# activity report '10

associated laboratory centre for research in ceramics and composite materials





cover and back-cover SEM images of glass powder compacts from composition (a) 9 and (b) 9-Bi3 heat treated at 800 C for 1 h. in International Journal of Hydrogen Energy 35 (2010) 6911-6923

> **report | design** Dora dos Santos - CICECO

> > **layout and review** João Rocha Luís Dias Carlos Dora dos Santos

director João Rocha

vice-directors Joaquim Vieira Luís Dias Carlos

associated laboratory centre for research in ceramics and composite materials

ciceco

# www.ciceco.ua.pt

university of aveiro campus universitário de santiago 3810-193 aveiro - portugal e-mail: ciceco@ua.pt phone: (351) 234 372 571 fax: (351) 234 401 470

40° 37´48N 8° 39´22O





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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 departments.

CICECO 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 Technolgy. CICECO is regularly evaluated by international panels and has been rated 'Excellent', in 2010.

This document reports the main activities developed in 2010.



#### general aims

- To 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;

- To develop new materials and functional coatings for industrial applications and materials with improved structural properties;

- To design recycling/reuse alternatives for wastes and by-products in ceramic or cement-like materials;

- To 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;

- To develop biomedical and biomimetic materials and methods.

#### mission

To develop the scientific and technological knowledge base required for the innovative production and transformation of ceramic and composite materials.

#### vision

- To become a leading inter-disciplinary European research laboratory in the field of materials;

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

Ceramics and Glass Engineering Dept. (1992) Arg. Alcino Soutinho



Physycs Dept. (1994) Arq. Alfredo Matos Ferreira



Complexo dos Laboratórios Tecnológicos (2009) Arg. José Rebelo de Andrade



Chemistry Dept. (1993) Arq. Alcino Soutinho



Laboratório Central de Análises (1993) Arq. Fernando Gomes da Silva

#### research team

**CICECO** is the largest Portuguese institute in the field of materials. On 31st December 2010 CICECO hosted 448 people, an increase of 9.54% relatively to the previous year.

Almost 31.5% of the Research Team hold a PhD degree.

#### scientific output

CICECO is one of the most productive research institutes in the country in all scientific areas, with an average publication of 4.5 - 5 SCI papers per year per academic staff or full-time researcher in 2010.



#### management structure

The Management structure encompasses the Scientific Council (SC), Directors, Directing Board (DB), International Advisory Board, Research Lines and Research Groups, integrating also the Centre for Imaging and Structure of Materials (CISM), Centre for Design and Technology of Materials (CDTM) and the new Centre for the Study of Science, Education and Technology (CIETE).

#### **Scientific Council**

Is the most important body of CICECO, gathering all members with a PhD degree. Meets 1-2 times/year and approves the year's scientific and financial report, the following year scientific and financial plans, and discusses general issues. It has the power to recommend the Rector the discharge of the Directors. Its President is elected for 3 years.

#### **Directing Board**

The General Director is Prof. João Rocha and the Vice-Directors are Profs. Joaquim Vieira and Luís Dias Carlos. The Directing Board is appointed by the Directors (meets once a month) and includes 12 other researchers (2 are full-time researchers).

#### **Centre for Imaging and Structure of Materials**

**CISM**, headed by the Directors, gathers all the medium and large-scale equipment and has been a very effective way of managing a large number of facilities. All CICECO members have free access to the equipment available. Service to external users is also provided.

#### **Centre for Design and Technology of Materials**

CDTM is a knowledge transfer centre and interface with industry financed by CICECO at a basal level (2 people).

#### Centre for the Study of Science, Education and Technology

**CIETE** focuses on the understanding and development of systems, processes and contexts that favour and sustain the creation and use of knowledge in universities, research centres, schools and companies.

#### **Research Lines and Research Groups**

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

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

- motivation to develop new and stimulating scientific and technological fields.

The research lines and groups Coordinator's are appointed by the Directors.

