

associated laboratory centre for research in ceramics and composite materials

CICECO



Model of a double-walled carbon nanotube (DWCNT) section

back-cover Cover DWCNT model and respective transmission electron microscopy (TEM) image simulation. The nanotube is a (7,7)@(13,12) DWCNT and the TEM parameters correspond to those of the JEOL 2200FS instrument installed at the University of Aveiro Scale bar: 1 nm.

Dora dos Santos - CICECO

lay-out and review João Rocha Luís Dias Carlos Dora dos Santos

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associated laboratory centre for research in ceramics and composite materials CICECO

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In Memoriam of Prof. Helena Maria Correia Seixas Carapuça

After prolonged illness, Professor Helena Carapuça passed away in 2008. As a member of the Chemistry Department and CICECO, she enthusiastically contributed to our community as a teacher and as a scientist. This annual report still includes her contribution in electrochemistry-related research. We will miss her friendship. Her courage and dedication are an example to us.



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associated laboratory centre for research in ceramics and composite materials CICECO





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about

The **centre for research in ceramics and composite materials** (**CICECO**), is an interdisciplinary laboratory in the University of Aveiro (Portugal) with researchers from Chemistry, Ceramics and Glass Engineering and Physics.

CIČECO was created in 2000, as a result of the fusion of two research units of the University of Aveiro: Centro de Química Inorgânica e de Materiais and Unidade de Investigação em Materiais Cerâmicos.

In March 2002, CICECO was awarded the status of Associated Laboratory by the Portuguese Ministry of Science and Thechnolgy.

CICECO is regularly evaluated by international panels and has been rated as '**Excellent**' in the last assessment was conducted in 2004.

This document reports the rmain activities developed in 2008 as well as the actions aimed for 2009.

mission vision

Develop the scientific and technological knowledge base required for the innovative production and transformation of ceramic and composite materials. Become a leading inter-disciplinary European research laboratory in the field of materials.

Contribute to the development of a scientific culture at a national level; stimulate innovation within the industrial sector.





Chemistry Department

Physics Department Develop novel nano- and micro-structured materials, and innovative methods of synthesis and processing, leading to the foundation of basic scientific knowledge, which allows the study of structure-property (electrical, magnetic, optical...) relationships and the design of devices for communications technologies. Much attention will be devoted to organic-inorganic hybrids, multifunctional materials and multiferroics;

Develop new materials and functional coatings for industrial applications and materials with improved structural properties;

general aims

Design recycling/reuse alternatives for wastes and by-products in ceramic or cement-like materials; develop, in the frame of the biorefinery concept, the scientific and technological knowledge of the chemical and biological processes of production and transformation, at the laboratory, pilot and industrial scale, of polymeric materials and lignocellulosics, adding value to forestry materials and industrial wastes, while minimising the environmental impacts;

Develop biomedical and biomimetic materials and methods.





Complexo de Laboratórios Tecnológicos

Ceramics and Glass Engineering Department

associated laboratory centre for research in ceramics and composite materials CICECO

research is organised in 3 lines and 8 interdisciplinary groups from the Departments of Chemistry, Ceramics and Glass Engineering and Physics, considering:

surrounding industrial environment (ceramics, chemical and forest-based companies);

our skills and expertise; and

motivation to develop new and stimulating scientific and technological fields.

research lines

research areas

advanced micro- and nanostructured materials for communications technologies

research groups

g1 | inorganic functional nanomaterials and organicinorganic hybrids

g2 | electroceramics

g3 | magnetostructural and multiferroic modulation of strongly correlated electric materials

advanced materials for industrial applications

g4 | reactive ceramic components for process control

g5 | ceramic composites and functional coatings for structural applications

g6 | wastes recycling and green products

biorefineries and biomaterials

- g7 | macromolecular materials and biorefineries
- g8 | biomedical and biomimetic materials



sientific output

CICECO is one of the most productive research institutes in the country in all scientific areas, with an average publication of 5-5.5 SCI papers per year per academic staff or full-time researcher in 2008.

	'02	'03	'04	'05	'06	'07	'08	total
PhD theses	14	13	11	14	19	20	10	101
MSc theses	10	8	7	17	16	41	75	174
SCI papers (IF>= 5)	1	3	4	5	7	17	23	60
SCI papers (IF< 5)	204	225	283	310	374	273	396	2065
books	-	-	1	1	1	-	3	6
books chapter	4	14	12	10	5	17	36	98
national patents	7	3	1	6	6	6	4	33
international patents	2	-	-	-	1	4	1	8

02	03	.03	.04	.05	.06	07	.08	
47	47	47	50	52	53	50	48	professor and lecture
5	9	9	12	16	20	23	29	full-time researcher
23	22	22	29	47	46	47	51	pos-doctoral associates
16	13	13	12	10	23	46	14	collaborators
54	60	60	61	51	67	69	81	PhD students
26	44	44	54	63	49	39	116	MSc and other students
4	8	8	5	5	5	4	4	laboratory technicians
1	3	3	5	6	7	7	7	administrative personel
176	206	206	228	250	270	285	350	total
23 16 54 26 4 1	22 13 60 44 8 3 206	22 13 60 44 8 3 206	29 12 61 54 5 5 228	47 10 51 63 5 6 250	46 23 67 49 5 7 270	47 46 69 39 4 7 285	51 14 81 116 4 7 350	pos-doctoral associa collaborators PhD students MSc and other studer laboratory technician administrative persor total

research team

CICECO is the largest Portuguese institute in the field of materials. On 31st December 2008 CICECO hosted 350 people, an increas of 22.8% relatively to the previous year and almost 100% since 2002.

Almost 37% of the Research Team hold a PhD degree.

Under the Government Programe for hiring researchers for the National Scientific and Technological System, CICECO hired 4 researchers in 2008 and 9 researchers in 2009.

08 | about CICECO



Transmission Electron Microscopy (High resolution)



Solid Nuclear Magnetic Resonance (NMR)



Chromatography (Gas and HPLC)

facilities

CICECO is one of the best equipped materials science centres in the country

in the recent FCT equipment programme we have been awarded over 4.4 M€

the Centre for Imaging and Structural Studies manages, in an integrated way, medium and largescale equipment, granting free access to all members. Some 250 k€/year from FCT budget are allocated to maintain and upgrade equipment

main instruments have service contracts and dedicated technicians. Academic users from Aveiro and other institutions in Portugal and Europe have privileged access conditions. Industrial users pay a larger fee (exception for those engaged in CICECO-industry consortia) electron microscopes are part of the national microscopy network and the access conditions to Portuguese academic users are very favourable

our Nuclear Magnetic Resonance spectrometers are much demanded by academic users. Until 2008, most researchers north of Lisbon would come to Aveiro to run their spectra

our single-crystal X-ray diffraction facility was granted through a joint proposal with Associated Laboratory, REQUIMTE, which secures up to 25% of the users time

recently, we started CICECO's computer cluster, which is housed and embedded in the Aveiro computer centre



High-temperature graphite furnace

Platform for physical measurements at low temperatures with a magnetic field up to 10 Tesla





Single-Crystal X-Ray

technology transfer and valorisation of knowledge are important concerns of CICECO

stable collaboration with Portuguese industry is difficult because most companies are SMEs and multinationals have their research centres elsewhere. CDTM is our interface with industry

centre for design and technology of materials cdtm

CDTM has been exploring the following important initiatives:

Spin-off Companies

in 2006 CDTM and research unit QOPNA (U Aveiro) started 'FoodMetric SA'

(http://www.foodmetric.com), which raised funds from the venture capital company Change Partners SCR. FoodMetric gained 3 entrepreneurship awards. It provides solutions to food and drink companies through the implementation of fast and reliable methods of instrumental analysis and chemometrics.

'Tetracarbon' is also being created, in collaboration with a second Associated Laboratory (I3N) of U Aveiro. The solutions developed are based on advanced ceramics and diamond coated materials, and target end-users such as ceramics, moulding, chemical, wood, and metal industries. With a staff of 4 people, CDTM assists CICECO in management of R&D:

consortia/services/projects with companies

identifying products and processes of commercial interest and securing intellectual property protection

creation of spin-off companies

licensing of technologies

identifying funding programmes, particularly European, and submitting proposals

marketing CICECO's image

organisation of training courses and technical workshops

Technology Platforms

These are CICECO-companies clubs where the companies have exclusive prior access to research output, against a 7.5 k€ annual fee. They also have special access to equipment and services, consulting, literature search, etc. The first one, created in 2006, is IDPoR-Polymers from Renewable Resources (http://idpor.ciceco.ua.pt), and it aims at developing scientific and technological knowledge driven by the needs of 6 national companies. 5 Ph.D. theses are in progress. IDPoR is involved in the Network for Competence in Polymers with other companies and U Porto, and financed for 2 years by AdI with 1 M€, to promote new investments and business opportunities.

Competitiveness Cluster

In the case of Ceramics, the technology platform may take the form of a competitiveness cluster networked with a similar cluster in Limoges, France. In the French system, 'Pole de compétitivité' is a combination in a given geographical area of companies, training centres and public sector or private research facilities, all committed to a partnership approach in order to create synergy around innovative projects. Contacts have been established and there is a good possibility that this competitiveness cluster will soon be created. Some 30 Portuguese Ceramics companies are interested in this initiative, which has progressed during 2008.

research projects selected examples

The number of Projects in progress in 2008 was 121, similar to the last five years. The main sources of funding are FCT, National Science Foundation (75%), and the European Funding Agencies and Programmes, European Commission, FEDER, (24%). Section 5 lists all projects funded.

Projects with local Governments

URBACT: project supported by UNIC aiming at promoting sustainable economical development of local ceramic industries. Partners - Municipalities of Aveiro, Limoges, Pécs, Delft and Selb

POVT Suitanable Water Management in Public Buildings: with Aveiro Municipality

VOUGAPARK: we assist the Sever do Vouga Municipality in the creation of a research and technological lab within the technological park VOUGAPARK

National Network Action

Institute of Molecular Materials, Processes, and Products (M2P2): consortium CICECO-Associated Laboratories REQUIMTE and LSRE-LCM.

CICECO heads the national facilities networks on electron microscopy (http://www.ua.pt/ rnme/default.aspx) and nuclear magnetic resonance (http://ptnmr.dq.ua.pt/).

Nanomedicine Research Networks: we participate in several such Portuguese-Spanish networks.

House of the Future Programme: consortium between University of Aveiro and several companies.

QREN cluster "Plataforma para a Construção Sustentável"

scientific highlights '08

controlled integration of nanocrystals in inverted hexagonal nano-pits at the surface of light-emitting GaN based heterostructures

metal-organic nanoporous structures with anisotropic photoluminescence and magnetism for sensing purposes

atomic layer deposition of metal oxides onto solid substrates using surfactant free and non-aqueous routes

structural studies and cytotoxicity evaluation of inclusion organometallic complexes in beta cyclodextrin

interconvertable modular framework and layered lanthanide(III)-etidronic acid coordination polymers combining zeolite-type behavior with reversible photoluminescence behaviour one-step synthesis of Vitamin B-3 and other nitrogen-containing pharmaceutical chemicals with a single-site heterogeneous catalyst

applications of scanning probe microscopy: observation of intense THz emission from PZT nanotube arrays

synthesis of well crystallized meso-structured BaTiO₃ via a simple sol-precipitation process

assessing a new form of multiferroic material in charge-ordered manganites, using hyperfine local probing with radioactive isotopes

spectroscopic guidelines for optimization of mixed conducting & electrocatalytic properties of ceramic materials

mechanosynthesis of single phase nanocrystalline powders with enhanced sinterability, and corresponding preparation of high quality ceramic microstructures

detection of limitations and compensation of potentiometric sensor readings

International Network Action

EU Network of Excellence (2005-08): 'Functionalised Advanced Materials and Engineering of Hybrids and Ceramics-FAME' (6th framework programme, ca. 200 researchers and 50 Ph.D. students in 7 countries, http://www.famenoe.org/), which has now evolved to European Multifunctional Materials Institute-EMMI.

Network with Brazil: 'Molecular and Interfaces Nanotechnology Research Network'.

European Projects (selection)

MAEIF-CT-2006-041632 - MULTIFERRO-SOL-GEL

Multiferroic nanostructures: a non-aqueous sol-gel approach (multiferro-sol-gel)

NMP3-CT-2006-032616 – MULTICERAL Multifunctional Ceramics Layers with High Electromagnetoelastic couplin in complex geometries

NMP2-CT-2004-515960 ULCOS ULTRA LOW CO2 STEELMAKING

Strp 033410 Matsilc Matsilc-Novel Materials for Silicate Based Fuel Cell

Multi-Level Protection of Materials for Vehicles by 'Smart' Nanocontainers

WACHEUP - New Concepts for Upgrading Pulp Mill Waste Streams to Values - Added Chemicals - Fp6 2002 Nmp/1 (Ip 500311-2)

SUSTAINPACK - Innovation and Sustainable Development in the Fibre Based Packaging Value Chain

development of minute pipettes capable of store and release Cul on-demand

adequacy of nanocrystalline diamond (NCD) sliding systems for biotribological applications with very low wear rates

applications of direct coated NCD tools for sintered hardmetal, graphite and Al-alloys

demonstration that NCD films induced human osteoblast and fibroblast proliferation

demonstration of high mechanical sealing with NCD coated Si_3N_4 rings

development of self-healing coatings based on nanocontainers

development of new experimental methods to investigate corrosion in micro-confined coatings

patented novel solid-contact ion-selective microelectrodes

design of novel pigment structures for substitution of expensive chromophors (Co or Ni) new cellulose and other polysaccharide-based functional materials

different chemical and biochemical approaches for the implementation of the bio-refinery concept in forest based industries

sudy of water interaction and low temperature behaviour of biofuels, and development of models for their description

PMMA-modified HA bone cements with multiwalled carbon nanotubes (fatigue resistant implants and coatings)

first evidence that amniotic fluid reflects metabolic changes in malformed human foetuses, showing changes in glycolysis and gluconeogenesis and kidney development

new cyclodextrin (CD) inclusion compound $[CpMo(H_2biim)(CO)_2](BF_4)$ (H2biim = 2,2'biimidazole) / heptakis(2,6-di-O-methyl)-ß-CD showed increased cytotocicity against K1735-M2 mouse melanoma cells (estimated as > 50 µM for the non-included complex).

trainnig activity

U Aveiro Ph.D. and M.Sc. Courses: highlight - 10 Ph.D. and 76 M.Sc. theses terminated in 2008. We lecture a number of M.Sc. degrees of the Departments of Chemistry, Physics and Ceramics and Glass Engineering. Until recently, in CICECO (and Portugal) most students got their degrees through the traditional supervisor-student route. CICECO is now involved in Ph.D. courses (starting soon) with other research units in Aveiro in Chemistry, Chemical Engineering, Nanosciences and Nanotechnologies and Materials Science and Engineering.

Bilateral Ph.D. Programmes: 5 these in progress with U Montpellier, U Bordeaux, U Zaragoza, U Santa Catarina (Brazil). Informal schemes of student's exchange with other foreign laboratories are also in operation. ERASMUS MUNDUS M.Sc. Programmes: 'EMMS-Joint European Masters Programme in Materials Science' with the universities of Aalborg and Hamburg, which is now in its fifth edition (http://emms.web.ua.pt/);

and a FAME-promoted programme (http://www.fame-master.com/) in its year 2.

Workshops: on January, a 2 days general workshop was organised in the format of a conference, with oral communications and poster presentations; seminars are organised every ca. 2 weeks and aimed at all our members. Supervisors-students group meetings take place on a regular basis.

Summer Schools: regularly organised, for example in the frame of NoE FAME/EMMI. The last such events (ca. 100 attendants) took place on July 2008 near Aveiro ('School on Inorganic Functional Materials').

Specialised courses: for post-graduate students and industrialists, e.g. 'Polymer Science' and 'Physics and Chemistry of Surfaces and Interfaces'

outreach/ society and science	Coordination of over 33 activities with 28 schools, including visits to Chemistry laboratories, conferences in schools, demonstrations, School Science Fairs, and Science Cafes.
	TV and radio programmes, newspapers
	Cooperation with Aveiro Science Centre

future aims

Develop novel nano- and micro-structured materials, and innovative methods of synthesis and processing, leading to the foundation of basic scientific knowledge, which allows the study of structure-property (electrical, magnetic, optical...) relationships and the design of devices for communications technologies. Much attention will be devoted to organic-inorganic hybrids, multifunctional materials and multiferroics.

Develop new materials and functional coatings for industrial applications and materials with improved structural properties.

Design recycling/reuse alternatives for wastes and by-products in ceramic or cement--like materials.

Develop, in the frame of the biorefinery concept, the scientific and technological knowledge of the chemical and biological processes of production and transformation, at the laboratory, pilot and industrial scale, of polymeric materials and lignocellulosics, adding value to forestry materials and industrial wastes, while minimising the environmental impacts.

Develop biomedical and biomimetic materials and methods.

The same type of general activities of knowledge transfer, networking, internationalisation and outreach described in the other items of this report, will be carried out.

research line

advanced micro- and nanostructured materials for communications technology

line coordinator Luis Dias Carlos Icarlos@ua.pt

general aims

design, prepare, process and characterise novel inorganic and organic-inorganic hybrid, functional and multifunctional materials and nanostructures, of different dimensionality (0-3D), for communications technologies (optical and magnetic properties) and heterogeneous catalysis

improve understanding of electroceramics, and develop new low-cost materials and devices for dielectric, piezoelectric, ferroelectric and multiferroic applications

understand nanosize effects and properties in bulk, films and nanocomposites

study magnetic properties, and their interplay with structural and electronic correlations, of magnetic oxides, superconductors, bulk and thin-film metal alloys and nanoparticles

develop solid-state NMR and apply at the highest level: photoluminescence, vibrational and X-ray absorption spectroscopies, XRD, electron and scanning probe microscopies, magnetisation, magnetoresistance and magnetothermal analyses, impedance spectroscopy, ferroelectric and piezoelectric analyses, hiperfine local probing using radioactive isotopes; quantum mechanics and molecular dynamics modelling

research groups

g1 | Inorganic Functional Nanomaterials and Organic-Inorganic Hybrids

g2 | Electroceramics

g3 | Magnetostructural and Multiferroic Modulation of Correlated Electron Materials

research line

advanced materials for industrial applications



line coordinator Jorge Ribeiro Frade jfrade@ua.pt

general aims

study ionic or mixed conductors, electrocatalysts, etc, for energy conversion systems (ECS)

optimize materials properties for ECS (mixed transport, electrochemical, catalytic, etc) based on effects of composition-structure-microstructureredox-phase changes

enhance tolerance (chemical-structural-thermalmechanical) to harsh working conditions

develop nanodiamond and other ultra hard coatings for tribosystems with outstanding wear resistance and low friction

develop protective coatings for metallic materials, based on nanostructured hybrids, self-healing coatings, smart nanocontainers

develop novel solutions for industrial processes, with emphasis on correlations between powder and ceramic processing

develop use ceramic, cement and other technologies for reuse and recycling of wastes and byproducts

develop environment related technologies for remediation and cleanup of pollutants, carbon lean technologies, etc.

design green products based on secondary raw materials.

research groups

g4 | reactive ceramic components for process control

g5 | ceramic composites and functional coatings for structural applications

g6 | wastes recycling and green products

research line

3 biorefineries and biomaterials



line coordinator Carlos Pascoal Neto cneto@ua.pt

general aims

assess chemical structure / properties relationships on national relevant lignocellulosic materials, and the chemistry of its industrial processing; to apply this knowledge on the optimization and improvement of industrial processes (pulping and bleaching) and properties of end-products (pulp and paper) and identification of new routes to upgrade industrial by-products

develop new chemical and biochemical biomass conversion processes, including catalytic oxygen polyoxometalate catalyzed delignification

develop new materials and products from cellulose-fibres and by-products from forestbased industries

develop new processes using alternative green solvents (fluorocarbons and ionic liquids) for enhanced production in bioreactors

produce novel biomaterials for different medical uses

develop Nuclear Magnetic Resonance-based methods for the evaluation of the metabonomic effects of the new biomaterials

study biological recognition and membrane transport mechanisms

research groups

- g7 | macromolecular materials and biorefineries
- g8 | biomedical and biomimetic materials

research group

inorganic functional nanomaterials and organic-inorganic hybrids



research group

inorganic functional nanomaterials and organic-inorganic hybrids



group coordinator Tito Trindade tito@ua.pt

development of new microporous and layered lanthanide silicates showing unusual photoluminescence behaviour





structural studies and cytotoxicity evaluation of inclusion organometallic complexes in beta cyclodextrin

scientific highlights

controlled integration of nanocrystals in inverted hexagonal nano-pits at the surface of light-emitting GaN based heterostructures

metal-organic nanoporous structures with anisotropic photoluminescence and magnetism for sensing purposes

atomic layer deposition of metal oxides onto solid substractes using surfactant free and non-aqueous routes

structural studies and cytotoxicity evaluation of inclusion organometallic complexes in beta cyclodextrin

interconvertable modular framework and layered lanthanide (III)-etidronic acid coordination polymers combining zeolite-type behaviour with reversible photoluminescence bahaviour

functionalisation of glassy carbon electrodes using Kegging type polyoxosilicotungstates

development of atom transfer radical polymerizations to produce surface functionalized carbon nanofibers

one-Step synthesis of Vitamin B-3 and other nitrogen-containing pharmaceutical chemicals with a single-site heterogeneous catalyst

photopatternable di-ureasil-zirconium oxocluster organic-inorganic hybrids as cost effective integrated optical substrates *New Microporous Materials.* The hydrothermal synthesis and structural characterization of the lanthanide silicate system $[Na_6Ln_2Si_{12}O_{30} \cdot xH_2O]$ (Ln=La³⁺, Sm³⁺, Eu³⁺, Gd³⁺, and Tb³⁺), named AV-21, have been reported. Structural elucidation of the Sm³⁺ analogue (isomorphous with the Eu³⁺, Gd³⁺, and Tb³⁺ frameworks) reveal disorder in the Si(1) second coordination sphere. La-AV-21 presents a distinct framework. These materials combine microporosity and interesting photoluminescence features with structural flexibility that allows the introduction of a second or third type of lanthanide center.

Eu³⁺ has been incorporated into the pores of titanosilicates sitinakite and GTS-1. The Eu³⁺-doped materials display a stable room temperature ligth emission. Microporous zinc phosphate with DFT topology has been synthesized in an eutectic mixture (choline chloride and imidazolidone). The organic template was generated *in situ* by the decomposition of imidazolidone. By using 2-methylpentamethylenediamine (MPMD), microporous ZSM-48 and mesoporous SU-M have been obtained.

Vanadium has been incorporated into titanosilicate ETS-4 as five and six-coordinated V⁴⁺, partly replacing TiO₅ and TiO₆. This causes interruption of Ti–O–Ti chains and changes the thermal stability, which may be used to tune the properties of ETS-4.

Mn-doped AIPO-5 was employed as a single-site heterogeneous catalyst in pharmaceutically-interesting reaction of nitrogen-containing heterocyclic compounds. As a continuation of previous work, hypothetical zeolitic trinodal structures were systematically enumerated using tiling theory and investigated with a view of finding those most suitable for potential applications in heterogeneous catalysis and sorption.

AM-2 membrane has been prepared on porous TiO₂ tubular supports using organic Ti source. Well intergrown AM-2 membrane with a thickness of ca. 5 μ m has been obtained reproducibly. These membranes are able to separate H₂ from N₂ even in the presence of moisture, with good selectivity, being 45.2±3.8, together with H₂ permeance of 4.6±1.1×10⁻⁹ mol/(m²s Pa).

Water suspensions of microparticles of paramagnetic zeolite-type silicates containing Ln^{3+} ions in the framework (Ln-AV-9) very considerable r_2^* and r_2 relaxivities in water suspensions. The experimental results were explained by a theoretical model, which takes into account the residual diffusion effect in the static dephasing regime. The Dy-AV9 particles were found to be particularly efficient T_2 and T_2^* nuclear relaxation agents potentially useful as reporters in particulate MRI contrast agents.

Organic-Inorganic Hybrids Lacking Activating Centers. Three undoped di-urea cross-linked poly(oxyethylene) (POE)/siloxane hybrid matrices, classed as di-ureasils, incorporating POE segments with different lengths were prepared through the carboxylic acid solvolysis sol–gel method using formic acid. The hybrids' structure is essentially independent of the polymer chain length and the materials are room temperature white-light emitters with emission quantum yields of $10 \pm 1\%$ and room temperature lifetime average values between 2 and 4 ns. For the di-ureasil host with short polymer chains the solvolysis method favours the increase of the PL quantum yields (30-35 %) relatively to conventional sol–gel route.

New Hybrid Materials. A series of organic-inorganic di-ureasils modified by different concentrations (20-80 % wt.) of zirconium (IV) n-propoxide (ZPO) stabilized with methacrylic acid (McOH) were processed as thin films deposited in glassy substrates via spin coating and as transparent and shape controlled monoliths. The local-structure of these hybrids were modelled as Si and Zr- based nanobuilding units where for low Zr-OMc content the Si- and Zr-based networks are interconstrained (the Zr-based clusters are embedded in the polymeric phase between the siliceous domains) whereas segregation of the individual components at the 0.1 µm scale occurs for high contents. The aggregate size of the Zr-OMc clusters increases from 300-500 nm as the relative Zr-OMc content increases. Channel monomode waveguides and diffraction gratings were UV patterned using the Talbot interferometer and the Lloyd mirror interferometer experimental setups. The time dependence of the diffraction gratings efficiency was studied for hybrids containing different amounts of Zr-OMc. The number of propagating modes and the refractive index gradient within the waveguide region, determined as a Gaussian section located below the patterned channel, was evaluated and modelled.

Di-ureasil based nanocomposites were prepared *in situ* in the presence of organically capped CdSe quantum dots (QDs) or CdSe QDs coated with a ZnS shell. The QDs became well dispersed in the final nanocomposites whose microstructural homogeneity was evaluated by AFM and TEM analysis. Emission quantum yields up to 0.11 were measured in nanocomposites with ZnS coated CdSe QDs (particle size distribution of d~4.5 nm) that present a huge (between 3 and 6 orders of magnitude) increase in the lifetime, relatively to that of the isolated QDs, as a result of energy transfer occurring between the intimate mixed di-ureasil host and the QDs. Eu3+-containing di-ureasils were prepared as transparent monoliths and thin films via spin coating. Photoluminescence results point out that the Eu3+ ions occupy, at least, two distinct local environments. The processing method (thin films or monoliths) has influence on the energy levels of the hybrid host probably due to the lower degree of organization of the thin films structure; in particular it may be related to the lower degree of organization present in the thin films structure caused by the fast withdrawal of the solvents during the spin-coating process. Di-amide cross-linked alkyl/siloxane hybrid materials, termed as di-amidosils, were synthesized with different amounts of europium triflate (Eu(CF₃SO₃)₃), 200 <= n <= 8 (n is the number of oxyethylene units per Eu³⁺ ion). The Eu³⁺ ions bond to the C=O groups of the amide cross-links in the whole range of salt concentration examined. At n = 8 an ionic aggregate of unknown nature is formed. The hybrids are room temperature white light emitters due to the convolution of the hybrid host emitting centers (amide cross-linkages and siliceous nanodomais) and the Eu³⁺ intra-4f⁶ ⁵5D₀-->⁷F₀₋₄ transitions.

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Organic-inorganic hybrids formed of di-urethane cross-linked poly(oxyethylene) (POE)/siloxane, classed as diurethanesils, were modified by Eu(tta)3phen complex (tta=2-thenoyltriflluoracetonate; phen=1,10-phenantroline). The hybrids' emission depends on the excitation wavelength displaying the typical orange-red lines ascribed to the Eu³⁺ intra- intra-4f⁶ 5D₀—>⁷F₀₋₄ transitions for excitation wavelengths below 330 nm and showing the hybrid intrinsic emission overlapped by intra-4f⁶ lines for higher excitation wavelengths (330–400 nm). The complex incorporation into the hybrid host contributes to enhance the Eu³⁺ sensitization process. An hybrid matrix built from the cocondensation of two di-ureasils frameworks, one of which incorporates poly(oxyethylene) (POE) chains with about 15.5 repeat units and the other about 8.5 oxyethylene repeat units was prepared. The co-condensed di-ureasil network has been doped with the Eu(tta)₃(H₂O)₂. The co-condensation procedure promoted the establishment of an hydrogen-bonded network stronger than that formed in the single chain di-ureasils, in which stronger hydrogen-bonded aggregates, leading to their breakdown. The effective interaction between the lanthanide ions and the host hybrid structure accounts for the increase of the emission overall quantum yield (36%) and for the ⁵D₀ quantum efficiency (57%) with respect to those of the complex alone (29% and 27%, respectively). A sol–gel derived hybrid material (Eu-DBM-Si) covalently grafted with Eu(DBM-OH)₃•2H₂O was prepared through the primary β-diketone ligand DBM-OH and the resultant Eu-DBM-Si materials exhibited more efficient ligand-to-Eu³⁺ energy transfer. The periodic mesoporous organosilica materials (PMOS) containing Eu(tta)₃phen were synthesized by impregnation of Eu(tta)₃•2H₂O into PMOS that covalently grafting with phen through a ligand exchange reaction and showed higher emission quantum efficiency.

An organic molecule, $(EtO)_3Si(CH_2)_3NH(C=O)NH-(CH_2)_{12}-NH(C=O)NH(CH_2)_3Si(OEt)_3$, combining urea functionalities and a 12-carbon alkyl chain, underwent sol-gel reactions in the presence of an acid catalyst, a large excess of water and variable amounts of EuCl³, giving rise to the formation of crystalline hybrids through a self-directed organization process in which hydrogen bonding interactions play a key role. Three photoluminescent lamellar Eu³⁺-doped silsesquioxane hybrids incorporating 1.01, 1.83 and 15.04% Eu³⁺ were prepared. The lamellar hybrids are room temperature multi-wavelength emitters due to the convolution of the hybrid's emitting centres and the Eu³⁺ intra-4f⁶ transitions. Their emission colour can be easily tuned along the Commission Internationale d'Eclairage chromaticity diagram from the bluish-purple region to the pink area, either by changing the excitation wavelength or the Eu³⁺ amount. The Eu³⁺ first coordination shell is very similar for the three photoluminescent lamellar Eu³⁺doped silsesquioxane hybrids incorporating oxygen atoms of the carbonyl group, Cl atoms and water molecules. The 5D0 quantum efficiency (16.3–19.2), number of water molecules (1.7–2.0) and experimental intensity Ω_2 parameter (8.9–10.1 × 10⁻²⁰ cm²) are similar for all the Eu³⁺ content.

Porous alginate organic-inorganic hybrid materials incorporating Eu³⁺, Tb³⁺, and Eu³⁺/Tb³⁺ were processed in four states, hydrogel, alcogel, xerogel, and aerogel with nominal 3:1 carboxylate groups to lanthanide coordination. Under UV radiation, all hybrids are room temperature emitters in the visible spectral range. The Eu³⁺-alginate aerogel and alcogel exhibit the highest ⁵D₀ quantum efficiencies (9.9 and 8.2%, respectively), while the hydrogel and xerogel have lower quantum efficiency values (5.2 and 5.6%, respectively). The difference in the nonradiative transition probability was rationalized on the basis of the different number of OH oscillators present in the Eu³⁺-first coordination shell. The Tb³⁺/Eu³⁺ co-doped materials are multiwavelength emitters for which the emission color can be tuned across the chromaticity diagram by selecting the excitation wavelength. Magnetic studies in natural ferritin and iron oxide (ferrihydrite, maghemite, magnetite and others) nanoparticles incorporated into organic-inorganic hybrids and polymer matrices. The effect of partice size distributions on the magnetic properties/anisotropy and the analysis of the effect of magnetic dead layer were addressed. High Field (up to 50 Tesla) studies of Exchange Bias in nanoparticles (Grenoble, Niemegen and Toulouse) were also performed.

Mesoporous Materials. Luminescent mesostructured materials were prepared by incorporation of Eu^{3+} ß-diketonate complexes inside the channels of MCM-41-type ordered mesoporous silica via a noncovalent host-guest interaction or via complexation with surface-anchored pyridine ligands. In the first method, the ligand ethyl[3-(2-pyridyl)-1-pyrazolyl]acetate was first encapsulated by simple wet impregnation, followed by treatment with the complex Eu(NTA)₃(H₂O)₂ [HNTA = 1-(2-naphthoyl)-3,3,3-trifluoroacetone]. MCM-48 aluminosilicates with different aluminium contents were synthesised by a room temperature procedure

MCM-48 aluminosilicates with different aluminium contents were synthesised by a room temperature procedure using tetraethoxysilane and aluminium sulfate, isopropoxide or tert-butoxide as metal sources. The samples were characterised by X-ray diffraction, nitrogen adsorption at 77 K, and ²⁷AI MAS NMR and the catalytic activity tested in the reaction of 1-butene double bond position isomerisation.

Layered Materials. The first examples of nanoparticles of pure layered $Ln_2(SiO_4H)(OH)_2(H_2O)CI$ (where Ln = Eu, Gd, and Tb) and mixed microcrystalline layered lanthanide silicates containing different Eu/Gd and Tb/Gd ratios have been reported. These materials display interesting and tuneable photoluminescence properties and exhibit potential for sensing Cl⁻ ions.

The synthesis of new layered rare-earth silicates $K_3[Y_{1-a}EraSi_3O_8(OH)_2]$ (AV-22 materials) has been reported. The photoluminescence properties of Y/Er-AV-22 and the material resulting from its thermal degradation, $K_3[Y_{1-a}EraSi_3O_9]$ (Y/Er-AV 23), have been studied and compared. Both materials have a similar chemical makeup and structures sharing analogous building blocks, hence providing a unique opportunity for rationalising the evolution of the photoluminescence properties of lanthanide silicates across dimensionality.

A combination of physical methods such as conventional and synchrotron X-ray powder diffraction, EXAFS and fluorescence spectroscopy were used to fully characterise nanocomposite materials prepared by the intercalation of pyrene(tetra)sulfonate, pyrenecarboxylate, and oxomolybdenum catecholate complexes into layered double hydroxides. Dimerisation of the monomeric Mo^{VI} precursor complex during contact with the LDH supports resulted in the intercalation of oxobridged catecholate complexes.

Zn,Al–CO₃ compounds with the hydrotalcite-like (layered double hydroxide) structure were prepared by a coprecipitation method followed by hydrothermal treatment under microwave irradiation. The influence of the ageing treatment, heating temperature and of irradiation time was studied.

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Separation of the major components of landfill and natural gas by four adsorbent materials was investigated, and a high selectivity was obtained in some materials. The adsorbents, prepared from a natural clay, were two porous clay heterostructures (PCH) obtained by use of tetraethoxysilane (TEOS) and phenyltriethoxysilane (PhOS), and two other PCH prepared by use of 3-aminopropyltriethoxysilane (APTES) and TEOS. A pillared clay, with aluminum oxide pillars, was used also. CH_4 , C_2H_6 , and CO_2 high-pressure adsorption isotherms (measured up to 1000 kPa) were used to estimate the selectivity and phase diagrams for separation of binary mixtures of these gases.

Nanostructured Materials. A single-source approach was investigated to prepare morphological well-defined and coupled TiO₂/metal-sulfide nanocomposites. Metal *N*-alkyldithiocarbamates were used as the precursors to the metal-sulfide nanophases and, in particular, Ag₂S nanostructures were investigated in more detail. These were observed as nano-islands at the surface of TiO₂ (anatase) particles, which were used as substrates. Because the growth of the metal sulfide can be controlled at the surface of a photoactive substrate, we anticipate the potential of this synthetic method to chemical design reasonable amounts of semiconductor-sensitized TiO₂, such as Ag_2S/TiO_2 nanocomposites.

EuS nanocrystals encapsulated in poly(styrene) (PS) were investigated as the first example of a polymer based EuS nanocomposite prepared in situ. Comparatively to the starting powders of EuS nanocrystals (8 nm), in the final nanocomposites there was a decrease of the blocking temperature T_B and a change in the shape of the field-cooled susceptibility curve, indicating that the intensity of dipolar interactions decreases when the nanoparticles are incorporated into PS. Differences in the magnetic properties of the EuS nanocrystals and the EuS/PS nanocomposites were ascribed to surface phenomena occurring in EuS nanocrystals dispersed in the polymer matrix.

A series of chemically prepared Co^{2+} -doped ZnO colloids has been surface modified either by growing shells of ZnSe or by the in situ encapsulation in polystyrene. The surface modification effects using these two distinct chemical strategies on the magnetic properties of the nanocrystals were probed by electron paramagnetic resonance EPR. The results confirmed that in the core of these nanocrystals, Co was incorporated as Co^{2+} , occupying the Zn²⁺ sites in the wurtzite structure of ZnO. Additionally two Co signals stemming from the nanocrystals' shell were identified. The performed surface modifications clearly change the relative intensity of the EPR spectrum components, revealing the core and shell signals.

Synthetic strategies towards diverse nanobiocomposites have been investigated. In particular the influence of inorganic nanoparticles such as magnetite (Fe_3O_4), amorphous silica, titania, gold and silver on the rheological/optical properties of polysaccharides has been investigated. Mechanisms inherent to the nanocomposite behaviour have been proposed based on the combined effect of the nanoparticles and the type of matrix used in the synthesis (carrageenan gels or celluloses).

The work on ordered hybrid and doped nanostructures was continued especially by targeting new inorganic materials (e.g. phosphates and doped oxides), intercalating new organic moieties, performing advanced structural, optic and magnetic characterization techniques. By using this approach we could add new functionalities to these materials. Moreover, hybrid structure based on lanthanide doped strontium and barium aluminates were recently synthesized and were the scope of advanced optical and structural investigations.

synthesized and were the scope of advanced optical and structural investigations. An atomic force microscopy (AFM) tip has been coated with photoluminescent Eu³⁺-doped Gd₂O₃ nanorods using a dielectrophoresis technique, which preserves the red emission of the nanorods (quantum yield 0.47). The performance of the modified tips has been tested by using them for regular topography imaging in tapping and contact modes. These tips should find applications in scanning near-field optical microscopy and other scanning techniques.

We have investigated the correlations between the nanostructure and optical properties on epitaxial thin films and low dimensional heterostructures of wide bandgap semiconductors with technological interest for light emission. Device structures based on GaN and related alloys, including thin films, single (SQW) and multiple quantum wells (MQWs), diamond and electroceramic structures were studied by high-resolution X-ray diffraction in order to gain an insight regarding the effects of strain and composition on various material physical properties relevant in terms of device performance and functionality. Moreover, we have used the nitride light emitting MQWs, as a platform to integrate other material systems, namely metallic nanocrystals, achieving nanostructures tailored with nanometre scale control.

Hybrid inorganic-organic light emitters have been investigated. These devices combine recent developments in III–V nitride technology (including UV emitting micro-arrays and specifically tailored quantum wells) with conjugated polymers to access the entire visible spectrum. Two types of devices are studied, those based on down conversion of the quantum well emission by radiative transfer and those based on non-radiative resonant energy transfer. The spectral and operating characteristics of the devices have been described in detail. The thermal properties of bulk and nanostructured semiconductors were investigated theoretically. A general model for the thermal conductivity in the full temperature range considering the contribution of optical phonon decay into acoustic phonon of semiconductor structures has been developed and tested with reference to Ge, Si and AIN structures. The accuracy of the proposed model shows for the first time the fundamental role of the optical phonon in the thermal conductivity of semiconductor materials.

Research on polysaccharides nanocomposites (NC) has focussed on the effect of SiO₂ fillers surface modification on the properties of chitosan NC films. Kinetics studies on 3 different types of polysaccharides/NPs suspensions have been carried out under distinct pH and ionic strength conditions to get further understanding of their rheological properties.

As regards the development of synthetic strategies to prepare functional polymer based NC materials two main lines have been followed, (i) the grafting from approach using the RFAT mechanism and (ii) on the use of ILs as surfactants. In this context, synthetic strategies to modify the surface of luminescent SiO₂-coated Gd₂O₃:Eu³⁺ nanotubes and subsequent in situ polymerisation as well as the assembly of aligned structures using the LB technique have been developed. Work has also been developed regarding the use of macroRAFT agents for surfactant free synthetic strategies and the preparation of nanobags. Finally the use of the LB technique as a means to prepare Janus particles, and to mimic membrane models has been started.

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Well crystallized BaTiO₃ with meso-structure inside the crystallites was directly synthesized from the solution via a simple sol-precipitation process with cetyltrimethylammonium chloride (C16TMAC) as the cationic surfactant. Mesoporous structure (pore size distribution peaking at 1.5 nm) with single crystalline wall was obtained after removal of the template by calcination. The pores were locally ordered for some regions but wormhole-like on the whole view. The resulting materials were characterized with wide-angle and low-angle X-ray diffraction, SEM, TEM and low temperature nitrogen adsorption-desorption isotherms. A specific surface BET area of ~50 m²/ g was obtained. Formation mechanisms of the single-crystalline mesoporous structure were discussed. The present method avoids onerous heat treatment procedure for crystallization and provides an efficient way to synthesize mesoporous functional multi-metallic oxides with single-crystalline wall.

The hydrothermal synthesis of barium titanate particles by reaction of titanate layered nanotubes and barium hydroxide in aqueous solution at 90, 110 and 200 °C from 1 to 24 hours were studied. Anisotropic growth of barium titanate particles was observed when the synthesis temperature was 90 °C resulting in the formation of pseudo-cubic BaTiO₃ single crystal particles with a "wild" - type dendritic shape. Synthesis at 110 °C led to the formation of round-shaped, pseudo-cubic and tetragonal BaTiO₃ particles. At 200 °C, single crystal barium titanate "seaweed"-type dendritic particles with predominantly tetragonal structure were obtained. It was demonstrated that the anisotropic growth of barium titanate crystals can be controlled by manipulating the temperature and time of reaction and highlights the influence of the synthesis parameters on the anisotropic growth of BaTiO₃ crystals under hydrothermal conditions when using layered titanates with nanotube morphology as Ti precursor.

Non-Aqueous Chemistry Applied to Atomic Layer Deposition. Non-aqueous sol-gel approaches applied to the atomic layer deposition (ALD) technique were deeply investigated and new materials were deposited on different substrates. Such a novel approach brought several advantages compared to ordinary deposition and will permit the development toward more complicated materials. The deposition of relevant metal oxides on different supports such as carbon nanotubes for application in gas sensing was demonstrated. A combination of SEM and HRTEM was used for the characterization of nanostructured materials, ranging from organic materials to organic-inorganic hybrid materials, thin films and diluted magnetic semiconductor (DMS) nanoparticles. Especially, metal oxide thin films deposited by ALD on the surface of carbon nanotubes have been characterized in depth. In the case of V_2O_4 coated tubes, their behavior in gas sensing was studied.

Polyoxometalates. Research was developed on (i) new hybrid compounds with polyoxometalates (POM) and organic moleties, (ii) preparation of supported polyoxotungstates and (ii) studies of polyoxotungstates in the catalytic oxidation of organic compounds with H₂O₂. In particular, transition metal substituted (Co, Mn) Keggin polyoxotungstates were combined with cations like 1-butyl-3-methylimidazolinium, yielding new hybrid compounds. The work on iron and manganese substituted polyoxotungstates supported on functionalised silica was continued, coupled with the use of the prepared materials in heterogeneous oxidative catalysis of alkanes with hydrogen peroxide. The same anions (Keggin and sandwich-type) were also supported on silica nanoparticles and the products characterized by several techniques, including transmission electronic microscopy (TEM). These materials were found to be good catalysts for epoxidation reactions with H₂O₂, namely selective catalysts for the oxidation of geraniol. The use of the silica nanoparticles in heterogeneous catalysis were studied in several conditions and new experimental protocols had to be developed to cope with the small particle size of the new catalysts. Research was continued on the preparation of new organic-inorganic hybrid coordination compounds based on POMs. A series of organic-inorganic hybrids composed by lanthanopolyoxotungstates [Ln(W5O18)2]ⁿ⁻ (Ln(III) = Eu, Tb, Er and Yb) and 3-hydroxypicolinic acid were prepared using different lanthanide ions. The energy transfer processes from the organic ligand and the POM moiety to the lanthanide (antenna effect) in these compounds was studied by photoluminescence measurements. The application of the compounds in the preparation of POM based materials has been explored, namely by the preparation of mono or multilayered nanostructured films and incorporation into nanosized SiO₂.

The preparation of supramolecular organic-inorganic adducts containing dibenzo-30-crown-10 and $H_3PM_{12}O_{40}$ (M = W or Mo) was also investigated. Two novel compounds with the molecular formula $(H_3O)_3[PM_{12}O_{40}]$.3($C_{28}H_{40}O_{10})$ [where $C_{28}H_{40}O_{10}$ = dibenzo-30-crown-10 and M = W or Mo] were isolated in the solid state and their crystal structures were determined by single-crystal X-ray diffraction.

Crystal Engineering of Organic-Inorganic Hybrid Materials. Several new metal-organic framework (MOF) systems have been prepared and exhaustively studied for their properties, in particular for their structural features (using X-ray diffraction and solid-state NMR) and photoluminescence. With etidronic acid (H₅hedp) the first examples of single-crystal-to-single-crystal interconversion between 2D and 3D materials were discovered: Na₄[Ln₂(hedp)₂(H₂O)₂].*n*H₂O (Ln³⁺ = La³⁺, Ce³⁺, Nd³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Er³⁺) framework-type, layered orthorhombic [Eu(H₂hedp)(H₂O)₂].H₂O and Na_{0.9}[Nd_{0.9}Ge_{0.10}(hedp)(H₂O)₂], monoclinic [Ln(H₂hedp)(H₂O)].3H₂O (Ln³⁺ = Y³⁺, Tb³⁺) and triclinic [Yb(H₂hedp)].H₂O. The first modular MOFs containing 2,5-pyridinedicarboxylic (2,5-H₂pdc) and 1,4-phenylenediacetic acids (1,4-H₂pda) coordinated to binuclear units Ln³⁺ have been reported: [Ln₂(2,5-pdc)₂(1,4-pda)(H₂O)₂]. In particular, for stochiometric mixed-lapthapide compounds it was observed the existence of an effective room temperature Tb³⁺.

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With naphthalene-2,6-dicarboxylic acid (H_2NDC) and Ho^{3+} a layered [$Ho_2(NDC)_3(H_2O)_6$] and a 3D framework [$Ho_4(NDC)_6(H_2O)_5$]•1.75H₂O were found to co-crystallise from the same hydrothermal batch. Using the [Eu(DPA)(HDPA)(H_2O)_2]•4H_2O polymer (where H2DPA = pyridine-2,6-dicarboxylic acid) it was demonstrated that the Sparkle/PM3 model arises as a valid and efficient alternative to the simulation and prediction of the photoluminescent properties of MOFs when compared with other methods traditionally employed.

In the realm of the synthesis of MOFs, a new synthetic approach was developed combining concepts from both ionothermal and hydrothermal synthetic approaches: coined as hydro-ionothermal synthesis. A new bisphosphonate system, Ln(Hpmd)(H₂O)] (where Ln³⁺ = Ce³⁺ and Pr³⁺; H₄pmd = 1,4-phenylenebis(methylene)diphosphonic acid), has been prepared using this approach which was further shown to be the only route for the preparation of the mentioned material. A new research area in MOFs combining transition metals and lanthanides was also started with the preparation and extensive structural/properties studies of a photoluminescent and magnetic cyano-bridged Tb³⁺-Mo⁵⁺ layered material.

We have synthesized, by rational design, novel crystalline MOFs containing rare-earth ions that combine hydrophobicity, high adsorption capacity, high thermal resistance, anisotropic photoluminescence, and magnetic properties. These materials preserve their photoluminescence properties in the presence of water and show excellent sensor capabilities. The spacer used was 4,4'-(hexafluoroisopropylidene)- bis(benzoic acid) (HFIPBB). Under appropriate synthesis conditions and in the presence of HFIPBB, new Ln³⁺-based materials ITQMOF-1 and ITQMOF-2 with similar properties but different crystallographic structures, have been obtained. This new family of nanoporous, multifunctional rare-earth MOFs displays emission quantum yields and efficiencies that are the highest reported for solid-state Eu³⁺ compounds with organic ligands and magnetic properties.

C60 Phase Transitions Under High-Pressure. Structural analysis of a cubic carbon clathrate obtained from C60 compressed at 10GPa is performed. Although the experimental data has not enough resolution to determine the atomic structure, an approximate structure was obtained by symmetry and rigid-body constraints. Massive computer simulations (employing both DFT and Molecular Dynamics methods) on the structure of carbon clathrates were performed.

Development of Spectroscopic Techniques. Setting up high-resolution ¹H NMR experiments in solids is timeconsuming and not trivial, and this has discouraged their use by materials scientists. To change this status quo, we have discussed some important aspects of the experimental implementation of CRAMPS (Combined Rotation And Multiple-Pulse Spectroscopy) techniques, such as FSLG (Frequency Switched), and windowed and windowless PMLG (Phase Modulated). In particular, we discussed the influence on the quality of the ¹H NMR spectra of the different parameters at play, for example Lee-Goldburg pulses, radio-frequency phase, frequency switching, and pulse imperfections, using model compounds. The efficiency and robustness of the different NMR schemes was also illustrated on organo-phosphorus ligand and inorganic–organic hybrid materials. The use of such advanced ¹H-based NMR techniques combined with synchrotron PXRD and DFT calculations allowed to fully characterise the hydrogen-bonding network in the interlayer space of organically templated titanium phosphate materials. ⁹¹Zr Quadrupolar Carr-Purcell Meiboom-Gill (QCPMG) spectra of some zirconium silicates were obtained at different magnetic fields from which the quadrupolar and chemical shift parameters were extracted. The work shows that using sensitivity enhancement techniques such as QCPMG and performing NMR experiments at the highest possible magnetic fields allow one to probe low-gamma, quadrupolar metal centers in microporous materials. Spectroscopic studies of nanostructured surfaces were carried out. In particular the development of new SERS (Surface-Enhanced Raman Scattering) substrates was investigated. Synthetic Ag-bacterial cellulose nanocomposites were reported and their performance as SERS substrates was investigated using thiosalicylic acid and 2,2'dithiodipyridine as analytes. These nanocomposite materials act as natural sponges when immersed in aqueous or ethanolic solutions allowing capture and SERS detection of certain dissolved molecules. The detection limits are considerably lower than the conventional vegetable cellulose analogs. Furthermore, we anticipate that the use of these nanocomposites has a beneficial consequence for the development of handy and active cellulosic SERS substrates, in particular for bioanalysis, as we experimentally demonstrated by testing the amino acids Lphenylalanine, L-glutamin and L-histidine.

Cyclodextrins. We have studied the interaction between various cyclodextrin molecules (methylated and unsubstituted α - and β -cyclodextrins) with sodium decanoate micelles in water, using SANS. Ruthenium trithiacyclononane ([9]aneS3) complexes bearing planar amines are suitable anti-tumour candidates due to their DNA intercalating abilities. Native β -CD and TRIMEB inclusion compounds of [Ru[9]aneS₃(bpy)CI]CI were prepared (bpy = 2,2'-bypiridine). A Monte Carlo optimisation run on the powder XRD pattern of the microcrystalline TRIMEB adduct showed that the inclusion compound crystallises in the monoclinic system with the space group P2₁, and a hypothetical structural model of the crystal packing was presented.

Cyclodextrins were also tested as molecular electrical insulators for the emitting material of an OLED (organic light emitting device). In particular TRIMEB was shown to increase the durability and high-voltage stability of an OLED using Eu(1-(2-benzoyl)-3,3,3-trifluoroacetone)₃(bpy), an emitting complex that is otherwise unstable under high applied voltages.

Computer Aided Characterization of Materials and Properties. Molecular modelling is recognized to play a key role in the success of several recent papers of this group, and during 2008 an effort has been done towards the building-up of the CICECO's computational cluster. A new cluster of computers was bought in May 2008 and is now installed at the University of Aveiro. It consists of 8 blades BL460c from HP with characteristics (Dual Xeon Quad-core Intel E5430, 2.66 GHz; 8GiB FB-DIMM DDR2-667; Dual Gigabit Ethernet; Dual 146GB 10K RPM SAS HDD in RAID1). The OS is Gentoo linux and several computational codes were already optimized for parallel execution, namely, *CPMD 3.13.1, DL POLY 2.19, Quantum Espresso, Gaussian 03 Rev. C.01, Gromacs, VASP 4.6.34* and *WIEN2k 08.2*. More details are reported here: http://wikis.ua.pt/flamingo/index.php. A web interface (WebMO) was also installed for control and execution of Gaussian runs and is located here: http://flamingo.ciceco.ua.pt/. The results from this effort start to arise in 2008, but several works with relevant contributions from computational chemistry – including polymorphism in molecular crystals, fatty acids behaviour, structure of cyclodextrin inclusion compounds, and water clusters in hybrid organic-inorganic framework – are currently submitted or in preparation.

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Calculations based on the Density functional theory (DFT) were carried out aiming at the understanding of the decomposition of azomethane catalyzed by Pt(111) after the consideration of three main elementary steps implying either the cleavage of N-N or C-N bonds. It was found that kinetics play a crucial role in the reaction and the most favored reaction path was suggested to be that leading to the least stable reaction products (anti-Brönsted-Evans-Polanyi). DFT was also used to study the reconstruction of a stepped Au(321) surface by deposition of oxygen atoms. Importantly, several thermodynamically planar configurations were found and suggested to act as examples of oxidized gold surfaces. The role of low coordinated Au atoms was also analyzed taking the CO oxidation as a test case.

DFT calculations combined with experimental thermochemistry were used to ascertain the stability of several species in the gas-phase, namely, indole and indoline, cyanobenzoic acids and methylbenzophenones. Furthermore, the strength of N-O bonds in derivatives of quinoxaline was also studied since they are used as a measure of their anti-tumor potential. DFT calculations were also used in the structural and energetic characterization of silicates in the gas-phase. Then, these calculations were used to tailor a potential for Molecular Dynamics (MD) simulations.

The performance of the M06 family of hybrid meta generalized gradient approximation DFTs was analyzed using the CO adsorption on MgO(001) as a case study. These methods were compared with other functionals and were found to be the first ones to provide a simultaneous satisfactory description of adsorbate geometry, vibrational frequency shift and adsorption energy. The importance of Car-Parrinello Molecular Dynamics simulations in the study of silicates in water was also tested.

The CPMD and Espresso codes were installed and tested aiming at the calculation of NMR shifts of solids for direct comparison with experimental data determined in our laboratory. An example of such studies is the calculation of the 1H NMR chemical shifts of NAH_2PO_4 with numbers that were found to be in excellent agreement with very-fast MAS experimental values.

Chemical Modification of Electrodes With Functional Materials. The electrochemistry of the immobilized hybrids was assessed, namely the redox reversibility and formal potentials as well as the effects of the solution pH on the overall behaviour. Layer-by-layer assembled electrodes were prepared on glassy carbon substrates using polyelectrolytes (mainly PEI) as builders. Some studies on the preparation of composite materials incorporating the polyoxotungstates and polymer/carbon-based mixtures, plus mineral oil/ionic liquid as homogenisers were also performed.

New Microporous Materials. Work on the synthesis of new microporous and related materials will continue. New organic templates and non-aqueous solvents will be carefully selected and used in this work. The modification of our previously innovated new materials in context of real applications will continue. The preparation of macrostructured microporous materials will be studied. The optimization of preparing faujasite, ZSM-5, AM-3 and MCM-48 membranes will also continue. New membranes, such as zeolite A, sodalite and stannosilicate AV-7 will be prepared. The applications of microporous materials to remove heavy metal in aqueous solution will continue.

New Hybrid Materials. Development of innovative organic-inorganic hybrids, such as di-ureasils modified by of zirconium (IV) n-propoxide (ZPO) stabilized with methacrylic acid (McOH) to produce new cost effective integrated optics devices. Emphasis will be given to UV patterning of optical power splitters, optical filters and couplers. The effect of the ZPO concentration on the emission mechanisms will be also evaluated via steady-state, time resolved emission and emission decay curves in the temperature range 12-300 K.

Design of new functional hybrids hierarchically ordered through self-assembled organization. The relationship between the local structure, the lanthanide ion concentration and the photoluminescence features will be addressed. Emphasis will be given to the combination of urea functionalities and 12-carbon alkyl chain, in the presence of a mixture of ethanol, water, amonium fluoride and variable amounts of europium chloride. The incorporation of organic aromatic ligands as spacers between the inorganic domains will be also studied. Enhancement of the photoluminescence efficiency and chemical stability under ultraviolet radiation exposure of lanthanide based tris-beta-diketonate complexes incorporated in organic-inorganic hybrids Aiming at preparing higher efficient and higher UV stable organic-inorganic hybrids, new lanthanide based complexes will be incorporated into innovative organic/inorganic hybrid matrixes. Different neutral ligands will be employed. The effective interaction between the lanthanide ions and the host hybrid structure, the emission overall quantum yield and the 5D0 quantum efficiency will be estimated and compared with those of the isolated complexes. A series of di-ureasils resulting from different organic precursors (jeffamines) co-doped with lanthanide (Ln=Nd, Sm, Dy, Er and Yb) complex and metal nanoparticles, such as Ag and Au, will be synthesized. The factors that affect the luminescence properties, such as the kind of the jeffamines, the concentration of Ln complex, the size of metal nanoparticles and their concentrations in the hybrid materials will be investigated. Hybrid materials derived from amino acids and alkoxides will be prepared using a sol-gel method. The influence of the reaction conditions (e.g. the amino acid and alkoxides, the ratio of functional groups, and the methods of preparation) on the network buildup and product properties will be studied and examined.

Mesoporous Materials. Mesoporous membranes with a cubic structure, based on MCM-48, will be prepared on alumina supports by hydrothermal synthesis, starting from sols having CTABr and TPAOH structure directing agents. The inclusion of a zeolite (MFI-type) precursor during membrane synthesis will lead to partial zeolite incorporation into the porous structure, hopfully giving rise to a hydrothermally stable membrane. Membranes will be tested in the gas phase separation of binary organic (cyclohexane, benzene and n-hexane)/O₂ mixtures.

Layered Materials. Building on previous work, a layered double hydroxide pillared by 2,2'-bipyridine-5,5'dicarboxylate (BDC) anions will be used to complex neutral $MoO_2(NCS)_2$ and $CuCl_2$ fragments, with the aim of preparing heterogenised complexes of the type $MoO_2(NCS)_2(BDC)$ and $Cu(BDC)Cl_2$. The resultant materials will be examined as heterogeneous catalysts for liquid-phase oxidations involving olefins, ethylbenzene, cyclohexane, and benzyl alcohol, using either dimethyl sulfoxide, hydrogen peroxide or tert-butyl hydroperoxide as oxidant. Carboxylate-intercalated (terephthalate, TA, and oxalate, ox) layered double hydroxides (LDHs) will be aged under a microwave-hydrothermal treatment. The influence of the nature of the interlayer anion during the ageing process will be studied.

Nanostructured Materials. We intend to direct the work regarding the manipulation of various nanocrystals (NC) at the surface of In-containing Nitride heterostructures towards the nano-bio interface. We would like to exploit this integration platform to test Plasmon coupling concepts and eventually develop lab-on-a-chip device concepts related to nanomedicine. We will also extend our work on the theoretical modelling of basic semiconductor material properties at the nanoscale. In particular work is in progress to model thermal conductivity and melting temperature in technologically relevant semiconductor nanomaterials, such as Si, Ge, and group III Nitride nanowires. We will also continue to apply and develop high-resolution X-ray diffraction methods to the characterization of a wide range of advanced material systems including GaN based materials, diamond and electroceramic materials. The work on ordered hybrid and doped nanostructures will be continued especially by targeting new nanostructured inorganic materials. As an example we will functionalize or coat with various metal oxides nanostructures (e.g. nanotubes, nanowires) for application in various timely fields such as energy storage, (photo)-catalysis and gas sensing. Advanced structural characterization techniques will be applied for a deep understanding of the structureproperties relation. By using this approach will be able to add new functionalities targeting the foreseen applications. Research on nanocomposites will be continued, using both synthetic and natural polymers. In particular we will focus on new multifunctional nanocomposites whose fillers are engineered inorganic nanoparticles that confer functionalities of interest for nanomedicine, biosensing and environmental remediation processes. The use of single molecule precursors to produce nanocomposites will be continued. In particular we would like to initiate the application of advanced characterization techniques to elucidate the type of interactions between nanophases deposited at the surface of diverse substrates.

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Research aiming to develop biosensors based on polymer based NC and the LbL technique will be developed. Work on the use of macroRAFT agents for surfactant free synthetic strategies and the preparation of nanobags will continue in order to prepare well controlled functional NCs which are stimuli responsive. The use of the grafting from approach (via ATRP) from the surface of luminescent SiO₂-coated Gd₂O₃:Eu³⁺ nanotubes will be investigated. Finally the use of the LB technique as a means to: 1) prepare Janus particles as well as aligned luminescent nanotubes and 2) to mimic membrane models will continue. A thorough training on thermal and mechanical analyses will start aiming at detailed characterisation of polymer based NCs. Work on functional mortars will be continued.

The aims of research in this topic are the preparation of novel lanthanide luminescent systems at the molecular or supramolecular level together with systems supported in a nanosized material. Research will be continued on the synthesis of photoactive lanthanide complexes with aromatic ambidentate ligands, exploring the possibility of formation of multidimensional coordination compounds. The ligands ability to sensitize the lanthanide emission will be particularly investigated. The incorporation of those lanthanide compounds into nanosized SiO₂ and other substrates will be explored.

Work will continue on fabrication, structural and morphological characterization of anisotropic ferroelectric, piezoelectric and quantum paraelectric perovskites nanostructures. Identification of the optimal processing conditions, thermodynamics and kinetics for the hydrothermal synthesis of each crystallographic phase in certain 1D morphology will go on. The detailed kinetic studies of the morphogenesis of anisotropic barium titanate structures under hydrothermal conditions using layered titanates with nanotubular morphology as titanium precursor and barium hydroxide as Ba²⁺ source will be finished. Attempts for the fabrication of barium titanate 1D nanostructure based on the use of carbon nanotubes (CNTs) will continue.

The studies on mesoporous functional perovskites will continue with the design of multifunctional multimetallic oxide thin films by sol-gel technique in the presence of block copolymer directing agents and will evolve towards the fabrication of composite thin films. Mesoporous ferroelectric thin films will be used as a host in order to get a multifunctional material. Simultaneously the structural and electrical characterization of these films will continue.

Non-Aqueous Chemistry Applied to Atomic Layer Deposition. Non-aqueous sol-gel approaches applied to the atomic layer deposition technique will be further investigated and new materials will be deposited on different substrates targeting application in the field of energy and environment. The development of multiferroic materials will be continued using the approaches developed in the last few years.

Polyoxometalates. Research will be continued on the preparation of new organic-inorganic hybrid coordination compounds containing lanthanides, POMs and an organic ligand. The effects of the organic ligand and the POMs on the luminescent properties will be investigated in particular, considering the possibility that they might act as sensitizers of the lanthanide luminescence. The application of the compounds in the preparation of POM based materials will be explored, namely by the preparation of mono or multilayered nanostructured films, incorporation into nanosized SiO₂ and preparation of polyoxometalate-anion-pillared layered double hydroxides. The synthesis and study of new hybrid compounds with polyoxometalates and organic aromatic moieties, either as cationic species (namely dyes) or incorporated in metal complexes, will be continued. The obtained compounds will be assessed for their electrochemical or optical properties. Studies on homogeneous and heterogeneous catalysis will be continued with new substrates. The studies on the preparation of supported transition metal-substituted polyoxotungstates, to be evaluated as oxidative heterogeneous catalysts, will be continued. The preparation and characterization of chemically modified electrodes with polyoxotungstates will be continued. New efforts will be directed to ITO electrodes, using the modification methods more successful in the studies with carbon electrodes, namely the layer-by-layer film deposition approach. The electrochemistry of the immobilized hybrids will be assessed, as well as their possible uses in electrocatalysis.

Crystal Engineering of Organic-Inorganic Hybrid Materials. Efforts on the synthesis and characterisation of novel multi-dimensional metal-organic frameworks will continue to be centred in the use of lanthanide cations. Polyphosphonic acid ligands such as (carboxymethyl)iminodi(methylphosphonic acid (H₅cmp) will be selected to self-assemble with lanthanide cations under typical hydrothermal conditions. As in previous investigations, micro-crystalline powders are expected to be isolated. The structure of these materials will be elucidated from a combination of high-resolution powder X-ray diffraction data (collected from a synchrotron source at the ESRF in Grenoble, France) with solid-state NMR data, TGA, SEM, EDS, FT-IR and FT-Raman and elemental composition (CHN and metal content from ICP analysis) studies. Some compounds have already been preliminary identified such as [Ln(H₂cmp)]•xH₂O [x < 1; Ln³⁺ = Nd³⁺ and Eu³⁺] and [RE(H₂cmp)(H₂O)] [RE³⁺ = Y³⁺, La³⁺, Pr³⁺, Nd³⁺, Sm³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Dy³⁺, Ho³⁺ and Er³⁺].

The coordination flexibility of 2,5-pyridinedicarboxylic acid (H₂pydc) with lanthanide centres will continue to be explored under both hydrothermal and solvothermal synthetic conditions. Recent results show that this system readily crystallises as large single-crystals with the resulting materials being amenable to full structural elucidation from single-crystal X-ray diffraction. Initial results evidence the formation of the 3D networks $(CH_3)_2NH_2[Ln(pydc)_2]^{\bullet}/_2H_2O$ [Ln3+ = Eu3+ or Er3+], [Er₄(OH)₄(pydc)₄(H₂O)₃] •H₂O and [PrIII₂PrIV_{1.25}O(OH)₃(pydc)₃]. The use of microwave irradiation will be attempted for photoluminescent systems with residues of H2pydc with the final objectives to significantly reduce the reaction times, improve yields, control crystal morphology and reduce the amount of chemical residues from the synthesis.

Crystalline (Hbipy)₂[Ge(C₂O₄)₃] and (Hphen)₂[Ge(C₂O₄)₃]•2(H₂O) [Hbipy⁺ is the 2,2'-bipyridinium cation (C₁₀H₉N₂), and Hphen+ is the 1,10'-phenathrolinium cation (C₁₂H₉N₂)] will be prepared using hydrothermal syntheses and their structures and hydrogen-bond networks elucidated by single-crystal XRD and other techniques.

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C60 Phase Transitions Under High-Pressure. C60-compressed samples display complex diffraction patterns (multi-phase, twinning, etc), for which the traditional diffraction techniques do not give a complete structural characterization and structure determination. To overcome this difficulty, a newly developed technique, X-ray diffraction tomography, will be employed to characterize the C60-pressurized samples. In this way, a proposal was submitted to the E.S.R.F., which is already accepted. Very recently, computational simulations performed by different teams gave new results on carbon clathrates structures. We intend to initiate collaboration with one of those teams in order to clarify, through a joint theoretical-experimental effort, the structures of the different carbon clathrate phases.

Development of Spectroscopic and Electron Microscopy Techniques. Development and implementation of a set of tools for the advanced characterization of nanostructured materials based on analytical TEM with a special focus on electron energy loss spectroscopy and the simulation and interpretation of spectra via density-functional-theory based calculations of the electronic structure. The toolbox will be developed and adapted for the JEOL 2200FS TEM with the goal to use the instrument at its full analytical power. Three classes of suitable nanostructured composite materials have been chosen as benchmark systems:

-Core-shell hybrid nanoparticles

-Metal oxide thin films on high surface area supports

-Metal nanoparticles supported on graphene sheets

We shall focus on methodological developments suitable for ultra-fast (up to 70 kHz) ¹H NMR MAS combined with CRAMPS. We will design high-resolution multi-dimensional ¹H-¹H DQ recoupling and ¹H-X (X=¹⁹F, ¹³C, ²³Na,...) HETCOR NMR experiments suitable for the ultra-fast MAS rates now available. Work will be carried out in CICECO and on the 800 MHz facility of the national NMR network (ITQB, Lisbon).

The potential of SERS (Surface-Enhanced Raman Scattering) in the study of the interaction of metal nanocrystals with molecular adsorbates will be continued, in particular for the investigation of adsorption modes and orientation of molecules on the surfaces, with relevance in heterogeneous catalysis and nanoparticle assembly studies. Studies will also be continued on the use of SERS for trace detection. The development of new SERS substrates will also be investigated.

Cyclodextrins. A new SANS experiment at Laboratoire Léon Brillouin (CEA/Saclay, France) is scheduled for 2009, to clarify the interaction between methylated and unsubstituted cyclodextrins with AOT reverse micelles.

Oxomolybdenum Catalysts. Work will continue on the synthesis of new and improved oxomolybdenum(VI) catalysts for oxidation reactions such as the epoxidation of olefins and sulfoxidation. Complexes of the type $[MoO_2Cl_2(L)_2]$ (L = N,N-dialkylamide), $[MoO_2Cl(L)][X]$ (L = tridentate tris(benzimidazolyl) ligand) and [MoO2(L)] (L = tetradentate bis(oxazoline) ligand) will be studied. The cyclopentadienyl dicarbonyl complexes Cp'Mo($\eta^{3-}C_{3}H_{5}$)(CO)₂ (Cp' = e.g. $\eta^{5-}C_{5}H_{4}Me$) will also be prepared and examined as convenient precursors to catalytically active organometallic oxides.

Computer Aided Characterization of Materials and Properties. The research already pursued on this subject will acquire an increased importance within the general activities of line 1. Particular attention will be given to the description of materials from combining computational modelling with spectroscopic and diffraction techniques. The development and optimization of new methodologies for the study of molecular crystals at ab initio level and their further extension to functional materials and hybrids are two main goals proposed for this subject. Contacts with groups with expertise in the computational approach to problems such as SERS effect and rare-earth luminescence quantum yield are widening our modeling skills – and improving the links between the computational bench and the conventional laboratory bench.

DFT calculations on the reactions of inorganic and organic species at gold surfaces. A study of the N-O bond dissociation of NO on clean or H-covered Au surfaces was recently sent for publication where it is shown that the presence of H adatoms lowers the energy required for N-O bond scission by up to 7 times. The comparison of the water gas shift reaction catalyzed on planar and stepped copper surfaces is in progress. The adsorption of small gases in the channels of periodic materials will be also studied since it is essential for the understanding of some experimental results obtained in our laboratory.

DFT and MD calculations will be performed for a better understanding of the initial stages of the synthesis process of periodic mesoporous silica. The DFT calculations will extend previous work that will now include explicit solvent and individual template molecules. The collective interactions involving silicates, templates and solvent will be studied by MD. These two types of calculations will offer the possibility of developing a kinetic Monte Carlo model that is able to describe silica condensation, hydrolysis and deprotonation in porous silica synthesis solutions. Computational thermochemistry used to complement experimental determinations and to ascertain the gas-phase stability of sulfur containing compounds. Data for these compounds is lacking in the literature. This kind calculations will be also extended to small portions of periodic materials such as chitosan.

DFT calculations will be used for the calculation of NMR chemical shifts of solids. These results will be used in the interpretation of experimental NMR data.

future research

general aims

design, to prepare and characterise novel inorganic and organic-inorganic hybrid, functional and multifunctional materials ans nanostructures, of different (0-3D) dimensionality, for communications technologies (optical and magnetic properties), catalysis and (new areas) biological and environmental applications

develop solid-state NMR methods (1H and quadrupolar nuclei) and apply at the highest level the following characterisation techniques: photolumiescence, vibrational and X-Ray absorption spectroscopies, signlecrystal and powder XRD, and TEM

develop SMARTER (Structure Elucidation by Combining Magnetic Resonance, Computational Modelling and Differactions) approaches to materials

future research

specific aims

Inorganic Materials

design and prepare novel oxide-based materials and nanostructures, particularly dense, microporous and layered silicates and phosphates, and polyoxometalates of transitions-metals (TM) and lanthanides (Ln), via hydrothermal and sol-gel methods. To process these materials in the form of powders, membranes and films (including thin films by atomic layer deposition) characterise their structures and explor applications in photoluminescence, magnetism and catalysis

Organic-Inorganic Hybrids

design and prepare by aqueous and non-aqueous sol-gel routes amorphous and crystalline organic-inorganic hybrids, particularly amine- and amidebased ormosils (organically-modified silicates) doped with TM and Ln. To process these materials in the form of powders, membranes and films, characterise their structures and explore applications in lighting (phosphors), integrated optics (planar waveguides, diffraction gratings), and magnetism

design and prepare by hydrothermal and solvothermal (including microwave) routes crystalline metal organic (carboxylates, aminoacids, phosphonates, fluorinated ligands) frameworks of TM and Ln. To explore applications in photoluminescence and magnetism. To prepare oriented films nanoparticles.

explore the host-guest chemistry of ordered mesoporous silicas, layered metal hydroxides and cyclodextrines, derivatised/ intercalated with TM and Ln complexes, and organic molecules. To explore applications in optics, magnetism, catalysis and medicine (e.g. CO-release)

investigate polymer-based composites containing surface derivatised inorganic nanoparticles and to assess their optical, magnetic and thermal properties. To develop biofunctionalised nanocomposites based on natural and synthetic polymers for in vitro clinical diagnosis (SERS bioanalytes detection, MRI and optical bio-tagging of cell)
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nanobelts



books chapters

2 electroceramics

scientific highlights

Applications of scanning probe microscopy: i) first observation of local symmetry breaking in macroscopically symmetric materials

ii) observation of abnormal (agains the applied electric field) domain switching in $Pb(Zr_XTi_{1-x})O_3$ attributed to the charge compensation effect at the boundaries of the grain with rhombohedral structure and

iii) observation of intense THz emission from PZT nanotubes arrays, wich was totally absent in flat films or bulk, and these results have a great potential as effective THz emitters are indispensable for the materials characterization and security checks

Nanoscale and nanostructured materials:

i) synthesis of well crystallised meso-structured BaTiO₃ via a simple sol-precipitation process

ii) identification of the factors controlling the anisotropic growth of barium titanate crystals under hydrothermal conditions when using layered titanates with nanotube morphology as Ti precursor

Incipient ferroelectrics:

first observation of a 'multiglass' scenario of two different glassy states in Sr_{0.98} Mn $_{0.02}$ TiO₃ ceramics. It was proposed that due to a strong spin-phonon interaction within the incipient ferroelectric host crystals SrTiO₃, large higher order magnetoelectric coupling occurs between both glass systems



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Ferroelectric films:

i) development of a new method, based on a commercially available fotonic sensors, for measurments of electric field-induced displacements in cylindrical geometry optical fiber covered with piezoelectric film

ii) optimization of the dielectric response of 0,37BiScO₃-0,63PbTiO₃ thin films; in particular, the remarkable low Ec of ~33kV/cm of these films adds value to the potential application of BiScO₃-PbTiO₃ films in high temperature ferroelectric memories



bulk resonators

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Microwave Dielectric Materials. The crystal structures of the perovskites $La_{1/3}NbO_3$ and $La_{1/3}3TaO_3$ were studied between 10 and 350 K using high-resolution neutron powder diffraction and compared with their radio-frequency dielectric response over the same temperature range. The structure of $La_{1/3}NbO_3$ remains orthorhombic *Cmmm*, while $La_{1/3}TaO_3$ undergoes continuous transition from the high-temperature tetragonal P4/*mmm* to *Cmmm* phase at about 220 K. This transition is tricritical in nature and accompanied by no dielectric anomaly. In $La_{1/3}NbO_3$, the frequency-dependent peak of the dielectric permittivity is associated with an atypical increase of the lattice parameters below about 80 K.

The temperature variation of the dielectric permittivity and loss of the solid solutions (1-x)La(Mg_{1/2}Ti_{1/2})O₃xBi(Mg_{1/2}Ti_{1/2})O₃ [(1-x)LMT-xBMT] (0<=x<=0.3) measured at radio, microwave and far infrared frequency ranges has been analyzed in comparison with that observed in other bismuth-containing and bismuth-free perovskite ceramics based on LMT. It has been found that the low temperature dielectric response of the (1-x)LMT-xBMT compositions with x>=0.1 is frequency-dependent over a wide range from radio- to microwave frequencies. The considerable compositional growth dependence of the dielectric permittivity and loss associated with amount of bismuth in the system was not dependent on the lattice polar phonon modes. The effect was suggested to be relate to the low temperature dielectric relaxation process due to a hopping movement of charge carriers in crystallographic A-sites of the perovskite lattice. Particular role of local lattice distortions caused by the anisotropic chemical bonds involving bismuth 6s²-electrons in a localization of hopping charge carriers in perovskites and other oxygen-octahedral compositions is considered. The characteristic features of the Bi-induced dielectric other oxygen-octanedral compositions is considered. The characteristic relatives of the bi-induced dielectric relaxation and those typical of the ferroelectric relaxors are compared and discussed. The crystal structure and phase transition in the perovskite La($Mg_{1/2}Ti_{1/2}$)O₃ (LMT) have been investigated using high-resolution neutron powder diffraction in the temperature range 60-1414 K. Between 1246 and 1310 K LMT undergoes the monoclinic-to-rhombohedral (P2_{1/n} – R3) crossover required by Landau theory to be a first-order. The temperature dependences of the unit cell parameters and the octahedral tilt angles suggest a discontinuous phase transition. Specific variations of both the metal-oxygen bond lengths and the octahedra volume in LMT are correlated with the dielectric anomalies observed at the same temperature ranges. The uncommon dielectric correlated with the dielectric anomalies observed at the same temperature ranges. The uncommon dielectric behaviour in the vicinity of room temperature has been interpreted in terms of deformations of the TiO₆ octahedra, which change their polarizability and thereby contribute to the dielectric response of LMT. It is suggested that in spite of a generally negligible effect, such a contribution to the relative permittivity can occur in compositions containing oxygen octahedra as structural elements.

The dielectric properties of the solid solutions $(1-x)(Na_{1/2}Bi_{1/2})TiO_3-xLa(Mg_{1/2}Ti_{1/2})O_3$ (0<=x<=0.4) have been studied over the temperature range 650-1030 K by measuring their impedance spectra at the frequency range of 25-10⁶ Hz. Specifically, the Curie temperature of the solid solutions was determined as a function of their composition. The temperature dependences of both the dc component and the polarization component of the conductivity were estimated. Observed variations in the dielectric parameters were analyzed and associated with the structure phase transitions and phase coexistence in these (Na_{1/2}Bi_{1/2})TiO_3 - based solid solutions. An alternative approach to tailor TC_Er of high Q dielectric BaO–Re₂O₃–TiO₂ (Re – rare earth elements) thick films was presented. 10 to 80 µm thick BaNd₂Ti₅O₁₄ (BNT) films were fabricated by electrophoretic deposition on Pt foils under different processing conditions. The observed anisotropic grain growth is facilitated by the constrained sintering. The increase of the sintering temperature increases markedly the aspect ratio of the grains, decreases the dielectric permittivity and TC_Er changes from -114 to +12 ppm/°C. By controlling the sintering temperature, near – zero TC_Er, high Q thick films can be fabricated with 45< ϵ r<70. These findings are of technological relevance since they demonstrate that control of substrate constraint and sintering conditions can be used to control grain anisotropy and thus microwave properties of the BaO-Re₂O₃-TiO₂. The thick films facilitate scaling to small device sizes for high frequency operation. Similar observations are expected in other MW systems thus opening further technological opportunities.

Ferroelectric Ceramics. Textured $SrBi_2Ta_2O_9$ (SBT) ceramics were fabricated via templated grain growth (TGG) technique using platelet-like SBT single crystal templates. The templates (5 wt%) were embedded in a fine-grain SBT powder matrix containing 3 wt% of Bi_2O_3 excess that were subjected to uniaxial pressing and sintering at 1000–1250 °C for up to 24 h. Microstructural characterization by SEM was performed to establish the effect of sintering parameters on the grain growth and texture development. It was found that the ceramics developed a bimodal microstructure dominated by a large number of big anisometric grains at the final stage of the TGG process. A fast increase in the volume fraction of large anisometric grains was observed after 2 h of sintering time at 1250 °C. The time evolution of the microstructure revealed that the number of large anisometric grains at the late stage of the TGG process is almost four times greater than that at the early stage. Therefore, new large anisometric grains appear in the matrix acquiring similar platelet-like morphology and alignment as the original seeds. It was suggested that the aligned templates induced the alignment of the small matrix grains showing a face-to-face contact, which bonded to each other to form new large anisometric grains. $CaCu_3Ti_4O_{12}$ ceramics with high dielectric constant (2-4 x 10⁴) and low loss (0.04) has been prepared by the sol-gel process and sintered at different temperatures and times. The influence of sintering time on the values of the dielectric constant and nonlinear coefficient of ceramics has been studied towards tailor dielectric constant and nonlinear coefficient.

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Ferroelectric Fibers, Single Crystals and Films. The development of a new method for measurements of electric field-induced displacements in a cylindrical geometry optical fiber with the deposited piezoelectric film was developed. The measurement setup is based on a commercially available Fotonic Sensor MTI 2000 MTI Inc. Major disadvantages of measurement by standard techniques e.g., interferometry such as low reflectivity, high roughness of the coating resulting in poor fringe quality, and big displacement range are successfully avoided using a special configuration of an optical probe and a sample. The method allows performing investigations of electromechanically induced vibrations in a broad frequency range from 0 up to 150 kHz and various combinations of ac and dc voltages. The capabilities of the proposed method are validated by strain measurements of an optical fiber cantilever beam covered by PbZrTiO₃ thick film.

 $Bi_{3,25}La_{0,75}5T_3O_{12}$ ferroelectric thin films were prepared and characterized. The synthesis was by sol-gel using a solvent alternative to the highly toxic 2-methoxyethanol. Pyrochlore-free thin films were obtained at 500-700°C. The ferroelectric behaviour and the dielectric loss and constant of the films increase with increasing annealing temperature. The substitution of 2-methoxyethanol by another solvent does not affect the electrical properties of BLT thin films.

Dielectric/ferroelectric properties of morphotropic phase boundary (MPB) $0.37BiScO_3-0.63PbTiO_3$ thin films with a PbTiO_3 seed-layer deposited on platinized silicon substrates by sol-gel were examined. Room temperature dielectric constant of >1600 and dielectric loss of 0.02 were achieved (100 Hz). A well-defined hysteresis loop was observed with a Pr of ~23µC/cm². In particular, the remarkable low *Ec* of ~33kV/cm of these films adds value to the potential application of BiScO₃-PbTiO₃ films in high temperature ferroelectric memories. The influence of PbTiO₃ seed-layer on the electric properties and the relation with the phase formation process, crystallinity and microstructure of the films was established.

The study of the alteration of sintering PZT thick films on Cu foil by using of different sintering aids and in inert atmosphere has been continued. PZT thick films on copper foils were deposited by EPD. Microstructural studies revealed that PZT film with 1wt% of sintering aids (PbO+V₂O₅) and sintered at 850°C exhibit a sharp interface, dense microstructure and good piezoelectric response, suitable for applications as embedded components.

Incipient Ferroelectrics. The incorporation of chromium on the strontium site of the perovskite lattice of $SrTiO_3$ ceramics and its influence on the structural, microstructural and low-frequency dielectric properties was studied. Dense $Sr_{1-1.5x}Cr_xTiO_3$ (x = 0, 0.0005, 0.0010, 0.0015) ceramics were prepared from powders obtained by a solgel method. The lattice parameter ~3.906 Å and average grain size ~2.5 µm is almost identical for all the ceramics under study. On the other hand, the dielectric constant increases from circa 7000 for x = 0 to >16000 for x = 0.0005. Detailed investigations of the low-temperature dielectric properties showed that small contents of Cr into Sr site result also in a remarkable increase of the nonlinearity of the dielectric constant as a function of dc bias field and a significant enhancement of the tunability of the dielectric constant, but does not induce a ferroelectric or relaxor-like behavior in strontium titanate. These results imply that the incorporation of small amounts of Cr into the Sr site expands the use of ST based materials for possible tunable application at cryogenic temperatures. The studies on the magnetoelectric properties of SrTiO₃ doped ceramics revealed that when replacing Sr²⁺ ions in SrTiO₃ by a small amount of magnetic Mn²⁺ ions, two processes are activated at low temperatures. On one hand, the Mn²⁺ ions take the role of electric and elastic pseudospins and undergo a transition into a polar 6-state Potts glass. On the other hand, the S 1/4 5=2 spins, being attached to the Mn²⁺ ions, couple via frustrated antiferromagnetic super- exchange, reinforced by ME two-spin-pseudospin inter- action. They freeze into a spin glass state after the polar degrees of freedom come to rest below T eg 1/4 38 K. Both glassy phases are independently evidenced by their specific memory effects. Strong ME coupling via both the generic "magnetocapacitive" E2 H2 and the probably spurious 'paramagnetoelectric' EH2 effects manifests the importance of quantum fluct

The structure-property relations of Mg doped $SrTiO_3$ (ST) sol-gel thin films deposited on Pt/TiO₂/SiO₂/Si substrates were investigated in order to determine the effect that Mg dopants have on the dielectric properties of $SrTiO_3$ thin films. For $Sr_{1-x}Mg_xTiO_3$ (SMT) (x <= 0.30) films annealed at 750 °C all Mg ions were accommodated in the perovskite lattice and for SMT films annealed at 900 °C, the solubility limit of Mg was x = 0.10, above which a Mg rich ilmenite second phase was observed. Irrespective of the higher solid solubility limit of Mg in the ST lattice for sol gel ST films compared to equivalent ceramics, no ferroelectric or relaxor phase transition was observed, refuting the reported predictions.

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Nanoscale Properties of Ferroelectrics and Related Materials. The observation of abnormal (against the applied electric field) domain switching in $Pb(Zr_xTi_{1-x})O_3$ (PZT) films by piezoresponse force microscopy was reported. It was shown that in some grains polarization orients opposite to the external field in the presence of the applied field while the rest of the film volume switches in a normal way. This effect was observed in thin film capacitors, which excludes charge injection effect and spontaneous backswitching due the built-in field as possible reasons for this behaviour. The abnormal switching behaviour was then attributed to the charge compensation effect at the boundaries of the grains with rhombohedral structure.

An intense THz emission from PZT nanotube arrays was observed, which was totally absent in flat films or bulk. THz radiation is emitted within 0.2 ps, and the spectrum exhibits a broad peak from 2 to 8 THz. This is a gap in the frequency spectrum of semiconductor THz devices, such as ZnTe and an order of magnitude higher frequency peak than that in the well-studied p-InAs. The results have a great potential as effective THz emitters are indispensable for the materials characterization and security checks. The results are the joint work within EU project "Multiceral" coordinated by CICECO.

Bias-induced phase transitions underpin a wide range of applications ranging from data storage to energy generation and conversion. The mechanisms behind these transitions are extremely sensitive to local defects that act as centers for local transformations or pinning. Using ferroelectrics as an example, we reviewed methods for probing bias-induced phase transitions in the range of materials and discuss the current limitations and challenges for extending the methods to other fields.

Pure SrTiO₃ ceramics were studied by PFM. Piezoelectric contrast observed on polished surfaces in both vertical and lateral modes was attested to the surface piezoelectricity due to flexoelectric effect (strain gradient-induced polarization) caused by the surface relaxation. The observed enhancement of piezoresponse signal at the grain boundaries was explained by the dipole moments associated with inhomogeneous distribution of oxygen vacancies. This is the first observation of local symmetry breaking in macroscopically symmetric material. Graded PZT films with Zr% varied across the thickness direction were deposited on Si substrates by sol-gel. The up- and down-graded PZT films exhibited perovskite polycrystalline structure and shifted hysteresis. Good dielectric and ferroelectric properties as well as the low-temperature processing suggested that the compositionally graded PZT films are promising for memory and MEMS applications.