#### research line advanced micro- and nanostructured materials for communications technology

line coordinator: Luis Dias Carlos (lcarlos@ua.pt)

#### general aims

i) To 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.

 ii) To improve understanding of electroceramics, and develop new low-cost materials and devices for dielectric, piezoelectric, ferroelectric and multiferroic applications. To understand nanosize effects and properties in bulk, films and nanocomposites.
 iii) To study magnetic properties, and their interplay with structural and electronic correlations, of magnetic oxides, superconductors, bulk and thin-film metal alloys and nanoparticles.

iv) To 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

 i) High T energy conversion, based on improving materials performance by mastering correlations between properties/applicability and composition, structure and microstructural features;

 ii) Conversion or processing of fuels, with emphasis on conversion of natural gas to syngas;

 iii) Improved performance of hard materials and coatings (wear, friction, toughness), including industrial products, and new concepts based on nanostructured materials;
 iv) Highly performing nanostructured materials for functional applications (e.g.biomedical);

 v) Corrosion protection based on active protection, self-healing, multi protection, and methods for their applications or non destructive monitoring;
 vi) Development of novel electrochemical devices; characterisation methods (expertise)

synchrotron radiation (diffraction, EXAFS XANES, SAXS) microscopy (optical, SEM, TEM, scanning probe) electrical properties characterisation (impedance spectroscopy, ferroelectric, electromechanical)

photoluminescence

solid & liquid state

other spectroscopies (IR,UV,Raman, perturbed angle correlation spectrosc.)

diffractometry (single-crystal and powder lab XRD)

magnetic properties (VSM)

mechanical properties

mass spectrometry

thermal analyses

#### application fields

optoelectronics

magnetism

electroceramics

fuel conversion electrodes, electrolytes, ion conductivity heterogeneous

ion-exchange & gas

coatings

biorefinery & biomass

biology & medicine

wastes recycling

## synthesis & shaping methods

hydro(solvo)thermal / sol-gel methods

coordination chemistry and organometallic synthesis methods organic chemistry synthesis and polymerisation methods

thin films processing chemical solution deposition, sputtering, CVD, MOCVD, ALD...

ceramics processing (green processing in dry & liquid medium, sintering) vii) New products and added-value materials based on recycled wastes and by-products, used as raw materials, or to eliminate toxic wastes;
viii) Lower CO<sub>2</sub> footprint in materials processing;
ix) Heat management/storage.

#### 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 biorefineries and biomaterials

line coordinator: João Coutinho (jcoutinho@ua.pt)

#### general aims

i) Implementation of the forest-based biorefinery, focused on characterization of agro-forest biomass components and extraction of valuable components, using benign extraction systems and assessment of potential technologies for industrial implementation;

ii) Development of new polysaccharide based materials and composites, including functional materials bearing inorganic nanophases;

iii) Development of novel polymeric materials based on biomass derived monomers;
 iv) Conversion of biomass components into valuable chemicals for: efficient catalytic conversion for production of platform chemicals from polysaccharides and biotechnological processes for conversion of biomass components into fine chemicals and biofuels;

v) Production of novel biomaterials for medical uses;

vi) Study biological recognition and membrane transport mechanisms; vii) Production of new drugs and drug molecular transporters along with toxicity assessment;

viii) Application of metabonomics for evaluation of metabolic profiles and fluxes in biological processes: disease, exposure to drugs/biomaterials.

#### research groups

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

#### facilities Centre for Imaging and Structure of Materials

Technicians: Maria do Rosário Soares (rosarios@ua.pt) Marta Ferro (marta.ferro@ua.pt) Maria Celeste Azevedo (cazevedo@ua.pt)

<b>g</b> 1,2,4		<b>g</b> 1	<b>g</b> 8	<b>g</b> 1,7	<b>g</b> 1
<b>g</b> 1		<b>g</b> 1	<b>g</b> 8	<b>g</b> 1	
<b>g</b> 2	<b>g</b> 1			<b>g</b> 1,7	
<b>g</b> 1,2 <b>g</b> 3,5		<b>g</b> 1	<b>g</b> 8	<b>g</b> 1	<b>g</b> 4
g2,4 g5,6			<b>g</b> 8	<b>g</b> 1	<b>g</b> 5,6

organic materials

oxides

Jybrids

colloids.

softmatter



Transmission Electron Microscopy (High resolution)



Solid Nuclear Magnetic Resonance (NMR)



Chromatography (Gas and HPLC)

#### 08 | about CICECO

CICECO is one of the best equipped materials science centres in the country. In the recent FCT equipment programme we have been awarded over 5.5MEur.