Piezoelectric and electrostrictive sensors and actuators are very important for the applications, especially due to automobile production, active vibration damping, navigation systems, and medical imaging. In our contribution to the book "Smart Materials#, we overviewed the principles of piezoelectric and electrostrictive transducers along with the properties of the most useful materials and examples of successful devices. The possibility of inducing a polarization state in PLZT relaxor ceramics under exposure to external electric fields and intensive light illumination at room temperature was demonstrated. Such polarization state was studied by pyroelectric technique It was established that a fairly stable polarization state can also be created in PLZTceramics when studying it by PFM. In the latter case, hysteresis loops of a local piezoelectric response demonstrated bias-induced phase transition.

Multifunctional Ceramic Films and Composites. Room-temperature crystal structure, local ferroelectric, and magnetic properties wer studied in BiFeO₃ doped with Gd. A sequence of the composition-driven structural phase transitions $R_{3c} \rightarrow Pn_{21\alpha}$ and $Pn_{21\alpha} \rightarrow Pnm\alpha$ was revealed. Gd substitution has been shown to effectively induce the appearance of the spontaneous magnetization, thus indicating a promising way for improving multiferroic properties of antiferromagnetic BiFeO₃.

The effect of heterovalent Ca, Sr, Pb, and Ba substitution on the crystal structure, dielectric, local ferroelectric, and magnetic properties of the BiFeO₃ was studied. It was shown that the crystal structure of the compounds is described within the space group R3c, permitting the spontaneous polarization whose existence was confirmed by the PFM. Experimental results suggested that the increase in the radius of doping ion leads to the effective suppression of the spiral spin structure of BiFeO₃.

suppression of the spiral spin structure of BiFeO₃. Ni₂MnGa films were deposited onto Si(100) substrates and LaNiO₃/PZT ferroelectric buffer layer. The prepared samples were characterized using conventional XRD, SQUID and EDS from SEM observations. Optimized films deposited under high radio frequency (RF) power and low Ar pressure presented good surface quality and high textured phase crystallization. This low temperature process appears to be very promising, allowing separated control of the functional layers' properties, while trying to achieve high electromagnetoelastic coupling.

Polarization-Induced Self-assembly of Organic and Biomolecules. Computer simulations in P(VDF-TrFE) using quantum-chemical methods were performed. The simulated data were calculated for different copolymer contents. The PFM measurements of the local hysteresis loop (at fixed tip position) of the LB samples demonstrated clear ferroelectric switching. The molecular dynamic simulation performed by HyperChem 7.52 tool for the molecular model of 4 free polymer chains slab provides very fast rotation (relaxation) time 0.4 ps. The analysis show that this model is most close to thick LB films, while in thin LB films the strong electrostatic-dipole interaction with substrate must be taken into account.

Ferroelectric properties of the PVDF/TrFE – phospholipid composite films were studied. The surface roughness and thickness of the films are verified by AFM. The films show first order ferroelectric-paraelectric phase transition, capacitance-voltage hysteresis and dielectric hysteresis loops that are similar to ones of PVDF/TrFE. The composites, in contrast to pure PVDF/TrFE films, are highly leaky and their polarization switching curves, such as capacitance-voltage and polarization-voltage are shifted due to the presence of inhomogeneous internal local electric fields.

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Microwave Dielectric Materials. The work on the preparation of tungsten bronzoids thick dielectric films by EPD for MW applications will include the following aspects: i) preparation of BaO-Ln₂O₃-TiO₂ (Ln = Nd, La) composite thick films; ii) continuation of the investigation of the effect of different solvents on the EPD these thick films; iii) constrained sintering studies of BaO-Ln₂O₃-TiO₂ (Ln = Nd, La) and iv) continuation of the assessment of the dielectric properties of some of these thick films at MW frequencies.

The requirement for low sintering temperature is particular important for low-temperature-cofired-ceramics (LTCC) and base-metal electrode multilayer ceramic capacitors (BME-MLCCs) applications. Titanium tellurite, TiTe₃O₈ ceramics and films will be studied in terms of fabrication and dielectric property characterization. TiTe₃O₈ thick films will be fabricated by electrophoretic deposition (EPD) on Si platinised substrates using TiTe₃O₈ powders synthesized by a conventional solid-state-reaction. The permittivity of TiTe₃O₈ films at different frequency and the temperature coefficients of permittivity of TiTe₃O₈ films will be studied.

temperature coefficients of permittivity of TiTe₃O₈ films will be studied. Systematic studies on the effect of doping MgTiO₃ thin films with isovalent cations, Ni²⁺and Zn²⁺ will be undertaken. A sol gel based wet-chemical synthesis will be used. The modification of Ni²⁺ and Zn²⁺ doping on the crystal structure, microstructure, and RF dielectric properties of sol gel derived MgTiO₃ films will be discussed.

Ferroelectric Ceramics and Ferroelectric Fibers, Single Crystals and Films. The study of the alteration of sintering EPD PZT thick films on Cu foil by using of different sintering aids and in inert atmosphere will be continued. Based on previous results the sintering aids composition will be optimised. The optimum EPD conditions will be established. The role of the sintering aids on the microstructure development and electrical properties of PZT thick film will be evaluated.

Pb(Zr_{0.53}Ti_{0.47})O₃ PZT (53/47) fibers will be prepared using acrylic (C₃H₄O₂) acid to acidify the sol-gel precursors. The structure of the precursors, pyrolysis and crystallization behavior, and microstructure of the obtained PZT fibers will be studied and compared with the characteristics of fibers prepared with methacrylic (C₄H₆O₂) acid. The effect of the type and content of organic acid on the length and strength of the PZT fibers will be discussed. Studies on the preparation and properties of Aurivillius oxides with n>=5 will continue. Starting with Sr- and Cabased compositions, the required Bi contents and heat treatment conditions for obtaining dense and single phase ceramics will be exploited. Electrical characterization studies for establishing the ferroelectric properties of the obtained ceramics will be carried out. The compositions having the best schedule of properties will be selected as targets for thin films preparation.

Other topics include the preparation of: Bi-layered perovskites (BLP) thin films by sol-gel and physical deposition techniques; targets by conventional oxides route; stable sols for sol-gel deposition of thin films; crystalline BLP thin films at low temperature with optimized ferroelectric characteristics.

The study on high Curie temperature relaxor $BiScO_3$ -PbTiO_3 (BSPT) thin films will be continued. Morphotropic Phase Boundary 0.37BiScO_3-0.63PbTiO_3 films (here abbreviated as BSPT) will be fabricated by sol-gel on $IrO_2/TiO_2/SiO_2/Si$ substrates and the influence of IrO_2 electrodes on the dielectric/ferroelectric properties and leakage current behaviour will be assessed. Particular attention will be paid to the interface between the film and the electrode.

Fatigue endurance studies in ferroelectric systems, such as BSPT and PZT thin films will be conducted. The preparation and characterization of $Ba_xSr_{1-x}TiO_3$ thin films on commercial flexible polymeric substrate "Kapton" via a short-time hydrothermal process will be aimed. The morphology, stoichiometry and electric properties of $Ba_xSr_{1-x}TiO_3$ films grown by hydrothermal synthesis on Kapton will be investigated and discussed. Assessment of polar domains in the annealed hydrothermal BaTiO₃ films will be conducted.

 $CaCu_3Ti_4O_{12}$ thin films will be prepared on various substrates by chemical solution deposition method. Deionized water, 1,2-propanediol as different solvents will be used for aqueous and non-aqueous precursors, respectively. The influence of the solvents on the phase composition, microstructure, dielectric and nonlinear properties of CCTO thin films will be analyzed and discussed.

Incipient Ferroelectrics. The work within incipient ferroelectric ceramics will continue along the following lines: Potassium tantalate single crystals will be grown by a modified flux growth method. Small amounts of B_2O_3 will be used in the K_2CO_3 flux mixture. The processing conditions will be optimized to obtain large and high quality single crystals and decrease the growth temperature. The evaluation of the grown crystal structure will be performed by X-ray diffraction analysis (XRD). Preliminary dielectric characterization will be conducted. The effect of nonstoichiometry on the densification of SrTiO₃ ceramics with Sr/Ti ratios from 0.997 to 1.02 will be systematically addressed. The densification kinetics will be investigated and analyzed to access the effects of the nonstoichiometry on the mass transport mechanisms. The dielectric response of nonstoichiometric ST will be analyzed by impedance spectroscopy to separate the contributions of bulk and grain boundaries from the overall dielectric response of the material. Complex impedance measurements will be performed in a selected range of temperature and complemented with electron microscopy (SEM) and (TEM) to clarify the role of nonstoichiometry on the simultaneously alterations of the microstructure, grain boundary structure and dielectric response of ST ceramics.

Continuation of the preparation by RF magnetron sputtering thin films based on KTM (1-x)-(KTaO₃)-x(MTaO₃) systems.

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Nanoscale Properties of Ferroelectrics and Related Materials. During the year 2009 the investigations of the local properties of ferroelectric thin films, single crystals and ceramics will be extended into macroscopically non-ferroelectric materials like SrTiO₃ and ZnO. Symmetry breaking and local dipole moments that influence macroscopic properties will be studied. In addition, the research will be continued on lead-free materials (KNN), and nanostructures (multilayers, nanotubes, nanorods, nanocrystals) based on multiferroics (e.g., BiFeO₃) and ferroelectrics (PZT, KNN). Domains will be studied in terms of their stability as a function of time and temperature. These studies should reveal the local switching mechanism and local coercive field. The programs will be modified, so that to study local relaxation, local butterfly hysteresis and measurements in the resonance. Studies on ferroelectric relaxors will be extended into the pure PMN and PMN where a surface phase transition has been recently observed by PFM. Also, lead-free and artificial relaxors will be studied such as BFO/BTO and PMN/PT based on multilayers. The comparison with the results of macroscopic measurements will reveal valuable information on the nature of relaxor state and giant piezoelectric effect recently observed in solid solutions. This will be translated into the giant magnetoelectric predicted by calculations.

Multifunctional Ceramic Films and Composites. BiFeO₃ nanotubes will be studied to reveal their usefulness for the demonstration of giant magnetoelectric effect.

In terms of multiferroic materials the incorporation of components with ferroelectric and magnetic properties, such as $Pb(Fe_{0.5}Nb_{0.5})O_3$ or BiFeO₃ with PZT and the formation of composites may represent a real potential for applications based on the Magnetoelectric effect. These composite thick films will be prepared by an hybrid solgel process on platinised and iridium oxide silicon substrates. PZT precursor solutions will be prepared by solgel. $Pb(Fe_{0.5}Nb_{0.5})O_3$ or BiFeO₃ powders will be synthesized by mechano-chemical synthesis or conventional solid state method. Novel composites such as PZN-PT/PFN will be sintered and investigated. Novel composite thick film materials (Ni_3FeO_4/PZT) will be fabricated by using hybrid sol-gel method.

Polarization-Induced Self-Assembly of Organic and Biomolecules. Polarization-induced assembly will be studied in phospho- and glycolipids. The switching and recognition phenomena related with the dynamics of ferroelectric domains (lipid-PVDF) during application of external electric field will be also investigated.

Materials for Piezoelectric Harvesting. Mechanical energy can be converted into electrical energy using piezoelectric, electromagnetic or electrostatic mechanism. Piezoelectric transducers are the most suitable because the efficiency can be very high and there are no moving parts. We will explore the possibility of preparation and integration of several ferroelectric materials (including lead-free) into viable devices capable to collect vibrational energy in remote locations and charge batteries for various sensors.

future research

general aims

fabricate optimized new electroceramics for dielectric, piezoelectric, ferroelectric and multiferroic applications

develop high quality materials for compatible integration at low costs and low temperatures

understand nanosize effects and nanotechnology aspects of electroceramics

develop scanning probe microscopy (SPM): piezo force, scanning capacitance and spreading resistance microscopies

use at the highest level electrical and structural characterization tools (impedance spectroscopy, piezo- ferroelectric analysis, high resolution electron microscopy. Raman spectroscopy)

future research

specific aims

microwaves materials:

fabricate thick films by Electrophoretic Deposition for MW applications, namely BaO-Re $_2O_3$ -TiO $_2$ bronzoids, on conducting/ non conducting substrates; investigations of EPD processing variables and assessment of dielectric properties at MW

fabricate thin dielectric multistructures, namely TiO_2 based (SrTiO_3, CaTiO_3 and MgTiO_3) by chemical solution deposition and rf sputtering for MW applications; to characterize structure-microstructure-properties and exploit thermostable applications at MW

ferroelectric, incipient ferroelectric and piezoelectric materials and composites

prepare/ characterize high Tc $xBiScO_3 - (1-x) PbTiO_3$ (BS-PT) thin films by sol gel and rf sputtering. To study BS-PT films reliability characteristics (fatigue, endurance, leakage) on different substrates towards piezo- and ferroelectric applications at high temperatures (e.g. automobiles)

modify sintering behaviour of PZT thick-films on Cu foils by using alternative approaches (sol infiltration and core shell particles). To assess microstructure and electrical properties of PZT thick capacitors for embedded applications

prepare $CaCu_3Ti_4O_{12}$ (CCTO) ceramics and films with high dielectric constant and low loss by the sol-gel for high dielectric permittivity applications

nanoscale and nanostructured materials

polarization-induced assembly in selected phosphor- and glycolipids materials. Characterization by macroscopic and local techniques (electric potential, charge, electric field, conductivity, piezoresponse)

fabrication of 1D nano ferroelectric materials via polymer-assisted hydrothermal synthesis. Use of carbon nanotubes (CNTs) as templates. Description of anisotropic growth thermodynamic and kinetic models

SPM analysis of hybrid nanostructure and nano-materials to application of biomedical and microbiological systems

multifunctional ceramic films and composites

fabrication of BiFeO₃/ BaTiO₃ and BiFeO/ BiMnO multilayers, novel composites such as PZN-PT/ Terfenol D and novel composite thick film materials Ni₂FeO₄/ PZT Ni₂FeO₄/ KNN by hybrid sol-gel method.

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sputtering thin film deposition

magnetostructural and multiferroic modulation of correlated electron



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scientific highlights

assessing a new form of multiferroic material in charge-ordered manganites, using hyperfine local probing with radioactive isotopes

bias-induced phase transitions in manganites: local properties modification by voltage from tip of scanning microscope and piezoelectric state detection (Piezoforce Microscopy). Application on magnetic induced ferroelectric behaviour in chargeordered oxides (manganite)

development of electromagnetic coupled structures: magnetic shape memory alloys sputtered on ferroelectrics

effects of the interplay of magnetic, structural and electronic degrees of freedom on the magnetic entropy and magnetocaloric properties of complex magnetic materials, with first or second-order phase transitions. New modelling techniques for magnetocaloric analysis

development of experimental technique to directly measure the magnetocaloric effect using noncontact optical sensing

preparation using magnetron sputtering and processing of oxide thin films on Si and sapphire substrates. Study of epitaxy and microstructure. Magnetic and electrical properties studies on heterostructures containing thin layers of Mg-B. Electric properties modifications with layer structure

induced piezoelectric phase



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Multifunctional/multiscale Phenomena in Magnetic Oxides/Manganites. A main topic of study is the complex interplay of lattice structure, oxygen vacancy, defects and doping on the properties of CMR and multiferroic manganites. This leads to phase segregation at different length scales: charge or orbital ordered; insulator vs metallic. Ferroelectricity driven by magnetic order or charge/orbital order.

Multiferroic hexagonal manganites: REMnO₃ (RE=Er, Lu, Eu ferroelectric) and composites (ferromagnetic/ferroelectric): Thin film preparation (sputtering), structural studies (X-ray diffraction) for phase purity and calculation of lattice parameters and temperature study of structural phase transitions. Magnetic studies: (i) physical properties in the vicinity of phase transitions; (ii) application of Landau theory of phase transitions to provide a systematic understanding, (iii) application of mean field approaches to the study of magnetic interactions and magnetostructural coupling.

Hyperfine local probe using implanted radioactive isotopes at ISOLDE-CERN, with Perturbed Angular Correlation Spectroscopy and Emission Channeling: to provide local and element selective information on doping mechanisms. Lattice site and electronic characterisation of the doping elements, disorder and quenched random field effects at the Mn site, in the vicinity of the charge or orbital ordered/ferromagnetic phase instability. Polaron dynamics and percolative effects in lightly doped ferromagnetic insulator manganites. Effect of charge/orbital ordering and local electrical polarization on hyperfine measurements.

Ab-initio calculations of the electronic structure and local hyperfine parameters: application to oxides and magnetic semiconductors (MnAs). New field in the development of electromagnetic coupled structures: magnetic shape memory alloys sputtered on ferroelectrics.

New field of studies started on bias-induced phase transitions in manganites: local properties modification by voltage from tip of scanning microscope and piezoelectric state detection (Piezoforce Microscopy)

Magnetocaloric Effect and Application to Magnetic Cooling. Manganite samples: a)La-(Ca,Sr)MnO₃ and Rareearth (Er,Eu) doped and derived with vacancies in A and B site: effect of RE substitution on the cooling power for near-room-temperature applications. Study of magnetic entropy in competing phase systems (Ferromagnetic and charge-order)

Intermetallic alloys: Pr (Ni-Co), MnAs, NiMnGa shape memory alloy and metal/metalloid Gd-Si-Ge: martensitic transitions and electronic density coupled to magnetic entropy changes. Modelling of magnetocaloric properties with mean field theory. Development of experimental techniques to directly measure the magnetocaloric effect using noncontact optical sensing. Magnetocaloric Prototype design and development of materials.

High Temperature Superconductors. Studies in new MgB₂-type superconductors: preparation and HIP processing. Magnetic and electrical properties studies: superconducting fraction and critical currents. Weak link effects. Preparation using magnetron sputtering and processing of thin films on Si and sapphire substrates. Study of epitaxy and microstructure. Magnetic and electrical properties studies. Mg-B heterostructures. Electric properties modifications with layer structure.

Thin Film Preparation with RF Sputtering Deposition System. The main result is the deposition and growth of non-polar (100) oriented ZnO thin films. Deposition of ultra-thin (1-5 nm) buffer layers on oxide/oxide and p-silicon/oxide interface for microelectronic applications. The main goals are to create an oxygen diffusion barrier between adjacent layers and to prevent the formation of the SiO₂ interface layer, during deposition and post-deposition processing of oxide thin films on silicon (cases studied: hafnium oxide and zinc oxide).

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Advanced Materials

- Iron oxide nanoparticles (maghemite, magnetite and ferritin): high magnetic field studies to analyze the antiferromagnetic component and crystal field effects on magnetic properties and magneto-structural coupling. Modelization of inhomogeneous distributions (size/anisotropy)

- Linear chain compounds with s=1/2 copper ions and dimmers/trimer cluster associations. Mixed Fe-V ferrimagnetic clusters and Ge-Cu-O linear systems. Cubane Ru complexes in polyoxometalates.

- Multifunctional magnetic nanoparticles, for biomedical applications (development of magneto-optical functionalities) and removal of heavy ions (using functionalized particles). New project at ISOLDE-CERN (Radioactive probe studies of coordination mechanisms of heavy metal ions from natural waters to functionalized magnetic nanoparticles) for hyperfine studies using implanted radioactive isotopes (Hg).

Study of thermal entanglement in magnetic materials for applications in Quantum Information and Quantum Computation. Design of materials (those with transition metals chain/cluster) with quantum entanglement at high/room temperature, based on previous knowledge of magnetic behaviour of materials. Connections of thermal entanglement with strucutural properties. Possible aplication in solid-state quantum chips. Connections with Tsallis non-extensivity. Pulsed Electron Paramagnetic Ressonance for addressing logical gates in molecular magnets. - Development of magnetic hamiltonians to understand the microscopic mechanisms that rule the magnetic behavior of linear chains and cluster compounds. Application to S=1/2 and higher cases

Strongly Correlated Electron Systems: Theory and Experiment

a) Colossal magnetoresistive, multiferroic materials and their magneto-electro-elastic coupling effects. Thin film preparation with RF sputtering deposition system: structural (X-ray), magnetic and electrical properties. Systems studied: La-Sr and La-Ba manganites with highest Tc (above room temperature) and multiferroic structures

LaSrMnO₃-REMnO₃, BaTiO₃-LaBaMnO₃. - Doping of ZnO, TiO₂ and Ta₂O₅ thin films for optical applications. - Growth of MgO and HfO as dielectric layers for electronic applications and buffer layer in metal-oxide structures. - Hyperfine studies using implanted radioactive isotopes at ISOLDE-CERN. New international project in CERN. Hyperfine techniques, addressing charge/orbital order and electronic phase segregated systems; competition and interface effects; measurements of electric field gradient and hyperfine magnetic field in magnetic oxides. - Multiferroic oxide materials: hexagonal manganites REMnO₃ (RE=Er,Gd,Lu,...), multiferroic composites of barium hexaferrite (BaFe₁₂O₁₉) and barium titanate. Study of structural, magnetic and electrical properties; Raman spectroscopy. New materials will be created on the basis of the ferroelectric Aurivillius family by introducing magnetically-active transition metal ions in B- sites of the Bi-containing perovskite-type units to form a long-range magnetic ordering without suppressing the polar displacements.

Physical characterization studies of oxide magnetic materials prepared by LFZ (manganite fibers) - Multiferroic structures: bilayer/multilayer systems of magnetic shape-memory /ferroelectrics. Work in the collaboration MULTICERAL project: shape memory alloy films Ni₂MnGa on ferroelectric layers and active substrates and also ferrites/ferroelectric composites.

 Measurements of ferroelectric, magnetic and magnetoelectric properties will be conducted in order to prove which materials are best for room temperature magnetoelectric applications. The work will be done within EU-funded project "Multiceral"

- First-principles calculation (DFT) of structural, electronic and hyperfine properties of materials (oxides). Application to multiferroic manganite oxides and magnetic semiconductors.

b) Local bias induced phase transitions in multiferroic materials.

-The possibility of study and modification of atomic arrangements and electronic structures at the nanometer scale was recently revealed by using Scanning Probe Microscopy methods. We will use Piezoresponse Force Microscopy for studying bias-induced ferroelectric properties in manganites and create artificial multiferroic materials and memory cells. Studies under application of sufficiently high magnetic field and low temperatures in manganites will be carried at Oak Ridge National Laboratory within joint project.

c) Theoretical study of magnetic systems and phase transitions.

-Magneto-electro-elastic coupling mechanisms. Development of mean-field approaches for data analysis and modeling. Application of original method to analyse and separate contributions to the magnetic properties of ferromagnetic systems. Study of inhomogeneous states in manganites using analysis of cluster persistence (scaling approach).

-New approaches to the study of magnetic properties of (Mn1-xMx)As and the role of phase mixing in magnetic first-order phase transition: Combined study of Calorimetry, XRD (micrometer coherence), Magnetic Force Microscopy (100 nm range) and Hyperfine studies using implanted radioactive isotopes at ISOLDE-ČERN (nm range). Firstprinciples calculation (DFT) of structural, electronic and hyperfine properties.

-Development of fundamentals of Tsallis non-extensive statistics and applications to strongly correlated electron systems and other complex inhomogeneous magnetic systems. Theoretical analysis of NMR tomography to measure (non-extensive) systems out of equilibrium; i.e., excitation of two 1/2-spin nucleus to build a non-equilibrium density matrix; from this result it is possible to obtain all desired thermal properties, such as specific heat, magnetization and other quantities.

Magnetocaloric Effect and Its Applications: Theory, Experiments and Prototype

 Optimization of intermetallic/metalloid compounds for magnetocaloric applications: systems under study are mainly containing rare-earths and transition metals to provide magneto-structural coupling: Ni₂MnGa, (Mn_{1-x}M_x)As (M=Cu, Cr, Co and other metals) and also manganites. Additional hyperfine studies using broad band Nuclear Magnetic Resonance of intermetallics.

- Modeling of magnetic entropy contributions for the understanding of material properties: this topic is developed in connection with item 2.3, focusing on magnetic entropy. Examples: mapping the magnetic stability among different phases (in first and second-order phase transitions), with magnetostructural effects. Development of a new process to optimize thermo-magnetic cycles, in the sense of the magnetocaloric effect. Modelling of components and building of a prototype for magnetocaloric refrigeration near room temperature. Development of pilot experiments on dynamic magnetocaloric effect.

Scientific Instrumentation

- Upgrading of RF sputtering materials deposition system: design of a control system for co-deposition and multilayer deposition enabling automatic sequential control of power sources of targets and shutters - Experimental set-up for electric measurements, with thermal-magneto expansion and magneto-resistance, from 77 K up to 500 K and from -1 Tesla up to 1 Tesla (rotating field, from 0° to 360°): final calibration procedures of the measurements.

- Experimental set-up for direct magneto-electric coupling measurements, with ac- based magnetic excitation. - Development of new experimental techniques up to 10 Tesla and temperature 1.6 K-300K in the VSM magnetometer cryostat/magnet: (i) new adjustments in the VSM probe (previous problems solved); (ii) use of a Cu-Be pressure cell (up to 10 kBar); (iii) electrical resistivity and magnetoresistance measurements with already available measurement cell requiring measurement adaptation and performance tests for optimization and automation; (iv) design of specific heat and thermal-magneto-expansion techniques.

Thin Film Preparation With RF Sputtering Deposition System. Growth, structural (X-ray, optical), magnetic and electrical characterization of: i) La-Sr and La-Ba manganites with highest Tc (above room temperature) and multiferroic structures, such as LaSrMnO₃-REMnO₃, BaTiO₃-LaBaMnO₃; ii) SMA (shape memory alloys, e.g. NiMnGa) on active substrates (PZT, PNMPT); iii) doped ZnO, TiO₂ and Ta₂O₅ thin films for optical applications; iv) buffer layers for oxide/oxide multilayered structures and silicon/oxide for electronic applications.

future research

general aims

The combination of macroscopic and local probing techniques with the theoretical calculation of electronic structure/energy parameters (hyperfine fields, EELS) using and magnetic modelling is a strong point in our research strategy, particularly for the defects, local distortions and dynamic processes effects on the properties of complex materials (such as oxides). This is essential for a multi-perspective understanding of multiferroic materials, allowing a prospective materials design sustained in microscopic and ab-initio approaches. In particular, radioactive probe hyperfine techniques and filtered energy high resolution TEM (FE-HRTEM) combined with density functional theory will be used to elucidate the effects of cation ordering and cation/vacancy substitutions on observed magnetodielectric coupling, assessing oxidation states and electronic structures at the nanometer scale.

Biasing or enhancing external fields effects by local perturbations and boundary conditions will be studied and explored for materials and structures performance optimization: nanorods, thin films and heterostructures (thin oxide layers for oxygen/charge control, multiferroic structures, ferroelectric/ferromagnetic layers, interface engineering). Manganites, ferrites and double layer perovskites materials will be the main focus of research.

Modelling of components and building of a prototype for magnetocaloric refrigeration near room temperature, with pilot experiments on dynamic magnetocaloric effect already performed. Study and optimization of refrigerant magnetic materials (alloys and oxides) including thermal efficiency in magnetic cycles. Studies for the improvement and understanding of multifunctional materials, particularly nanoparticles and composites for bio-medical applications (optical and magnetic) are in progress with collaborative PhD thesis.

Investigation of optical excitation of multiferroic effects: local voltages, strain under light. Modern theoretical issues such as quantum entanglement of spin systems and non-extensive statistics will be investigated further in magnetic chain compounds and manganites.

Instrumental development envisaged: 1-upgrading the RF sputtering system, adding a pre-chamber for clean insertion of substrates, additional power source and design of a control system for codeposition and multilayer deposition enabling automatic sequential control of power sources of targets and shutters. 2-Development of new experimental techniques in the VSM magnetometer cryostat/magnet: Electrical resistivity and magnetoresistance with available measurement cell, use of a Cu-Be pressure cell and design of specific heat and thermal-magneto-expansion techniques. A magneto-optic set-up is also under consideration. 3-Analysis and development of a new multiferroic mode in Force Microscopy using magnetocapacitance. 4-Further development of FE-HRTEM technique with the help of density functional theory applied to EELS spectra.

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at 31st december '08

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4 reactive ceramic components for process control



spectroscopic guidelines for optimization of mixed conducting and electrocatalytic properties of ceramic materials, with emphasis on Fe-based

mechanosynthesis of single phase nanocrystalline powders with enhanced sinterability, and corresponding preparation of high quality ceramic microstructures with submicron grain sizes (e.g.

detection and compensation of potentiometric sensor readings



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experimental setup and results of methane processing showing selective syngas formation for SrFe0.3Al0.7O3-d.

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Materials for High Temperature Electrochemical Applications. Studies of solid electrolytes included assessment of YSZ and other materials such as cerias, apatites and pyrochlores, and mixed conductors have been studied as electrode materials for solid electrolytes. The work was based on characterization of transport properties, surface exchange and electrode kinetics of a wide variety of electrode materials and solid electrolytes (with emphasis on ZrO_2 -, CeO_2 -, $LaGaO_3$ - and $La_{10}Si_6O_{27}$ -based materials). One found that proposals of rate determining steps often disagree, possibly due to other factors such as thermomechanical stability, compatibility with solid electrolytes, unsuitable processing or microstructural degradation. Our most recent interests are on perovskites $Sr_{0.7}Ce_{0.3}Mn1$ -yCryO₃- δ and RP phases $LaSr_2Mn2$ -yNiyO₇- δ , which were prepared, characterized and tested as potential cathode materials for $La_{10}Si_5AlO_{26.5}$ -based electrolytes. Studies included structural characterization and stability ranges, thermal and chemical expansion, and transport properties based on dependence of conductivity and Seebeck coefficient on pO_2 and T, and oxygen permeation. Electrode performance was studied by impedance spectroscopy and steady state polarization. Poor performance as cathodes was ascribed mainly to cation interdiffusion and microstructural degradation.

Glass ceramics were prepared as potential seals for solid state electrochemcal cells. The most relevant compositions contained significant fractions of La_2O_3 and Cr_2O_3 , and additions of TiO₂ and NiO to adjust their crystallization. These studies also comprised structural and thermal characterization.

One addressed the issue of electrode polarization in other solid state electrochemical cells, including potentiometric oxygen sensors. One found significant errors resulting from minor electronic conduction and electrochemical leakage through the solid electrolyte, and proposed a method to analyse electrode polarization. One also found that cell thickness plays an important role and described its effects.

Microstructural Effects. Microstructure-properties relations were studied to overcome the blocking character of grain boundaries and their sensitivity to contaminants. This was based on heterogeneous solid electrolytes (e.g. ceria-apatite), to circumvent contamination with silica, or core-shell structures as demonstrate for modified grain boundaries in LSGM or cerias. One also studied negative effects of heterogeneities on Yb₂Ti₂O₇. Low T mechanosynthsis or other suitable powder processing methods may yield better behaviour in these cases. These studies included impedance spectroscopy to de-convolute the contributions of bulk, grain boundaries and electrode processes. One demonstrated applicability of alternative representations based on minima of Z" to extract the relevant parameters.

Mixed Conductors and Catalysts for Oxygen Separation or Partial Oxidation of Hydrocarbons. La₂(Ni,M)O_{4+δ} with M=Fe,Cu and other layered RP phases were prepared and studied as mixed conducting materials for applications based on oxygen permeation. Transport properties were characterized by dependence of total conductivity, Seebeck coefficient and oxygen stoichiometry on pO₂ and T; this was used to revise the defect chemistry, including and effects of composition. Mossbauer spectroscopy was used for characterization of materials containing Fe and to analyse the impact on electronic and ionic conductivities.

Sr(Fe,AI) O_3 - δ -based membranes show better redox stability than most other mixed conducting materials and are obvious choices for partial oxidation of hydrocarbons. Asymmetric porous/dense ferrite-based ceramic mixed membranes were processed to combine a thin mixed conducting layer with a porous ceramic support (La_{0.5}Sr_{0.5}FeO₃- δ). One confirmed the stability of these membranes under air/CO₂ and air/(CH₄+CO₂) gradients. CO₂ tolerance was ascribed to slight Sr-defficiency. Combination with Pt/LaNiO₃/Al₂O₃ catalyst yields high conversion of methane and selectivity for syngas, probably due to nanostructured Ni particles formed under reducing conditions. The team has also studied other mixed conductors based on A(Fe,M)O_{3- δ} or Ln(Fe,M)O₃ perovskites (with alkali earth A=Ca,Sr,Ba, rare earths Ln=La,Pr,Nd,Sm and M=Ni,Al,...). Perovskite materials allow extensive composition changes which result in tuned redox behaviour, adjusted thermal and chemical expansion, and enhanced stability, studied by structural characterization and revealed by abnormal drops in electrical properties. Transport properties and their dependence on working conditions (P and pO₂) were characterized by electrical methods (total conductivity and Seebeck coefficient) and solid state electrochemical methods (oxygen permeability and oxygen stoichiometry). Defect chemistry was analysed by combining effects of relevant factors on transport properties and structural studies. Interesting guidelines were obtained for the effects of different alkali earths and rare earths on structure, stability, bulk transport properties and surface exchange kinetics. Fe species were characterized by Mossbauer spectroscopy. One also studied effects of Ni on transport properties, and its impact on structural and thermochemical stability, and on thermal expansion.

Other materials have been studied as model materials for different structures (e.g. $CaFe_2O_4$). Dependence of total conductivity and Seebeck coefficient showed p-n transition, and revealed that the ionic transport number is low. One interpreted the lower tolerance of $CaFe_2O_4$ to compositions changes, difficulties in enhancing its transport properties, and structural changes under reducing conditions.

LnBaCo₂O_{5.5} materials (with Ln=Y, Nd) were studied as interesting materials with good mixed conduction and unusual structure-property relations. Neutron powder diffraction and Rietvelt analysis were used for structural characterization and to study phase transitions.

Materials for Other Electrochemical Processes. One studied the applicability of $La_{1-x-y}Sr_xCo_{1-z}AlzO_3-\delta$ and $La_2Ni_1-_xMexO_{4+}\delta$, with Me = Co, Cu), as ceramic anodes for electrolytic processes in aqueous alkaline media. In this case, one found that electrochemical performance is determined both by the transport properties and redox kinetics of ceramic anodes, as well as selective leaching by the aqueous medium, and formation of hydroxides.

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Materials for High Temperature Electrochemical Applications. Most of the work planned for 2009 will still be based on materials for solid state electrochemical systems, mainly solid electrolyte, electrode materials and sealants for SOFC, etc., and mixed conducting membranes for alternative electrochemical systems, including concepts which avoid dilution of CO₂ and facilitate its sequestration. Studies of solid electrolytes will include continuation of previous work, and strategies to obtain ceramic components with improved microstructures, or to obtain dense ceramics at lower temperatures. New La_{10-δ}(Si,Al,B,P)₆O_{26+x} and BaZrO₃-based compositions will be prepared to assess the effects of different additives on sintering ability and transport properties. Other sintering studies will be based on more classical solid electrolytes to obtain ceramics with finer grain sizes and improved microstructures, and their potential impact on mechanical properties. Solid electrolytes with designed heterogeneities will be prepared to attain better understanding of effects on bulk and grain boundary properties. Representative examples will be based on TZP+YSZ powder mixtures. Different powder preparation methods or precursor powders will be used to prepare Yb₂Ti₂O₇ and La_{10-δ}(Si,Al,B,P)₆O_{26+x} ceramics, and to assess the role of heterogeneities induced by unsuitable powder preparation methods. Yb₂Ti₂O₇-based materials will also be used as a model for induced or spontaneous anti-site heterogeneities, their dependence on powder preparation and ceramic processing, including cooling from sintering temperatures, or long term annealing at operation temperatures. Proper assessment of applicability of La_{10-δ}Si₆O_{26+x}-based solid electrolytes imply further attempts to develop suitable electrode materials. This work will include studies of electrolytes in contact with the air and/or fuel electrodes. In addition, one will attempt to develop electrode architectures with designed porosity patterns.

Microstructural Effects. Microstructure-property relations will be explored with combination of electron microscopy and impedance spectroscopy. Special attention will be given to impedance spectroscopy, including modifications of experimental procedures, alternative representation to assist de-convolution of those spectra, and examination of conditions which might lead to misleading interpretations.

Mixed Conductors and Catalysts for Oxygen Separation or Partial Oxidation of Hydrocarbons. Novel approaches will also be used to design alternative mixed conductors with good redox stability based on $Ce_{1-x}Pr_xxO_{2-\delta}$. This should allow good ionic conductivity and electronic contributions with p-n transition. In addition, one will attempt to induce core-shell microstructures with enhanced transport properties along grain boundaries, by selective segregation of mixed valence additives.

Further work on mixed conducting materials will include surface modifications for materials with oxygen exchange limitations, and reexamination of redox stability of promising mixed conductors such as La_2NiO_{4-5} and $Sr(Fe,AI)O_{3-5}$ -based materials. By tunning the redox behaviour one expects enhanced performance for conversion of hydrocarbons to syngas, while avoiding carbon deposition. One will also examine the tolerance of mixed conductors (e.g. $Sr(Fe,AI)O_{3-5}$) and solid electrolytes (e.g. $BaZrO_3$) to atmospheric gases (CO_2 , humidity) imposed by electrochemical conversion of methane and other prospective applications.

Materials for Other Electrochemical Processes. Our previous activities on liquid electrochemistry are now being extended to understanding the electrode kinetics in the presence of suspensions in alkaline media, and the development of hard and yet active electrode surfaces.

future research

general aims

the team is pursuing its role in new energy conversion systems, namely low cost materials for energy systems, alternative electrochemical technologies for energy and environmental issues, and energy management. The emphasis of these activities will be on high temperature systems, namely fuel cells and related systems (steam electrolysers, oxygen separation, partial oxidation by mixed conducting membranes, etc.)

to pursue these objectives, the team started research on electrocatalysts with less common structures and/or assisted by redox-induced phase changes. The team is also dedicating a great deal of attention to nanostructured systems, which are expected to give higher performance, mainly at intermediate or lower temperatures, as planned for the recently started Project NANOCOFC. Ongoing activities include processing of structures ceramics with grain sizes from the nano to microscale range, both dense and highly porous, and nanostructured catalysts. Some activities are also based on hybrid nanostructured materials for low or intermediate temperature the team is dedicating efforts to alternative low cost materials for fuel cells and related electrochemical systems, with emphasis on silicate (Project MatSILC) and carbonate containing electrolytes (NANOCOFC), and nanostructured mixed conducting oxide catalysts, to replace noble metals

the team is also seeking activities on wider areas of energy conversion and management, including the hydrogen vector, solar energy, and heat storage

energy related environmental issues stimulated our participation in the ongoing ULCOS project. This consortium is seeking another large project on carbon dioxide lean technologies, including electrolytic processes. Our future interests include on CO_2 sequestration by suitable materials, and production of pure oxygen as electrolytic by-product

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5 ceramic composites and functional coatings for structural applications



ceramic composites

and functional coatings for structural applications

scientific highlights

in a collaboration with the National Institute for Materials Science (Japan), minute pipettes capable of store and subsequently release on-demand Cul on the scale of 10⁻¹⁸ grams were developed based on carbon nanotubes (CNTs)

using of ZnS nanowires doped with Ga and sheeted with carbon layers on preparing heterostructured nanotubes composed of ZnO and ZnGa₂O₄ grains

study of the behaviour of nanotubes with various morphologies, structures and compositions subjected to a gradient electric field generated through biasing an STM tip inside a high resolution transmission electron microscope (HRTEM)

adequacy of homologous nanocrystalline diamond (NCD) sliding systems for biotribological applications proved by very low wear rates in the range of $\sim 10^{-9}$ – 10^{-8} mm³•N⁻¹m⁻¹

turning of sintered hardmetal, graphite and Alalloys with direct coated NCD tools with very low cutting forces and minimized tool wear NCD films induced human osteoblast and fibroblast proliferation and stimulated specific metabolic activities supporting the potential of NCD as a coating for articular prosthesis and odontological tools

mechanical sealing with NCD coated Si_3N_4 rings at PxV=4.8 MPa.m/s for long running times of 24 h (300 km) without measurable wear development of new smart self-healing coatings based on nanocontainers created using natural clay nanotubes, halloysotes, loaded with corrosion inhibitors and oppositely charged layers of polyelectrolytes doped with corrosion inhibitors



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new hybrid sol-gel derived nanocomposite thin films doped with corrosion inhibitors were investigated as perspective pre-treatments for aluminium and magnesium alloy

development of new experimental methods to investigate corrosion processes in micro-confined defects of organic coatings

novel solid-contact ion-selective micro-electrodes were created and patented

the effect of the Mn³⁺ ions content and charge order on the electrical behaviour of Mn(IV)-rich perovskite manganites Ca_{1-x}Ho_xMnO₃ was investigated by TEM and XRD

a correlation between the generation of extrinsic defects and the stress produced by the thermal expansion coefficient mismatch between CVD polycrystalline diamond films and the substrate material was demonstrated

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Diamond Coatings. Research on hard materials and coatings was dedicated to manufacturing advanced ceramics, as bare or coated with CVD nanocrystalline diamond (NCD), aiming better outstanding of wear resistance and friction for machine elements, metalworking processes, cutting tools for very abrasive materials and biomedical applications. Main results were:

Tribological systems for mechanical seals and articular prosthetic implants: in self-mated ball-on-flat configuration, microcrystalline diamond (MCD) coatings presented an outstanding behaviour, namely very low friction and wear coefficient, with delamination threshold load of 160N. In ring-on-ring configuration. nanocrystalline diamond (NCD) coatings guaranteed water sealing with very low and stable friction coefficient of 0.01, without measurable wear.
NCD coated inserts were used in turning of graphite (EDM grade). Wear was low, with forces were lower than 20 N. An important result is the absence of diamond film delamination showing high adhesion offered by the silicon nitride ceramic substrates for diamond coating.

- Correlations between extrinsic defects and stress produced by thermal expansion mismatch between CVD polycrystalline diamond films and the substrate material were established. This study was based on different ceramic substrate compositions with distinct thermal expansion. It was found that defect-free diamond grains are associated with low stressed coatings.

NCD films were assessed under lubrication of Hank's balanced salt solution (HBSS) and dilute fetal bovine serum (FBS), using a pin-on-flat test configuration. Friction coefficient values of 0.06 and 0.12 were measured under HBSS and FBS lubrication. Evidences of protein attachment and salt deposition were found, being responsible for enhanced friction under FBS relatively to HBSS. The wear rates measured for NCD films were in the range of 10⁻⁹ to10⁻⁸ mm³•N⁻¹m⁻¹. NCD biocompatibility withstand improved human osteoblast proliferation and the stimulation of differentiated markers, like ALP activity and matrix mineralization, compared with standard polystyrene tissue culture plates. Nanometric featuring of NCD, associated to its chemical affinity are key factors for bone regeneration purposes.

Other Hard and Ultra-Hard Materials. Composites prepared from WC powders sputter-coated with metals show increased ductility with Ni coatings and higher toughness versus hardness with stainless steels coatings, when com

pared with conventional composites. These benefits were attributed to the remaining high uniformity of phase distribution and nanocrystalline binder structure in the composites, coming from the coating process, despite partial degradation during sintering.

Processing Methods. Ti₂AIC and Ti₃AIC₂ carbides with laminated grain morphology and terraced structure of parallel laminated layers were prepared by combustion synthesis. A layered growth mechanism was proposed to describe their formation. These materials possess unique physical and mechanical properties, including high melting point, good thermal and electrical conductivity, high strength and modulus, and good machinability. In order to explore the high strength and hardness, good wear resistance, and excellent thermal shock resistance of SiAION materials, rod-like α -SiAION and of β -SiAION powders stabilised with single and multi-cations were prepared by combustion synthesis (CS) and used as reinforcing elements of structural sialon-based ceramics densified by pressureless sintering. SiAION whiskers with various morphologies were produced at the surface of hot-pressed bulk samples by heat treatment at 1800°C. Other than straight whiskers with or without nodules on their heads, curved bow-like and kinked whiskers were also observed. The VLS (vapour–liquid–solid) growth mechanism was proposed as the main growing mechanism for the whiskers. The VS mechanism could become active on exhausting liquid droplets.