The Centre for Imaging and Structural Studies manages, in an integrated way, medium and large-scale equipment, granting free access to all members. Some 250 kEur/ 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 CICECOindustry consortia). Electron microscopes and Nuclear Magnetic Resonance spectrometers are part of national networks (coordinated by CICECO) and the access conditions to Portuguese academic users are very favourable.

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.



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



Single-Crystal X-Ray Diffraction



High temperature mechanical testing system



High-temperature graphite furnace



**Coordination:** Joaquim Vieira (jvieira@ua.pt) **Executive Director:** Ana Daniel (anadaniel@ua.pt)

#### technology transfer Centre for Design and Technology of Materials

Maria Paula Seabra (pseabra@ua.pt) Paula Sousa Pais (sousa.pais@ua.pt) Vera Fernandes (verafernandes@ua.pt) Rute Duarte (rute.duarte@ua.pt)

**CDTM**, CICECO Technology Transfer Unit, is an interface structure with the purpose of transferring the knowledge created within CICECO to society, fostering its valorisation. The unit main goals are:

- Promotion of CICECO's Intellectual Property Valorisation and Entrepreneurship;
- Promotion and support to CICECO-industry interaction
- Funding programmes identification & support to proposals submission;
- Promotion of CICECO image to society.

The **protection of intellectual property and the valorization of R&D** results are one of CDTM main purpose and several support actions were offered to researchers to increase the awareness on IP protection rules and benefits. After the government support, offered to universities in 2009, to promote international IP protection, it is natural that the numbers of patents have somehow decreased after this pressing period, continuing nevertheless the same trendline observed in the previous years (Graphic 1). Concerning the support and promotion of CICECO entrepreneurship, CDTM actively seeks to identify products and processes with commercial interest, to promote an entrepreneurship culture within CICECO and to support the development of business plans and the creation of spin-offs. In 2010, one of CICECO business plans resulted in the creation of a spin-off "NANOSMARTEK – Nanotechnology solutions applied to the protection against corrosion". Two other technology valorization projects, CERQUT – High performance variable RF and - THIN FILM TEC - Advanced Processing Solutions (TFT-APS), are in the business plan development stage. The promotion and support of CICECO - Industry interaction was another CDTM major goal in 2010. In this line of action, several activities were performed to support the creation of cooperation R&D projects and to promote CICECO consultancy and technical services as well as to develop new projects for MSc & PhD thesis in Industrial context. Within these goals, CDTM staffs visited with several Portuguese companies to present CICECO competences and outline possible cooperation, leading to some new R&D projects and contracts.

This continuous effort enables CICECO of having more than 120 protocols and contracts with 65 different companies

As an output of this effort, 36 specific R&DT projects/services contracts with companies were in progress in 2010, 15 of which began this year. This represented a total net income of approximately 420 thousand euros. Fortunately, CICECO presents a clear growing tendency of industry base revenues more praiseworthy when considering the international economic crisis and serious problems faced by Portuguese companies (grap. 2).



Another line of action still framed by the CICECO-Industry interaction objective is the promotion and support of technology platforms and/or competence poles within CICECO areas of expertise, with the intent to foster new innovative and collaborative approaches of working with industry.



The Technological Platform IDPoR - Research and Development in Polymers from Renewable Resources, created by CICECO and the Chemistry Department in 2006, is now seen by many as a case study of university-industry cooperation and technology transfer. The platform envisages the development of scientific and technological knowledge driven by the needs and competitive challenges of a group of six national major companies. In 2010, IDPoR strengthened its participation in several R&D projects, either at national or international level, pursuing innovative products, technologies and processes with green label, namely the implementation of the proof of concept of the patent of liquefaction of biomass residues, a project financed by QREN, in consortium with one of the associated companies.