Formation of titanium nitride (TiN) by combustion of Ti particles in air was proposed to occur through controlled reaction by delayed gas infiltration behind the combustion wave. Formation of TiN was enhanced by addition of NH₄Cl or carbon black. As-synthesized TiN grains showed terraced morphology with parallel layers stacked in the normal direction.

Advanced structural ceramics based on SiAIONs, with good friction and wear behaviour, were consolidated by colloidal techniques and pressureless sintered. The friction and wear behaviour were investigated using a pinon-disk tribometer under dry sliding conditions at room temperature, against steel DIN-Ck45K. The results obtained revealed excellent hardness and thermal shock resistance.

Combustion synthesis (CS) and solid-state reaction were also used to prepare powders of Al₂O₃, MgAl₂O₄ spinel, and 20wt.% ZrO₂–MgAl₂O₄ and to study effects of preparation on sintering, microstructural features, and mechanical properties. It was concluded that agglomeration of CS powders hinders densification. Agglomeration of ZrO2 powders determine the microstructures of porous ceramics and their thermal conductivity. Porous ceramics with nonuniform microstructures have wider pore and grain size distributions, relative to those with uniform microstructures. An effective medium approach was used to describe thermal conductivity of porous ceramics. This analysis revealed that grain size distribution has a significant impact on thermal conductivity of porous ceramics. Thermodynamic calculations and TGA studies allowed one to describe the relevant reactions of AIN ceramics consolidated from aqueous suspensions after protecting the AIN powder against hydrolysis with phosphate species. This correlated well with detected secondary phases, and explained the microstructures and density of AIN samples, and their properties (e.g. thermal conductivity). A similar approach was used to control surface properties of submicron and nanosized SiC particles modified with aluminium oxy-hydroxide and to tailor their colloidal suspensions; this also acted as sintering additive.

TEM and EELS were used for unmatched spatial and composition resolution of advanced materials such as AlxGa1-xN light emitting diodes and laser diodes, nanotubes and nanowires.

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Corrosion Protection Methods. Research on corrosion protection was focused on novel protective coatings and new methods for characterization of passive and active protection. Protection included pre-treatments, anticorrosion inhibitors, polymer coatings and surface modification for specific metals and alloys. Corrosion mechanisms were studied by multi-scale approach, from macro to nano. Other approaches were based on electrodeposition of films and 1D nanostructures using ionic liquids. Smart self-healing coatings were based on nanoreservoirs of corrosion inhibitors, using clay nanotubes and halloysotes loaded with corrosion inhibitors, introduced to hybrid sol-gel coatings. Nanocontainers were also developed by application of Layered Double Hydroxides doped with corrosion inhibitors. Oppositely charged layers of polyelectrolytes doped with corrosion inhibitors were used for active protective coating. These systems release active substance in response to the presence of aggressive corrosion.

New hybrid organosilane and sol-gel derived nanocomposite thin films doped with corrosion inhibiting compounds were investigated as perspective pre-treatments for aluminium alloys and magnesium alloy. Mechanisms of corrosion inhibition for aluminium alloys using organic and inorganic corrosion inhibitors were studied. New experimental protocols were developed for application of SVET/SIET techniques to investigate corrosion processes in micro-confined defects of organic coatings. Solid-contact ion-selective micro-electrodes were developed and patented. Novel anodic oxide films were produced by electric discharge method on titanium and studied, with emphasis on semiconductive and protective properties.

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Diamond Coatings. The main activities will be based on hard materials and films for structural applications, and biomedical applications, namely:

- Development and application of tribosystems based on multilayered micro/nanocrystalline diamond (MCD/NCD) coated surfaces with superior friction and wear resistance, including cutting tools, hip joint prosthesis and mechanical seal rings. The innovation proposed deals with the combination of both the superior adhesion of MCD, as first layer, to the surface properties of NCD, as top layer, in a multilayered composite. Alternating MCD and NCD thin films will prevent MCD grains to grow excessively. Fracture toughness will be enhanced by the crack-arresting role of interfaces between layers. Work is being carried out with industry support to create a spin-off company for manufacturing ceramic and diamond coated components.

- Production and characterization of carbon nanotubes (CNT)-containing bone grafts, namely: i) CNT 3D-scaffolds. ii) CNT reinforced ceramic matrix to further improve the mechanical properties. CNT 3D-structures will be produced by direct growth of CNT on a patterned bed of catalyst or by shaping CNT after been aligned produced. For the second approach, the ceramic matrix to be mixed with functionalized CTN is a P205-glass reinforced hydroxyapatite (GRHA) material.

Other Hard and Ultra-Hard Materials. WC-stainless steel composites will be obtained fast consolidation techniques, such as, microwave sintering, to densify sputter-coated and conventionally prepared powder compacts. These materials will be characterized for their relevant technological properties, including composites prepared in laboratorial and at industrial scale (Hard Metal company).

Processing Methods. One aims preparation of SiAION based ceramics with rod-like α -SiAION particles, to attain high strength and hardness, good wear resistance, and excellent thermal shock resistance. Ceramics will be densified by pressureless sintering, hot pressing, HIPing and spark plasma sintering. The impact of processing on mechanical and tribological properties will also be assessed. Other composite materials based on Al₂O₃, MgAl₂O₄ spinel, ZrO₂–MgAl₂O₄ and Al₄O₃-ZrO₂ will be also processed and characterized for their relevant properties. Continuation will be given to the previous work on che colloidal processing and sintering of SiC ceramics. - Development of innovative methods to measure properties of nanostructured materials via in-situ transmission electron microscopy, with emphasis on mechanical behaviour of nanowires and nanotubes. One is also seeking a suitable protocol for reproducible and efficient synthesis of carbon nanotubes by thermal CVD.

Corrosion Protection Methods. The main activities will be dedicated to development of active corrosion protective coatings with self-healing ability in frame of several European and national scientific projects, mainly: - New nanocontainers of corrosion inhibitors based LDH structures, mesoporous particles and other host-guest nanostructures, to be applied as anticorrosive pigments in coatings.

- A variety of organic and inorganic compounds will be screened to find new effective corrosion inhibitors for the different steel, aluminum alloy and magnesium alloy substrates. The new screening approach using multi-electrode micro-cells will be used in combination with localized electrochemical methods.

- New experimental protocols for probing the self-healing properties in protective coatings will be developed on basis of Scanning Vibrating Electrode Technique (SVET) and Scanning Ion-selective Electrode Technique (SIET). The new ion-selective electrodes for measurement of active species in the electrolyte near the active metal surface will be developed and applied.

- Novel anodic oxide films on titanium, magnesium and aluminium will be produced by electric discharge. - Electrodeposition from ionic liquids will be employed to create 1D – 2D metal-based nanostructures which have potentiality for several applications like protective coatings, semiconductive materials and materials for energy systems.

- Development of electrically conductive NCD coatings for all-diamond microelectrodes to be tested by and used in Scanning Electrochemical Microscopy (SECM) and Scanning Vibrating Electrode Technique (SVET) applied to corrosion and to plant cells studies. The construction of the microelectrodes involves sharpening of W or Mo filaments, coating with an inner layer of conducting NCD and an outer shell of electrically insulating NCD or microcrystalline diamond. One aims to improve spatial resolution, time of response, sensitivity, stability, robustness and lifetime. A collaboration with INMETRO, Brazil, is expected. Advanced Ceramics and Composites: development of reliable processes based on direct consolidation techniques to obtain large/bulky ceramic/metallic components and thus overcoming the limitations of traditional approaches involving spray-drying, dry pressing (uniaxially, and/or isostatically) followed by green machining in CNC machines to confer the desired shape. These traditional approaches are time-consuming, leading to less homogeneous materials and high sintering temperatures, and require very heavy and expensive equipment

Functional Coatings for Mechanical Applications:

i) deposition of multilayer coatings of CVD microcrystalline and nanocrystalline diamond (MCD/NCD) that will combine both the superior adhesion of MCD and the surface properties of NCD in a composite coating for practical tribosystems. Alternate MCD/NCD thin layers will prevent MCD grains to grow excessively allowing a smooth surface by depositing a top NCD layer, while enhanced fracture toughness is achieved by careful interlayer design

ii) starting of a research line on processing, characterization and application of carbon nanotubes (CNTs). This is an evolution of the know-how acquired on the CVD growth of carbonaceous species and will profit from a newly integrated full-time researcher (P.M.F.J. Costa) with expertise on the field. Hybrid composites of nanocrystalline diamond (NCD) and CNTs will be investigated aiming technological applications such as wear-resistant coatings, thermal management of integrated circuits, field emission devices and electrical field shielding in NEMS\MEMS and microelectronics. In addition, both forms were proven to be biocompatible, displaying high bio-chemical selectivity after being functionalized

future research

general aims

Functional Protective Coatings:

i) novel self-healing protective coatings for metallic materials based on multi-level active protection approach. The idea is to combine different protective mechanism in one coating providing synergistic protection

ii) new "smart" nanocontainers of corrosion inhibitors and other protective agents to be incorporated to the coatings. The intelligent nanocontainers should provide release of active protective agents only on demand under action of specific triggers originated from the aggressive environment

iii) new method and experimental protocols to study active corrosion and healing processes in micro- and nano-confined defects allowing deeper understanding of self-healing mechanisms

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at 31st december '08

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0% MRP 30% MRP 37,5% MRP 45% MRP

research group

wastes recycling and green products

scientific highlights

Design of new and green products, such as pigments is high value-added alternative for the valorisation of secondary raw materials. Metalrich wastes may act as colouring agent, or may be combined with other materials acting, in this case, as hosts for diverse colouring species, so they can be regarded as supplementary raw materials for pigments production. In particular, we developed a novel pigment structure, based on hibonite (CaAI12O19) structure that give interesting blue hues, consuming low amount of chromophor (Co or Ni)

Sustainable Built Environment is particularly interesting area for collaboration with the Habitat cluster companies and also with municipalities, which face difficult questions concerning wastes and its management in their daily activity of local governance. This effort has been coordinated by the Sustainable Construction Platform (www.centrohabitat.net)



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Blue Pigment

novel (non-catalogued) blue pigment based on the hibonite structure (CaAl_{12}O_{19})

Ultrasonic pulse velocity measurement was used as a non-destructive technique to assess the density and delamination of ceramic tiles. It was assumed that an increase in travel time for a given thickness would indicate the presence of delamination, as the sound wave travels around the flat pore. Measurement uncertainty and repeatability were also discussed.

Industrial sludges derived from cutting and polishing natural stones (granite and quartzite) have been characterised and incorporated as main components in redclay-based stoneware tiles, with up to 60–70 wt.% incorporation. Resulting rustic tiles obtained by extrusion showed 8–9% water absorption and a flexural strength of 17–18MPa, with significant improvements, fulfilling the requirements of the ISO 13006 standard.

Chromium-rich ashes derived from incinerating leather residues from shoes industry were used as colouring and fluxing agent for industrial porcelain tile formulations with sintering temperatures 1120-1180°C. Incorporation of these wastes resulted in lower water adsorption, and improved density and bending strength. Coulouring could be adjusted from cream to dark brown by changing the amount of ashes and sintering temperature.

ZnO-containing glazes were developed for hard tableware porcelains, with enhanced densification behaviour, widened maturing temperature range, better mechanical properties and whiteness, and lower shrinkage than conventional hard porcelains. A physicochemical mechanism was proposed for continuous production of hydrogen by reaction of aluminum with water. The oxidised scale breaks on exceeding a critical equilibrium pressure of H₂, thus re-exposing Al for reaction with water. Fotocatalytic decontamination systems based on unidirectional porous glass structure coated with a nanometer TiO₂ thin film was successfully fabricated by freezing a water-based slurry of sheet glass while controlling the growth direction of ice crystals, followed by sublimation under vacuum. The green body was sintered to produce porous glass with unidirectional pores. Then, the sintered porous glass was infiltrated by a titanium (IV) butoxide solution, dried and calcined at a moderate temperature to generate a nonostructured TiO₂ film on pore walls with high surface area.

The main activities will be focused on recycling industrial wastes and by-products to prepare new added-value materials. The current research works will be extended to other types of residues in order to find suitable solutions to clean the environment, preserve natural and non-renewable resources, save energy, while improving some of the actually existing products or developing new ones with new functionalities. Recycling will also be used as a strategy to minimize the environmental impact of materials and their processing. One of the main emphasis of this work will be on designing cement formulations with lower CO2 footprint and to assess the potential of concrete residues for long term sequestration of atmospheric CO2, and to identify the main factors that promote or hinder sequestration.

Some work is also been performed on materials for heat management in buildings and domestic appliances, including phase change materials for heat storage. activity report 2008

activity plan 2009

In the future, the Habitat cluster (building materials and related activities) will continue to play a key role in sustainable development. Transformation industries, such as those involving Ceramics, Glasses and Cements production, are critical because high tonnage of materials and energy are involved. Waste and recycled materials are being utilized extensively in high-volume ceramics such as glasses, cements and many vitreous materials. Their use will be extended where economic or legislative drivers are present. There will be increasing use of wastes as aggregate in bound and unbound civil engineering applications. New ceramic products will arise and come to market manufactured from sintered or melted wastes. Within a few years, in many countries we will see an emerging industry base (often small enterprises) that will take waste, sort and separate it out and seek applications and potential markets. Because of the increasing cost of landfill, more waste incineration units are being built worldwide, and while there has been much research into applications for the ashes produced, a greater commercial take-up based on this research is needed

within the next five years, we expect to see development of cements that set by reaction with atmospheric CO2: carbon negative cement systems. There will be increasing understanding of the potential of room-temperature glasses such as geopolymers and room-temperature ceramics such as phosphate cements. Cost-effective vitrification technologies will evolve for problematic hazardous wastes, making them inert and reusable based on plasma or cold-crucible melting technologies. There is already a clear shift in public opinion and marketing so that products made from secondary materials are seen as desirable, and this will continue. Major civil engineering projects in many countries will be assessed for their sustainability by the amount of secondary materials used in construction. In the 5–10 years time frame, we will see evidence of increasing globalization of research into, and implementation of, sustainable development. There will be growing realization of the importance of recycling and reuse of materials and immobilization of hazardous wastes. More international research programs in this area, of the sort already in place in Europe, will be initiated

future research general aims

waste recycling and valorisation is one of the key aspects for a Sustainable Built Environment and as such is a particularly interesting area for collaboration with the Habitat cluster companies but also with municipalities, which face difficult questions concerning wastes and its management in their daily activity of local governance

our future work will be a natural continuation of the research themes already pursued and will focus on the characterization and recycling of several industrial wastes aiming at achieving the following general objectives:

(i) Lower production costs and energy saving of ceramic/cement formulations

(ii) Preserve natural resources, namely inorganic primary raw materials

(iii) Clean the environment and reduce land fill

(iv) Maximise waste incorporation

(v) No changes in intermediate processing steps of the recycled products

(vi) Prserve, or improve the final product properties

(vii) Obtaining new products and new functionalities.

research team at 31st december '08

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research group

7 macromolecular materials and biorefineries

scientific highlights

Our research results strongly contributed the undertstanding of the specific chemical features of Eucalyptus globulus wood and to the improvement of the associated industrial transformation processes.

i) Novel environmentally friendly polyoxometalate-catalyzed delignification processes were developed and reached the pilote-scale level.

ii) New cellulose and other polysaccharidebased functional materials were developed.

iii) Different chemical and biochemical approaches for the implementation of the biorefinery concept in forest based industries, including the conversion of carbohydrates into furfural were proposed.

The characterization of the properties of ionic liquids and the development of group contribution methods for the development of CAMD approaches was completed with success.



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The study of water interaction and low temperature behaviour of biofuels, and the development of models for their description was successfully achieved.



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Novel Biomass-Derived Materials and Composites. The research on the development of novel materials based on polysaccharides (vegetal cellulose, bacterial cellulose, chitosan and starch) was continued. Cellulose fibers, previously modified with fatty acids were used as reinforcing elements in composites with both polyethylene and poly(ethylene sebacate) matrices. The obtained materials were characterized in terms of thermal and mechanical properties, morphology, water uptake and biodegradability. The chemical modification of cellulose with fatty acids was also applied to cellophane films and bacterial cellulose membranes and the materials characterized as referred above. Additionally, these materials were also characterised in terms of barrier properties (H₂O and atmosphere gases permeability). Cellulose fibers modified with several perfluorinated reagents, were also tested in the preparation of new composites with perfluorinated polymer matrices. The characterization of these new materials will be carried out in the next period. The using of these perfluorinated cellulose derivatives for the inclusion of Eu³⁺, aiming to produce novel photoluminescent materials was also started during this period. Surface chemical modifications of cellulose fibres, aiming to improve mechanical properties of paper while preserving hydrophilicity, were carried out with different anhydride molecules.

The studies on the coating of paper sheets with chitosan and one water soluble chitosan derivative were continued. Additionally, mixtures of chitosan (and its derivative) and bacterial cellulose fibers, were also tested in this context. The coated papers revealed very promising mechanical, and barrier properties, as well as enhanced printability. In a more fundamental perspective, and in order to clarify some conflicting reports, a systematic study of the surface energy of chitin and chitosan, was carried out using contact angle measurements before and after different purification procedures. The results obtained, showed that the non-polar impurities found in these natural substrates (in variable amounts) might affect substantially their surface energies, and inevitably their subsequent transformations/applications.

New materials based on thermoplastic starch and bacterial cellulose were also prepared and characterised. These new biocomposites show enhanced mechanical properties when compared to unfilled thermoplastic starch, even when very low fiber loads were used (1-5%).

The development of new cellulose-based nanocomposites was pursued. Particular attention was devoted to materials incorporating silver and gold nanoparticles and Fe(III) oxide nanophases, both on vegetable cellulose as well as on bacterial cellulose.

Polymers Derived from Renewable Resources. The synthesis of monomers bearing furan and maleimide functionalities suitable for the synthesis of polymer materials through the Diels-Alder cyclo-addition (DA) was continued. A range of bisfuran (AA), bismaleimide (BB), and trismaleimide (B3) monomers were prepared, The DA/retro-DA cycle was applied to linear (AA+BB systems) and crosslinked (AA+B₃ system) polymers. These systems were analyzed in terms of (i) the kinetics of the linear polymerization (based on preliminary studies on monofunctional model compounds) followed by UV and ¹H-NMR spectroscopy; (ii) the changes in the viscosity of the reaction medium, as a function of temperature; (iii) the equilibrium position of each system, assessed by the same techniques, as a function of temperature; (iv) the structure and molecular weight of the ensuing polymers; (v) the glass transition temperature determined by DSC; and (vi) the thermal depolymerization followed by TGA.A new research line, dealing with the synthesis of new polyesters derived from 2,5-furandicarboxylic acid (FDCA) was started during this period. The exploratory work carried out involving the synthesis of poly(ethylene 2,5-furandicarboxylate) PEFDCA showed that this novel material bore properties entirely comparable with those of poly(ethylene terephthalate) PET, namely in terms of high thermal stability, crystallinity, with a mp ~215 °C and a Tg ~80 °C. These preliminary results show that FDCA polyesters might have a high potential to replace the fossilderived terephthalic acid (FA) counterpart.

The development of new polyesters derived from cork suberin components (relatively complex mixtures of long chain ω -hydroxyacids and α, ω -diacids) involved the optimization of the experimental conditions related to their polytransesterification, as well as enzymatic and emulsion polycondensations, accompanied by parallel studies with model systems. Polyesters with average molecular weights in the range of 3800- 4600 Da were obtained, with Tgs below room temperature and melting points around 80 °C.

Other Polymer Systems. We have been focusing our research activities in the construction of a permeability apparatus, using the time-lag technique, and the measurements of permselectivities of membranes, especially those related with poly(lactic acid) (PLA) and additivated PLA. The separation of paraffins/olefins has been addressed and the architectural features of PLA have been manipulated in order to optimize the separation factor.

Upgrading Lignocellulosics and Wood Pulping by-Products: Biorefineries. The study of the chemical composition of cork by-products was focused during this period on the GC-MS and LC-MS analysis of the phenolic fractions and on the evaluation of their antioxidative properties. Other cork fractions (i.e. suberin) previously studied in detail, were exploited as raw materials for polymer synthesis (see above).

The chemical composition of the triterpenic fractions of *E. globulus* bark and other biomass fractions was studied in detail. Some of the studied fractions and, particularly, outer bark and the outer layer of stems, are very rich in triterpenic acids (mainly ursolic and oleanolic acids). Additionally the phenolic/tannin fractions of *E. globulus* bark and wood aqueous extracts were studied and their application in leather tanning accessed. The results obtained so far show that *E. globulus* tannin fractions have a promising potential in leather tanning. The by-products from acidic sulfite pulping (evaporation condensates and sulfite spent liquor (SSL)) have been investigated aiming to develop new approaches for their processing to added value products. An approach was developed for acetic acid and furfural recuperation from evaporation condensates. Liquid-liquid extraction was the better separation alternative, using MTBE (Methyl Tert-Butyl Ether) as extraction solvent. MTBE has low solubility on water and is very volatile, allowing a less expensive regeneration, compared with other solvents. The kinetic study of oxidation of lignosulphonates (LS) from the eucalyptus with molecular oxygen under alkaline conditions has been carried out to evaluate the potential of syringaldehyde (SA) and vanillin (VA) production. Upon optimized conditions and using the copper salts as catalysts the yields of aromatic aldehydes may be increased up to 25% and of aromatic acids up to 3%. The sugar fraction of SSL can be used as a substrate for the production of diverse products including ethanol. One of the objectives was to propose a biotechnological approach to produce bioethanol from SSL using a xylose fermenting yeast *Pichia stipitis*. However, ethanol yield and productivities obtained were reduced due to the presence of inhibiting compounds like acetic acid (about 8 gL-1), hydroxymethylfurfural and lignosulfonates. Another approach involved different detoxification methods including biological methods with different de-acidifying yeasts, and sugar fraction separation using ion-change resins. The best te-acidification was reached with *Saccharomyces cerevisiae* allowing the total acetic acid removal during 30h.

Studies on oxypropylation (liquefaction) of biomass residues were pursued. A patent was filled on this subject. Contacts were initiated with industrial partners aiming to assess the technical and economical feasibility and the implementation of this process at a pilote-scale.

Research on the flash pyrolysis of *E. globulus* wood (liquefaction) has been initiated. First results obtained using an ablative reactor allowed rather promising results.

Studies on the extraction and upgrading of grape seed oil, including enzymatic pre-treatment and super-critical extraction were initiated.

Wood Pulping, Bleaching and Papermaking. The effect of the final hydrogen peroxide stage in a conventional ECF sequence DEOPDP and in a ECF-light sequence OQ(PO)DP on the eucalypt pulp brightening, mechanical strength and brightness reversion have been investigated. The conditions of the last hydrogen peroxide stage were optimised. The new research was focused on the understanding of the nature of chromophores in pulps and their behaviour under pulp ageing.

A Sequential Batch Reactor (SBR) was used for the pulp kraft effluent treatment by Trametes versicolor as an alternative to the activated sludge. The presence of Trametes Defined Medium (TDM) in the fermentation was required to obtain a significant COD reduction. Experiments in batch reactor confirmed, in general, the predicted results of optimization developed from Erlenmeyer batch assays. A *T. versicolor* culture remained active during the 42 days of studies, in the SBR, providing approximately 80% of COD reduction.

results of optimization developed from Erlenmeyer batch assays. A *T. versicolor* culture remained active during the 42 days of studies, in the SBR, providing approximately 80% of COD reduction. The α -Keggin heteropolyanion [SiW₁₁V^VO₄0]⁵⁻ was employed as electrochemically reversible catalyst in the delignification of eucalypt kraft pulp. This approach allowed the highly selective pulp delignification, which was limited, however, to 45% under the applied conditions. The electrochemical pre-bleaching stage was considered to be an economically feasible tool to decrease the ECF bleaching costs without deterioration of pulp strength properties.

A series of experiments were done on pilot equipment for the paper coating with new formulations based on cellulose-silica hybrids. The coated papers revealed ink-jet better printing properties than all conventional industrial analogues.

Structural Studies on Lignocellulosic Materials. The structural characterization of macromolecular components of eucalypt and some perspective lignocellulosic materials (grape residues and *Paulownia*) has been carried continued. In particular, the heteroxylan from hybrid *Paulownia elongata/Paulownia fortunei* has been characterised for the first time using a series of wet chemistry, NMR and advanced mass spectrometry techniques (ESI-MS/MS and MALDI-TOF). In addition, the glucan-glucuronoxylan complex was characterised for the first time using NMR and electrospray ionization tandem mass spectrometry. The results of structural analysis indicated that glucan's chains are bonded to glucuronoxylan (GX) via terminal 4-O-methylglucuronic residues (MeGIcA). The presence in glucan backbone of (1?6)-linked glucopyranosyl units, attached to MeGIcA of GX, explained the easy degradation of glucan-glucuronoxylan complex under acidic and alkaline conditions. The chemical composition of national wine grape constituents (skin and stalk) has been studied for the first time and the chemical structure of macromolecular components were preliminary elucidated.

The role of several depolymerising enzymes and fungi on the detailed nanostructure of cork has been continued, with strong emphasis on the direct characterisation of the complex material by NMR and FTIR methods.

Chemical Conversion of Biomass Into Chemicals. Studies on the chemical valorisation of carbohydrates using porous heterogeneous catalysts were pursued. We have discovered promising solid acid catalysts for the dehydration of D-xylose into furfural, which is produced on an industrial scale from pentosan rich biomass (sulfuric acid is commonly used as catalyst). Particularly interesting are materials derived from a layered zeolite Nu(6)-1, prepared from the lamellar precursor Nu-6(1), namely H-Nu-6(2), and a material with enhanced specific surface area obtained after swelling/ultrasonication/calcination of Nu-6(1), which performed quite well in comparison to some H-MOR and H-Y zeolites. We have studied also the aqueous phase base catalyzed isomerization of glucose (monomer unit of the abundant natural polysaccharide cellulose) into fructose over microporous and layered metallosilicates containing non-framework or framework alkali metals (ETS-10, ETS-4, AM-4, AV-1, AV-2, and a synthetic analogue of tobermorite). Fructose yields of 20–40% were obtained within 2 h reaction, at 100 °C, which is similar to or better than those achievable with the commercial zeolite Na-X or aqueous NaOH.

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Biofuels. Our studies on biodiesel production address the modelling of the phase equilibria between biodiesel and the various other compounds present in the process such as water, alcohols and glycerol. We have been measuring both VLE and LLE of binary and ternary mixtures of fatty acid methyl esters (FAMEs) with these compounds because, surprisingly, the information about these phase equilibria is very scarce in the literature. These data is used to develop and test models for the description of these phase equilibria. We have been in particular addressing the development of a new equation of state, CPA-EoS, to the description of these complex systems with water and alcohols and non polar compounds such as esters. Our ultimate goal on this subject is the modelling and optimization of a biodiesel purification plant.

Another aspect of biodiesel production that we have been addressing is the enzymatic synthesis of biodiesel from free fatty acids. Commercial and home-produced lipases have been used to optimize the conditions to produce biodiesel from oleic acid using both methanol and ethanol.

The last aspect concerning biodiesel production is the optimization of the mixtures of raw materials. Vegetable oils have prices that depend on the oil type, their origin and that have important market fluctuations. The production of a biodiesel able to fulfil the standard specifications cannot be based on a single oil. This means that a biodiesel producer has to have indications that allow him to use a formulation that meets the specifications and optimizes the cost of the raw materials used.

lonic Liquids. lonic liquids are novel solvents with many interesting properties that are being applied in a number of different technological areas with surprising results. We have been exploring their potential for separation purposes and characterizing their properties.

Aiming at developing a Computer Aided Molecular Design (CAMD) approach to task specific ionic liquids, correlations for various thermophysical properties of ionic liquids have been produced (densities, compressibilities, expansivities, heat capacities diffusion coefficients, thermal conductivities, viscosities, refraction indexes...) based on data measured by ourselves and others. An online application for the estimation of these properties was developed and is now available to the general public at http://path.web.ua.pt/thermophil.asp.

Since the extraction of biomolecules from aqueous solutions can be one of the most interesting areas of application of ionic liquids we have been addressing the mutual solubilities of ionic liquids and water, and the effect of salts on these solubilities.

A new project on the sweetening of natural gas and CO2 capture using ionic liquids was started in 2008. The first results for high pressure solubilities were reported.

Development of Analytical Approaches. A new non-degradation methodology was proposed for the distinction and identification of lignins, according to their biological origin and/or isolation methodology, using an electronic aroma sensing system (electronic nose). The system, once trained with representative lignins, could quickly and objectively be used as a simple tool by providing, in real-time, information about the lignin origin, based on their headspace volatile composition.

The application of new electronic tongue (ET) multisensor system for the real-time monitoring of polyoxometalates (POM) re-oxidation with molecular oxygen has been initiated. Sensors contained trioctyl phosphine oxide and octylphenyl-N,N-diisobutylcarbamoylmethyl phosphine oxide as active substances were applied to follow the *in situ* changes in particular POM structures containing vanadium (IV/V) atoms upon re-oxidation with molecular oxygen.

Novel Biomass-Derived Materials and Composites. Within the scope of the development of new polysacharidebased materials, future work will focus mainly on the development of:

-New hybrid materials obtained by modification with reactive triethoxysilanes, and products of subsequent solvolysis. -New transparent nanocomposite films composed of chitosan (or derivatives) and nanocellulose fibers (bacterial and nano fibrillated cellulose), as well as with inorganic nanoparticles (e.g Au, Ag and Cu). -New thermo-reversible gels based on modified chitosan bearing furan moieties and a bismaleimide cross-linking agent.

-New materials derived from bacterial cellulose, following different strategies, (e.g. incorporation of other polymeric materials in the wet membranes, incorporation of reactive monomers, followed by *in situ* polymerization etc.). Bacterial cellulose membranes (with or without modification) will be studied as subtracts for controlled release of drugs (including kinetic studies of the migration into the membrane and the subsequent release). -New composite materials based on modified cellulose fibers (and/or other natural substrates) and thermoplastic matrices (particularly biodegradable polymers)

The production of papers coated with chitosan and bacterial cellulose fibers will be optimized, and the use of nanofibrilated cellulose will also be considered. Particular attention will be devoted to chitosan films re-enforced with cellulose nanostructures

A new research activity will also be started involving the implementation of the laboratorial production of bacterial cellulose membranes. This activity will supply bacterial cellulose membranes for local consumption and for some key research collaborations.

The development of new cellulose-based nanocomposites will be extended to other polysaccharide substrates, including chitosan, as well as nanofibrilated structures and to other inorganic nanophases, namely, Cu, Pt and Pd. The research activity focused on nanofibrilated cellulose will be part of a new FP7 European project starting during 2009.

Polymers from Renewable Resources. The development of the research activities dealing the synthesis of new polymeric materials based on the Diels-Alder reaction will be focused on the preparation of AB, AB₂ and A₂B monomers, and on their use in linear polymerization studies with AB and in the construction of hyperbranched macromolecules from AB₂ and A₂B. A thorough characterization of the ensuing materials, in terms of structure and properties, will then be conducted.

Considering the high potential of FCDA-based polyesters suggested by the preliminary studies carried out in the last period, the synthesis of a wide variety of polyesters and co-polyesters derived from this diacid, using several diols from renewable resources, as well as those derived from petrochemistry, will be investigated using different polycondensation and polytransesterification conditions. Copolyesters incorporating FCDA and FA residues will also be prepared. The detailed properties of the ensuing materials will be evaluated and the synthesis of the most promising materials optimized.

A new project involves the preparation of macromonomers derived from fatty acids/glycerides/vegetable oils, to be used in radical and cationic (co)polymerization.

The development of polymeric aqueous dispersions for coating applications will be initiated. This new research topic involves an industrial PhD program, which aims at developing new polymeric materials with specific properties, including mechanical performance and dirt repellence, for coating applications and their dispersion in aqueous media with the aid of surfactants from renewable resources.

Other Polymer Systems. The permeability of gases in polymer membranes is going to be studied using the permeability apparatus built. Diffusivity and solubility properties are going to be derived and the mechanisms governing permeability are going to be explored. The influence of water content in several proposed modifications will be measured and analysed.

The incorporation of ionic liquids in polymer films either to tailor/improve polymer specific properties (change Tg, change permeabilities) or perform a specific task (e.g. active transport) will be addressed.

Upgrading Lignocellulosics and Wood Pulping by-Products: Biorefineries

The development of adequate and environmentally friendly processes for the extraction fractionation and purification of high value components (e.g. phenolics, triterpenic acids) from cork and *E. globulus* by-products will be the main focus during the year. Special attention will be paid to extraction/fractionation techniques based on supercritical CO₂.

The studies on the bio-processing of sulfite spent liquor (SSL) will continue. The major efforts will be done for the combined bio-treatment of SSL with fungi (for the deacidifation/detoxification of substrate) and fermenting yeast to produce bioethanol. An initiative work will be started for bio-processing of SSL with mixed cultures to produce polyhydroxybutanoates (PHA).

The study on the chemical and structural characterization of grape skins and stalks will continue. The new applications for the obtained materials will be envisaged.

Initiatives aiming at assessing the technical and economical feasibility of the biomass oxypropylation process will be pursued with our industrial partners.

Grape seed (*Vitis vinifera L.*) is a well known oilseed crop containing typically 8-15% (w/w) of oil and antioxidantrich compounds. In terms of applications, it is becoming increasingly popular for pharmaceutical, cosmetics, and medical purposes. Hence, we intend to study the supercritical fluid extraction of grape seed oil, optimizing the operating conditions to produce high quality oil in terms of antioxidant properties. Simultaneously, an enzymatic pre-treatment to increase the extraction yield will be investigated. After that, we plan to extract the procyanidins fraction of the defatted seeds, since it has high therapeutic application, namely as inhibitor of the angiotensin converting enzyme (responsible for high blood pressure). The modelling of the supercritical fluid extraction will be also accomplished.

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Wood Pulping, Bleaching and Papermaking. The work on highly selective polyoxometalate (POM) catalysis in oxygen delignification of kraft pulp using POMs will be continued.

The study on the structure of chromophoric groups in pulps and the new bleaching sequences will continue. The study on the paper surface modification with perspective formulations prepared using sol-gel process will continue. In addition, the new functional cellulose-silica hybrid materials doped with POMs will be synthesised, characterised and tested in the redox catalysis with air pollutants.

The study of the surface chemical modifications of the fibers to be used in the paper production will be continued. The modified fibres will be employed in the paper production and the mechanical properties of the paper sheet will be evaluated. It will be also studied the efficiency of additive retention during the paper production.

Structural Studies of Lignocellulosic Materials. The studies on specific structural features of hemicelluloses and lignin employing ESI-MS/MS and MALDI-TOF will continue.

The study on the chemical composition of macromolecular components of the natural hybrid of *Paulownia elongata* and *Paulownia fortunei* will continue. The attention will be paid to the elucidation of papermaking properties of this wood.

Chemical Conversion of Biomass Into Chemicals. We will investigate the dehydration of oligo/di/monosaccharides into furfural and 5-hydromethylfurfural, using porous heterogeneous catalysts or acid ionic liquids (ILs). The latter approach may be promising as ILs may enhance the dissolution of some saccharides in comparison to water and combine the low volatility and the ease of separation from the reaction products normally associated with solid acid catalysts, and may give relatively high reaction rates.

We will study the application of castor oil for the production of dielectric oils. We will start by the kinetic studies of the reactions involved, as well as the development of the indispensable analytic methods.

Biofuels. The CPA-EoS development to the description of systems of relevance to the purification of biodiesel should be completed during this year. In collaboration with a biodiesel producer, Prio, process data for a biodiesel purification process will be acquired to be used for the test of the model in process simulation. The study of the enzymatic synthesis of biodiesel will be extended to high pressures to evaluate the effect of this parameter on the conversion rate and the reaction kinetics.

Aiming at making the lipase production more economical and the enzymatic synthesis more competitive we will study the production of lipase in solid state fermentation.

New titanosilicate-based membranes will be synthesised and characterised, and evaluated for the separation of hydrogen containing mixtures. At the moment, steam reforming, partial oxidation of hydrocarbons, autothermal reforming, and gasification of biomass are the best economically viable options towards a hydrogen economy. Therefore its separation is an important target.

lonic Liquids. Concerning the ionic liquids we plan to extend our activities towards the separation and purification of aminoacids, proteins and alkaloids in aqueous biphasic systems using the knowledge developed on the aqueous solubilities of ionic liquids and the impact of salts on these systems.

Investigation on the nature of the vapour phase of these "non-volatile" solvents is also going to another central topic of research. This goal is going to be achieved through the measurements of the vapour pressure and heat of vaporization of selected families of ionic liquids. Other insights will also be obtained by vapour-liquid equilibrium studies of ionic liquids and volatile organic solvents.

The use of ionic liquids towards the dissolutions of cellulose and other polysaccharides will be a major goal of our activities during the current year. We will try to understand the interactions between ionic liquids and the simple sugars and polysaccharides aiming at developing ionic liquids able to selectively dissolve these compounds. The capture of acid gases will address the use of basic ionic liquids based on conjugated basis of fatty acids. The development of a CAMD methodology will be further pursued during this year based on the correlations developed previously.

Development of Analytical Approaches. The application of electronic tongue (ET) sensor array system for the monitoring of POMs re-oxidation mechanisms will be accomplished.

future research

general aims

The creation of CICECO contemplated a research line on Chemistry & Technology of Polymeric and Lignocellulosic Materials & Biomaterials that was divided in three groups: Macromolecular Materials and Lignocelullosics; Biomedical and Biomimetic Materials; Process Development and Optimisation.

The main objective of the Lignocellulosics Group were the deep study of the chemical composition of lignocelullosic materials, with focus on relevant species in the national context (eucalyptus and cork oak), of their behaviour during industrial processing (with particular emphasis on pulping and bleaching processes); the valorisation of industrial processing by-products was also among the key objectives of the group. While achieving such objectives the group also aimed to reach a high level of scientific productivity, the integration in international research networks and also to contribute the development of this sector in Portugal.

The Process Development Group was concerned with polymers from renewable sources, the development of processes using alternative green solvents (fluorocarbons and ionic liquids) for enhanced production in bioreactors, the production of enzymes of relevant industrial application such as laccase and lipase, and energy issues related to conventional fuels. However, the focus of this research area has changed dramatically in the last few years as a result of the emergence of the "Biorefinery" concept which aims to develop new pathways to produce chemicals, materials, fuels and energy from (renewable) biomass. Inevitably pulp and paper companies, and researchers in this area, are pursuing the growing potentialities of the Biorefinery concept. In this vein this group also oriented part of the research efforts to this emerging area.

The best approach to adequately address this new scenario was found to be the merging of the Lignocellulosics and the Process groups into an integrated group, which will allow a more coherent integration of the research activities of the line under the broad area of biorefinery.

Our main objective now is to become a reference research group in the Biorefinery domain in Europe with a network of international academic and industrial collaborations.

We will be addressing both the chemical and biotechnological conversion of renewable materials as well as the separation and purification of value added products.

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research group



biomedical and biomimetic materials





novel Bone cement

0.1% MWCNT-PMMA/HA nanocomposite

(a),(b): Interfaces with a titanium prosthesis after a fatigue test for one million cycles;

(c),(d): delamination and cracks after the same type of fatigue test for a PMMA-only nanocomposite

research group

biomedical and biomimetic materials

scientific highlights

establishment of best analytical approaches for efficient cell metabonomics by NMR spectroscopy

new method for preparing strong PMMA-modified HA bone cements with multiwalled carbon nanotubes (fatigue resistant implants and coatings)

preparation of materials for biological applications: biocatalysis and toxicity studies on algae

first evidence that amniotic fluid reflects metabolic changes in malformed human foetuses, showing changes in glycolysis and gluconeogenesis and kidney development; these results establish the basis for possible NMR-based diagnostic methods for fetal malformations

new cyclodextrin (CD) inclusion compound [CpMo(H₂biim)(CO)₂](BF₄) (H₂biim = 2,2'biimidazole) / heptakis(2,6-di-O-methyl)- β -CD showed increased cytotocicity against K1735-M2 mouse melanoma cells (estimated as > 50 µM for the non-included complex)



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new ruthenium(II) complexes, containing [9]aneS₃ and N-bridging planar amines prepared and their possible biological interaction mechanisms studied. - Binucler Ru(II) complexes show kinetic interaction selectivity for AT tracts or mixed-sequence ct-DNA and the relative selectivity of [-bidppz([12]aneS₄])2Ru₂]⁴⁺ was studied



calixarene derivative in a phospholid bilayer

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Biomaterials. The synthesis of sol-gel derived $SiO_2-CaO-P_2O_5-Ag_2O$ bioglass system has been achieved successfully and their in vitro antibacterial and biological activity has been evaluated and the results were compared with the $SiO_2-CaO-P_2O_5$ glass systems, which has no incorporated silver ions. The antibacterial activity and biological properties were evaluated by determining the minimum inhibitory concentrations (MICs). The results have proved that the Ag-bioglass not only acts bacteriostatically but it also elicited a rapid bactericidal action. The antibacterial action of Ag-bioglass was exclusively attributed to the leaching of Ag⁺ ions from the glass matrix thus confirming significant influence of incorporated silver into the glass matrix.

A novel tool involving Cryo-X-ray analysis was adapted to investigate the physicochemical reactions at the bioglass/biological fluid interface. The out come of the investigation was found effective in analyzing the elemental distribution at the periphery of bioglass particles in their native state. This technique also allows studying the process of physicochemical reactions at a sub micrometer scale. A detailed *in vitro* electrochemical characterization of electrochemically deposited fluorine doped apatite coatings has shown better corrosion resistive behaviour of the coated implants when compared to the uncoated Ti₆Al₄V alloy. A detailed investigation has also been made on the effectiveness of metallic implants for biomedical applications.

Silicon-substituted hydroxyapatite bioceramic materials were prepared by incorporating small amounts of silicon into the structure of hydroxyapatite through a sol–gel method. A series of silicon substitutions ranging from 0, 1, 3 and 5 mol%, which are comparable to the measured silicon contents in natural bone, were performed. Single-phase Si-HAP was obtained upon calcining the as-prepared powders up to 800 °C since no secondary phases. The responses of human osteoblast-like cells to the silicon doped hydroxyapatite were investigated and the results were compared with pure hydroxyapatite. The silicon-substituted hydroxyapatite showed a significant increase in cell growth density with culture time irrespective of the amount of silicon substituted in HAP. A high silicon content (5 mol%) appears to promote rapid bone mineralization but on the other it was also found that a high silicon content may result in fast dissolution of the material, owing to a decrease of HAP crystallite size, which might not be ideal for cell attachment for prolonged time periods. An optimum level of silicon appears to exist at 3 mol%, which balances these effects.

The biological behaviour of porous scaffold structures of bonelike materials, which are suitable for either direct clinical use or tissue engineering applications has been evaluated. Porous cylindrical specimens (8 mm diameter, 10 mm height) were implanted in the lateral aspect of the tibia of 13 patients (mean age 54 years), during osteotomy surgery for the treatment of medial compartment osteoarthritis of the knee. Implanted cylinders were retrieved at the same time as the removal of the blade plates at 3, 6, 9 and 12 months. The implant material has permitted the effective vascularization and bone ingrowth, and therefore was fully osteointegrated. The results have shown the potential for complete ingrowth of osseous tissue and restoration of vascularization throughout the defected site for the investigated porous structures.