#### 10 | about CICECO

The promotion of advanced training programs at master and doctoral level in industrial context have also been reinforced, as well as other training courses and seminars promoted by the platform.

Still within this line of actions CICECO started, in 2010, to assess its own resources and competences in the field of Materials for Energy (**Energy@CICECO**) with the intention of creating an integrated platform in this area. The project will continue throughout 2011.

Additionally to the work performed with the Sustainable Habitat Cluster (Pole of Competence of QREN), another initiative is being pursued with the intent of creating a new cooperation platform between University and Industry in the field of Ceramics. Several visits and contacts have been made in the last years with the European Centre of Ceramics, located in Limoges, France.

Following to another of the four key objectives, **identification of funding opportunities and support to proposals submission**, CDTM developed several initiatives designed to promote internationalization of CICECO research and members, as well as to find additional financing. CDTM advertised and supported all opportunities for networking grants and scholarships, namely the Treaty of Windsor Programme, training programmes at CERN, ESA or ESO, etc...

But the two main framework programmes targeted were the 7th Research Framework Programme and the Portuguese Strategic Reference Framework Programme - QREN (Quadro de Referência Estratégico Nacional). Several strategies were used by CDTM to increase the researcher's awareness of these funding opportunities (working sessions, ex: "Development of Successful Project Applications – economic and financial concepts", info session: "FP7 Info Session: HEALTH, NMP and KBBE opportunities", mailing with pertinent opening calls, information in CICECO newsletter, etc...).

CDTM provided technical and info support to several CICECO proposals (6) in the development of FP7 applications, in the elaboration of projects budgets, in the filling of administrative forms, in support to FP7 regulations and eligibility criteria, among others. In order to increase CDTM competences in the support of applications, CDTM staff received several training courses (concerning the preparation of FP7 proposals and critical factors and in more specific subjects as Grant agreements contracts and IP protection in FP7).





Regarding QREN program, the Portuguese Government program to foster companies' innovation, the window of opportunity to researchers and CICECO associated companies was also actively promoted by CDTM. In 2010, 5 Co-promotion projects (supported by CDTM) were in full development representing more than 1,5 million euros of funding to CICECO. Several other applications where supported namely in the typologies of Co-promotion projects, Individual projects and R&D Cheques.

As mentioned above, CICECO actively seek to contribute to the enhancement of the regional and national competitiveness, by promoting a closer cooperation not only with industry but also with other regional key players. One of these examples is the participation of CICECO in the project UNIC - Urban Network for Innovation in Ceramics, promoted in the frame of the URBACT programme, which aims at exchanging experiences between European cities, to promote innovation in Ceramic



sector. The Municipality of Aveiro, the Aveiro Industrial Association (AIDA – Associação Industrial do Distrito de Aveiro) and the National Association of Ceramic Producers – APICER are also partners of this project. The Local Action Plan, defined at the beginning of the project, was developed throughout 2010 with the purpose of fostering local economy, building upon industrial ceramic heritage and enhancing competitive factors.

Still following the internationalization strategy and in order to enhance CICECO competences and visibility in the area of knowledge transfer, CDTM is continuously screening for funding and network opportunities to increase CICECO R&D valorization not only to the national market but also to the international market.



As a result of this strategy, CICECO integrated, in 2010, a consortium institutions of R&D and Innovation in the frame of the European Program INTERREG IV B – Atlantic Area (involving Portugal, France, Spain, Ireland and United Kingdom) to develop a project called ENERMATaa, with a total budget of nearly 500 thousands €.

This project aims at promoting R&D and Technology Transfer networking among partners, in the field of Materials for Energy, by creating a sustainable transnational network between public research institutions and also with industry in the Atlantic Area. CICECO is one of seven partners and leads one of the project main activities: Activity 3 - *"Sharing and Cross-Referenced Running of Technological Platforms"*. CICECO has representatives in the project Executive and Decisional Boards. CDTM is operationally managing the project due to the transversal character of the thematic and its focus on the knowledge transfer between the network and to industry. In the beginning the project activities (May 2010), CDTM conducted a survey to identify CICECO main competence in the field of Materials for Energy, namely on the topics suggested by the WP2 leader. On June 2 & 3, 2010, CDTM organised CICECO participation at the project kick-off meeting, crucial step to refine project activities, make operational decisions and revaluate and detail the project calendar.