A synthetic route has been achieved to develop a apatite that simulates the inorganic component of natural bone. The essential trace elements involving Na⁺, Mg²⁺, K⁺, Cl⁻ and F⁻ have been incorporated into the apatite structure in appropriate proportions so that the resultant apatite has simulated natural bone. A detailed structural investigation by Rietveld analysis of X-ray powder diffraction has been done to investigate the structural behaviour of the resultant apatite due to the incorporation of essential elements. The results have given sufficient information on the effective role of substituents in the apatite structure with the properties of enhanced thermal stability of the resultant apatite and better mechanical properties when compared with stoichiometric apatite. Hybrid nanomaterials were prepared by two step sol-gel process using different inorganic and organic precursors. Synthesized hybrid silica nanobiomaterials were amorphous, exception of the samples containing chitin. FT-IR spectra of these materials showed the presence of Si-O-R (CH₃ and C₂H₅) and Si-C groups indicating the existence of strong chemical bonds between the inorganic and the organic components. The AFM results indicate the presence of nanostructures with well defined nanounits. The surface roughness of the obtained hybrids depends on the type of silica precursors and the nature and quantity of organic components. Investigated hybrid materials containing chitin can be successfully applied for cell immobilization. Synthesized silica hybrids containing kcarragean can be applied as carriers for obtaining active biocatalysts. Their enzyme activity towards different aliphatic and carboxylic nitriles was established. The biodegradation process performed in the two steps bioreactor proved no washout allowing high and stable process efficiency even under toxicity and at high temperature. Chemically derivatised biomaterials based on magnetic nanoparticles (e.g. magnetite/carrageenan) have been functionalised for antibody specific recognition. These systems have been made to comprise a thermoreversible matrix of polysaccharide which should enable thermally-switched release of magnetic particles, one recognition occurs between the composite particle and the target cells. Compositional variations are under study in order to incorporate gold nanoparticles in the system, in order to enable localised heating mechanisms to be used. The controlled release of magnetic particles from within the composite particle is being characterised and monitored and different bioconjugation mechanisms are currently being investigated.

Novel Si-free glass compositions of the Ti-Ca-P system have been developed. In vitro degradability of these glasses either in accellular or in the presence of cells was studied and related with the respective glass structure, assessed by spectroscopic techniques. Powders of selected glass compositions have been tested in mice and histological studies performed in kidneys liver and spleen. A number of Ti-based glass compositions showed the capability to induce the precipitation of Ca-P layers in SBF, the ability to promote cell adhesion and proliferation and the absence of adverse reactions in *in vivo* situations.

Glass scaffolds of the Si-Ca-P-Mg system were produced by a salt sintering process and it was possible to obtain porous structures with ~60 % porosity, containing macropores with diameters between 150 and 400 μ m and micropores < 60 μ m. Glass compositions of both systems Ti-Ca-P and Si-Ca-P-Mg have been incorporated in polymer matrices to develop new cements formulations (PMMA-based mixtures) and scaffolds for tissue engineering applications (PLLA-based). A high interconnectivity with pores >150 μ m was obtained for the PLLA-bioglass scaffolds. In vitro mineralization was observed in a significant number of cements and PLLA-glass scaffolds. Hydroxyapatite (HA) particles were produced by wet chemical and hydrothermal synthesis. Depending on solution pH, micrometric bundlelike-or nanometric needlelike particles were obtained by wet chemical synthesis. Mesostructured nano-sized particles were obtained by hydrothermal synthesis.

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The in vitro response of two cell lines (L929 and ROS 17/2.8) to spray dried HA micro granules loaded with the chemotherapeutic agent 5-fluorouracil (5-FU) showed a dose dependent decrease in cell proliferation in response to 5-FU and the response towards the granules varied with cell type.

Mixtures containing bovine bones heated at different temperatures were applied to the purification of acid mine drainage waters. This work originated a master degree thesis and showed results to be developed in the future. The use of synthetic hydroxyapatite and other synthetic amendments to mine contaminated soils remediation as well as the time evolution of soils behaviour when in long lasting contact with water and aqueous solutions were also studied.

The growth and building principle of nacre formed by gastropod mollusks and the role of the surface membrane in assembling the individual aragonite platelets that build up the nacre has been studied. This fascinating material demonstrates how hierarchical structuring can lead to enhanced properties, such as, in the case of nacre, a high mechanical stability at low weight. Such bio-inspired building principles are important for the design of new advanced materials that are based on hierarchical structuring at the nanometer scale.

Artificial Receptors for Pharmaceutical and Environmental Applications. The research activity of the molecular modeling group was focused on the development of artificial receptors with potential pharmaceutical and environmental applications and anion binding recognition phenomena. Theoretical methods, molecular mechanics and molecular dynamics simulations were applied extensively on the molecular design of the novel receptors and in the understanding of the molecular recognition mechanisms.

The tetraprotonated form of a dioxatetraazamacrocycle was used as receptor of carboxylate anions of different shapes, sizes, and charges: succinate, cyclohexanetricarboxylate, phthalate, isophthalate, terephthalate, and benezenetricarboxylate. Molecular dynamics simulations were carried out for the associations with tph²⁻ and btc³⁻ anions in water solution. These simulations established the existence of multiple and cooperative N–H/O=C hydrogen bonding interactions. The binding free energies were estimated by MM-PBSA methodologies agreeing well with the experimental ones.

The cooperative and ion pair recognition ability of new heteroditopic calix[4]diquinone receptors were investigated extensively by molecular dynamics simulations approaches including conformational analyses, conventional molecular dynamics simulations in solvent and free energy calculations by thermodynamic integration. These receptors, composed of calix[4]diquinone and isoftalamide fragments linked by polyether spacers of different length, are capable to bind contact ion pairs cooperatively (MX, M= alkali cation or NH_4^+ and X = halide) with an unprecedented AND recognition phenomenon being observed to operate in certain cases, in which receptors display no affinity for either of the individual "free" cation or anion, but bind the cation and anion ion-pair strongly. The interaction mechanism was established by molecular dynamics simulation and involves the folding of the receptors to allow π -stacking interactions between the calix[4]diquinone unit and the isophthalamide fragment allowing the proximal arrangement of the anion- and cation-binding sites independently of the size of the appended macrocycle. The anion-templated assembly of mechanically bonded molecules, catenanes and pseudo-rotaxanes, were also investigated by means of molecular dynamics simulations. Two [2]catenanes were studied being mediated by sulfate and chloride anions respectively. The catenane cavity of one of them has binding domains for the recognition of sulphate, chloride and acetate. The dynamic behaviour of the binding associations with these anions was evaluated theoretically in solution showing that the molecular recognition of sulphate and chloride anions occurs inside of catenane cavity through the hydrogen bonds, while the acetate anion occurs outside from catenane cavity. One of these receptors (1+) was the first example of a catenane capable of performing a circumrotation via an anion switching methodology. The deprotonation of a phenol group upon base addition leads to the phenolate anion, which induces the intra ring rotation of one macrocycle around the other leading to a structure stabilized by hydrogen bonds between the positively charged pyridinium cleft and negatively charged phenolate anion. It is also noteworthy that phenol conformation is locked by the coordination of the chloride in the catenane cavity even upon base addition. The structures of two phenol and phenolate forms of the [2]catenane and the binding association 1⁺.Cl⁻ were established by molecular dynamics simulations coupled with MMR data. Another related project undertaken was the sulfate anion templation of a pseudorotaxane assembly between a neutral indolocarbazole thread and an isoftalamide macrocycle in a tetrahedral fashion. The formation of pseudo rotoxane structure was evaluated by molecular dynamics with estimation of the entalphic and entropic contributions. Some work was also performed on the field of inorganic coordination chemistry of mixed valence complexes. A series of nine complexes incorporating [Rull/IIICl([n]aneS₃)] (n = 12, 14, 16) metal centers bridged by monodentate pyrazine, 4,4'-bipyridine, and 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine were synthesized. An experimental analysis of the intervalence charge transfer bands for the complexes revealed that, despite possessing the same donor sets, the electronic delocalization within these systems is modulated by the nature of the coordinated thiacrown. Density functional theory and TD-DFT methods offers further evidence of interaction between metal centers and provides insights into how these interactions are mediated.

Analytical Tools on Biological Systems. Work has been initiated and developed along the following main parallel lines: (i) systematic evaluation of the influence of sampling, storage and manipulation procedures on the integrity and metabolic profiles of human cells (lung and osteosarcoma cells), and optimization of protocols for the assessment of their metabolic response to chemotherapy drugs; (ii) characterization of lung cancer metabolic phenotype through the NMR analysis of tissue biopsies and biofluids; (iii) identification of biomarkers of fetal malformations in human amniotic fluid through NMR-based metabonomics, (iv) Nutritional metabonomics studies towards a better understanding of food/organism relationship.

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The NMR characterisation of biofluids and biological tissues has been pursued for application in: (i) study of pregnancy disorders, (ii) heart failure and diabetes incidence, (iii) detection of inborn errors in newborn babies and (iv)) biological tissues analysis for cancer diagnosis. Nutritional metabonomic studies have also been initiated through the analysis of biofluids of subjects subjected to a fibre-rich diet. These type of studies often comprise a through compositional characterisation of the foods themselves and this approach has been pursued within a collaboration with the brewing industry, aiming at characterising beer composition and relating it to product quality, effects on consumer health and, ultimately, general consumer satisfaction. This work comprises a multidisciplinary project on the study of the chemistry of beer ageing, making use of a range of analytical methods in tandem with FTIR and NMR spectroscopy, in order to detect quality markers and identify new natural compounds. The metabonomic study of osteosarcoma cells has been pursued by HR-MAS NMR, in order to establish the normal metabolic profiles of these cancer cells. This information will be used as backgraound knowledge for the understanding of the metabolic effects of newly synthetised drugs, delivered within cyclodextrin/inorganic composite systems.

Bio-Inorganic Systems and Toxixity Studies. Ruthenium(II) complexes proved to interact with bio-macromolecules and DNA. Complexes containing [9]aneS₃ and N-bridging planar amines were explored by positive mode ESI-MS-MS/MS to explain their fragmentation in relation to structural/ spectroscopic properties to get insights into their biological interaction mechanisms.

Binuclear Ru(II) complexes showed kinetic interaction selectivity for AT tracts or mixed-sequence ct-DNA. [μ -bidppz([12]aneS₄])₂Ru₂]⁴⁺ was studied by combining circular dichroism and luminescence to investigate their selectivity against poly(dAdT)₂ when intercalating, compared with other analogous Ru(II) complexes. Inclusion systems have been obtained resulting from the interaction of Ru(II)-thioether/polypirydilic or α -aminoacids complexes and several types of cyclodextrins. Elucidation of the molecular structure and patterns of fragmentation in the cases of {(Ru[9]aneS₃)(α -aminoacid)}⁺ molecular set continued to be studied.

Some chemotherapeutic agents such as titanocene compounds were investigated in *in vivo* studies for their effects on male mice fertility. Lesions were observed in the blood-testis barrier, and epidydimis, underlying significant adverse reactions on reproductive organs.

Several chromium compounds (eg, chromium picolinate) considered to show biologically relevant functions, have been tested due to a current important controversy about their essentiality. Mice, previously intoxicated with controlled levels of different metal complexes, were used as pre-clinical models, in order to evaluate the role of those compounds, following their routes in the body, aiming to better understand their paths *in vivo*. Their adverse effects were investigated using slices of target organs (kidney, liver and testis), prepared for histological, histochemical and ultrastructural methods. Complementary approaches, such as flow-cytometry that allows, in real time, a multiparametric assay of cells, have been also used to get more complete insights into the underlying mechanisms of toxicity. Altogether, these methodologies are good contributions for the evaluation of the toxicological effects of some heavy metals in public health.

Cyclodextrins (CDs) are drug vehicles that sometimes act as activity enhancers. 2-(N,N-dimethylaminomethyl)ferrocenecarboxamide, with an IC50 (at 24h) of 71.2 μ M against EAC, was included in heptakis-2,3,6-tri-O-methyl-ß-CD and 2-hydroxypropyl-ß-CD yielding adducts with lowered IC50 values of 25.2 and 20.0 μ M, respectively.

and 20.0 μ M, respectively. Inclusion of [CpMo(H₂biim)(CO)₂](BF₄) (H₂biim = 2,2'-biimidazole) into heptakis(2,6-di-*O*-methyl)-ß-CD increased its cytotocicity against K1735-M2 mouse melanoma cells (estimated as > 50 μ M for the non-included complex). This effect may be related to the Monte Carlo calculated inclusion geometry showing the BF₄⁻ anions inside the polar DIMEB cavity whilst the [CpMo(H₂biim)(CO)₂]⁺ cations remain in the intermolecular void spaces, thus being readily available for biological activity. Cell interaction studies using epifluorescence microscopy show that the adduct induces mitochondrial alterations leading to major cell morphology changes and ultimately to inviabilisation.

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Biomaterials. The research activities on the synthesis of calcium phosphate (CaP) powders doped with several substituting elements and the colloidal processing of dense and porous scaffolds for bone regeneration, bone augmentation, tissue engineering, and drug delivery systems will be pursued. Doped calcium phosphate powders will be used to prepare calcium phospate cements (CPC) with improved injectability and mechanical properties. Composite materials will be developed based on the CaP powders and biopolymers. The current studies on the synthesis and characterization of bioactive glasses will be continued for uses as thin films of bulk materials for different biomedical applications. High strength disilicate (LD) glass-ceramic which can mimic the properties of tooth enamel will be produced to provide aesthetic appearance for implants and protection of teeth against fracture including those treated by bioactive glass graft.

Chemically derivatised newly developed biomaterials based on magnetic nanoparticles (magnetite/carrageenan, magnetite/gold/carrageenan) will be further functionalised for antibody specific recognition of cancer cells and their efficiency tested in vitro. The controlled release of magnetic particles will be characterised and monitored. Nanostructured hybrid materials containing alumina will be synthesised by sol-gel using a new silica source and different hydrolysis conditions and characterized by XRD, FTIR, SEM, AFM and ²⁹Si MAS-NMR. The effect of aluminium content, hydrolysis conditions and pyrolysis temperature on the morphology and thermal stability of the prepared hybrid materials will be investigated.

Researchers from Biology and Medicine will be involved in the study of Glasses and glass-based scaffolds and Glass-polymer composites developed so far, aiming to pursue the materials engineering work carried out during the Masters recently completed. One of the main objectives of this task is to understand the effect of the ionic dissolution products on cells behaviour, namely on gene-expression profile of human bone cells. New glass fillers will be tested in the cement formulations aiming to improve bone bonding capability without loosing the control of processing parameters and workability of the composite mixtures.

The effects of experimental parameters, including spray drying temperature and HA precursor suspension formulation on the properties and releasing behaviour of a HA based drug delivery system, will be studied. The influence of different HA nanoparticles synthesized by wet chemical and hydrothermal methods on cells behavior as well as its use as potential drug delivery systems, will be investigated.

behavior as well as its use as potential drug delivery systems, will be investigated. The formation of the nacreous layer in gastropods will be studied in detail. Cooperation with the Fritz-Haber-Institute gives access to high quality TEM sample preparation of this highly sensitive material. This will allow revealing new structural details relevant for an understanding of the process of biomineralization.

Artificial Receptors for Pharmaceutical and Environmental Applications. The research activity of the molecular modelling group will be focussed on the development of artificial receptors for the selective binding of the substrates with biological relevance and medicinal application. This work will be carried out using experimental and theoretical methods. A particular attention will be dedicated to the following specific topics:

a) Development of novel aza-bridged calixarene receptors based on calix[2]arene[2]triazine architectures for medicinal chemistry: molecular design and synthesis of artificial receptors composed of two phenyl rings and two triazine rings linked by nitrogen bridges. These receptors will be used on the binding studies with chiral drugs from the families of barbiturates, 1,4-dydropyridines and nucleoside derivatives. The calix[2]arene[2]triazine platforms will be also used to design synthetic receptors for the transport of anions with biological relevance (typically chloride, phosphate) across membranes. The molecular modelling studies will be used extensively as a complementing and a supportive tool to enhance our understanding the binding affinity and/or amphiphilic properties of synthetic receptors.

b) Molecular design of artificial receptors for anion and ion pair recognition: molecular design of receptors for the molecular recognition of anions and ion pairs with biological relevance via simulation tools. The receptors include molecular machines, rotaxanes and catenanes, as well as heteroditopic receptors with ionophore properties. c) Computational studies of the diffusion of delivery-systems in cellular membranes models: computational simulation of the molecular recognition mechanisms between synthetic receptors and substrates with pharmacological interest. Furthermore, the interaction and diffusion of these host-guest systems with model membranes also will be addressed. At the long term this project aims the *in silico* design of new transporters with enhanced diffusion capacities through the cellular membranes and which are capable to act as drug-delivery systems. d) Self-Assembled of Metallocycles with fotochemical and electrochemical properties: thioether fragments will be used to self-assemble bridging ligands in metalo-macrocylces hosts. These metal fragments may incorporate multivalence states and have hydrophobic cavities suitable for molecular recognition of substrates such as aromatic carboxilates. The modelling work consists on DFT and TD-DFT calculations to explore the UV-Vis properties of these new materials. Their conformational preferences will be determined by molecular dynamics calculations.

Analytical Tools on Biological Systems. The NMR characterisation of biofluids and biological tissues will be pursued in the following areas: a) study of pregnancy disorders, b) heart failure and diabetes incidence, c) detection of inborn errors in newborn babies, d) biological tissues analysis for cancer diagnosis (lung, brain and bone cancers), e) nutritional effects of specific diet components and food thorough characterisation for quality control and human effects evaluation. Statistical analysis of the spectral data will be applied in order to develop models for the rapid detection of markers of the diseases under consideration and develop increasingly non-invasive methods (that is, through urine or plasma analysis).

Particularly new aspects of this work are: the metabonomic study of ostheocarsome cells by HR-MAS NMR and using 13C-enriched nutrients, in order to establish the normal metabolic profiles of these cancer cells and then go on to study the effects of several new drugs under chemical development; the monitoring of the metabolic behavior of tumor cells (lung and osteosarcoma) in response to anticancer drugs, applied directly and through controlled release systems; the NMR characterization of biomaterials for drug delivery applications (e.g. bacterial cellulose) and of their interaction with biological and biomimetic systems; the identification of metabolic patterns in lung tumor tissues and patients biofluids, which will provide insights into lung cancer metabolism and form the basis for new adjunct diagnosis tools; the metabonomic approach for the understanding of the role of selected diet components (e.g. fibre, beer) in the human organism, comprising both characterization of the food components (in the solid and liquid states, respectively, for fibre and beer) and of the human biofluids reflecting metabolic effects. This latter study will make use of a range of analytical methods (GC-MS, MS/MS, FTIR, NMR), in order to detect food quality markers and identify new natural compounds, develop prognosis models for product quality, develop an analytical platform for sensorial product analysis, establish relationships between product metabolic profile and consumer health and acceptance.

Bio-Inorganic Systems and Toxixity Studies. New designed compounds, for molecular recognition, of transition metals and polypyridyl and/or thioether ligands (square or triangle type). Also, synthesis of ruthenium(II) complexes with coordinated α -aminoacids as models of peptide/protein and DNA interactions. New Ru(II) compounds bearing new organic molecules (models of extracted natural products with biological properties) will continue to be synthesised and characterised by the usual spectroscopic techniques (namely solution NMR), X-ray single crystal diffraction analysis and ESI-MS spectrometry.

Synthesis and characterization of ruthenium(II) complexes with quinone-type ligands to be tested in oxidative catalysis, together with other, previously prepared, promising Ru(II) complexes, in order to optimize both the ligand design and the catalytic experimental conditions.

Chromium compounds taken as models for relevant intermediates in the intracellular-Cr(VI) reduction will continue to be studied. Additionally some chromium compounds widely used as nutritional (and controversial) supplements have already been synthesised and will be tested (*in vivo*) and studied by ultra-structural techiques, to clear the suspicion of provoking damages *in vivo*.

Chromium compounds, in different oxidation states, will continued to be tested in in vivo studies with mice in order to localise degenerative damages in animal target organs and quantify the amounts of this element in those organs. Histology, histochemistry and ultra-structural techniques will continue to be used.

Several different compounds frequently used as chemotherapeutic agents will be investigated, namely on the male mice reproductive system. Traditional diagnostic techniques (biopsies) will continued to be compared with faster, reliable and cheaper ones (flow-citometry and fluorescence microscopy) in order to do the quantification of "dose-effect" relationships.

Studies on cyclodextrins (CDs) as protecting and controlled release vehicles for ruthenium coordination complexes biological chemistry will continue. Native ß-cyclodextrin and heptakis(2,3,6-tris-O-methyl)-ß-cyclodextrin (TRIMEB) inclusion compounds of [Ru[9]aneS₃(1,10-phenanthroline-5,6-dione)CI]CI will be prepared and characterised by powder XRD, TGA and the effect of cyclodextrin inclusion upon their antitumoural activity will be determined. Selective activity toward osteosarcoma of these Ru(II) complexes will be tuned by resource to biomimetic design. [Ru[9]aneS₃(glycine)]Cl and [Ru[9]aneS₃(tryptophan)]Cl complexes will be prepared and tested as cytotoxic and antiproliferative drugs against osteosarcoma cell lines. After encapsulation in different cyclodextrin the cytotoxic effect is expected to increase.

Ru(II) complexes will also be tested as potential antimicrobial agents due to their broad spectrum cytotoxic action, namely [Ru[9]aneS₃(1,10-phenanthroline)CI]CI, both free and encapsulated in β -cyclodextrin and TRIMEB. Cyclodextrins are expected to reduce the minimum inhibitory concentration (MIC) of complex, and following this line of thought the drugs chloranphenicol and triclosan will also be encapsulated to probe the cyclodextrin effect on their MIC.

future research

general aims

new Biomaterials for:

Bone regeneration, drug delivery and cement substitution applications:

i) glass-polymer composites and glass-based scaffolds for localized drug delivery

ii) calcium phosphates of improved thermal stability, mechanical and osteoinductive properties

iii) bioactive glasses and glass-ceramics for osteoinductive and dentistry applications

iv) porous scaffolds with partially resorptive, osteoconductive and osteoinductive properties

v) nanoparticle reinforced bioactive PMMA bone cements

vi) pastes for rapid production of tailored scaffolds for surgical repair of craniofacial traumas

Environmental applications:

i) biomaterials for environmental remediation and use of native plants for phytostabilization of contaminated zones

ii) synthesis of Si biomaterials for the biodegradation of toxic environmental pollutants

new drugs and drug and molecular transporters:

i) synthesis and cyclodextrin encapsulation of new anti-tumoral agents for osteosarcoma; incorporation into polymeric or metal bone grafts for direct local action

ii) new polysaccharide encapsulated magnetic nanoparticles for use as contrast agents in magnetic resonance and drug delivery

iii) development of novel aza-bridged calixarene receptors for medicinal chemistry

iv) computational studies of the diffusion of delivery systems in cellular membrane models

v) molecular recognition studies of heme-binding proteins for application to disease-related issues and biomaterials/porphyrin chemistry

biological Metabonomics/In vivo studies:

i) metabolic profiling for studying biomaterials behavior in interaction with biofluidos/tissues/cells

ii) monitoring in vivo efficacy of drugs and drug delivery systems through the metabolic effects on cell/animal models

iii) in vivo/metabonomic studies of the effects of Ti-based chemotherapeutic agents, Ti-Al-V and Cr-Co-Mo alloys (orthopedic surgery) and new Cr(V) compounds

iv) metabonomics for disease diagnosis and treatment planning

v) metabonomics of the effect of mistranslation/heat shock on the longevity/stress of model organisms

research team at 31st december '08

professors & lectures

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Other student

Ana Sofia Pereira Moreira André Miguel da Costa Lopes Carla Cristina Portela C. Anjos Cláudia Manuela Mesquita da Rocha Heber Charles Joana Teixeira A. G. Marques Patrick Manuel Fernandes de Sousa Paula Maria Torres Rita Maria Cerejeira Matos Sílvia Diaz

collaborators

Anjos L Macedo Cristina Martins Moiteiro Glória C Ferreira João Miguel da Cruz M Agostinho Caio Rui Correia

associated laboratory centre for research in ceramics and composite materials CICECO

PhD theses MSc theses

Ferroelectric and Electromechanical Properties of Sol-Gel Pzt Films With Single-Composition and Compositionally Graded Structures Panya Khaenamkaew. Supervisor: Andrei Kholkine Prince of Songkla University, Hat Yai, Thailand.

A Pulverização Catódica na Produção de Compósitos de Carboneto de Tungsténio

Cristina Maria da Silva Fernandes. Supervisor: Ana Maria Oliveira E Rocha Senos

University of Aveiro. 2008

Dissolução e Precipitação de Xilanas Durante o Cozimento Kraft de E. Globulus:

Supervisor: Carlos de Pascoal Neto; Co-Supervisor: Dmitry Rvtuguin. University of Aveiro. 2008

Electrólitos Sólidos para Sensores Electroquímicos Eduarda Manuela Carvalho Lopes Gomes Pereira de Lima. Co-Supervisor: Filipe Miguel Henriques Lebre Ramos Figueiredo University of Aveiro. 2008

Estratégias para o aumento de retenção de polisscarídeos durante a produção de pasta Kraft de Eucalypyus Globulus Ana Sofia Vila Mona Santiago. Supervisor: Carlos Pascoal Neto. University of Aveiro. 2008

Estudo de condutores iónicos à base de Pirocloros Yb2ti2o7 Ana Lúcia Horovistiz, Orientadores: Jorge Frade e João Abrantes University of Aveiro. 2008

Fabrication and characterization of modified Macroporous Bioceramics for bone regeneration

Isabel Alexandra Fernandes Lemos. Supervisor: José Maria da Fonte Ferreira

University of Aveiro. 2008

Filmes espessos de band2ti5o14 para a microelectrónica fabricados por deposição electroforética Zhi Fu. Supervisor: Paula Maria Lousada Silveirinha Vilarinho, Angus

Zhi Fu. Supervisor: Paula Maria Lousada Silveirinha Vilarinho, Angus Kingon

University of Aveiro. 2008

Síntese e caracterização de nanoestruturas compósitas Márcia Carvalho Neves. Supervisor: Tito Silva Trindade University of Aveiro. 2008

Síntese, modificação superficial e propriedades de nanocristais de semicondutores

Ângela Sofia dos Santos Pereira. Supervisor: Tito Silva Trindade University of Aveiro. 2008 A Pulverização Catódica na Produção de Compósitos de Carboneto de Tungsténio

Cristina Maria da Silva Fernandes. Supervisor: Ana Maria Oliveira E Rocha Senos University of Aveiro. 2008

Análise citogenética de doenças hemato-oncológicas Rosa Angélica Alves De Sousa. Co-Supervisor: Maria De Lourdes Pereira

University of Aveiro, 2008

Análise estrutural de farinhas e alguns dos seus componentes Andreia Mariana Valinho Dias. Supervisor: Ana Maria Pissarra Coelho Gil

University of Aveiro, 2008

Análise e potencialidades de espécies químicas presentes no licor negro

Sušana Paula Dos Santos Teixeira. Orientador: Dmitry Victorovitch Evtyugin

University of Aveiro, 2008

Análise de variáveis processuais do cozimento ao sulfito acido de e. globulus

Cátia Cardoso Rolo Da Silva. Orientador: Dmitry Victorovitch Evtyugin University of Aveiro, 2008

Aplicabilidade da sinterização em duas etapas na obtenção de cerâmicos com tamanho de grão submicrométrico Maria Adelina Miranda Lourenço. Co-Orientador Filipe Miguel Henriques Lebre Ramos Figueiredo University of Aveiro, 2008

Aplicação De ferramentas de análise do ciclo de vida na sustentabilidade da construção - estudo de caso Ana Cláudia Furtado Correia Da Silva. Supervisor: Vitor Miguel Carneiro de Sousa Ferreira University of Aveiro, 2008

Argilas para aplicação na indústria de louça sanitária: design e fabrico Cláudia Marina Da Rocha Miranda, Supervisor: António Tomás Fonseca; Co-Supervisor: Maria Margarida Almeida University of Aveiro, 2008

Avaliação das características de ligação do cimento de fosfato de magnésio em moldes de Areia Para Fundição Nuno Miguel Pinto Neves. Supervisor: Ana Maria Bastos Costa

Segadães

University of Aveiro, 2008

Bioprocessamento de pentoses do licor de cozimento ao sulfito ácido Ana Sofia Nunes Pontes. Supervisor: Ana Maria Rebelo Barreto Xavier; Co-Supervisor: Dmitry Victorovitch Evtyugin University of Aveiro, 2008

Caracterização de membranas microporosas de titanossilicatos por permeação de um gás puro

Sara Margarida Baía Barros. Supervisor: Carlos Manuel Santos da Silva

University of Aveiro, 2008

Cinética de formação de aldeído siríngico durante a oxidação de Ienhossulfonatos com oxigénio em meio alcalino Sónia Goreti Maia Santos. Supervisor: Dmitry Victorovitch Evtyugin University of Aveiro, 2008

Caraterização química do engaço da uva e possíveis aplicações Sónia Oliveira Prozil. Orientador: Dmitry Victorovitch Evtyugin; Co-Orientador: Luisa Paula Valente da Cruz Lopes University of Aveiro, 2008

Coeficientes de actividade de aminoácidos em solução aquosa Simão André Pinto Ferreira Alves. Orientadores: Carlos Manuel Santos Da Silva and Francisco Avelino da Silva Freitas University of Aveiro, 2008

Conversas em casa sobre ciência - um estudo piloto Andreia Sofia Pereira da Silva Ramos. Supervisor: Julio Domingos Pedrosa Luz Jesus University of Aveiro, 2008

Critérios ambientais na utilização de materiais de construção Sandra Manuel Simaria De Oliveira Lucas. Supervisor: Vitor Miguel Carneiro de Sousa Ferreira; Co-Supervisor: Joao Antonio Labrincha **Batista**

University of Aveiro, 2008

Desacidificação biológica de mostos e vinhos com Susana Clara Ribeiro. Supervisor: Maria Ines Purcell de Portugal

Branco; Co-Supervisor: Ana Maria Rebelo Barreto Xavier University of Aveiro, 2008

Desenvolvimento de suportes porosos para aplicações biomédicas a partir de materiais vítreos do sistema Si-Ca-P-Mg Erika Davim Orientadora: Maria Helena Vaz Fernandes; Co-Orientadora: Ana Maria Oliveira Rocha Senos University of Aveiro, 2008

Desenvolvimento de um vidrado opaco brilhante

Isabel Gomes dos Santos Ladeira. Supervisor: Maria Margarida Almeida; Co-Supervisor: Raquel Matias Fonseca University of Aveiro, 2008

Deslenhificação de materiais lenhocelulósicos para bioconversão Gil André Serrão Freitas, Orientador: José Albino Gomes Alves Dias; Co-Orientador: Dmitry Victorovitch Evtyugin Universidade De Trás-Os-Montes E Alto Douro, 2008

Determinação do indice de octano a partir de dados cromatográficos Márcia Patrícia Ferreira Gonçalves. Co-Supervisor: João Manuel da Costa e Araujo Pereira Coutinho University of Aveiro, 2008

Determinação do número de octano por cromatografia gasosa Marcia Gonçalves.Supervisors: Armando Silvestre and João Coutinho University of Aveiro, 2008

Development and optimization of paint formulations with vocs Maria João Marques, Supervisor: Ana Barros and Co-Supervisor: João Coutinho University of Aveiro And Resiquímica. 2008

Diagnóstico pre-natal em citogenética

Cláudia Marlene Oliveira de Almeida. Co-Supervisor: Maria de Lourdes Pereira

University of Aveiro, 2008

Dissolução e Precipitação de Xilanas Durante o Cozimento Kraft de E. Globulus

Supervisor: Carlos de Pascoal Neto; Co-Supervisor: Dmitry Rvtuguin. University of Aveiro. 2008

Efeito do ph na remoção De Cd2+ em solução aquosa com Ets-4, Lidiana Domingues Barreira. Supervisor: Carlos Manuel Santos da Silva Silva and Maria Eduarda Pereira University of Aveiro, 2008

Efeitos do Cca (Crómio-cobre-arsenato) em ratinhos: estudos morfológicos e analíticos

Rita Maria Cerejeira Matos. Supervisor: Maria de Lurdes Gomes Pereira

University of Aveiro, 2008

Electrólitos Sólidos para Sensores Electroquímicos Eduarda Manuela Carvalho Lopes Gomes Pereira de Lima. Co-Supervisor: Filipe Miguel Henriques Lebre Ramos Figueiredo University of Aveiro. 2008

Estratégias para o aumento de retenção de polisscarídeos durante a produção de pasta Kraft de Eucalypyus Globulus Ana Sofia Vila Mona Santiago. Supervisor: Carlos Pascoal Neto. University of Aveiro. 2008

Estudo do comportamento de ligas de alumínio 6061 E 6082 MMM Martins, Supervisor: Fernando Bico Marques University of Aveiro, 2008

Estudo e optimização de materiais para aplicações termo-magnéticas José Carlos Vieira Leitão, Orientadores: Vitor Brás De Sequeira Amaral E Mário De Sousa Reis Júnior University of Aveiro, 2008

Estudo sobre a composição química e possíveis aplicações do folhelho de uva

Joana Andreia Saraiva Mendes. Orientador: Dmitry Victorovitch Evtyugin; Co-Orientador: Luisa Paula Valente Da Cruz Lopes University of Aveiro, 2008

Estudos de degradação do glifosato Ana Raquel Figueiredo Marques. Orientador: Valdemar Inocêncio Esteves; Co-Orientador: Dmitry Victorovitch Evtyugin University of Aveiro, 2008

Evolução da composição de vidrados mates para revestimento de monoporosa e pavimento de grés porcelânico: substituição de Zno Helder, José C. Oliveira. Supervisor: João Labrincha University of Aveiro, 2008

Extracção de óleo de grainha de uva com Co2 supercrítico Ana Luisa Carvalho Magalhães. Supervisor: Carlos Manuel Santos da Silva and Manuel António Coimbra University of Aveiro, 2008

Extracção e isolamento de triterpenoides de elevado valor comercial a partir da casca de E. Globulus, Rui Domingues, Supervisors: Armando Silvestre and Carlos Pascoal Neto University of Aveiro, 2008

Ferramentas odontológicas de si3n4 revestidas com diamante Cvd Ermelinda Da Conceição Portela Salgueiredo. Orientadores: Filipe José Alves Oliveira and Rui Ramos Ferreira e Silva University of Aveiro, 2008

Ferroelectric and Electromechanical Properties of Sol-Gel Pzt Films With Single-Composition and Compositionally Graded Structures Panya Khaenamkaew. Supervisor: Andrei Kholkine Prince of Songkla University, Hat Yai, Thailand

Fotodegradação de soluções de laranja ii e efluentes da indústria têxtil por camadas de Tio2 E Zno, serigrafadas em peças cerâmicas Elisabete Bárbara Maia Rego. Supervisor: Joao Antonio Labrincha Batista

University of Aveiro, 2008

Influência do par iónico na partição de fluoroquinolonas Ana Isabel da Graça Barranqueiro, Orientadoras: Isabel Maria Marrucho

University of Aveiro, 2008

Isotérmicas de adsorção de água de materiais híbridos O/I à base de celulose

Vânia Manuela Mendes Dias. Orientador: Maria Ines Purcell De Portugal Branco; Co-Orientador: Dmitry Victorovitch Evtyugin University of Aveiro, 2008

lattice dynamics and relaxation mechanisms in doped strontium titanate ceramics

Tatiana Correia. Supervisor: Paula Maria Vilarinho University of Aveiro, 2008

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Magnetoelectric composites based on hexagonal ferrites Ekaterina Konstantinovna Selezneva. Supervisor: Andrei Leonidovitch Kholkine University of Aveiro, 2008

Mecanossíntese, processamento cerâmico e caracterização eléctrica de La1-Xsrxga1-Y-Zmgyalzo3-d Eddy Michael Pedro Domingues. Orientador Filipe Miguel Henriques Lebre Ramos Figueiredo University of Aveiro, 2008

Medição de propriedades termofísicas de perfluorocarbonetos e líquidos iónicos

Pedro Jorge Marques de Carvalho. Supervisor: Joao Manuel da Costa e Araujo Pereira Coutinho University of Aveiro, 2008

Modelação da circulação dos Npe'S Na produção de pastas celulósicas

Maria Goreti Fernandes Martins. Orientador: Dmitry Victorovitch Evtyugin; Co-Orientador: Maria Ines Purcell De Portugal Branco University of Aveiro, 2008

Modelação da solubilidade de compostos aromáticos policíclicos com Cpa eos

Vera Lúcia Henriques de Oliveira. Supervisor: Joao Manuel da Costa e Araujo Pereira Coutinho University of Aveiro, 2008

Nanocompósitos de celulose e metais (Au, Ag) Ricardo João Borges Pinto. Supervisor: Carlos Pascoal Neto; Co-Supervisor: Tito Silva Trindade

University of Aveiro, 2008

Obtención y caracterización de pectinas y sus hidrogeles a partir de cáscara de naranja del estado de sonora Verónica Acuña Ortiz. Orientadores: Waldo Argüelles Monal E

Alessandro Gandini Centro De Investigation En Alimentación Y Desarrollo, Guaymas,

Sonora, Mexico.

Optimização do tratamento biológico com o sistema bioamp gt em áduas residuais

Ana Sofia Mendes Margues Ameixoeiro. Supervisor: Ana Maria Rebelo Barreto Xavier. Co-Supervisor: João Manuel da Costa e Araujo Pereira Coutinho University of Aveiro, 2008

Polimerização de pmma em microemulsão com lis tensioactivos Marisa Vendeira Valente. Supervisors: Isabel Maria Marrucho and Ana Timmons Barros University of Aveiro, 2008

Polyamide 12 / alumina nanocomposites - thermal and mechanical

properties Montira Sriyai. Supervisors: Ana Barros-Timmons And Karl Schulte University of Aveiro, 2008

Preparação e avaliação da permeabilidade de substratos de celulose modificados

Liliana Sofia Carvalho Tomé. Supervisor: Carmen Sofia da Rocha Freire Barros and Isabel Marrucho University of Aveiro, 2008

Preparação e caracterização de novos biocompósitos baseados em amido termoplástico

Ivo Marcelo Guilherme Martins. Supervisors: Carmen Sofia Rocha Freire and Alessandro Gandini University of Aveiro, 2008

Preparação e caracterização de novos materiais compósitos baseados em fibras de celulose

Tânia Freitas Fernandes. Supervisors: Carmen Sofia Rocha Freire and Alessandro Gandini University of Aveiro, 2008

Preparation and characterization of functional mortars Júlio César Longo. Supervisor: Ana Margarida Madeira Viegas de Barros Timmons University of Aveiro, 2008

Previsão de pontos de turvação de biodieseis Joana Cristina Alberto Lopes. Supervisor: Joao Manuel da Costa e Araujo Pereira Coutinho

University of Aveiro, 2008

Processamento coloidal de cerâmicos de espinela Mgal2o4 Paula Curveira Pinho. Supervisors: Margarida Almeida and Augusto l opes University of Aveiro, 2008

Processamento de híbridos orgânicos-inorgânicos para óptica integrada

Carlos Miguel Santos Vicente. Supervisor: Maria Rute de Amorim e Sa Ferreira Andre University of Aveiro, 2008

Produção de ácido acético e furfural a partir do condensado de cozimento ao sulfito ácido

Nelson Correia Martins. Supervisors: Dmitry Victorovitch Evtyugin and Carlos Manuel Santos da Silva University of Aveiro, 2008

Produção de amoníaco e sua optimização

Marta de Jesus Roque. Supervisor: Francisco Avelino da Silva Freitas University of Aveiro, 2008

Produção de bioetanol a partir de licor de cozimento ao sulfito ácido Mariana Fernandes Correia. Supervisor: Ana Maria Rebelo Barreto Xavier; Co-Supervisor: Dmitry Victorovitch Evtyugin University of Aveiro, 2008

Produção de celulose microcristalina a partir de pasta sulfito ácido Andreia Filipa Bastos Figueiredo. Supervisor: Dmitry Victorovitch Evtyugin University of Aveiro, 2008

Projecto, instalação e modelação de uma unidade de extracção supercrítica

Rui Alberto Magueta da Silva. Supervisor: Carlos Manuel Santos da Silva

University of Aveiro, 2008

Quantificação de club drugs em amostras biológicas em toxicologia forense

André Lobo. Supervisor: Armando Silvestre University of Aveiro, 2008

Reacção pozolânica de metacaulinos e diatomites em argamassas de reabilitação

Edson Miguel da Silva Tavares. Supervisor: Vitor Miguel Carneiro de Sousa Ferreira University of Aveiro, 2008

Reactividade superficial de vidros com tio2 em soluções fisiológicas simuladas

Ana Margarida Batista da Silva. Supervisor: Maria Helena Figueira Vaz Fernandes

University of Aveiro, 2008

Regeneração da espermatogénese e qualidade espermática em ratinhos expostos a Cdcl2 António José Coelho. Supervisor: Maria de Lourdes Pereira University of Aveiro, 2008

Relação entre a resposta eléctrica macroscópica e microscópica em polímeros electroactivos Jivago Nunes. Co-Supervisor: Paula Maria Vilarinho University of Aveiro, 2008

Remoção de Cd2+ em solução aquosa usando titanossilicato Ets-10

Elizabeth Domingues Camarinha. Supervisor: Carlos Manuel Santos da Silva and Maria Eduarda Pereira University of Aveiro, 2008

Revestimento de papéis com formulações à base de alcóxidos e sua aptidão para impressão Rui de Figueiredo Duarte. Supervisor: Dmitry Victorovitch Evtyugin University of Aveiro, 2008

Revestimentos decorativos cumprindo covs 2010 impostos no DI 181/06

Maria João Madaíl Ferreira Margues. Co-Supervisor: Joao Manuel da Costa e Araujo Pereira Coutinho University of Aveiro, 2008

Scaholds a base de polímeros piezoeléctricos para regeneração óssea

Natália Braz Barroca. Supervisor: Paula Maria Lousada Silveirinha Vilarinho; Co-Supervisor: Maria Helena Figueira Vaz Fernandes University of Aveiro, 2008

Síntese de pigmentos inorgânicos azuis com base em lama de anodização de alumínio Ana La Salete Pereira Leite. Supervisor: Joao Antonio Labrincha Batista

University of Aveiro, 2008

Sintese e caracterização de materiais hibridos de Caco3 e celuloses modificadas

Carla Andreia Cunha Vilela. Supervisor: Carlos Pascoal Neto; Co-Supervisor: Tito Silva Trindade University of Aveiro. 2008

Síntese e caracterização de nanocompósitos funcionais Susana Maria Rodrigues Peixoto. Supervisor: Ana Margarida Madeira Viegas de Barros Timmons University of Aveiro, 2008

Solubilidade de polímeros biodegradáveis em solventes verdes/equilíbrio líquido-líquido em sistemas álcoois fluorados e líquidos iónicos

Rui Manuel Cordeiro Ferreira. Supervisor: Joao Manuel da Costa e Araujo Pereira Coutinho University of Aveiro, 2008 Studies on polymer/carbon based nanoparticles Madhuphani Namburi. Supervisor: Ana Margarida Madeira Viegas de Barros Timmons University of Aveiro, 2008

Synthesis of alumina ceramics with bimodal pore size distribution Bussara Lapamnuayphon. Supervisor: Anja Borchert, Rolf Janssen and Joaquim Manuel Vieira University of Aveiro, 2008

Transformações microestruturais nas ligas de alumínio arrefecidas desde o domínio semi-sólido Natalia Ribeiro de Oliveira. Supervisor: Rui Ramos Ferreira e Silva University of Aveiro, 2008

Valorização da grainha de uva: óleo e procianidinas Joana Patrícia do Vale Afonso. Supervisor: Carlos Manuel Santos da Silva and Manuel António Coimbra University of Aveiro, 2008

books intenational Abrantes LM, Amir N, Aoki K, Aurbach D, Barcena Soto D, Baucke FGK, Bobacka J, Bond AM, Bund A, Chasid O, Correia J, Dölling R, Donten M, Echegoyen LE, Eshel H, Feldberg SW, Fisher A, Fletcher A, Garay F, Gavaghan D, Gillow K, Gründler P, Gofer Y, Gulaboski R, Guth U, Hamnett A, Heinze J, Hepel M, Hermes M, Heyrovsky M, Holze R, Horanyi G, Hümmelgen IA, Inzelt G, Kahlert H, Kakiuchi T, Katz E, Kharton VV, Koltypin M, Komorsky-Lovric S, Kulesza PJ, Kutner W, Kuznetsov AM, Kvarnström G, Lang GG, Larosh L, Levi E, Levi M, Levi N, Lewera A, Lohrengel MM, Lovric M, Ludvik J, Marken F, Markevich E, Markovsky B, Matthews S, Meyer B, Milchev AA, Mirceski V, Mortimer RJ, Murray RW, Myland J, Oldham KB, Opallo M, Osakai T, Pajkossy T, Pethig R, Petrii OA, Polak E, Ragoisha G, Salitra G, Samec Z, Scheller F, Schmickler W, Scholz F, Schröder U, Schuhmann W, Soffer A, Stojek Z, Strehblow HH, Tallmann DE, Talyossef Y, Tang XC, Tsirlina G, Vayenas CG, Volkov AG, Vorotyntsev MA, Wang J, Wollenberger U, Yosypchuk B, Zinigrad E, Zoski CG, Zuman P. 2008. Electrochemical Dictionary. Edited by Bard AJ, Inzelt G, Scholz F. Springer, Heidelberg-Berlin, ISBN: 978-3-540-74597-6, DOI 10.1007/978-3-340-74598-3, 723 pages.