The ENERMAT project contemplates a number of events that promote the sharing of experiences among researchers and industrials, and the definition of the network research themes that will form the basis for joint projects. The *"First Transnational Research and Business Meeting"*, was the first of these events and took place in Liverpool, on November 2 & 3, 2010. This event was focused on the themes: Thermoelectric, Photovoltaic, Superconductivity, Hybrid Materials and Fuel Cells and one of CICECO researcher's was invited to be a keynote speaker. The event gathered nearly 100 representatives from across the network, who reported their work through oral presentations and posters. CICECO was represented by sixteen people, with four oral presentations and six posters and CDTM organized the attendance to the event, gathering and organizing all the information needed. Parallel to the scientific event, there were workgroup meetings to address project Activity 3 and 4. CICECO, as Activity 3 leader, conducted on of the meetings and other CDTM staff represented CICECO in the other workgroup meeting. Another important part of the project is the construction of a web platform to foster ENERMAT communication internally and externally. CDTM has also been disseminating all ENERMAT events to CICECO members along with project reports which have been periodically published in Life@CICECO. This allows the tracking of the main events and project developments.

The last of the four CDTM key objectives is the **promotion of CICECO image in society**, namely in industry and to other potential R&D partners. In order to accomplish this goal, CDTM offers support to all CICECO events organisation (ex: *VII Jornadas do CICECO*, January 28-29, 2010), represents CICECO in Technology Transfer and Innovation events (ex: *Portugal Tecnológico 2010* or 2<sup>*I*/d</sup> *UTEN Annual Conference 2010* – *Science and Technology Commercialization in a Globally Networked Economy*). In the same line of action, CDTM organizes different promotional, dissemination and training events, as described above, that play various roles: to promote CICECO R&D valorisation, Technology Transfer and Entrepreneurship mainly to CICECO researchers (ex: *CICECO working session "Successful Paths for Technology Commercialization"*, January 15, 2010 – UA); to promote and enhance CICECO-Industry interaction (ex: *"RMN & Indústria: Applications of Nuclear Magnetic Resonance (NMR) in industry*" October 22, 2010 – UA); to divulge, promote and support CICECO applications to funding programmes (ex: Workshop *"FP7 Funding Opportunities in NMP, KBBE and Health"*, March 30, 2010 – UA or *CICECO Working Session "Development of Successful Project Applications – economic and financial concepts*" September 29, 2010 – UA). Additionally, CDTM is also responsible for the edition of CICECO newsletter: life@ciceco, an internal communicational tool which serves to divulge CICECO news and opportunities.

#### creation and use of knowledge Centre for the Study of Science, Education and Technology

**Coordination:** Júlio Pedrosa (julio.pedrosa@ua.pt)

#### mission

CIETE is a CICECO structure devoted to contributing to the understanding and development of systems, processes and contexts that favour and sustain the creation and use of knowledge in universities, research centres, schools and enterprises.

#### main goals

To contribute to the development and understanding of modes of creating and using knowledge; To investigate models, processes and contexts of governance, management and evaluation of Science and Education Institutions;

To contribute to the development of novel approaches to the use and understanding of Science in schools, public services and companies.

#### programmes

a) Developing platforms for the cooperation of Universities and Research Centres with society This is a programme aimed at designing, testing and evaluating platforms to promote knowledge share, transfer and development in research centres and organisations outside universities; this programme was associated with the establishment of IDPOR, in 2006. At present the focus is on the creation of a platform for the cooperation between University researchers, schools and municipalities.

b) Developing the understanding and value of education and science in schools and local communities: - School/Science at home: this is part of the project 'A Escola em Casa', aiming at developing and testing instruments and materials to promote and support conversations between children and their parents at home, that is being financed by the Gulbenkian Foundation since 2004.