Belgacem Mohamed Naceur, Gandini Alessandro, 2008, Monomers, Polymers and Composites from Renewable Resources, Elsevier, Amsterdam, ISBN: 978-0-08-045316-3.

books Ribeiro-Claro P, Coutinho J, Neto CP, 2008, Chemistry@UA 03-07, Chemistry Department (Ed.), ISBN 978-972-789-271-6.

book chapters intenational

Amaral PFF, Coelho MAZ, Marrucho IM, Coutinho JAP. 2008. Biosurfactants from yeasts: Characteristics, production and application. In Biosurfactants, R Sen (ed), Landes Bioscience

Chmielewská E, Sabová L, Wu A, Aranyosiová M, Velic D. 2007. Surface charging or templating by carbonaceous substances to broaden the adsorption performance of clinoptilolite-rich tuff. In ANALES, Wladyslaw Rudzinski (Ed.), UNIVERSITATIS MARIA E CURIE – SKLODOWSKA, LUBLIN – POLONIA, VOL. LXII, 4 SECTIO AA, Chap. 4, pp. 35-48. (ISBN: 0137-6853)

Gamelas J, Evtuguin DV, Gaspar A. 2008. Transition Metal Complexes in the Delignification Catalysis. In: "Transition Metal Chemistry: New Research", B. Varga and L. Kis, Eds., NovaPublishers, Huntington NY 11743 USA, pp. 15-57

Gil AM, Rodrigues JR. 2008. Methods for the characterization of beer by nuclear magnetic resonance spectroscopy. in Beer in Health and Disease Prevention, Preedy, Victor R. Ed., Elsevier, London, Chapter 93, 935-942, 2008 (ISBN 978-0-12-373891-2)

Golberg D, Costa PMFJ, Mitome M, Bando Y. 2008. In-situ TEM electrical and mechanical probing of individual multiwalled Boron Nitride nanotubes. In Nanotubes, Frontier-Books Publisher, Tokyo, Japan, p. 306-314.

Kholkin AL, Kiselev DA, Kholkine LA, Safari A. 2008. Smart ferroelectric ceramics for transducer applications. In "Smart Materials", Ed. Mel Shwartz, CRC Press, 592p, pp. 9.1-9.11

Kholkin AL, Pertsev NA, Goltsev AV. 2008. Piezoelectricity and crystal symmetry. In "Piezoelectric and Acoustic Materials for Transducer Applications", Eds. Safari A, Akdogan K, Springer, pp. 17-38.

Labrincha JA. 2008. Reutilització de residus sòlids o fangs en matrius ceràmiques per vitrificació. In La Nostra Ceràmica – Art, indústria i recerca en la ceràmica valenciana, Chapter 9, ed. E. Gual, V. Cantavella, G. Monrós, Agrupació Borrianenca de Cultura, Valencia, ISSN: 1130-4235

Naceur BM, Alessandro G. 2008. The State of the Art. In Monomers, Polymers and Composites from Renewable Resources. Naceur BM, Alessandro G. Elsevier, Amsterdam, Chap.1, pp.1-16.

Naceur BM, Alessandro G. 2008. Materials from Vegetable Oils: Major Sources, Properties and Applications, In Monomers, Polymers and Composites from Renewable Resources, Naceur BM, Alessandro G. Elsevier, Amsterdam, Chap.3, pp.39-66

scientific production 2008 | 87

Naceur BM, Alessandro G. 2008. Furan Derivatives and Furan Chemistry at the Service of Macromolecular Materials, In Monomers, Polymers and Composites from Renewable Resources, Naceur BM, Alessandro G. Elsevier, Amsterdam, Chap.6, pp.115-152

book chapters intenational

Naceur BM, Alessandro G. 2008. Lignins as Components of Macromolecular Materials, In Monomers, Polymers and Composites from Renewable Resources, Naceur BM, Alessandro G. Elsevier, Amsterdam, Chap.11, pp.243-272

Naceur BM, Alessandro G. 2008. Partial or Toral Oxypropilation of Natural Polymers and the Use of the Ensuing Materials as Composites or Polyol Macromolecules, In Monomers, Polymers and Composites from Renewable Resources, Naceur BM, Alessandro G. Elsevier, Amsterdam, Chap.13, pp.273-288

Naceur BM, Alessandro G. 2008. Surface Modification of Cellulose Fibers, In Monomers, Polymers and Composites from Renewable Resources, Naceur BM, Alessandro G. Elsevier, Amsterdam, Chap.18, pp. 385-400

Naceur BM, Alessandro G. 2008. Chemical Modification of Wood, In Monomers, Polymers and Composites from Renewable Resources, Naceur BM, Alessandro G. Elsevier, Amsterdam, Chap. 20, pp. 419-432

Neri G, Pinna N. 2008. Resistive chemical sensors from metal oxides nanocrystals synthesized in organic solvents. In: "Nanomaterials: New research developments", Nova Science Publishers 217-252

Neto CP, Silvestre AJD, Gandini A. 2008. Cork and suberins: major sources, properties, applications. In Monomers, oligomers, polymers and composites from renewable resources. M.N. Belgacem, A. Gandini (Eds), Elsevier, Oxford, cap. 14, 305-320

Oliveira L, Evtuguin DV, Cordeiro N, Silvestre AJD, Silva MAS. 2008. Chemical composition and lignin structural features of banana plant leaf sheaths and rachis. In: "Characterization of Lignocellulosic Materials", Ed. Thomas Q. Hu, Blackwell Publ., Vancouver, Canada, Chapter 10. pp. 171-188

Pai IK, Terdalkar S, Pereira ML, Morgado F. 2008. Diel vertical migration of zooplankton in Andaman Sea. In: Arvin Kumar & Harbhajan Kaur (Eds.), Ecology of Aquatic Insects, Daya Publishing Housse, Delhi, Chap. 3, p. 24-5

Pasquini D. 2008. Química dos Compostos de Coordenação. In: Série Licenciatura em Química/Universidade de Uberaba – Educação à Distância, M. A. R. F. Santos (Eds.), Universidade de Uberaba, Uberaba – MG, Etapa V – Volume 1 – Roteiro de Estudo 3, p.61-80. ISBN: 978-85-7777-155-4

Pasquini D. 2008. Análise de Compostos Orgânicos por Métodos Químicos. In: Série Licenciatura em Química/Universidade de Uberaba – Educação à distância, M. A. R. F. Santos (Eds.), Universidade de Uberaba, Uberaba – MG, Etapa VI – Volume 2 – Roteiro de Estudo 5, p.79-103. ISBN: 978-85-7777-244-5

Pasquini D. 2008. Destilação Simples e Destilação por Arraste de Vapor. In: Série Licenciatura em Química/Universidade de Uberaba – Educação à distância, M. A. R. F. Santos (Eds.), Universidade de Uberaba, Uberaba – MG, Etapa VI – Volume 4 – Roteiro de Estudo 2, p.41-56. ISBN: not attributed yet

Pasquini D., Dias R.A. 2008. Cinética Química: Parte II. In: Série Tecnologia em Produção Sucroalcooleira/Universidade de Uberaba – Educação à Distância, A. L. T. Fernandes (Eds.), Universidade de Uberaba, Uberaba – MG, Etapa IV – Volume 2 – Roteiro de Estudo 1, p.55-79. ISBN: not attributed yet

Silva CM, Liu H. 2008. Modeling of Transport Properties of Hard Sphere fluids and its Applications. In Theory and Simulation of Hard-Sphere Fluids and Related Systems, A. Mulero (Ed.), Lecture Notes in Physics Vol. 753, Springer-Verlag, Chap. 9, p. 389-501

Silvestre AJD, Gandini A. 2008. Rosin: sources, properties and applications. In Monomers, oligomers, polymers and composites from renewable resources. M.N. Belgacem, A. Gandini (Eds), Elsevier, Oxford, cap. 4. 67-88

Silvestre AJD, Gandini A. 2008. Terpenes: major sources, properties and applications. In Monomers, oligomers, polymers and composites from renewable resources, M.N. Belgacem, A. Gandini, Elsevier, Oxford chap. 2. 17-38

Cavaleiro AMV. 2008. Polyoxometalates in oxidative catalysis of organic compounds. In Catalysis from theory to applications, J. L. Figueiredo, M. M. Pereira, J. Faria (Eds.), Coimbra University Press, Coimbra, Chap. 5, p. 335-354.

book chapter national

sci papers IF> =5

Ananias D, Ferdov S, Paz FAA, Ferreira RAS, Ferreira A, Geraldes C, Carlos LD, Lin Z, Rocha J. 2008. Photoluminescent layered lanthanide silicate nanoparticles. Chemistry of Materials 20:205-212.

Costa PMFJ, Golberg D, Mitome M, Hampel S, Leonhardt A, Buchner B, Bando Y. 2008. Stepwise Current-Driven Release of Attogram Quantities of Copper Iodide Encapsulated in Carbon Nanotubes. Nano Letters 8:3120-3125.

Graca G, Duarte IF, Goodfellow BJ, Carreira IM, Couceiro AB, Domingues MD, Spraul M, Tseng LH, Gil AM. 2008. Metabolite profiling of human amniotic fluid by hyphenated nuclear magnetic resonance spectroscopy. Analytical Chemistry 80:6085-6092.

Harbuzaru BV, Corma A, Rey F, Atienzar P, Jorda JL, Garcia H, Ananias D, Carlos LD, Rocha J. 2008. Metal-organic nanoporous structures with anisotropic photoluminescence and magnetic properties and their use as sensors. Angewandte Chemie-International Edition 47:1080-1083.

Kalinin SV, Rodriguez BJ, Jesse S, Maksymovych P, Seal K, Baddorf AP, Kholkin A, Proksch R. 2008. Bias induced phase transitions, Materials Today 11: 16-27.

Kharton VV, Kovalevsky AV, Patrakeev MV, Tsipis EV, Viskup AP, Kolotygin VA, Yaremchenko AA, Shaula AL, Kiselev EA, Waerenborgh JC. 2008. Oxygen nonstoichiometry, mixed conductivity and Mössbauer spectra of Ln0.5A0.5FeO3-? (Ln = La-Sm, A = Sr, Ba): Effects of cation size. Chemistry of Materials 20:6457-6467.

Kowalchuk CM, Paz FAA, Ananias D, Pattison P, Carlos LD, Rocha J. 2008. Photoluminescent Microporous Lanthanide Silicate AV-21 Frameworks. Chemistry-a European Journal 14:8157-8168.

Lamaka SV, Shchukin DG, Andreeva DV, Zheludkevich ML, Möhwald H, Ferreira MGS. 2008. Sol-Gel/Polyelectrolyte Active Corrosion Protection System. Advanced Functional Materials 18:3137 – 3147.

Lankshear MD, Dudley IM, Kar-Man C, Cowley AR, Santos SM, Félix V, Beer PD, 2008, Cooperative and ion-pair recognition by heteroditopic xalix[4]diquinone receptors, Chemistry, European Journal, 14, 2248-2263.

Lopes AML, Araujo JP, Amaral VS, Correia JG, Tomioka Y, Tokura Y. 2008. New phase transition in the Pr1-xCaxMnO3 system: Evidence for electrical polarization in charge ordered manganites. Physical Review Letters 100:155702.

Mafra L, Rocha J, Fernandez C, Castro GR, Garcia-Granda S, Espina A, Khainakov SA, Garcia JR. 2008. Characterization of layered gamma-titanium phosphate (C2H5NH3)[Ti(H1.5PO4)(PO4)](2)center dot H2O intercalate: A combined NMR, synchrotron XRD, and DFT calculations study. Chemistry of Materials 20:3944-3953.

Oliveira DC, Macedo AG, Silva NJO, Molina C, Ferreira RAS, Andre PS, Dahmouche K, Bermudez VD, Messaddeq Y, Ribeiro SJL, Carlos LD. 2008. Photopatternable di-ureasil-zirconium oxocluster organic-inorganic hybrids as cost effective integrated optical substrates. Chemistry of Materials 20:3696-3705.

Pereira SMD, Martins MA, Trindade T, Watson IM, Zhu D, Humphreys CJ. 2008. Controlled integration of nanocrystals in inverted hexagonal nano-pits at the surface of light-emitting heterostructures. Advanced Materials 20:1038-+.

Pinna N, Niederberger M. 2008. Surfactant-free nonaqueous synthesis of metal oxide nanostructures. Angewandte Chemie-International Edition 47:5292-5304.

Raja R, Thomas JM, Greenhill-Hooper M, Ley SV, Paz FAA. 2008. Facile, one-step production of niacin (Vitamin B-3) and other nitrogen-containing pharmaceutical chemicals with a single-site heterogeneous catalyst. Chemistry-a European Journal 14:2340-2348.

Rauwel E, Clavel G, Willinger MG, Rawel P, Pinna N. 2008. Non-aqueous routes to metal oxide thin films by atomic layer deposition. Angewandte Chemie-International Edition 47:3592-3595.

Scott JF, Fan HJ, Kawasaki S, Banys J, Ivanov M, Macutkevic J, Blinc R, Laguta VV, Cevc P, Liu JS, Kholkin AL. 2008. THz emission from PZT nanotubes. Nano Letters 8: 4404-4409.

Shi FN, Cunha-Silva L, Ferreira RAS, Mafra L, Trindade T, Carlos LD, Paz FAA, Rocha J. 2008. Interconvertable modular framework and layered lanthanide(III)-etidronic acid coordination polymers. Journal of the American Chemical Society 130:150-167.

Shvartsman VV, Bedanta S, Borisov P, Kleemann W, Tkach A, Vilarinho PM. 2008. (Sr,Mn)TiO3 - a magnetoelectric multiglass. Physical Review Letters 101, 165704-1 -165704-4.

Singh MK, Tolou S, Gracio JJA, Sousa ACM, Fereira JMF, Garmestani H, Ahzi S. 2008. Hydroxyapatite Modified with Carbon-Nanotube-Reinforced Poly(methyl methacrylate): A Nanocomposite Material for Biomedical Applications. Advanced Functional Materials 18: 694–700

Surendran KP, Wu AY, Vilarinho PM, Ferreira VM. 2008. Sol-gel synthesis of low-loss MgTiO3 thin films by a nonmethoxyethanol route. Chemistry of Materials 20:4260-4267.

Willinger M-G, Neri G, Rauwel E, Bonavita A, Micali G, Pinna N. 2008. Vanadium oxide sensing layer grown on carbon nanotubes by a new atomic layer deposition process. Nano Lett 8, 4201.

sci papers IF< 5

Abrantes JCC, Ferreira AAL, Horovistiz AL, Frade JR. 2008. Interpretation of impedance spectra based on local minima of imaginary Z vs frequency. Electrochimica Acta 53:8222-8227.

Abreu CS, Salgueiredo E, Oliveira FJ, Fernandes AJS, Silva RF, Gomes JR. 2008. CVD diamond water lubricated tribosystems for high load planar sliding. Wear 265:1023-1028.

Abreu MM, Matias MJ, Magalhães MCF, Basto MJ. 2008. Impacts on water, soil and plants from the abandoned Miguel Vacas copper mine, Portugal. Journal of Geochemical Exploration 96:161-170.

Aguiar H, Solla EL, Serra J, Gonzalez P, Leon B, Almeida N, Cachinho S, Davim EJC, Correia R, Oliveira JM, Fernandes MHV. 2008. Orthophosphate nanostructures in SiO2-P2O5-CaO-Na2O-MgO bioactive glasses. Journal of Non-Crystalline Solids 354:4075-4080.

Albuquerque CM, Labrincha JA. 2008. Removal of contaminants from aqueous solutions by beds made of rejects of the lightweight aggregates production. Ceramics International 34:1735-1740.

Albuquerque R, Neves MC, Mendonca MH, Trindade T, Monteiro OC. 2008. Adsorption and catalytic properties of SiO2/Bi2S3 nanocomposites on the methylene blue photodecolorization process. Colloids and Surfaces A-Physicochemical and Engineering 328: 107-113.

Almeida A, Correia TM, Chaves MR, Vilarinho PM, Kholkin A. 2008. Study of inelastic light scattering in KaxSr1-1.5xTiO3. Materials Science Fórum 587-588:148-152.

Almeida FA, Oliveira FJ, Sacramento J, Silva RF. 2008. Micro- and nano-crystalline CVD diamond coated tools in the turning of EDM graphite. Surface and Coatings Technology 203:271-276.

Almeida T, Ferreira B, Loureiro J, Lopes T, Correia RN, Santos C. 2008. In vitro toxicity of novel bone cement PMMAco-EHA. Tissue Engineering Part A 14:867-867.

Alonso JC, Neves P, Silva C, Valente AA, Brandao P, Quintal S, de Brito MJV, Pinto P, Felix V, Drew MGB, Pires J, Carvalho AP, Calhorda MJ, Ferreira P. 2008. Immobilisation of eta(3)-allyidicarbonyl complexes of Mo-II with bidentate nitrogen ligands within aluminium-pillared clays. European Journal of Inorganic Chemistry:1147-1156.

Amaral F, Rubinger CPL, Henry F, Costa LC, Valente MA, Barros-Timmons A. 2008. Dielectric properties of polystyrene-CCTO composite. J Non-Crystalline Solids 354:5321–5322.

Amaral JS, Reis MS, Araújo JP, Mendonça TM, Tavares PB, Amaral VS, Vieira JM. 2008. Phase Separation of La0.70-xErxSr0.30MnO3 and its Effect on Magnetic and magnetocaloric properties. Materials Science Forum 587-588:338

Amaral JS, Tavares PB, Reis MS, Araújo JP, Mendonça TM, Amaral VS, Vieira JM. 2008. The effect of chemical distribution on the magnetocaloric effect: a case study in second-order phase transition manganites Journal of non-crystalline solids, 354:5301

Amaral L, Senos AMR, Vilarinho PM. 2008. Nonstoichiometry effects in SrTiO3 ceramics assessed by Transmission Electron Microscopy. Microscopy and Microanalysis 14: 5-6.

Amaral M, Abreu CS, Oliveira FJ, Gomes JR, Silva RF. 2008. Tribological characterization of NCD in physiological fluids. Diamond and Related Materials 17:848-852.

Amaral M, Dias AG, Gomes PS, Lopes MA, Silva RF, Santos JD, Fernandes MH. 2008. Nanocrystalline diamond: In vitro biocompatibility assessment by MG63 and human bone marrow cells cultures. Journal of Biomedical Materials Research Part A 87A:91-99.

Amaral M, Gomes PS, Lopes MA, Santos JD, Silva RF, Fernandes MH. 2008. Nanocrystalline diamond as a coating for joint implants: cytotoxicity and biocompatibility assessment. Journal of Nanomaterials Article ID 894352, 9 pages, doi:10.1155/2008/894352.

Amaral PFF, Freire MG, Rocha-Leao MHM, Marrucho IM, Coutinho JAP, Coelho MAZ. 2008. Optimization of oxygen mass transfer in a multiphase bioreactor with perfluorodecalin as a second liquid phase. Biotechnology and Bioengineering 99:588-598.

Amarante TR, Coelho AC, Klinowski J, Goncalves IS, Paz FA. 2008. 1-hydroxy-1,1,3,3,3-pentaphenyldisiloxane, [Si2O(OH)(Ph)(5)], at 150 K. Acta Crystallographica Section E-Structure Reports Online 64:O239-U4733.

Amorin H, Kholkin AL, Costa MEV. 2008. Templated grain growth of SrBi2Ta2O9 ceramics: Mechanism of texture development. Materials Research Bulletin 43:1412-1419.

Andrade-Dias, C, Lima, S, Teixeira-Dias, JJC, Teixeira, J. 2008. Why do methylated and unsubstituted cyclodextrins interact so differently with sodium decanoate micelles in water? Journal of Physical Chemistry B 112: 15327-15332.

Balula SS, Cunha-Silva L, Santos ICMS, Paz FAA, Rocha J, Nogueira HIS, Cavaleiro AMV. 2008. Catalytic Performance of Copper-Substituted Polyoxotungstate Materials and X-ray Structure of a New Sandwich-Type Compound. Advanced Materials Forum IV, Materials Science Forum 587-588:538-542.

Barradas NP, Alves E, Pereira S, Watson IM. 2008. RBS analysis of InGaN/GaN quantum wells for hybrid structures with efficient Forster coupling. Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms 266:1402-1406.

Barroca NB, Daniel-da-Silva AL, Fernandes MHV, Vilarinho PM. 2008. Porogen Effect of Bioactive Glass on Poly(Llactide) Scaffolds: Evidences by Electron Microscopy. Microscopy and Microanalysis, 14:65-66.

Bastos AC, Zheludkevich ML, Ferreira MGS. 2008. A SVET investigation on the modification of zinc dust reactivity. Progress in Organic Coatings 63:282-290.

Bdikin IK, Kholkin AL, Morozovska AN, Svechnikov SV, Kim SH, Kalinin SV. 2008. Domain dynamics in piezoresponse force spectroscopy: Quantitative deconvolution and hysteresis loop fine structure. Applied Physics Letters 92: 182909.

Belton CR, Itskos G, Heliotis G, Stavrinou PN, Lagoudakis PG, Lupton J, Pereira S, Gu E, Griffin C, Guilhabert B, Watson IM, Mackintosh AR, Pethrick RA, Feldmann J, Murray R, Dawson MD, Bradley DDC. 2008. New light from hybrid inorganic-organic emitters. J Phys. D: Appl. Phys. 41: 094006.

Benito P, Guinea I, Labajos FM, Rocha J, Rives V. 2008. Microwave-hydrothermally aged Zn,Al hydrotalcite-like compounds: Influence of the composition and the irradiation conditions. Microporous and Mesoporous Materials 110:292-302.

Bogomolov A, Solnyshkin A, Lasarev V, Kiselev D, Kholkin AL. 2008. Polarization of surface layer in PLZT relaxor ceramics. Ferroelectrics 374: 144-149.

Braga SS, Coelho AC, Goncalves IS, Santos G, Fonseca FJ, Andrade AM, Peres M, Simoes W, Monteiro T, Pereira L. 2008. Luminescence properties of the TRIMEB inclusion compound of a europium tris-beta-diketonate. Journal of Non-Crystalline Solids 354:2736-2739.

Bruno SM, Coelho AC, Ferreira RAS, Carlos LD, Pillinger M, Valente AA, Ribeiro-Claro P, Gonçalves IS, MCM-41 derivatised with pyridyl groups and its use as a support for luminescent europium(III) complexes. European Journal of Inorganic Chemistry:3786-3795.

Bruno SM, Ferreira RAS, Carlos LD, Pillinger M, Ribeiro-Claro P, Goncalves IS. 2008. Synthesis, characterisation and luminescence properties of MCM-41 impregnated with an Eu3+ beta-diketonate complex. Microporous and Mesoporous Materials 113:453-462.

Bystrov V, Bystrova N, Kisilev D, Paramonova E, Kuhn M, Kliem H, Kholkin A. 2008. Molecular model of polarization switching and nanoscale physical properties of thin ferroelectric Langmuir-Blodgett P(VDF-TrFE) films. Integrated Ferroelectrics 99:31-40.

Caço A, Varanda FR, Melo JMP, Dias AM, Dohrn R, Marrucho IM. 2008. Solubility of Antibiotics in Different Solvents. Part II: Non-Hydrochloride Forms of Tetracycline and Ciprofloxacin. Industrial & Engineering Chemistry Research 47: 8083-8089.

Caetano M, Oliveira FJ, Silva RF, Simoes F, Trindade B. 2008. Effect of Cu on the sintering ability of a surface modified Ti5Si3-based alloy synthesized by mechanical alloying. Reviews on Advanced Materials Science 18:339-343.

Carlos LD, Faustino WM, Malta OL. 2008. Comment on trivalent europium lifetimes in the presence of intramolecular energy transfer processes. Journal of the Brazilian Chemical Society 19:299-301.

Carvalho J, Carvalho P, Labrincha JA. 2008. Alkaline activation of mixtures of natural clay and glass culet rejects. Clay Minerals 43:531-541.

Carvalho MD, Ferreira P, Waerenborgh JC, Tsipis E, Lopes AB, Godinho M. 2008. Structure and magnetic properties of Ca2Fe1-xMnxAIO5+delta. Journal of Solid State Chemistry 181:2530-2541.

Carvalho PJ, Freire MG, Marrucho IM, Queimada AJ, Coutinho JAP. 2008. Surface tensions for the 1-alkyl-3methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids. Journal of Chemical and Engineering Data 53:1346-1350.

Carvalho S, Delgado R, Drew MGB, Felix V, Figueira M, Henriques RT.2008.Cascade dicopper architectures of a dibenzodioxatetraazamacrocycle, Polyhedron, 27(2), 679-687.

Cassiede M, Pauly J, Milhet M, Rivaletto M, Marrucho IM, Coutinho JAP, Daridon JL. 2008. A quartz crystal microbalance technique to study wax crystallization in the presence of gas. Measurement Science & Technology 19.

Castanho JM, Vieira MT, Fernandes CM, Senos AMR, Matos M. 2008. Coated WC powders by sputtered nanostructured Ni and stainless steel. Vacuum 82:1404-1406.

Castro G, Almeida FA, Oliveira FJ, Fernandes AJS, Sacramento J, Silva RF. 2008. Dry machining of silicon-aluminium alloys with CVD diamond brazed and directly coated Si3N4 ceramic tools. Vacuum 82:1407-1410.

Chelebaeva E, Larionova J, Guari Y, Ferreira RAS, Carlos LD, Paz FAA, Trifonov A, Guerin C. 2008. A luminescent and magnetic cyano-bridged Tb3+-Mo5+ coordination polymer: toward multifunctional materials. Inorganic Chemistry 47:775-777.

Chernev G, Samuneva B, Djambaski P, Kabaivanova L, Emanuilova E, Salvado IMMiranda, Fernandes MHV, Wu A. 2008. Synthesis and structure of new biomaterials containing silica and chitosan. Physics and Chemistry of Glasses-European Journal of Glass Science and Technology Part B 49:11-14.

Chernev G, Samuneva B, Djambaski P, Kabaivanova L, Emanuilova E, Salvado, I M. Miranda, Wu A. 2008. Synthesis and selected properties of silicate hybrids containing sepharose. Advanced Materials Research vols 39-40:53-56

Chmielewski MJ, Zhao LY, Brown A, Curiel D, Sambrook MR, Thompson AL, Santos SM, Felix V, Davis JJ, Beer PD, 2008.Sulfate anion templation of a neutral pseudorotaxane assembly using an indolocarbazole threading component, Chemical Communications, 27, 3154-3156.

Clavel G, Willinger MG, Zitoun D, Pinna N. 2008. Manganese-doped zirconia nanocrystals. European Journal of Inorganic Chemistry: 863-868.

Coelho AC, Amarante TR, Klinowski J, Goncalves IS, Paz FAA. 2008. 1-hydroxy-1,1,3,3,3-pentaphenyldisiloxane, [Si2O(OH)(Ph)(5)], at 100 K. Acta Crystallographica Section E-Structure Reports Online 64:O237-U4707.

Coelho AC, Brandão P, Santos AM, Rocha J, Gonçalves IS. 2008. Immobilisation of ferricinium cation into ETS-10 by ion exchange under microwave irradiation. Materials Science Forum 587-588: 453-457.

Coelho C, Rocha J, Madhu PK, Mafra L. 2008. Practical aspects of Lee-Goldburg based CRAMPS techniques for high-resolution H-1 NMR spectroscopy in solids: Implementation and applications. Journal of Magnetic Resonance 194:264-282.

Correia SL, Hotza D, Segadaes AM. 2008. Predicting porosity content in triaxial porcelain bodies as a function of raw materials contents. Journal of Materials Science 43:696-701.

Costa BFO, Amaral VS, Le Caër G, Braga ME, Amado MM, Rocco DL, Sousa JB. 2008. Magnetic and Transport Studies of ?-phase Fe50V50 Alloys with Different Thermal History. Journal of non-crystalline solids, 354:5287.

Costa G, Della VP, Ribeiro MJ, Labrincha JA. 2008. Forming black spinel pigment from industrial sludges. Amer. Ceram. Soc. Bull. 87[7]:9101-9107.

Costa G, Della VP, Ribeiro MJ, Oliveira APN, Monros G, Labrincha JA. 2008. Synthesis of black ceramic pigments from secondary raw materials. Dyes and Pigments 77:137-144.

Costa G, Ribeiro MJ, Labrincha JA, Dondi M, Matteucci F, Cruciani G. 2008. Malayaite ceramic pigments prepared with galvanic sludge. Dyes and Pigments 78:157-164.

Costa PMFJ, Golberg D, Mitome M, Bando Y. 2008. Electrical properties of CNx nanotubes probed in a transmission electron microscope. Applied Physics A – Materials Science and Processing 90: 225-229.

Costa PMFJ, Golberg D, Shen G, Mitome M, Bando Y. 2008. ZnO low-dimensional structures: electrical properties measured inside a transmission electron microscope. Journal of Materials Science 43: 1460-1470.

Cunha AG, Fernandes SCM, Freire CSR, Silvestre AJD, Neto CP, Gandini A. 2008. What is the real value of chitosan's surface energy? Biomacromolecules 9:610-614.

Cunha-Silva L, Brandao P, Rocha J, Paz FAA. 2008. The dehydrated copper silicate Na-2[Cu2Si4O11]: a threedimensional microporous framework with a linear Si-O-Si linkage. Acta Crystallographica Section E-Structure Reports Online 64:I13-U47

Cunha-Silva L, Girginova PI, Trindade T, Rocha J, Klinowski J, Paz FAA. 2008. Bis(tetramethylamonium) bis(2,4,5-carboxybenzoate)-benzene-1,2,4,5-tetracarboxylic acid (1/1). Acta Crystallographica Section E-Structure Reports Online 64:O69-U3138.

Cunha-Silva L, Shi FN, Klinowski J, Trindade T, Rocha J, Paz FAA. 2008. Decaaquadioxidobis[mu(3)-N-(phosphonatomethyl) iminodiacetato]dizinc(II)divanadium(IV)dihydrate. Acta Crystallographica Section E-Structure Reports Online 64:M39-U422.

Cunha-Silva L, Soares-Santos PCR, Nogueira HIS, Trindade T, Klinowski J, Rocha J, Paz FAA. 2008. Poly[[aqua-mu(3)-picolinato-mu(2)-picolinato-dipicolinatopotassium(I)ter bium(III)] 2.5-hydrate]. Acta Crystallographica Section E-Structure Reports Online 64:M529-U188.

Daniel-Da-Silva AL, Loio R, Lopes-Da-Silva JA, Trindade T, Goodfellow BJ, Gil AM. 2008. Effects of magnetite nanoparticles on the thermorheological properties of carrageenan hydrogels. Journal of Colloid and Interface Science 324:205-211.

Daniel-Da-Silva AL, Pinto F, Lopes-Da-Silva JA, Trindade T, Goodfellow BJ, Gil AM. 2008. Rheological behavior of thermoreversible kappa-carrageenan/nanosilica gels. Journal of Colloid and Interface Science 320:575-581.

Daniel-da-Silva AL, Trindade T, Goodfellow BJ, Gil AM. 2008. Magnetic carrageenan nanospheres for medical imaging. Tissue Engineering Part A 14:875-875.

Davim EJC, Fernandes MHV, Senos AMR. 2008. In vitro reactivity of a porous SI-MG-CA-P glass scaffold. Tissue Engineering Part A 14:865-866.

Di W, Willinger M-G, Ferreira RAS, Ren X, Lu S, Pinna N. 2008. Citric acid-assisted hydrothermal synthesis of luminescent TbPO4:Eu nanocrystals: controlled morphology and tunable emission. Journal of Physical Chemistry C 112: 18815

dos Santos AM, Coelho AC, Paz FAA, Rocha J, Goncalves IS, Carlos LD. 2008. Spectroscopic studies of an europium(III) tris-beta-diketonate complex bearing a pyrazolylpyridine ligand. Journal of Alloys and Compounds 451:344-346.

Dul'kin E, Mojaev E, Roth M, Kamba S, Vilarinho PM. 2008. Burns, Neel, and structural phase transitions in multiferoic Pb(Fe2/3W1/3)O-3-xPbTiO(3) detected by an acoustic emission. Journal of Applied Physics 103: :083542, 1-5.

Evans RC, Ananias D, Douglas A, Douglas P, Carlos LD, Rocha J. 2008. Energy transfer and emission decay kinetics in mixed microporous lanthanide silicates with unusual dimensionality. Journal of Physical Chemistry C 112: 260-268.

Evans RC, Carlos LD, Douglas P, Rocha J. 2008. Tuning the emission colour in mixed lanthanide microporous silicates: energy transfer, composition and chromaticity. Journal of Materials Chemistry 18: 1100-1107.

Fajín JLC, Cordeiro MNDS, Gomes JRB. 2008. DFT study of the CO oxidation on the Au(321) surface. Journal of Physical Chemistry C 112:17291-17302.

Ferdov S, Ferreira RAS, Lin Z. 2008. Optical properties and local structure of Eu3+-doped synthetic analogue of the microporous titanosilicate mineral sitinakite. Journal of Luminescence 128:1108-1112.

Ferdov S, Ferreira RAS, Lin Z. 2008. Photoluminescence of Eu3+-doped nanosized microporous titanosilicate - A structural analogue of the mineral pharmacosiderite. Journal of Alloys and Compounds 451:125-127.

Ferdov S, Lin Z, Ferreira RAS, Correia MR. 2008. Hydrothermal synthesis, structural, and spectroscopic studies of vanadium substituted ETS-4. Microporous and Mesoporous Materials 110:436-441.

Ferdov S, Lin Z, Ferreira RAS. 2008. Syntheses of mesoporous and microporous materials via 2-methylpentamethylenediamine. Chemistry Letters 37:100-101.

Ferdov S, Reis M, Lin Z, Ferreira RAS. 2008. Hydrothermal synthesis, crystal structure and magnetic properties of a new inorganic vanadium (III) phosphate with a chain structure. Inorg. Chem. 47:10062-10066.

Fernandes AC, Fernandes JA, Paz FAA, Romão CC. 2008. Activation of B-H bonds by an oxo-rhenium complex. Dalton Trans. 6686-6688.

Fernandes CM, Senos AMR, Vieira MT, Antunes JM. 2008. Mechanical characterization of composites prepared from WC powders coated with Ni rich binders. International Journal of Refractory Metals & Hard Materials 26:491-498.

Fernandes CM, Senos AMR, Vieira MT. 2008. Microscopic Characterization of the Thermal Evolution of Stainless Steel Coatings Sputter-deposited onto WC Particles. Microscopy and Microanalysis-online Journal. 14: 39-40

Fernandes DM, Simoes SMN, Carapuca HM, Cavaleiro AMV. 2008. Functionalisation of glassy carbon electrodes with deposited tetrabutylammonium microcrystalline salts of lacunary and metal-substituted alpha-Keggin-polyoxosilicotungstates. Electrochimica Acta 53:6580-6588.

Fernandes M, Bermudez VD, Sa Ferreira RA, Carlos LD, Martins NV. 2008. Incorporation of the Eu(tta)(3)(H2O)(2) complex into a co-condensed d-U(600)/d-U(900) matrix. Journal of Luminescence 128:205-212.

Fernandes M, Goncalves MC, Bermudez VZ, Ferreira RAS, Carlos LD, Charas A, Morgado J. 2008. Optical material composed of a di-urethanesil host hybrid and a europium complex. Journal of Alloys and Compounds 451:201-205.

Fernandes S, Freire CSR, Neto CP, Gandini A. 2008. The bulk oxypropylation of chitin and chitosan and the characterization of the ensuing polyols. Green Chemistry 10:93-97.

Fernandes TA, Nunes CD, Vaz PD, Calhorda MJ, Brandao P, Rocha J, Goncalves IS, Valente AA, Ferreira LP, Godinho M, Ferreira P. 2008. Synthesis and catalytic properties of manganese(II) and oxovanadium(IV) complexes anchored to mesoporous MCM-41. Microporous and Mesoporous Materials 112:14-25.

Ferreira BJM, Magalhães MCF, Correia RN. 2008. In vitro formation of apatites and other biologically related calcium phosphates: influence of temperature and pH on the nature of the mineral phases, Materials Science Fórum 587-588:7-11.

Ferreira R, Blesic M, Trindade J, Marrucho I, Lopes JNC, Rebelo LPN. 2008. Solubility of fluorinated compounds in a range of ionic liquids. Cloud-point temperature dependence on composition and pressure. Green Chemistry 10:918-928.

Frade JR, Kharton VV, Shaula AL, Marques FMB. 2008. Interfacial effects in potentiometric oxygen sensors: The role of transport properties and thickness of solid electrolyte ceramics. Sensor Letters 6:370-380.

Freire CSR, Silvestre AJD, Pascoal Neto C, Gandini A, Martin L, Mondragon I. 2008. Composites based on acylated cellulose fibers and low-density polyethylene: Effect of the fiber content, degree of substitution and fatty acid chain length on final properties. Composites Science and Technology 68: 3358-3364.

Freire MG, Carvalho PJ, Gardas RL, Santos L, Marrucho IM, Coutinho JAP. 2008. Solubility of Water in Tetradecyltrihexylphosphonium-Based Ionic Liquids. Journal of Chemical and Engineering Data 58:2378-2382.

Freire MG, Ferreira AGM, Fonseca IMA, Marrucho IM, Coutinho JAP. 2008. Viscosities of liquid fluorocompounds. Journal of Chemical and Engineering Data 53:538-542.

Freire MG, Ventura SPM, Santos L, Marrucho IM, Coutinho JAP. 2008. Evaluation of COSMO-RS for the prediction of LLE and VLE of water and ionic liquids binary systems. Fluid Phase Equilibria 268:74-84.

Froimowicz P, Belgacem MN, Gandini A, Strumia MC. 2008. Design, synthesis and photo-cross-linking of a new photosensitive macromonomer from tetra-branched poly(ethylene oxide)s. European Polymer Journal 44: 4092-4097.

Fu LS, Ferreira RAS, Fernandes M, Nunes SC, Bermudez VD, Hungerford G, Rocha J, Carlos LD. 2008. Photoluminescence and quantum yields of organic/inorganic hybrids prepared through formic solvolysis. Optical Materials 30:1058-1064.

Gago S, Costa T, de Melo JS, Goncalves IS, Pillinger M. 2008. Preparation and photophysical characterisation of Zn-Allayered double hydroxides intercalated by anionic pyrene derivatives. Journal of Materials Chemistry 18: 894-904.

Gandini A, Coelho D, Silvestre AJD. 2008. Reversible click chemistry at the service of macromolecular materials. Part 1: Kinetics of the Diels–Alder reaction applied to furan–maleimide model compounds and linear polymerizations. European Polymer Journal 44: 4029-4036.

Gandini A. 2008. Polymers from Renewable Resources: A Challenge for the Future of Macromolecular Materials. Macromolecules. 4: 9491–9504.

Garcia H, Barros AS, Goncalves C, Gama FM, Gil AM. 2008. Characterization of dextrin hydrogels by FTIR spectroscopy and solid state NMR spectroscopy. European Polymer Journal 44:2318-2329.

Gardas RL, Costa HF, Freire MG, Carvalho PJ, Marrucho IM, Fonseca IMA, Ferreira AGM, Coutinho JAP. 2008. Densities and derived thermodynamic properties of imidazolium-, pyridinium-, pyrrolidinium-, and piperidinium-based ionic liquids. Journal of Chemical and Engineering Data 53:805-811.

Gardas RL, Coutinho JAP. 2008. A group contribution method for heat capacity estimation of ionic liquids. Industrial & Engineering Chemistry Research 47:5751-5757.

Gardas RL, Coutinho JAP. 2008. A group contribution method for viscosity estimation of ionic liquids. Fluid Phase Equilibria 266:195-201.

Gardas RL, Coutinho JAP. 2008. Applying a QSPR correlation to the prediction of surface tensions of ionic liquids. Fluid Phase Equilibria 265:57-65.

Gardas RL, Coutinho JAP. 2008. Estimation of speed of sound of ionic liquids using surface tensions and densities: A volume based approach. Fluid Phase Equilibria 267:188-192.

Gardas RL, Coutinho JAP. 2008. Extension of the Ye and Shreeve group contribution method for density estimation of ionic liquids in a wide range of temperatures and pressures. Fluid Phase Equilibria 263:26-32.

Gardas RL, Dagade DH, Coutinho JAP, Patil KJ. 2008. Thermodynamic studies of ionic interactions in aqueous solutions of imidazolium-based ionic liquids [Emim][Br] and [Bmim][Cl]. Journal of Physical Chemistry B 112:3380-3389.

Gardas RL, Dagade DH, Terdale SS, Coutinho JAP, Patil KJ. 2008. Acoustic and volumetric properties of aqueous solutions of imidazolium based ionic liquids at 298.15 K. Journal of Chemical Thermodynamics 40:695-701.

Gautam UK, Bando Y, Zhan JH, Costa PMFJ, Fang XS, Golberg D. 2008. Ga-doped ZnS nanowires as precursors for ZnO/ZnGa2O4 nanotubes. Advanced Materials 20: 810-814.

Ghislandi M, Prado L, Oyerviedes AD, Wittich H, Schulte K, Barros-Timmons A. 2008. Functionalization of carbon nanofibers (CNFs) through atom transfer radical polymerization for the preparation of poly(tert-butyl acrylate)/CNF materials: Spectroscopic, thermal, morphological, and physical characterizations. Journal of Polymer Science Part a-Polymer Chemistry 46:3326-3335.

Goel A, Tulyaganov DU, Kharton VV, Yaremchenko AA, Ferreira JMF. 2008. The effect of Cr2O3 addition on crystallization and properties of La2O3-containing diopside glass-ceramics. Acta Materialia 56:3065-3076.

Gomes E, Figueiredo FM, Margues FMB. 2008. Grain boundary Fe-doping effects in LSGM. Solid State Ionics 179:900-903.

Gomes E, Marques FMB, Figueiredo FM. 2008. Microstructural effects on the electrical properties of grain boundary Fe-doped LSGM. Solid State Ionics 179:1325-1328.

Gomes JRB, Cordeiro M, Jorge M. 2008. Gas-phase molecular structure and energetics of anionic silicates. Geochimica Et Cosmochimica Acta 72:4421-4439.

Gomes SR, Margaça FMA, Ferreira LM, Salvado IMMiranda, Falcão NA 2008. Thermal analysis of hybrid materials prepared by gamma irradiation, Journal of Thermal Analysis and Calorimetry 1-5

Gomes SR, Margaca FMA, Salvado IMM, Leal JP, Marques C, Alves E, Ferreira LM, Falcao AN. 2008. Elemental and RBS analysis of hybrid materials prepared by gamma-irradiation. Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms 266:288-294.