- 'Caminhar Juntos para Gostar de Aprender e Aprender com a Escola' is a three years project financed through a protocol signed by: Universidade de Aveiro; Agrupamento de Escolas Gândara Mar, Tocha; Direcção Regional de Educação do Centro, Câmara Municipal de Cantanhede e Junta de Freguesia da Tocha. The Project is financed by the latter two partners and started in September 2009.

- Interdisdiplinarity in research and teaching: this programme is just starting, with the aim of understanding the foundations and identifying the relevant conditions to promote interdisciplinarity in higher education.

c) Governance of Science and Education Institutions: at present, this programme is the basis for two doctoral theses, one focusing on knowledge management in research centres and the other on the design and implementation of policies for the development of higher education.

#### research projects selected examples

The number of ongoing Projects in 2010 was 120, similar to the last years. The main sources of funding are FCT, National Science Foundation (78%), and the European Funding Agencies and Programmes, European Commission, FEDER, (14%). Section 3 lists all projects funded.

CICECO participated in many networks in the country, with Brazil (Molecular and Interfaces Nanotechnology Research Network, RENAMI), Spain (Integrated Lab on Chip for Medical Diagnosis) and with other EU countries. An important example of the latter was the Network of Excellence (NoE) 'Functionalised Advanced Materials and Engineering of Hybrids and Ceramics', FAME, financed by the 6th framework programme European. FAME finished in 2008 and CICECO is among the 12 Universities involved in the continuation of this NoE in the so-called European Multifunctional Materials Institute-EMMI (whose Vice-Director is the Director of CICECO), which is now a legal entity (http://www.emmi-materials.eu/). It is also important to note that almost 15% of present our present budget comes from international projects.

#### highlights

#### projects with local Governments

- URBACT: project supported by UNIC and aims at promoting sustainable economical development of local ceramic industries. Partners - Municipalities of Aveiro, Limoges, Pécs, Delft and Selb;
 - POVT Sustainable Water Management in Public Buildings: with Aveiro Municipality;
 - Sustainability Park of Aveiro, with Aveiro Municipality; Parcerias para a Regeneração Urbana (QREN) (2009-2011).

#### national Network Action

- CICECO participates in 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, e.g. NANO/NMed-SD/0140/2007, "Integrated Platform for Medical Diagnostics"- QREN cluster "Plataforma para a Construção Sustentável"

#### 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'.
 COST Action FP0901: "Analytical Techniques for Biorefineries".

- ENERMATaa: new materials for energy, centred in 7 European public institutes.

Magnetotransduction: development of magnetic nanoparticle-viral vector complexes for therapeutic gene delivery in the senile brain, EULANEST:Argentine/Germany/Portugal/Spain
 Marie Curie FP7-PEOPLE-2009-RG-256509, Oxalkanes - Sustainable catalytic oxidation of alkanes

Coordination of three international projects at CERN (ISOLDE) involving researchers from institutions in Europe, Korea, and Japan: CERN-IS-487, Study of Local Correlations of Magnetic and Multiferroic Compounds; CERN-IS-515 Radioactive probe studies of coordination modes of heavy metal ions from natural waters to functionalized magnetic nanoparticles; CERN-I-132 Radioactive Local Probing and Doping on Graphene - NMP2-CT-2004-515960 ULCOS, ULTRA LOW CO2 STEELMAKING

- CP-IP 228589-2, AFORE - Forest Biorefinery: Added Value Chemicals and Polymers by new integrated separation, fractionation and upgrading technologies

- SUNPAP - Scale-up of Nanoparticles in Modern Papermarking

- ERA-IB/BIO/0001/2008-ERA-NOEL, Novel Enzyme Tools for Production of Functional Oleochemicals from unsaturated lipids (ERA-NOEL)

#### trainning activity

CICECO is much involved in advanced training activities, such as the University of Aveiro doctoral programmes in 'Nanosciences and Nanotechnologies', 'Materials Science and Engineering', 'Chemistry' and 'Chemical Engineering', or the national programme 'EngIQ' aimed at people from the Portuguese petrochemical and chemical industries. CICECO was also one of the few institutions in Portugal to receive from EU the status of Marie Curie training centre. We have also been involved in two international M.Sc. Erasmus Mundus Programmes: 'European Masters in Materials Science' with Technical U Hamburg, Aalborg University, and the 'European Maters in Functionalised Advanced Materials and Engineering', with the FAME network (Belgium, France, Germany, Israel, Portugal, Spain, UK).