Gomes SR, Margaça FMA, Salvado IMMiranda, Falcão NA, Almásy L, Teixeira J 2008. Nuclear Instruments and Methods in Physics Research B 266: 5166-5170.

Gomes SR, Margaca FMA, Silva DF, Ferreira LM, Salvado IMM, Falcao AN. 2008. Novel way to control PDMS cross-linking by gamma-irradiation. Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms 266:1105-1108.

Goncalves CMB, Coutinho JAP, Marrucho IM. 2008. Light olefins/paraffins sorption in poly(lactic acid) films. Journal of Polymer Science Part B-Polymer Physics 46:1312-1319.

Goncalves G, Marques P, Trindade T, Pascoal C, Gandini A. 2008. Superhydrophobic cellulose nanocomposites. Journal of Colloid and Interface Science 324:42-46.

Gonçalves P, Canales-Vázquez J, Figueiredo FM. Mechanosynthesis of Nanocrystalline CaTi_1-x Mn_x O_3-d . 2008. Boletín de la Sociedad Española de Cerámica y Vidrio, 47[4]:233-236.

Gonçalves P, Figueiredo FM. 2008. Mechanosynthesis of La1-xSrxGa1-yMgyO3-delta materials. Solid State Ionics 179:991-994.

Gonçalves P, Figueiredo FM. Mechanosynthesis of La_0.95 Sr_0.05 Ga_0.90 Mg_0.10 O_3-d. 2008. Materials Science Fórum, 587-588: 931-935.

Goncalves VMF, Evtuguin DV, Dominguesa MRM. 2008. Structural characterization of the acetylated heteroxylan from the natural hybrid Paulownia elongata/Paulownia fortunei. Carbohydrate Research 343:256-266.

Graca G, Duarte IF, Goodfellow BJ, Carreira IM, Couceiro AB, Domingues MD, Spraul M, Tseng LH, Gil AM. 2008. Metabolite profiling of human amniotic fluid by hyphenated nuclear magnetic resonance spectroscopy. Analytical Chemistry 80:6085-6092.

Graca MPF, da Silva MGF, Sombra ASB, Valente MA. 2008. The dielectric behavior of a thermoelectric treated B2O3-Li2O-Nb2O5 glass. Journal of Non-Crystalline Solids 354: 3408-3413.

Graca MPF, da Silva MGF, Valente MA. 2008. Influence of thermal and thermoelectric treatments on structure and electric properties of B2O3-Li2O-Nb2O3 glasses. Journal of Non-Crystalline Solids 354: 901-908.

Graca MPF, da Silva MGF, Valente MA. 2008. Structural and electrical characteristics of LiNbO3 embedded in a 34% SiO2 glass matrix. Journal of the European Ceramic Society 28: 1197-1203.

Granadeiro CM, Ferreira RAS, Soares-Santos PCR, Carlos LD, Nogueira HIS. 2008. Photoluminescent hybrid materials based on lanthanopolyoxotungstates and 3-hydroxypicolinic acid. Journal of Alloys and Compounds 451:422-425.

Guisbiers G, Kazan M, Van Overscheide O, Wautelet M, Pereira S. 2008. Mechanical and thermal properties of metallic and semiconductive nanostructures. Journal of Physical Chemistry C 112:4097-4103.

Guisbiers G, Van Overschelde O, Wautelet M. 2008. Theoretical investigation of size and shape effects on the melting temperature and energy bandgap of TiO2 nanostructures. Applied Physics Letters 92.

Guo XM, Guo HD, Fu LS, Zhang HJ, Carlos LD, Deng RP, Yu JB. 2008. Synthesis and photophysical properties of novel organic–inorganic hybrid materials covalently linked to a europium complex. Journal of Photochemistry and Photobiology A: Chemistry 200: 318-324.

Guo XM, Wang XM, Zhang HJ, Fu LS, Guo HD, Yu JB, Carlos LD, Yang KY. 2008. Preparation and luminescence properties of covalent linking of luminescent ternary europium complexes on periodic mesoporous organosilica. Microporous and Mesoporous Materials 116: 28-35

Harbuzaru BV, Corma A, Rey F, Atienzar P, Jorda JL, Garcia H, Ananias D, Carlos LD, Rocha J. 2008. Metal-organic nanoporous structures with anisotropic photoluminescence and magnetic properties and their use as sensors. Angewandte Chemie-International Edition 47:1080-1083.

Hiebl B, Fuhrmann R, Costa MEV, Almeida MM, Frank RP. 2008. In vitro 3D assay to test angiogenic effects of human CD14+ monocytes seeded on macroporous PLGA/CaP polymers with a CaP nanostructured surface. Clinical Hemorheology and Microcirculation 40:37-50

Holec D, Costa PMFJ, Cherns PD, Humphreys CJ. 2008. A theoretical study of ELNES spectra of AlxGa1-xN using Wien2k and Telnes programs. Computational Materials Science 44: 91-96.

Holec D, Costa PMFJ, Cherns PD, Humphreys CJ. Electron energy loss near edge structure (ELNES) spectra of AIN and AIGaN: a theoretical study using Wien2k and Telnes programs. Micron 39: 690-697.

Horovistiz AL, Abrantes JCC, Fagg DP, Frade JR. 2008. Effects of Yb : Ti ratio on transport properties of Yb2 +/- xTi2 +/- xO7 +/-delta. Solid State Ionics 179:1046-1049.

Hou RZ, Ferreira P, Vilarinho PM. 2008. A facile route for synthesis of mesoporous barium titanate crystallites. Microporous and Mesoporous Materials 110:392-396.

Ivanova D, Kovalevsky A, Kharton VV, Marques FMB. 2008. Silica-scavenging effects in ceria-based solid electrolytes. Bol. Soc. Esp. Ceram. Vidrio 47: 201-206.

Ivanova D, Lima E, Kovalevsky A, Figueiredo FML, Kharton VV, Marques FMB. 2008. Heterogeneous ceramics formed by grain boundary engineering. Ionics 14:349-356.

Jeridi K, Hachani M, Hajjaji W, Moussi B, Baccour H, Medhioub M, Lopez-Galindo A, Kooli F, Zargouni F, Labrincha JA, Jamoussi F. 2008. Technological behaviour of some Tunisian clays prepared by the dry ceramic process. Clay Minerals 43:339-350.

Jin M, Xu JY, Wu AY, Li XH, Shen H, He QB. 2008. Investigation of domain structures in PZNT93/7 crystals by chemical etching. Crystal Research and Technology 43:666-669.

Jordao CIC, Farinha ASF, Enes RF, Tome AC, Silva AMS, Cavaleiro JAS, Ramos CIV, Santana-Marques MG, Paz FAA, Ramirez J, de la Torre MDL, Nogueras M. 2008. Synthesis of [60]fullerene-glycopyranosylaminopyrimidin-4-one conjugates. Tetrahedron 64:4427-4437.

Kalinin SV, Rodriguez BJ, Jesse S, Maksymovych P, Seal K, Baddorf AP, Kholkin A, Proksch R. 2008. Bias induced phase transitions, Materials Today 11: 16-27.

Kaper H, Willinger M-G, Djerdj I, Gross S, Antonietti M, Smarsly BM. 2008. IL-assisted synthesis of V2O5 nanocomposites and VO2 nanosheets. Journal of Materials Chemistry 18: 5761–5769

Kazan M, Ottaviani L, Moussaed E, Nader R, Masri P. 2008. Effect of introducing gettering sites and subsequent Au diffusion on the thermal conductivity and the free carrier concentration in n-type 4H-SiC. Journal of Applied Physics 103.

Kazan M, Pereira S, Correia MR, Masri P. 2008. Contribution of the decay of optical phonons into acoustic phonons to the thermal conductivity of AIN. Physical Review B 77.

Kazan M, Pereira S, Coutinho J, Correia MR, Masri P. 2008. Role of optical phonon in Ge thermal conductivity. Applied Physics Letters 92.

Khaenakaew P, Bdikin IK, Kholkin AL, Muensit S. 2008. Microstructure and ferroelectric properties of sol-gel graded PZT (40/52/60) and (60/52/40) thin fims". Ceramics International. 34:1027.

Khalyavin DD, Argyriou DN, Amann U, Yaremchenko AA, Kharton VV. 2008. Low-temperature behavior of YBaCo2O5.5: Coexistence of two spin-state ordered phases. Physical Review B 77:064419.

Khalyavin DD, Prokhnenko O, Stusser N, Sikolenko V, Efimov V, Salak AN, Yaremchenko AA, Kharton VV. 2008. Crystal and magnetic structures of NdBaCo2O5+delta (delta similar to 0.75): A neutron diffraction study. Physical Review B 77:174417.

Kharlamova T, Pavlova S, Sadykov V, Kriger T, Alikina G, Mezentseva N, Muzykantov V, Boronin, Zaikovskii V, Ishchenko A, Rogov V, Uvarov N, Frade J, Argirusis C. 2008. Perovskite and composite materials for intermediate temperature solid oxide fuel cells. Eur. J. Inorg. Chem. 6:939-947

Kharlamova T, Pavlova S, Sadykov V, Lapina O, Khabibulin D, Krieger T, Zaikovskii V, Ishchenko A, Salanov A, Muzykantov V, Mezentseva N, Chaikina M, Uvarov N, Frade J, Argirusis C. 2008. Low-temperature synthesis and characterization of apatite-type lanthanum silicates, Solid State Ionics. 1018-1023

Kharton VV, Kovalevsky AV, Patrakeev MV, Tsipis EV, Viskup AP, Kolotygin VA, Yaremchenko AA, Shaula AL, Kiselev EA, Waerenborgh JC. 2008. Oxygen nonstoichiometry, mixed conductivity and Mössbauer spectra of Ln0.5A0.5FeO3-? (Ln = La-Sm, A = Sr, Ba): Effects of cation size. Chemistry of Materials 20:6457-6467.

Kharton VV, Tsipis EV, Kolotygin VA, Avdeev M, Viskup AP, Waerenborgh JC, Frade JR. 2008. Mixed conductivity and stability of CaFe2O4-delta. Journal of the Electrochemical Society 155:P13-P20.

Kharton VV, Tsipis EV, Naumovich EN, Thursfield A, Patrakeev MV, Kolotygin VA, Waerenborgh JC, Metcalfe IS. 2008. Mixed conductivity, oxygen permeability and redox behavior of K2NiF4-type La2Ni0.9Fe0.1O4+delta. Journal of Solid State Chemistry 181:1425-1433.

Kholkin AL, Bdikin IK, Ostapchuk T, Petzelt J. 2008. Room temperature surface piezoelectricity in SrTiO3 ceramics via piezoresponse force microscopy. Appl. Phys. Lett. 93: 222905.

Khomchenko VA, Kiselev DA, Bdikin IK, Shvartsman VV, Borisov P, Kleemann W, Vieira JM, and Kholkin AL. 2008. Crystal structure and multiferroic properties of Gd-substituted BiFeO3. Applied Physics Letters 93: 262905.

Khomchenko VA, Kiselev DA, Seluneva EK, Vieira JM, Lopes AML, Pogorelov YG, Araujo JP, Kholkin AL. 2008. Weak ferromagnetism in diamagnetically-doped Bi(1-x)A(x)FeO(3) (A=Ca, Sr, Pb, Ba) multiferroics. Materials Letters 62:1927-1929.

Khomchenko VA, Kiselev DA, Vieira JM, Jian L, Kholkin AL, Lopes AML, Pogorelov YG, Araujo JP, Maglione M. 2008. Effect of diamagnetic Ca, Sr, Pb, and Ba substitution on the crystal structure and multiferroic properties of the BiFeO3 perovskite. Journal of Applied Physics 103:024105.

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Khomchenko VA, Kiselev DA, Vieira JM, Rubinger RM, Sobolev NA, Kopcewicz M, Shvartsman VV, Borisov P, Kleemann W, Kholkin AL. 2008. Coexistence of spontaneous ferroelectricity and weak ferromagnetism in Bi0.8Pb0.2FeO2.9 perovskite. Journal of Physics-Condensed Matter 20:155207.

Khomchenko VA, Kopcewicz M, Lopes AML, Pogorelov G, Araujo JP, Vieira JM, Kholkin AL. 2008. Intrinsic nature of the magnetization enhancement in heterovalently doped Bi(1-x)A(x)FeO(3) (A = Ca, Sr, Pb, Ba) multiferroics. Journal of Physics D-Applied Physics 41:102003.

Khomchenko VA, Troyanchuk IO, Szymczak H. 2008. Influence of oxygen content on the magnetic properties of B-site deficient lanthanum manganites. Materials Chemistry and Physics 111:154-157.

Khomchenko VA, Troyanchuk IO, Szymczak R, Szymczak H. 2008. Negative magnetization in La0.75Nd0.25CrO3 perovskite. Journal of Materials Science 43:5662-5665.

Kiselev DA, Kholkin AL, Bogomolov AA, Sergeeva ON, Kaptelov EYu, Pronin IP. 2008. Pyro- and piezohysteresis in thin unipolar PZT films. Technical Physics Letters. 34:646-649.

Kleemann W, Shvartsman VV, Bedanta S, Borisov P, Tkach A, Vilarinho PM. 2008. (Sr, Mn)TiO3 - A Magnetoelectrically Coupled Multiglass, Journal of Physics Condensed Matter, 20: 434216 – 434222.

Kostova MH, Ananias D, Carlos LD, Rocha J. 2008. Photoluminescent layered Y/Er silicates. Journal of Alloys and Compounds 451:624-626.

Kovalevsky AV, Kharton VV, Snijkers FMM, Cooymans JFC, Luyten JJ, Frade JR. 2008. Processing and oxygen permeability of asymmetric ferrite-based ceramic membranes. Solid State Ionics 179:61-65.

Kowalchuk CM, Paz FAA, Ananias D, Pattison P, Carlos LD, Rocha J. 2008. Photoluminescent Microporous Lanthanide Silicate AV-21 Frameworks. Chemistry-a European Journal 14:8157-8168.

Krishnakumar T, Pinna N, Kumari KP, Perumal K, Jayaprakash R. 2008. Microwave-assisted synthesis and characterization of tin oxide nanoparticles. Materials Letters 62:3437-3440.

Kumar A, Singh T, Gardas RL, Coutinho JAP. 2008. Non-ideal behaviour of a room temperature ionic liquid in an alkoxyethanol or poly ethers at T=(298.15 to 318.15) K. Journal of Chemical Thermodynamics 40:32-39.

Lamaka SV, Karavai OV, Bastos AC, Zheludkevich ML, Ferreira MGS. 2008. Monitoring local spatial distribution of Mg2+, pH and ionic currents. Electrochemistry Communications 10:259-262.

Lamaka SV, Montemor MF, Galio AF, Zheludkevich ML, Trindade C, Dick LF, Ferreira MGS. 2008. Novel hybrid sol-gel coatings for corrosion protection of AZ31B magnesium alloy. Electrochimica Acta 53:4773-4783.

Lamaka SV, Shchukin DG, Andreeva DV, Zheludkevich ML, Möhwald H, Ferreira MGS. 2008. Sol-Gel/Polyelectrolyte Active Corrosion Protection System. Advanced Functional Materials 18:3137 – 3147.

Lehocky M, Amaral PFF, Stahel P, Coelho MAZ, Barros-Timmons AM, Coutinho JAP. 2008. Deposition of Yarrowia lipolytica on plasma prepared teflonlike thin films. Surface Engineering 24:23-27.

Lima S, Dias AS, Lin Z, Brandao P, Ferreira P, Pillinger M, Rocha J, Calvino-Casilda V, Valente AA. 2008. Isomerization of D-glucose to D-fructose over metallosilicate solid bases. Applied Catalysis a-General 339:21-27.

Lima S, Pillinger M, Valente AA. 2008. Dehydration of D-xylose into furfural catalysed by solid acids derived from the layered zeolite Nu-6(1). Catalysis Communications 9:2144-2148.

Lito PF, Silva CM. 2008. Comparison between Maxwell-Stefan and Nernst-Planck equations to describe ion exchange in microporous materials. Diffusion in Solids and Liquids III 273-276:776-781.

Liu FY, Carlos LD, Ferreira RAS, Rocha J, Gaudino MC, Robitzer M, Quignard F. 2008. Photoluminescent porous alginate hybrid materials containing lanthanide ions. Biomacromolecules 9:1945-1950.

Liu L, Kong Y, Xu H, Li JP, Dong JX, Lin Z. 2008. Ionothermal synthesis of a three-dimensional zinc phosphate with DFT topology using unstable deep-eutectic solvent as template-delivery agent. Microporous and Mesoporous Materials 115:624-628.

Lopes AML, Araujo JP, Amaral VS, Correia JG, Tomioka Y, Tokura Y. 2008. New phase transition in the Pr1-xCaxMnO3 system: Evidence for electrical polarization in charge ordered manganites. Physical Review Letters 100:155702.

Lopes AML, Araujo JP, Mendonça TM, Amaral JS, Pereira AM, Tavares PB, Amaral VS, Correia JG. 2008. Magnetic Hyperfine Field Study in the Pr1-xCaxMnO3 System. Journal of non-crystalline solids 354:5315.

Lopes CB, Lito PF, Otero M, Lin Z, Rocha J, Silva CM, Pereira E, Duarte AC. 2008. Mercury Removal with Titanosilicate ETS-4: Batch experiments and Modeling. Microporous and Mesoporous Materials. 115 (1-2): 98-105.

Lopes CB, Lito PF, Otero M, Lin Z, Rocha J, Silva CM, Pereira E, Duarte AC. 2008. Mercury removal with titanosilicate ETS-4: Batch experiments and modelling. Microporous and Mesoporous Materials 115:98-105.

Lopes CB, Pereira E, Duarte A, Lin Z, Rocha J. 2008. Uptake of Hg2+ from aqueous solutions by microporous titanoand zircono-silicates. Quim Nova 31(2): 321-325.

Lopes JCA, Boros L, Krahenbuhl MA, Meirelles AJA, Daridon JL, Pauly J, Marrucho IM, Coutinho JAP. 2008. Prediction of cloud points of biodiesel. Energy & Fuels 22:747-752.

Lopes PP, Ferreira B, Almeida NAF, Fredel MC, Fernandes MHV, Correia RN. 2008. Preparation and study of in vitro bioactivity of PMMA-co-EHA composites filled with a Ca-3(PO4)(2)-SiO2-MgO glass. Materials Science & Engineering C-Biomimetic and Supramolecular Systems 28:572-577.

Lopes PP, Ferreira B, Correia RN, Fernandes MHR, Fernandes MHV. 2008. Si and Ti-containing glasses as bone cement fillers: a bioactivity and biocompatibility study. Tissue Engineering Part A 14:908-908.

Lorenz K, Franco N, Alves E, Pereira S, Watson IM, Martin RW, O'Donnell KP. 2008. Relaxation of compressively strained AllnN on GaN. Journal of Crystal Growth 310:4058-4064.

Macedo AG, Ananias D, Andre PS, Ferreira RAS, Kholkin AL, Carlos LD, Rocha J. 2008. Functionalization of atomic force microscope tips by dielectrophoretic assembly of Gd2O3 : Eu3+ nanorods. Nanotechnology 19:275702.

Madja D, Paz FAA, Delgado-Friedrichs O, Foster MD, Simperler A, Bell RG, Klinowski J. 2008. Hypothetical zeolitic frameworks: In search of potential heterogeneous catalysts. J. Phys. Chem. C 112: 1040-1047.

Mafra L, Rocha J, Fernandez C, Castro GR, Garcia-Granda S, Espina A, Khainakov SA, Garcia JR. 2008. Characterization of layered gamma-titanium phosphate (C2H5NH3)[Ti(H1.5PO4)(PO4)](2)center dot H2O intercalate: A combined NMR, synchrotron XRD, and DFT calculations study. Chemistry of Materials 20:3944-3953.

Malyshkina OV, Movchikova AA, Pedko BB, Boitsova KN, Kiselev DA, Kholkin AL. 2008. Influence of Eu and Rh impurities on distribution of polarization of strontium-barium niobate crystals. Ferroelectrics 373: 114-120.

Marcos PS, Marto J, Trindade T, Labrincha JA. 2008. Screen-printing of TiO2 photocatalytic layers on glazed ceramic tiles. Journal of Photochemistry and Photobiology a-Chemistry 197:125-131.

Marques J, Anjo L, Marques MPM, Santos TM, Paz FAA, Braga SS. 2008. Structural studies on supramolecular adducts of cyclodextrins with the complex [Ru([9]aneS(3))(bpy)Cl]Cl. Journal of Organometallic Chemistry 693:3021-3028.

Marques P, Nogueira HIS, Pinto RJB, Neto CP, Trindade T. 2008. Silver-bacterial cellulosic sponges as active SERS substrates. Journal of Raman Spectroscopy 39:439-443.

Marques RFC, Garcia C, Lecante P, Ribeiro SJL, Noe L, Silva NJO, Amaral VS, Millan A, Verelst M. 2008. Electro-precipitation of Fe3O4 nanoparticles in ethanol. Journal of Magnetism and Magnetic Materials 320:2311-2315.

Marques SM, Antunes SC, Pissarra H, Pereira ML, Gonçalves F, Pereira R. 2008. Histopathological changes and erythrocytic nuclear abnormalities in Iberian green frogs (Rana perezi Seoane) from a uranium mine pond. Apr 29.

Marques VMF, Tulyaganov DU, Agathopoulos S, Ferreira JMF. 2008. Low temperature production of glass ceramics in the anorthite-diopside system via sintering and crystallization of glass powder compacts. Ceramics International 34:1145-1152.

Martins GF, Pereira AA, Stracçalano BA, Antunes PA, Pasquini D, Curvelo AAS, Ferreira M, Riul Jr A, Constantino CJL. 2008. Ultrathin films of lignins as a potential transducer in sensing applications involving heavy metal ions. Sensors and Actuators B: Chemical 129(2):525-530.

Martins MA, Santos C, Almeida MM, Costa MEV. 2008. Hydroxyapatite micro- and nanoparticles: Nucleation and growth mechanisms in the presence of citrate species. Journal of Colloid and interface science 318:210-216.

Mather GC, Figueiredo FM, de Paz JR, Garcia-Martin S. 2008. Strontium superstoichlometry and defect structure of SrCeO3 perovskite. Inorganic Chemistry 47:921-929.

Maxim F, Ferreira P, Vilarinho PM, Reaney I. 2008. Hydrothermal synthesis and crystal growth studies of BaTiO3 using Ti nanotube precursors. Crystal Growth & Design 8:3309-3315.

Micaelo NM, Felix VM, Macedo AL, Goodfellow BJ. 2008. Tetrapyrrole binding properties of the p22HBP protein. Febs Journal 275:172-172.

Milhet M, Pauly J, Coutinho JAP, Daridon JL. 2008. Solid-liquid equilibria under high pressure of nine pure n-alkylbenzenes. Journal of Chemical and Engineering Data 53:233-237.

Molina C, Sá Ferreira RA, Poirier G, Fu LS, Ribeiro SJL, Messsaddeq Y, Carlos LD. 2008. Er3+-based diureasil organicinorganic hybrids. Journal of Physical Chemistry C 112:19346-19352.

Monteiro B, Gago S, Paz FAA, Bilsborrow R, Goncalves IS, Pillinger M. 2008. Investigation of layered double hydroxides intercalated by oxomolybdenum catecholate complexes. Inorganic Chemistry 47:8674-8686.

Monteiro RCC, Figueiredo CF, Alendouro MS, Ferro MC, Davim EJR, Fernandes MHV. 2008. Characterization of MSWI bottom ashes towards utilization as glass raw material. Waste Management 28:1119-1125.

Monteiro, S, Silvestre, AJD, Silva, AMS, Cavaleiro, JAS. 2008. Synthesis of flavonoid-type compounds from methyl dehydroabietates. Monatshefte Fur Chemie, 139(9): 1119-1126.

Montemor MF, Ferreira MGS. 2008. Analytical characterisation and corrosion behaviour of bis-aminosilane coatings modified with carbon nanotubes activated with rare-earth salts applied on AZ31 Magnesium alloy. Surface & Coatings Technology 202:4766-4774.

Montemor MF, Simoes AM, Ferreira MGS, Carmezim MJ. 2008. Composition and corrosion resistance of cerium conversion films on the AZ31 magnesium alloy and its relation to the salt anion. Applied Surface Science 254:1806-1814.

Montemor MF, Trabelsi W, Lamaka SV, Yasakau KA, Zheludkevich ML, Bastos AC, Ferreira MGS. 2008. The synergistic combination of bis-silane and CeO2 center dot ZrO2 nanoparticles on the electrochemical behaviour of galvanised steel in NaCl solutions. Electrochimica Acta 53:5913-5922.

Mubarok F, Carrapichano JM, Almeida FA, Fernandes AJS, Silva RF. 2008. Enhanced sealing performance with CVD nanocrystalline diamond films in self-mated mechanical seals. Diamond and Related Materials 17:1132-1136.

Nader R, Kazan M, Moussaed E, Stauden T, Niebelschutz M, Masri P, Pezoldt J. 2008. Surface morphology of Ge-modified 3C-SiC/Si films. Surface and Interface Analysis 40:1310-1317.

Neri G, Bonavita A, Micali G, Rizzo G, Pinna N, Niederberger M, Ba J. 2008. Effect of the chemical composition on the sensing properties of In2O3-SnO2 nanoparticles synthesized by a non-aqueous method. Sensors and Actuators B-Chemical 130:222-230.

Neri G, Micali G, Bonavita A, Ipsale S, Rizzo G, Niederberger M, Pinna N. 2008. Tungsten oxide nanowires-based ammonia gas sensors for breath analysis in healthcare applications. Sensor Letters 6:590.

Neto MA, Fernandes AJS, Silva RF, Costa FM. 2008. Nucleation of nanocrystalline diamond on masked/unmasked Si3N4 ceramics with different mechanical pretreatments. Diamond and Related Materials 17:440-445.

Neves MC, Martins MA, Soares-Santos PCR, Rauwel P, Ferreira RAS, Monteiro T, Carlos LD, Trindade T. 2008. Photoluminescent, transparent and flexible di-ureasil hybrids containing CdSe/ZnS quantum dots. Nanotechnology 19:155601-155610.

Neves MC, Monteiro OC, Hempelmann R, Silva AMS, Trindade T. 2008. From Single-Molecule Precursors to Coupled Ag2S/TiO2 Nanocomposites. European Journal of Inorganic Chemistry 28:4380-4386.

Nobre SS, Brites CDS, Ferreira RAS, Bermudez VD, Carcel C, Moreau JJE, Rocha J, Man MWC, Carlos LD. 2008. Photoluminescence of Eu(III)-doped lamellar bridged silsesquioxanes self-templated through a hydrogen bonding array. Journal of Materials Chemistry 18:4172-4182.

Nunes CD, Pires J, Carvalho AP, Calhorda MJ, Ferreira P. 2008. Synthesis and characterisation of organo-silica hydrophobic clay hetero structures for volatile organic compounds removal. Microporous and Mesoporous Materials 111:612-619.

Nunes SC, Bermudez VD, Cybinska J, Ferreira RAS, Carlos LD, Legendziewicz J, Silva MM, Smith MJ, Ostrovskii D. 2008. Structure and photoluminescence of di-amidosil nanohybrids incorporating europium triflate. Journal of Alloys and Compounds 451:510-515.

Nunes SC, Bermudez VD, Ostrovskii D, Carlos LD, Silva MM, Smith MJ. 2008. Cation coordination and hydrogen bonding in potassium and magnesium based-di-amidosil hybrids. Journal of Molecular Structure 874:128-137.

Olekhnovich NM, Moroz, II, Pushkarev AV, Radyush YV, Salak AN, Vyshatko NP, Ferreira VM. 2008. Temperature impedance spectroscopy of (1-x)Na1/2Bi1/2TiO3-xLaMg(1/2)Ti(1/2)O(3) solid solutions. Physics of the Solid State 50:490-495.

Olhero SM, Ganesh I, Torres PMC, Ferreira JMF. 2008. Surface passivation of MgAl2O4 spinel powder by chemisorbing H3PO4 for easy aqueous processing. Langmuir 24:9525-9530.

Olhero SMH, Delgado J, Ferreira JMF, Pinho C. 2008. Development of porous ceramics for gas burners. Diffusion in Solids and Liquids lii 273-276:814-819.

Oliveira DC, Macedo AG, Silva NJO, Molina C, Ferreira RAS, Andre PS, Dahmouche K, Bermudez VD, Messaddeq Y, Ribeiro SJL, Carlos LD. 2008. Photopatternable di-ureasil-zirconium oxocluster organic-inorganic hybrids as cost effective integrated optical substrates. Chemistry of Materials 20:3696-3705.

Oliveira H, Spano M, Santos C, Pereira ML. 2008. Lead chloride affects sperm motility and acrosome reaction in mice. Cell Biology and Toxicology, Jul 2.

Oliveira IS, Sarthour RS, Souza AM, Soares-Pinto DO, Reis MS. 2008. Experimental determination of thermal entanglement in spin clusters using magnetic susceptibility measurements. Physical Review B 77:104402.

Oliveira MB, Marrucho IM, Coutinho JAP, Queimada AJ. 2008. Surface tension of chain molecules through a combination of the gradient theory with the CPA EoS. Fluid Phase Equilibria 267:83-91.

Oliveira MB, Varanda FR, Marrucho IM, Queimada AJ, Coutinho JAP. 2008. Prediction of water solubility in biodiesel with the CPA equation of state. Industrial & Engineering Chemistry Research 47:4278-4285.

Oliveira, L, Freire, CSR, Silvestre, AJD, Cordeiro, N. 2008. Lipophilic Extracts from Banana Fruit Residues: A Source of Valuable Phytosterols. Journal of Agricultural and Food Chemistry, 56(20): 9520-9524.

Ostapchuk T, Petzelt J, Kuzel P, Veljko S, Tkach A, Vilarinho P, Ponomareva I, Bellaiche L, Smirnova E, Lemanov V, Sotnikov AM. 2008. Infrared and THz Soft-Mode Spectroscopy of (Ba,Sr)TiO3 Ceramics. Ferroelectrics, 367, 139–148.

Papatriantafyllopoulou C, Jones LF, Nguyen TD, Matamoros-Salvador N, Cunha-Silva L, Paz FAA, Rocha J, Evangelisti M, Brechin EK, Perlepes SP. 2008. Using pyridine amidoximes in 3d-metal cluster chemistry: a novel ferromagnetic Ni-12 complex from the use of pyridine-2-amidoxime. Dalton Transactions:3153-3155.

Pasquini D, Teixeira EM, Curvelo AAS, Belgacem MN, Dufresne A. 2008. Surface esterification of cellulose fibres: processing and characterization of low-density polyethylene/cellulose fibres composites. Composites Science and Technology 68:193-201.

Paz FAA, Klinowski J. 2008. Poly[[mu(2)-aqua-tetraaquahexakis(mu(4)-naphthalene-2,6-dicarboxylato)te traholmium(III)] 1.75-hydrate]. Acta Crystallographica Section E-Structure Reports Online 64:M336-U610.

Paz FAA, Klinowski J. 2008. Poly[hexaaquabis(mu(3)-naphthalene-2,6-dicarboxylato)(mu(2)-naphthalene- 2,6-dicarboxylato)diholmium(III)]. Acta Crystallographica Section E-Structure Reports Online 64:M140-U1348.

Pecoraro E, Ferreira RAS, Molina C, Ribeiro SJL, Messsaddeq Y, Carlos LD. 2008. Photoluminescence of bulks and thin films of Eu3+-doped organic/inorganic hybrids. Journal of Alloys and Compounds 451:136-139.

Pereira A, Alonso CMA, Neves M, Tome AC, Silva AMS, Paz FAA, Cavaleiro JAS. 2008. A new synthetic approach to N-arylquinolino[2,3,4-at]porphyrins from beta-arylaminoporphyrins. Journal of Organic Chemistry 73:7353-7356.

Pereira AS, Ankiewicz AO, Gehlhoff W, Hoffmann A, Pereira S, Trindade T, Grundmann M, Carmo MC, Sobolev NA. 2008. Surface modification of Co-doped ZnO nanocrystals and its effects on the magnetic properties. Journal of Applied Physics 103 (7):07D140-07D140-3.

Pereira AS, Rauwel P, Reis MS, Silva NJO, Barros-Timmons A, Trindade T. 2008. Polymer encapsulation effects on the magnetism of EuS nanocrystals. Journal of Materials Chemistry 18:4572-4578.

Pereira CCL, Diogo CV, Burgeiro A, Oliveira PJ, Marques MPM, Braga SS, Paz FAA, Pillinger M, Goncalves IS. 2008. Complex formation between heptakis(2,6-di-O-methyl)-beta-cyclodextrin and cyclopentadienyl molybdenum(II) dicarbonyl complexes: Structural studies and cytotoxicity evaluations. Organometallics 27:4948-4956.

Pereira GA, Norek M, Peters JA, Ananias D, Rocha J, Geraldes C. 2008. NMR Transversal relaxivity of aqueous suspensions of particles of Ln(3+)-based zeolite type materials. Dalton Transactions:2241-2247.

Pereira SMD, Martins MA, Trindade T, Watson IM, Zhu D, Humphreys CJ. 2008. Controlled integration of nanocrystals in inverted hexagonal nano-pits at the surface of light-emitting heterostructures. Advanced Materials 20:1038++.

Pertsev NA, Petraru A, Kohlstedt H, Waser R, Bdikin IK, Kiselev D, Kholkin AL. 2008. Dynamics of ferroelectric nanodomains in BaTiO3 epitaxial thin films via piezoresponse force microscopy. Nanotechnology 19:375702.

Petrovski Z, de Matos M, Braga SS, Pereira CCL, Matos ML, Goncalves IS, Pillinger M, Alves PM, Romao CC. 2008. Synthesis, characterization and antitumor activity of 1,2-disubstituted ferrocenes and cyclodextrin inclusion complexes. Journal of Organometallic Chemistry 693:675-684.

Pinna N, Niederberger M. 2008. Surfactant-free nonaqueous synthesis of metal oxide nanostructures. Angewandte Chemie-International Edition 47:5292-5304.

Pinto ML, Pires J, Rocha J. 2008. Porous materials prepared from clays for the upgrade of landfill gas. Journal of Physical Chemistry C 112:14394-14402.

Pinto RJB, Marques P, Barros-Timmons AM, Trindade T, Neto CP. 2008. Novel SiO2/cellulose nanocomposites obtained by in situ synthesis and via polyelectrolytes assembly. Composites Science and Technology 68:1088-1093.

Poznyak SK, Kharton VV, Frade JR, Yaremchenko AA, Tsipis EV, Yakovlev SO, Marozau IP. 2008. Behavior of (La,Sr)CoO3- and La2NiO4-based ceramic anodes in alkaline media: Compositional and microstructural factors. Journal of Solid State Electrochemistry 12:15-30.

Poznyak SK, Zheludkevich ML, Raps D, Gammel F, Yasakau KA, Ferreira MGS. 2008. Preparation and corrosion protective properties of nanostructured titania-containing hybrid sol-gel coatings on AA2024. Progress in Organic Coatings 62:226-235.

Raicheff RG, Chernev G, Zaprianova VG, Ivanova DI, Djambaski PR, Samuneva B, Miranda Salvado IM. 2008. Electrochemical corrosion behaviour of silica hybrid sol-gel coatings. Bulgarian Chemical Communications 40: 295-299.

Raja R, Thomas JM, Greenhill-Hooper M, Ley SV, Paz FAA. 2008. Facile, one-step production of niacin (Vitamin B-3) and other nitrogen-containing pharmaceutical chemicals with a single-site heterogeneous catalyst. Chemistry-a European Journal 14:2340-2348.

Ramos AA, Lima CF, Pereira ML, Fernandes-Ferreira M, Pereira-Wilson C. 2008. Antigenotoxic effects of quercetin, rutin and ursolic acid on HepG2 cells: Evaluation by the comet assay. Toxicology Letters 177:66-73.

Raupp-Pereira F, Ball R, Allen K, Rocha J, Labrincha JA, Allen GC. 2008. New waste based clinkers: belite and lime formulations. Cement and Concrete Research 38[4]:511-521.

Raupp-Pereira F, Segadaes AM, Silva AS, Rocha J, Labrincha JA. 2008. AI-27 and Si-29 NMR and XRD characterisation of clinkers: standard phases and new waste based formulations. Advances in Applied Ceramics 107:37-45.

Rauwel E, Clavel G, Willinger MG, Rawel P, Pinna N. 2008. Non-aqueous routes to metal oxide thin films by atomic layer deposition. Angewandte Chemie-International Edition 47:3592-3595.

Rauwel E, Willinger MG, Ducroquet F, Rauwel P, Matko I, Kiselev D, Pinna N. 2008. Carboxylic acids as oxygen sources for the atomic layer deposition of high-kappa metal oxides. Journal of Physical Chemistry C 112:12754-12759.

Reis MS, Rubinger RM, Sobolev NA, Valente MA, Yamada K, Sato K, Todate Y, Bouravleuv A, von Ranke PJ, Gama S. 2008. Influence of the strong magnetocrystalline anisotropy on the magnetocaloric properties of MnP single crystal. Physical Review B 77:104439.

Ribeiro da Silva MAV, Cabral JITA, Gomes JRB. 2008. Experimental and computational study on the molecular energetics of indoline and indole. Journal of Physical Chemistry A 112:12263-12269.

Ribeiro MJ, Labrincha JA. 2008. Ceramic properties of alumina and alumina-mullite pressed bodies based on Al-rich anodising sludge. Materials Science Forum. 34:587-588.

Ribeiro MJ, Labrincha JA. 2008. Properties of sintered mullite and cordierite pressed bodies manufactured using Alrich anodising sludge. Ceramics International 34:593-597.

Rocha SM, Goncalves V, Evtuguin D, Delgadillo I. 2008. Distinction and identification of lignins based on their volatile headspace composition. Talanta 75:594-597.

Rodrigues MO, da Costa NB, de Simone CA, Araujo AAS, Brito-Silva AM, Paz FAA, de Mesquita ME, Junior SA, Freire RO. 2008. Theoretical and experimental studies of the photoluminescent properties of the coordination polymer [Eu(DPA)(HDPA)(H2O)(2)]center dot 4H(2)O. Journal of Physical Chemistry B 112:4204-4212.

Rubinger CPL, Costa LC, Esteves ACC, Barros-Timmons A, Martins JA. 2008. Hopping conduction on PPy/SiO2 nanocomposites obtained via in situ emulsion polymerization. Journal of Materials Science 43:3333-3337.

Russo PA, Carrott M, Carrott PJM, Lopes JM, Ribeiro FR, Rocha J. 2008. Structure and catalytic activity of Al-MCM-48 materials synthesised at room temperature: Influence of the aluminium source and calcination conditions. Microporous and Mesoporous Materials 114:293-302.

Salak AN, Ferreira VM, Ribeiro JL, Vieira LG, Pullar RC, Alford NM. 2008. Bismuth-induced dielectric relaxation in the (1-x)La(Mg1/2Ti1/2)O-3-xBi(Mg1/2Ti1/2)O-3 perovskite system. Journal of Applied Physics 104.

Salak AN, Prokhnenko O, Ferreira VM. 2008. Temperature evolution of the crystal structures in La(Mg1/2Ti1/2)O-3 perovskite: relation to the microwave dielectric properties. Journal of Physics-Condensed Matter 20.

Salak AN, Vyshatko NP, Khalyavin DD, Prokhnenko O, Ferreira VM. 2008. Low-temperature structural and dielectric phenomena in La1/3NbO3 and La1/3TaO3: comparative study. Appl Phys Lett 16: 162903(1-3).

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Salgueiredo E, Vila M, Silva MA, Lopes MA, Santos JD, Costa FM, Silva RF, Gomes PS, Femandes MH. 2008. Biocompatibility evaluation of DLC-coated Si3N4 substrates for biomedical applications. Diamond and Related Materials 17:878-881.

Samuneva B, Djambaski P, Kashchieva E, Chernev G, Kabaivanova L, Emanuilova E, Salvado IMM, Fernandes MHV, Wu AY. 2008. Sol-gel synthesis and structure of silica hybrid biomaterials. Journal of Non-Crystalline Solids 354:733-740.

Samuneva B, Kabaivanova L, Chernev G, Djambaski P, Kashchieva E, Emanuilova E, Salvado IMM, Fernandes MHV, Wu A. 2008. Sol-gel synthesis and structure of silica hybrid materials. Journal of Sol-Gel Science and Technology 48:73-79.

Santana-Marques MG, Madureira J, Santos TM, Felix V. 2008. Binuclear ruthenium(II) complexes with polypyridil bridging ligands: Gas-phase chemistry and ligand structure. International Journal of Mass Spectrometry 278:20-25.

Santiago AS, Neto CP, Vilela C. 2008. Impact of effective alkali and sulfide profiling on Eucalyptus globulus kraft pulping. Selectivity of the impregnation phase and its effect on final pulping results. Journal of Chemical Technology and Biotechnology 83:242-251.

Santiago AS, Neto CP. 2008. Anthraquinone addition to Eucalyptus globulus kraft pulping towards the reduction of operating sulfidity levels. Appita Journal 61:316-322.

Santiago AS, Neto CP. 2008. Eucalyptus globulus kraft process modifications: Effect on pulping and bleaching performance and papermaking properties of bleached pulps. Journal of Chemical Technology and Biotechnology 83:1298-1305.

Santiago AS, Neto CP. 2008. Impact of kraft process modifications on Eucalyptus globulus pulping performance and polysaccharide retention. Industrial & Engineering Chemistry Research 47:7433-7440.

Santos C, Franke RP, Almeida MM, Costa MEV, Fernandes MH. 2008. Behaviour of osteoblastic-like MG-63 cells cultured with hydroxyapatite and biphasic (Hap/beta-Tcp) porous granules. Tissue Engineering Part A 14:810-810.

Santos C, Franke RP, Almeida MM, Costa MEV. 2008. Nanoscale Characterization of Hydroxyapatite Particles by Electron Microscopy. Microscopy and Microanalysis 14:67-70

Santos C, Souza R, Fernandes MH, Almeida N, Almeida FA, Silva RF. 2008. Effect of the La2O3-rich glass addition on the sintering of zirconia based ceramics. Materials Science Forum 587-588:104-108.

Santos C, Souza RC, Almeida N, Almeida FA, Silva RF, Fernandes MHFV. 2008. Toughened ZrO2 ceramics sintered with a La2O3-rich glass as additive. Journal of Materials Processing Technology 200:126–132.

Santos G, Fonseca FJ, Andrade AM, Deichmann V, Akcelrud L, Braga SS, Coelho AC, Goncalves IS, Peres M, Simoes W, Monteiro T, Pereira L. 2008. Organic light emitting diodes with europium (III) emissive layers based on beta-diketonate complexes: The influence of the central ligand. Journal of Non-Crystalline Solids 354:2897-2900.

Santos I, Simoes MMQ, Balula MSS, Neves M, Cavaleiro JAS, Cavaleiro AMV. 2008. A new insight into the oxidation of cyclododecane with hydrogen peroxide in the presence of iron-substituted polyoxotungstates. Synlett:1623-1626.

Santos ICMS, Paz FAA, Simões MMQ, Neves MGPMS, Cavaleiro JAS, Klinowski J, Cavaleiro AMV. 2008. Catalytic homogeneous oxyfunctionalization with hydrogen peroxide in the presence of a peroxotungstate. Applied Catalysis A-General 351:166-173.

Sardo M, Amado AM, Ribeiro-Claro P. 2008. Pseudopolymorphic transitions of niclosamide monitored by Raman spectroscopy. J. Raman Spect., 39:1915–1924.

Sardo M, Ruano C, Castro JL, Lopez-Tocon I, Ribeiro-Claro P, Otero JC, 2008. Surface Enhanced Raman Scattering of trans-3-Hydroxycinnamic acid adsorbed on Silver Nanoparticles. Chemical Physics Letters 467: 101–104.

Sartor MN, Correia SL, Hotza D, Segadães AM, Labrincha JA, Novaes de Oliveira AP. 2008. Aluminum anodizing sludge as raw material in the fabrication of engobes, glazes and frits. Am. Ceram. Soc. Bul. 87:9201-9208.

Scharnweber T, Santos C, Franke R-P, Almeida MM, Costa MEV. 2008. Influence of Spray-dried Hydroxyapatite-5-Fluorouracil Granules on Cell Lines Derived from Tissues of Mesenchymal Origin. Molecules 13:2729-2739.

Scott JF, Fan HJ, Kawasaki S, Banys J, Ivanov M, Macutkevic J, Blinc R, Laguta VV, Cevc P, Liu JS, Kholkin AL. 2008. THz emission from PZT nanotubes. Nano Letters 8: 4404-4409.

Seabra MP, Labrincha JA, Ferreira, VM. 2008. Ageing Effect on Aerial Lime Mortars Rheology. Materials Science Forum, 587-588, pp. 872-876.

Sebastian V, Lin Z, Rocha J, Téllez C, Santamaría J, Coronas J. 2008. Improved Ti-silicate umbite membranes for the separation of H2. J Membr Sci 323:207-212.

Seco I, Neto CP, Silvestre AJD. 2008. Strategies to reduce the brightness reversion of industrial ECF bleached Eucalyptus globulus kraft pulp. Journal of Chemical Technology and Biotechnology 83:218-226.

Shchukin DG, Lamaka SV, Yasakau KA, Zheludkevich ML, Ferreira MGS, Mohwald H. 2008. Active anticorrosion coatings with halloysite nanocontainers. Journal of Physical Chemistry C 112:958-964.

Shi FN, Cunha-Silva L, Ferreira RAS, Mafra L, Trindade T, Carlos LD, Paz FAA, Rocha J. 2008. Interconvertable modular framework and layered lanthanide(III)-etidronic acid coordination polymers. Journal of the American Chemical Society 130:150-167.

Shi FN, Cunha-Silva L, Paz FAA, Hardie MJ, Klinowski J, Rocha J, Trindade T. 2008. 108. A novel germanium(IV) oxalate complex: [Ge(OH)2(C2O4)2]2-. Inorganic Chemistry Communications 11:283-287.

Shi FN, dos Santos AM, Cunha-Silva L, Costa BFO, Klinowski J, Paz FAA, Amaral VS, Rocha J, Trindade T. 2008. Synthesis, structure and magnetic behaviour of mixed metal leucophosphite. Journal of Solid State Chemistry 181:1330-1336.

Shi FN, Trindade T, Rocha J, Paz FAA. 2008. Hydro-ionothermal synthesis of lanthanide-organic frameworks with 1,4-phenylenebis(methylene)diphosphonate. Crystal Growth & Design 8:3917-3920.

Shvartsman VV, Bedanta S, Borisov P, Kleemann W, Tkach A, Vilarinho PM. 2008. (Sr,Mn)TiO3 - a magnetoelectric multiglass. Physical Review Letters 101, 165704-1 -165704-4.

Shvartsman VV, Dec J, Lukasiewicz T, Kholkin AL, Kleemann W. 2008. Evolution of the polar structure in relaxor ferroelectrics close to the Curie temperature studied by piezoresponse force microscopy. Ferroelectrics 373: 77-85.

Silva CM, Lito PF, Neves PS, Da Silva FA. 2008. PID Controller Design based on Transient Response Experiment. Chemical Engineering Education 42.

Silva CM, Neves PS, Silva FA, Xavier AMRB, Eusébio MFJ. 2008. Tangential Ultrafiltration of Aqueous Saccharomyces cerevisiae Suspensions. Journal of Chemical Education 85:130-132.

Silva NJO, Amaral VS, Carlos LD, Rodriguez-Gonzalez B, Liz-Marzan LM, Berquo TS, Banerjee SK, Bermudez VD, Millan A, Palacio F. 2008. Evidence of random magnetic anisotropy in ferrihydrite nanoparticles based on analysis of statistical distributions. Physical Review B 77:134426.

Silva NJO, Amaral VS. 2008. Comment on "Magnetization reversal in europium sulfide nanocrystals" [Appl. Phys. Lett. 89, 222501 (2006)]. Applied Physics Letters 92.

Silva RA, Costa FM, Silva RF, Andreeta JP, Hernandes AC. 2008. Electric field-modified segregation in crystal fibers of colossal magnetoresistive La0.7Ca0.3MnO3. Journal of Crystal Growth 310:3568-3572.

Singh MK, Shokuhfar T, Gracio JJD, de Sousa ACM, Fereira JMF, Garmestani H, Ahzi S. 2008. Hydroxyapatite modified with carbon-nanotube-reinforced poly(methyl methacrylate): A nanocomposite material for biomedical applications. Advanced Functional Materials 18:694-700.

Soares P, Pinto AT, Ferreira VM, Labrincha JA. 2008. Geopolymerization of lightweight aggregate waste. Materiales De Construccion 58:23-34.

Soares-Pinto DO, Morgado WAM. 2008. Exact time-average distribution for a stationary non-Markovian massive Brownian particle coupled to two heat baths. Physical Review E 77.

Soares-Pinto DO, Oliveira IS, Reis MS. 2008. Phase diagram of a 2D Ising model within a nonextensive approach. European Physical Journal B 62:337-340.

Soares-Santos PCR, Cunha-Silva L, Paz FAA, Ferreira RAS, Rocha J, Trindade T, Carlos LD, Nogueira HIS. 2008. Photoluminescent 3D lanthanide-organic frameworks with 2,5-pyridinedicarboxylic and 1,4-phenylenediacetic acids. Crystal Growth & Design 8:2505-2516.

Soares-Santos PCR, Cunha-Silva L, Sousa FL, Mafra L, Rocha J, Cavaleiro AMV, Trindade T, Paz FAA, Klinowski J, Nogueira HIS. 2008. Supramolecular organic-inorganic adducts containing dibenzo-30-crown-10 and H3PM12O40 (M = W or Mo). Journal of Molecular Structure 888:99-106.

Soares-Santos PCR, Ferreira RAS, Trindade T, Carlos LD, Nogueira HIS. 2008. Terbium(III) complexes of 2aminonicotinic, thiosalicylic and anthranilic acids: synthesis and photoluminescence properties. Journal of Alloys and Compounds 451:575-577.

Solnyshkin AV, Kiselev DA, Bogomolov AA, Kholkin AL, Kunster W, Gerhard R. 2008. Atomic force microscopy study of ferroelectric films of P(VDF-TrFE) copolymer and composites based on it. J. Surface Investigation: X-ray, Synchrotron and Neutron Techniques 2: 692-695.

Sousa AF, Gandini A, Silvestre AJD, Pascoal Neto C. 2008. Synthesis and characterization of novel biopolyesters from suberin and model comonomers. ChemSusChem 1:1020-1025.

Sousa D, Nunes MR, Silveira C, Matos I, Lopes AB, Jorge MEM. 2008. Ca-site substitution induced a metal-insulator transition in manganite CaMnO3. Materials Chemistry and Physics 109:311-319.

Souza AM, Reis MS, Soares-Pinto DO, Oliveira IS, Sarthour RS. 2008. Experimental determination of thermal entanglement in spin clusters using magnetic susceptibility measurements. Physical Review B 77.

Sun DL, Luo JQ, Xiao JZ, Zhang QL, Jiang HH, Yin ST, Wang YF, Ge XW. 2008. Effects of annealing treatment and gamma irradiation on the absorption and fluorescence spectra of Cr : GSGG laser crystal. Applied Physics B-Lasers and Optics 92:529-533.

Sun DL, Luo JQ, Zhang QL, Xiao JZ, Xu JY, Jiang HH, Yin ST. 2008. Gamma-ray irradiation effect on the absorption and luminescence spectra of Nd:GGG and Nd:GSGG laser crystals. Journal of Luminescence 128:1886-1889.

Sun DL, Wu AY, Yin ST. 2008. Structure, properties, and impedance spectroscopy of CaCu3Ti4O12 ceramics prepared by sol-gel process. Journal of the American Ceramic Society 91:169-173.

 $\label{eq:sum} \begin{array}{l} \mbox{Sun DL, Zhang QL, Xiao JZ, Luo JQ, Jiang HH, Yin ST. 2008. Influence of gamma-ray irradiation on absorption and fluorescent spectra of Nd : YAG and Yb : YAG laser crystals. Chinese Physics Letters 25:2081-2084. \\ \end{array}$

Suorti T, Gosselink R, Argiropoulos DS, Evtuguin DV, Suurnäkki A. 2008. Polymerization of lignins by laccase by M-L Mattinen. Ed de Jong, and T Tamminen. BioResources 3(2): 549-565.

Surendran KP, Wu AY, Vilarinho PM, Ferreira VM. 2008. Sol-gel synthesis of low-loss MgTiO3 thin films by a non-methoxyethanol route. Chemistry of Materials 20:4260-4267.

Tang CJ, Fu LS, Fernandes AJS, Soares MJ, Cabral G, Neves AJ, Gracio J. 2008. Simultaneous formation of silicon carbide and diamond on Si substrates by microwave plasma assisted chemical vapor deposition. New Carbon Materials 23:250-258.

Tang CJ, Neves AJ, Pereira S, Fernandes AJS, Gracio J, Carmo MC. 2008. Effect of nitrogen and oxygen addition on morphology and texture of diamond films (from polycrystalline to nanocrystalline). Diamond and Related Materials 17:72-78.
Teixeira JM, Ventura J, Araújo JP, Sousa JB, Amaral VS, Negulescu B, Rickart M, Freitas PP. 2008. Structural characterization of MnNi and MnPt antiferromagnetic materials for spintronic applications. Journal of non-crystalline solids, 354:5275

Teys S, Olshanetsky B, Zhachuk R, Pereira S, Norga G. 2008. Sr induced striped surface reconstructions formed on Si(111). Appl. Phys. Lett. 93: 161912.

Tkach A, Okhay O, Vilarinho PM, Kholkin AL. 2008. High dielectric constant and tunability of strontium titanate ceramics modified by chromium doping. Journal of Physics-Condensed Matter 20:415224.

Tkach A, Vilarinho PM, Reaney IM. 2008. Structure and Microstructure of Y-doped Strontium Titanate Ceramics. Microscopy and Microanalysis, 14: 11-12.

Tome LIN, Carvalho PJ, Freire MG, Marrucho IM, Fonseca IMA, Ferreira AGM, Coutinho JAP, Gardas RL. 2008. Measurements and correlation of high-pressure densities of imidazolium-based ionic liquids. Journal of Chemical and Engineering Data 53:1914-1921.

Trindade JR, Freire MG, Amaral PFF, Coelho MAZ, Coutinho JAP, Marrucho IM. 2008. Aging mechanisms of oil-in-water emulsions based on a bioemulsifier produced by Yarrowia lipolytica. Colloids and Surfaces a-Physicochemical and Engineering Aspects 324:149-154.

Tsipis EV, Kharton VV. 2008. Electrode materials and reaction mechanisms in solid oxide fuel cells: a brief review. I. Performance-determining factors. Journal of Solid State Electrochemistry 12:1039-1060.

Tsipis EV, Kharton VV. 2008. Electrode materials and reaction mechanisms in solid oxide fuel cells: a brief review. II. Electrochemical behaviour vs. materials science aspects. Journal of Solid State Electrochemistry 12:1367-1391.

Tsipis EV, Kiselev EA, Kolotygin VA, Waerenborgh JC, Cherepanov VA, Kharton VV. 2008. Mixed conductivity, Mössbauer spectra and thermal expansion of (La,Sr)(Fe,Ni)O3-? perovskites. Solid State Ionics 179:2170-2180.

Tsipis EV, Naumovich EN, Shaula AL, Patrakeev MV, Waerenborgh JC, Kharton VV. 2008. Oxygen nonstoichiometry and ionic transport in La2Ni(Fe)O4+delta. Solid State Ionics 179:57-60.

Valero R, Gomes JRB, Truhlar DG, Illas F. 2008. Good performance of the M06 family of hybrid meta generalized gradient approximation density functionals on a difficult case: CO adsorption on MgO(001). Journal of Chemical Physics 129:124710-124710-7.

Varanda FR, Vega LF, Coutinho JAP, Marrucho IM. 2008. Liquid-liquid equilibrium of substituted perfluoro-n-octane plus n-octane systems. Fluid Phase Equilibria 268:85-89.

Vasconcellos-Dias M, Nunes CD, Vaz PD, Ferreira P, Brandao P, Felix V, Calhorda MJ. 2008. Heptacoordinate tricarbonyl Mo(II) complexes as highly selective oxidation homogeneous and heterogeneous catalysts. Journal of Catalysis 256:301-311.

Ventura SPM, Pauly J, Daridon JL, Silva JAL, Marrucho IM, Dias AMA, Coutinho JAP. 2008 High pressure solubility data of carbon dioxide in (tri-iso-butyl(methyl)phosphonium tosylate plus water) systems. Journal of Chemical Thermodynamics 40: 1187-1192.

Vicente CMS, Pecoraro E, Ferreira RAS, Andre PS, Nogueira R, Messaddeq Y, Ribeiro SJL, Carlos LD. 2008. Waveguides and gratings fabrication in zirconium-based organic/inorganic hybrids. Journal of Sol-Gel Science and Technology 48:80-85.

Vila M, Carrapichano JM, Gomes JR, Camargo SS, Achete CA, Silva RF. 2008. Ultra-high performance of DLC-coated Si3N4 rings for mechanical seals. Wear 265:940-944.

Vila M, Lopes AB, Almeida A, Femandes AJS, Silva RF. 2008. Extrinsic stress induced defects in CVD diamond. Diamond and Related Materials 17:190-193.

Von Ranke PJ, De Oliveira NA, De Sousa VSR, Carvalho AMG, Gama S, Reis MS. 2008. Theoretical investigation on the anisotropic magnetocaloric effect: Application to DyAl2. Journal of Magnetism and Magnetic Materials 320:E143-E146.

Von Ranke PJ, Oliveira NA, Plaza EJR, de Sousa VSR, Alho BP, Magnus A, Carvalho G, Gama S, Reis MS. 2008. The giant anisotropic magnetocaloric e?ect in DyAl2. Journal of Applied Physics 104: 093906

Vyshatko NP, Vilarinho PM, Kholkin AL. 2008. Electromechanical measurements of electric field-induced displacements of fibers. Review of Scientific Instruments 78:015107.

Westerlund F, Nordell P, Blechinger J, Santos TM, Norden B, Lincoln P. 2008. Complex DNA binding kinetics resolvedby combined circular dichroism and luminescence analysis. Journal of Physical Chemistry B 112:6688-6694.

Willinger M-G, Neri G, Rauwel E, Bonavita A, Micali G, Pinna N. 2008. Vanadium oxide sensing layer grown on carbon nanotubes by a new atomic layer deposition process. Nano Lett 8, 4201.

Wu A, Vilarinho PM, Kingon AI, Reaney I. 2008. Microstructural Characterization of Thick PZT films on Cu Foils Deposited by Electrophoresis. Microscopy and Microanalysis, 14:23-26

Wu A, Vilarinho PM, Wu D, Gruverman A. 2008. Abnormal Domain Switching in Pb(Zr,Ti)O3 Thin Film Capacitors. Applied Physics Letters 93, 262906.

Xavier AMRB, Tavares APM, Agapito MSM, Evtuguin DV. 2008. Sequential batch Reactor for kraft pulp effluent treatment with Trametes versicolor. Journal of Chemical Technology Biotechnology. 83:1602-1608.

Xiao JZ, Wu AY, Vilarinho PM. 2008. Sol-gel derived morphotropic phase boundary 0.37BiScO(3)-0.63PbTiO(3) thin films. Applied Physics Letters 92:3.

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Yaremchenko AA, Bannikov DO, Kovalevsky AV, Cherepanov VA, Kharton VV. 2008. High-temperature transport properties, thermal expansion and cathodic performance of Ni-substituted LaSr2Mn2O7-?. Journal of Solid State Chemistry 181:3024-3032.

Yaremchenko AA, Kharton VV, Valente AA, Snijkers FMM, Cooymans JFC, Luyten JJ, Marques FMB. 2008. Performance of tubular SrFe(AI)O3-delta-SrAl2O4 composite membranes in CO2- and CH4-containing atmospheres. Journal of Membrane Science 319:141-148.

Yaremchenko AA, Kovalevsky AV, Kharton VV. 2008. Mixed conductivity, stability and electrochemical behavior of perovskite-type (Sr0.7Ce0.3)1-xMn1-yCryO3-d. Solid State Ionics 179:2181-2191.

Yasakau K.A., Zheludkevich M.L., Karavai O.V., Ferreira M.G.S. 2008. Influence of inhibitor addition on the corrosion protection performance of sol-gel coatings on AA2024. Progress in Organic Coatings 63:352-361.

Yasakau KA, Zheludkevich ML, Ferreira MGS. 2008. Lanthanide salts as corrosion inhibitors for AA5083. Mechanism and efficiency of corrosion inhibition. Journal of the Electrochemical Society 155:C169-C177.

Zheludkevich ML, Gusakov AG, Voropaev AG, Kozyrski EN, Raspopov SA, Vecher AA. 2008. "Superpermeability" and "pumping" of atomic hydrogen through palladium membranes. Journal of Membrane Science 320:528-532.

Zhu JF, Lin Z, Yan ZM, Huang YN. 2008. Zr-91 and Mg-25 solid-state NMR characterization of the local environments of the metal centers in microporous materials. Chemical Physics Letters 461:260-265.



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Projects finished during '08

BIO-TRIBODIAM - DLC and CVD Diamond coated Si3N4 Ceramics for tribological and biomedical purposes beginning date: 01-04-2006 | 24 month funding: European Commission | UA value (€): 129.870,31 international projects COST 539 ACTION - ELECTROCERAMICS FROM NANOPOWDERS PRODUCED BY INNOVATIVE METHODS-ELENA beginning date: 01-03-2005 | 36 month funding: European Commission | UA value (€): -FP6 2002 NMP/1 (IP 500311-2) SUSTAINPACK - INNOVATION AND SUSTAINABLE DEVELOPMENT IN THE FIBRE BASED PACKAGING VALUE CHAIN beginning date: 01-06-2004 | 48 month funding: European Commission | UA value (€): 218,360 FP6 2004 NMP3/CT (NOE 500159) - Network of Excellence: Functionalised Advanced Materials and Engineering of Hybrids and Ceramics (FAME) beginning date: 01-10-2004 | 48 month funding: European Commission | UA value (€): 219.408,75 MAEIF-CT-2006-041632 - MULTIFERRO-SOL-GEL - Multiferroic nanostructures: a non-aqueous sol-gel approach (multiferro-sol-gel) beginning date: 01-12-2006 | 24 month funding: European Commission | UA value (€): 138.246,64 WACHEUP - New Concepts For Upgrading Pulp Mill Waste Streams to Values - Added Chemicals beginning date: 01-06-2005 | 36 month funding: European Commission | UA value (€): 255,000 APPLICATION OF NMR-BASED METABONOMICS FOR EVALUATION OF DONOR HUMAN LIVERS FOR national TRANSPLANATION beginning date: 01-10-2004 | 48 month funding: CRUP | value (€): projects BIOACTIVE TEXTILES USING FUNCTIONAL BIOPOLYMERS beginning date: 01-07-2005 | 36 month funding: FCT | UA value (€): 33,000 Biorefinaria: Potencialidades do Licor de cozimento beginning date: 01-02-2007 | 18 month funding: CAIMA | UA value (€): 43.340,00 Biorefinaria: Aproveitamento de Condensados beginning date: 02-02-2006 | 24 month funding: CAIMA | UA value (€): 48.670,00 CARBIFINO 70/00090 CONCEPÇÃO DE NOVOS GRAUS DE METAL DURO DE GRANULOMETRIA SUB- A NANO-MÉTRICA COM ELEVADA RESISTÊNCIA AO DESGASTE EROSIVO beginning date: 02-01-2006 | 24 month funding: Adl | UA value (€): 74.375,00 CHARACTERIZATION OF HETEROPOLYSACCHARIDES USING MASS SPECTROMETRY beginning date: 01-10-2005 | 36 month funding: FCT | UA value (€): 64.500,00 Desenvolvimento de novas pastas para papeis especiais beginning date: 30-06-2007 | 12 month funding: Portucel | UA value (€): -DESENVOLVIMENTO TECNOLÓGICO APLICADO A MATÉRIAS-PRIMAS, PROCESSOS E PRODUTOS CERÂMICOS beginning date: 01-01-2005 | 48 month funding: GRICES | UA value (€): -Equilíbrio de Fases e Processos de Separação de Gorduras beginning date: 01-01-2005 | 36 month funding: FCT/GRICES | UA value (€): 6,000 FLAD 600-06/2006 - Development and characterization of novel multiferroic materials and structures beginning date: 01-01-2007 | 24 month funding: FLAD | UA value (€): 30.000,00 GRICES 4.1.1 CNR - Development and characterization of novel multiferroic ceramics and composites beginning date: 01-01-2007 | 24 month funding: GRICES | UA value (\in): 10.000,00

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IC-03-01-FDR00150 Extracção, Fraccionamento e caracterização de compostos polifenólicos da casca de Eucalyptus globulus para produtos de elevado valor acrescentado beginning date: 01-01-2008 | 12 month funding: ICENTRO | UA value (€): 17,368

ICentro IC-03-01-FDR-165 Eucaleather- Aplicação de Extractos Líquidos de Eucalyptus globulus no Curtume de Peles beginning date: 01-01-2008 | 12 month funding: ICENTRO | UA value (€): 13,500

IS-390 - STUDIES OF COLOSSAL MAGNETORESISTIVE OXIDES WITH RADIOACTIVE ISOTOPES beginning date: 01-01-2005 | 36 month funding: ISOLDE/CERN| UA value (€): -

Projecto Ideia (13-05-04-FDR-00044) - Revdimul (Desenvolvimento de revestimentos dinâmicos e multifuncionais) beginning date: 01-10-2007 | 15 month funding: POCI 2010 | UA value (€): -

POCI/AMB/55939/2004 - MODIFIED ELECTRODES: FROM VERSATILE MODELS TO FUNCTIONAL DEVICES FOR STUDYING DYNAMIC SPECIATION IN THE ENVIRONMENT beginning date: 01-01-2006 | 36 month funding: FCT | UA value (€): 61.794,00

POCI/CTM/58312/2004 - BIOTEX - BIOACTIVE TEXTILES USING FUNCTIONAL BIOPOLYMERS beginning date: 01-07-2005 | 36 month funding: FCT | UA value (€): 33.370,00

POCI/CTM/58507/2004 - Multifunctional anionic clays beginning date: 01-02-2005 | 36 month funding: FCT | UA value (€): 44.000,00

POCI/CTM/58570/2004 NOVEL CERAMIC MEMBRANES FOR SYNTHESIS GAS PRODUCTION beginning date: 01-05-2004 | 36 month funding: FCT | UA value (€): 64,000

POCI/CTM/59234/2004

DEVELOPMENT OF NEW NANOSTRUCTURED HYBRID SOL-GEL COATINGS MODIFIED WITH ORGANIC INHIBITORS FOR CORROSION PROTECTION OF METALLIC SUBSTRATES beginning date: 01-07-2005 | 36 month funding: FCT | UA value (€): 53.800,00

POCI/CTM/59425/2004 - PROCESSING AND CHARACTERIZATION OF ELECTROACTIVE POLYMERS AND COMPOSITES BASED ON PVDF FOR MICROELECTRONIC beginning date: 01-04-2005 | 36 month funding: FCT | UA value (€): 71.352,00

POCI/CTM/59449/2004 – NANODIAM NANOCRYSTALLINE DIAMOND (NCD) FILMS ON SILICON NITRIDE CERAMICS FOR TRIBOLOGICAL APPLICATIONS beginning date: 16-08-2005 | 36 month funding: FCT | UA value (€): 53.760,00

POCI/CTM/60064/2004 ELECTROPOLYMERIZED COATING USED AS PRE-TREATMENTS FOR ALUMINIUM ALLOYS beginning date: 15-07-2005 | 36 month funding: FCT | UA value (€): 17.340,00

POCI/CTM/60207/2004 SIMULTANEOUS PRECIPITATION AND IN SITU STABILISATION OF CALCIUM PHOSPHATE POWDERS FOR BIOMEDICAL APPLICATIONS IN BONE REPAIR AND CONTROLLED DRUG DELIVERY SYSTEMS beginning date: 01-06-2005 | 36 month funding: FCT | UA value (€): 29.510,40

POCI/CTM/60288/2004 DEVELOPMENT OF A NEW PHASE CHANGE MATERIAL COMPOSITE FOR ENERGY STORAGE AND THERMAL INSULATION beginning date: 01-06-2005 | 36 month funding: FCT | UA value (€): 71.162,00

POCI/CTM/61284/2004 - Materials Science and Fundamental Research On Nano-Stratified Rare Earth Based Compounds For Magnetic Refrigeration and Sensor Applications - Unusual Martensitic Transitions Driven by the Electronic Fluid beginning date: 01-05-2005 | 36 month funding: FCT | UA value (€): 28,202

POCI/EQU/58152/2004 SCREENING OF IONIC LIQUIDS FOR GAS SEPARATION beginning date: 01-09-2005 | 36 month funding: FCT | UA value (€): 63.000,00

POCI/EQU/59345/2004 - DEVELOPMENT OF A FIXED SITE CARRIER CERAMIC ULTRAMICROPOROUS MEMBRANE REACTOR FOR THE SELECTIVE SEPARATION AND OXIDATION OF CARBON MONOXIDE TO CARBON DIOXIDE beginning date: 01-12-2005 | 36 month funding: FCT | UA value (€): 26.100,00

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POCI/FP/63438/2005 - Studies of Colossal Magnetoresistive Oxides with Radioactive Isotopes beginning date: 16-11-2005 | 48 month funding: CERN | UA value (€): 36,000 POCI/FP/63953/2005 - Estudos de Óxidos Magnéticos aplicando Isótopos Radioactivos (ISOLDE-CERN) beginning date: 01-02-2007 | 12 month funding: FCT | UA value (€): 19,400 POCI/FP/81979/2007 - Estudo de Óxidos Magnéticos usando Isótopos Radioactivos no ISOLDE-CERN beginning date: 16-11-2007 | 12 month funding: FCT | UA value (€): 19,301,05 POCI/HEC/57890/2004 STUDY OF COMPATIBLE MORTARS FOR THE PRESERVATION OF THE BUILT HERITAGE beginning date: 01-09-2005 | 36 month funding: FCT | UA value (€): 47.472,00 POCI/QUI/56112/2004 Catalytic conversion of carbohydrates into furan derivatives beginning date: 01-04-2005 | 36 month funding: FCT | UA value (€): 45,500 POCI/QUI/56229/2004 MOULD PROTECTION BY SUBSTRATE BIOAVAILABILITY: DEPOLYMERISING ENZYMES LIKELY TO ALTER BIOPOLYMER NANOSTRUCTURE beginning date: 01-06-2005 | 36 month funding: FCT | UA value (€): 19.800,00 POCI/QUI/56534/2004 - Nanostructured hybrid organic-inorganic assemblies: development os layer-by-layer and single layer heteropolytungstate modified electrodes beginning date: 01-09-2005 | 36 month funding: FCT | UA value (€): 62.000,00 POCI/QUI/56569/2004 Molecular recognition of phthalate and phthalic acid esters pollutants by ditopic receptors or by cascade dicopper systems beginning date: 01-09-2005 | 36 month funding: FCT | UA value (€): 20.040,00 POCI/QUI/58377/2004 - NOVEL MULTIDIMENSIONAL LANTHANIDE-ORGANIC FRAMEWORKS: HYDROTHERMAL SYNTHESIS, STRUCTURAL CHARACTERISATION AND APPLICATIONS beginning date: 01-10-2005 | 36 month funding: FCT | UA value (€): 35.300,00 POCI/QUI/58887/2004 - Polyoxometalates: from discrete clusters to networks and materials beginning date: 01-09-2005 | 36 month funding: FCT | UA value (€): 57.500,00 POCI/V.5/A0067/2005 - PHOTOLUMINESCENCE-STRUCTURE RELATIONSHIP IN ORGANIC/INORGANIC HYBRIDS FOR OPTICAL APPLICATIONS beginning date: 01-08-2007 | 16 month funding: FCT | UA value (€): 58.520,60 POCTI/CTM/57536/2004 NOVA METODOLOGIA PARA A PRODUÇÃO DE COMPÓSITOS LEVES DE MATRIZ INTERMETÁLICA COM PROPRIEDADES MECÂNICAS MELHORADAS beginning date: 01-06-2005 | 36 month funding: AdI | UA value (€): 18,600 REDE/1509/RME/2005 - Rede de Microscopia Electrónica - UNIVERSIDADE DE AVEIRO beginning date: 01-09-2005 | 36 month funding: FCT | UA value (€): 2.000.910,68 SUB0 – AUMENTO DO TEMPO DE VIDA DE FERRAMENTAS E ORGÃOS DE MAQUINAS POR TRATAMENTO TERMICO **ESPECIFICO** beginning date: 01-04-2006 | 24 month funding: AdI | UA value (€): 21.600,00 VALORIZAÇÃO DE RESÍDUOS E SUB-PRODUTOS INDUSTRIAIS NO DESENVOLVIMENTO DE MATERIAIS CERÂMICOS

beginning date: 01-05-2005 | 24 month funding: GRICES | UA value (€): -

Projects in progress during '09

international projects 11783-2 MULTIPROTECT Advanced Environmentally Friendly Multifunctional Corrosion Protection by Nanotechnology beginning date: 01-03-2005 | 48 month funding: European Commission | UA value (€): 282.203,00

COLL-CT-2006 030338 ADOPTIC - ADDITIVE OPTIMISATION FOR IMPROVED CERAMICS beginning date: 01-09-2006 | 36 month funding: European Commission | UA value (€): 222.120,40

Design, engineering and application of nanosized calcium phosphate particles (CaP-NP) beginning date: $03-04-2006 \mid 36 \text{ month}$ funding: GKSS | value (€): -

FP 7 - Multi-level protection of materials for vehicles by 'Smart' nanocontainers beginning date: 01-05-2008 | 48 month funding: European Commission | UA value (€): 824.769,00

MATERIALS FOR IMPROVED WEAR RESISTANCE OF TOTAL ARTIFICIAL JOINTS beginning date: funding: European Commission | UA value (€): -

NMP2-CT-2004-515960 ULCOS ULTRA LOW CO2 STEELMAKING beginning date: 01-09-2004 | 60 month funding: European Comission | UA value (€): 316,406

NMP3-CT-2006-032616 – MULTICERAL Multifunctional Ceramics Layers with High Electro-magnetoelastic couplin in complex geometries beginning date: 01-11-2006 | 36 month funding: European Comission | UA value (€): 416.00,00

NMP3-CT-2007-032308 – NANOCOFC NANOTECHNOLOGIES AND NANOSCIENCES, KNOWLEDGE BASED MULTIFUNCTIONAL MATERIALS, NEW PRODUCTION PROCESSES AND DEVICES beginning date: 01-11-2006 | 36 month funding: European Comission | UA value (€): 34,650

PAIIPME-ATI-POAI-004 APLICAÇÕES EM TRIBOLOGIA beginning date: 01-03-2009 | ??? month funding: EuropeAid/120707/C/SER/Br | UA value (€): 11,730

Prediction of the kinetics of self-repaired of forming induced defects on thin functional primers for advances automotive applications beginning date: 01-07-2008 | 36 month funding: European Commission | UA value (€): 160.341,00

STRP 033410 MATSILC MATSILC-NOVEL MATERIALS FOR SILICATE BASED FUEL CELL beginning date: 01-12-2006 | 36 month funding: European Comission | UA value (€): 252,000

national	INTAS-05-1000008-8091 - Polarization-driven self-assemply of organics and biomaterials using ultrathin ferroelectric
projects	polymers beginning date: 01-11-2006 30 month
	funding: INTAS UA value (€): 16.400,00

POCI/QUI/59615/2004 - ESTUDO DA FOTODEGRADAÇÃO CATALÍTICA DO FENOL USANDO COMO CATALISADORES SEMICONDUTORES NANOCRISTALINOS beginning date: 01-02-2006 | 36 month funding: FCT | UA value (€): 3.060,00

PTDC/QUI/71198/2006 - Ansa-bridged Organorhenium(VII) oxides and their application as homogeneous and heterogeneous catalysts beginning date: 01-01-2008 | 36 month funding: FCT | UA value (€): 42.372,00

PTDC/QUI/65805/2006 - Water nanodrops in microporous and inorganic-organic hybrid materials beginning date: 01-01-2008 | 36 month funding: FCT | UA value (\in): 61.000,00

PTDC/CTM/73643/2006 - Developing Novel Microporous Powder and Membranes beginning date: 01-02-2008 | 36 month funding: FCT | UA value (€): 78.000,00

PTDC/QUI/67712/2006 - Nanoquímica de compósitos magnéticos/ luminescentes para aplicações de diagnóstico médico in vitro beginning date: 01-01-2008 | 36 month funding: FCT | UA value (€): 40.900,00

PTDC/ECM/72104/2006 - Estudo de argamassaa funcionais para uma construção sustentável beginning date: 01-01-2008 | 36 month funding: FCT | UA value (€): 81.600,00 Nanotubos e silicatos microporosos de terras raras fotoluminscentes

PDTC/CTM/73243/2006 - Nanot beginning date: 01-12-2007 | 36 month funding: FCT | UA value (€): 60.456,00

PPCDT/QUI/58377/2004 - Novel Multidimensional Lanthanide-Organic Frameworks: Hydrothermal Synthesis, Structural Characterisation and Applications beginning date: 01-01-2008 | 24 month funding: FCT | UA value (€): 23.700,00

<code>PTDC/CTM/65718/2006</code> - Fabrication of ordered mesoporous carbon networks for catalysts support beginning date: 02-01-2008 | 36 month funding: FCT | UA value (\in): -

Characterization of the geometric and electronic structure of CNT supported vanadium oxides at the nanometer scale beginning date: 01-01-2008 | 24 month funding: FCT | UA value (\in): 5.000,00

PTDC/CTM/72093/2006 - Híbridos orgânicos-inorgânicos auto foto-padronizáveis para dispositivos de baixo custo em óptica integrada beginning date: 01-01-2008 | 36 month funding: FCT | UA value (€): 74.746,00

PTDC/CTM/65667/2006 - Synthesis and characterization of multiferroic nanostructures synthetised via novel non-aqueous sol-gel routes beginning date: 01-11-2007 | 36 month funding: FCT | UA value (€): 151.000,00

PTDC/FIS/65233/2006 - Ternary and quaternary nitride alloys for lattice matches heterostructures: novel materials for high efficiency field effect transistors and optoelectronic devices beginning date: 01-07-2007 | 36 month funding: FCT | UA value (€): 59.520,00

PTDC/QUE-ERQ/66045/2006 - Use of membrane reactores in the water-gas shift reaction beginning date: 01-09-2007 | 36 month funding: FCT | UA value (€): 25.919,00

PTDC/CTM/67409/2006 - Complexos de Metais de Transição(III) e Lantanídeos(III) como Catalisadores na Polimerização de Olefinas beginning date: 01-07-2007 | 36 month funding: FCT | UA value (€): -

Acção nº E-93/08, Procº AI-E/07 - High-resolution solid-state NMR and powder diffraction two complementary techniques for the characterization of organic-inorganic hybrid nanomaterials based on metal phosphates beginning date: 01-01-2008 | 24 month funding: Acção Integrada | UA value (€): 4.000,00

Nanoscale characterization of ferroelectric films and devices beginning date: 01-01-2008 | 24 month funding: GRICES | UA value (€): 10.000,00

POCI/CTM/55648/2004 - PERIODIC MESOPOROUS ORGANIC-INORGANIC HYBRIDS beginning date: 01-05-2006 | 36 month funding: FCT | UA value (€): 55.000,00

PROGRAMA ESTÍMULO À EXCELÊNCIA - Paula Vilarinho beginning date: 14-02-2007 | 24 month funding: FCT | UA value (€): 10.000,00

PTDC/CTM/81442/2006 - Origem do estado polar em relaxores por microsocopia da sonda de varrimento beginning date: 15-05-2007 | 36 month funding: FCT | UA value (\in): 119.724,00

PTDC/CTM/68614/2006 - Estudos da solidificação em polímeros e nanocompósitos sob acção de esforços de corte beginning date: 01-12-2007 | 36 month funding: FCT | UA value (€): 13.531,00

PTDC/QUI/72584/2006 - Photocatalytic reduction of carbon dioxide into valuable hydrocarbon products beginning date: 01-01-2008 | 36 month funding: FCT | UA value (€): 41.200,00

PTDC/CTM/64805/2006 - Statics and dynamics if hight polarizable ultra-thin films and nano-layered superlattices beginning date: 01-02-2007 | 36 month funding: FCT | UA value (€): 107.505,00

PTDC/CTM/67575/2006 - PROCESSING AND CHARACTERIZATION OF MULTIFERROIC CERAMICS FOR SENSOR AND ACTUACTOR APPLICATIONS beginning date: 02-01-2008 | 36 month funding: FCT | UA value (€): 106.000,00

PTDC/CTM/73367/2006 - Colossal permittivity perovskite films by chemical solution deposition methods for microelectronic and sensor applications beginning date: 01-03-2008 | 36 month funding: FCT | UA value (€): 85.000,00

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PTDC/CTM/71643/2006 - Novos óxidos de aurivillius para applicações microelectrónica beginning date: 01-02-2008 | 36 month funding: FCT | UA value (\in): -

Production of Calcium Phosphate (CaP) nanoparticles and CaP modified surfaces for cell guiding and differentiation studies beginning date: 03-04-2006 | 36 month funding: GKSS | UA value (€): -

A-14/07 - Desenvolvimento de suportes porosos para aplicações biomédicas a partir de materiais vítreos beginning date: 01-02-2006 | 48 month funding: CRUP | UA value (€): 4.500,00

Rede Nacional de Microscopia Electrónica (RNME) - Financiamento do Contrato Programa FCT_RNME período 2009-2011 beginning date: 01-01-2009 | 36 month funding: Programa Nacional de Re-equipamento Científico (FCT) | UA value (€): 805 534,40

CERN/FP/83643/2008 - Estudos de Óxidos Magnéticos e Multiferróicos Aplicando Isótopos Radioactivos No Isolde-Cern V. S. Amaral (Ir) beginning date: 02-01-2009 | 12 month funding: FCT | UA value (€): 20,988

PTDC/CTM/64357/2006 NOVEL LAYERED FERRITE MATERIALS WITH MIXED IONIC-ELECTRONIC CONDUCTIVITY FOR APPLICATIONS IN ALTERNATIVE ENERGY SOURCES beginning date: 01-01-2008 | 36 month funding: FCT | UA value (€): 76,760

PTDC/CTM/65632/2006 Self-healing protective coating with 'intelligent' nanoreservoirs of corrosion inhibitors beginning date: 01-03-2008 | 36 month funding: FCT | UA value (€): 157.200,00

POCI/CTM/66195/2006 Desenvolvimento de microestruturas texturizadas e ultra-finas por fusão de zona com laser beginning date: 02-01-2008 |36 month funding: FCT | UA value (€): 115.697,00

Anodic films on light metals obtained by novel high-voltage pulsed anodizing technique beginning date: 01-01-2008 | 36 month funding: FCT | UA value (\in): 107.202,00

PTDC/CTM/6604/2006

Sensing the micro-distribution of chemical species in solution close to the active metal beginning date: 01-01-2008 | 36 month funding: FCT | UA value (€): 82.425,00

Self-Healing Corrosion Protection Systems with "Smart" Nanostructured Inhibitor Containers beginning date: 31-12-2008 | 36 month funding: GRICED-DAAD | UA value (€): 2,000

PTDC/CTM/66302/2006 Desenvolvimento de um betão refractário auto-escoante sem cimento para revestimentos monolíticos beginning date: 07-01-2008 | 36 month funding: FCT | UA value (€): 7.500,00

PTDC/QUI/68472/2006 Controlled chemical modification of polysaccharides for the development of novel materials beginning date: 01-01-2008 | 36 month funding: FCT | UA value (€): 69.300,00

PTDC/QUI/72903/2006 Determinação de Parâmetros Básicos para o Desenvolvimento de Modelos Fundamentais em Sistemsa de Sais Líquidos beginning date: 01-01-2009 | 36 month funding: FCT | UA value (€): 76,388

PTDC/EQU-FTT/65252/2006 Equilíbrio Líquido Vapor de Líquidos lónicos Puros e suas Misturas com Solventes Orgânicos beginning date: 01-10-2007 | 36 month funding: FCT | UA value (€): 104,970

PTDC/CTM/67444/2006 Novos Materiais Poliméricos Furânicos baseados na Reacção Reversível de Diels-Alder beginning date: 01-01-2009 | 36 month funding: FCT | UA value (€):73,440

PTDC/CTM/71491/2006 OLIVEPOL – Espumas de Poliuretano e Compósitos Termoplásticos baseados em caroço de azeitona oxipropilado. beginning date: 01-01-2009 | 36 month funding: FCT | UA value (€): 28,960

Estudo da variável penetração de resina no papel e do fenómeno de crescimento em papéis decorativos, e respectivas relações causa-efeito com os processos de impregnação e de produção de termolaminados de alta pressão beginning date: 01-09-2008 | 19 month funding: Sonae | UA value (€): 29,000

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Estudo sobre aplicações do engaço e do folhelho da uva beginning date: 01-02-2008 | funding: Grupo Tavfer | UA value (€):13,600 PTDC/QUI/68472/2006 Controlled chemical modification of polysaccharides for the development of novel materials beginning date: 01-01-2008 | 36 month funding: FCT | UA value (€):69,300 Shear-induced solidification studies on polymers and polymer-clay nanocomposites beginning date: 02-01-2008 | 36 month funding: FCT | UA value (\in): 150,000 PTDC/SAU-BEB/66896/2006 Implantable Scaffolds for local osteo-sarcoma chemotherapy beginning date: 01-09-2007 | 36 month funding: FCT | UA value (€): 172.000,00 PTDC/QUI/64203/2006 Structural and functional studies of the soul/hbp family of heme-binding proteins beginning date: 01-01-2008 | 36 month funding: FCT | UA value (€): 55.950,00 PTDC/QUI/68017/2006 Metabolic profiling and biochemical differentiation of human lung tumours by nuclear magnetic resonance (NMR) methods beginning date: 15-01-2008 | 36 month funding: FCT | UA value (€): 59.200,00 PTDC/QUI/68582/2006 Concepção molecular de novos receptores do tipo azacalixareno para química medicinal: encapsulamento de iões lantanideos e resolução de fármacos racémicos beginning date: 01-01-2008 | 36 month funding: FCT | UA value (€): -PTDC/QUI/66523/2006 Estudo metabonómico de desordens da grávida e do feto por espectroscopia de Ressonância Magnética Nuclear (RMN): caracterização bioquímica e métodos de diagnóstico beginning date: 15-01-2008 | 36 month funding: FCT | UA value (€): 64,960 Biochemical Characterisation of Stomach, Endometrial and lung tumour (HRMAS) nuclear magnetic resonance (NMR) Spectroscopy beginning date: 01-09-2006 | 36 month funding: CIMAGO | value (€): 9,000 PTDC/ECM/72104/2006 Estudo de argamassas funcionais para uma construção sustentável beginning date: 01-01-2008 | 36 month funding: FCT | UA value (€): -SÍNTESE E CARACTERIZAÇÃO DE NANOMATERIAIS CERÂMICOS COM APLICAÇÕES BIOLÓGICAS E ELETROQUÍMICAS beginning date: 01-08-2005 | 36 month funding: GRICES | UA value (€): -

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