#### highlights

- 21 Ph.D. and 89 M.Sc. theses from University of Aveiro terminated in 2010, 3 of the PhD theses are international works developed in collaboration with University of Limoges (France), Federal University of Rio Grande do Norte (Brazil) and University of Turku (Finland). We lecture a number of M.Sc. degrees of the Departments of Chemistry, Physics and Ceramics and Glass Engineering. CICECO is now involved in Ph.D. courses with other research units in Aveiro in Chemistry, Chemical Engineering, Nanosciences and Nanotechnologies and Materials Science and Engineering. It is also involved in MAP-Fis, a doctoral programme in Physics with Universities of Minho, Aveiro and Porto, and in EnglQ, a PhD programme aimed at people from the Portuguese petrochemical and chemical industries;

- Bilateral Ph.D. Programmes: 6 theses in progress with U Montpellier, U Bordeaux, U Zaragoza, U Santa Catarina (Brazil), Norwegian University of Science and Technology. Informal schemes of student's exchange with other foreign laboratories (particularly in Brazil) 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 sixth edition (http://emms.web.ua.pt/); and a FAME-promoted programme (http://www.fame-master.com/) in its year 3. 2 theses in collaboration with University of Aalborg (Denmark) were presented in 2010



- A general EMMI/FAME workshop (2 days) was organised on July, in the format of a conference, where the students presented his/her works as oral and poster communications. Seminars are organised every ca. 2 weeks and aimed at all our members. Supervisors-students group meetings take place on a regular basis; - Specialised courses for graduate students - Advanced Course in Biomaterials and Regenerative Medicine at the University of Aveiro (2 day); 8th International Tutorial Workshop on PFM and Nanoscale Electromechanics of Polar Materials, Beijing, China (2 days); 4rth Theoretical and Computational Chemistry Summer School of the University of Barcelona, Spain (1 day); "Workshop RMN and Industry", University of Aveiro (1 day).

#### outreach, society and science

CICECO has developed strong links with society through other actions. In this frame a wide-ranging programme of outreach activities targeted at high schools and the citizens in general (including radio and TV programmes and newspaper articles, organisation of the Chemistry Olympiads, activities with 'Ciência Viva', etc.). Another important commitment of CICECO is in transferring good practices to scientific institutions in deprived national regions, such as the 'Centre of Agricultural and Agrofood Biotechnology of Alentejo', CEBAL, a new and small research institution (6 Ph.D.s) located in Beja, Alentejo in the South of Portugal. CEBAL and CICECO have signed a cooperation agreement and CEBAL is under the scientific direction of the leaders of one of CICECO's group, Prof. A. Silvestre. Finally, some cooperation is also being developed with the local government of Aveiro (e.g. project URBAC).

#### highlights

#### promotion of science

- Within U Aveiro: Science & Technology week, summer academy;

- Cooperation with Secondary Schools (talks at schools, support to teachers), including organising the national Chemistry Olympiads;

Cooperation with Aveiro Science Centre;

- Cooperation with the National programme for the promotion of Science, 'Ciência Viva';

- TV and radio programmes, newspapers;

- Activities promoted by the Centre for Science, Education and Technology Studies (CSETS).

#### activities with schools

- Over 25 activities with over 20 schools, including visits to Chemistry laboratories, conferences in schools, demonstrations, School Science Fairs, and Science Cafes.

- Active participation in up to 15 activities, including demonstrations (Chemistry Show), School Science Fairs, and Science Cafes.

#### activities with families

**Talking About Science at Home.** This is a project promoted by CSETS that involves the development of a strategy for schools (4th, 5th and 6th grades) in which schools' heads, teachers and parents are engaged in promoting communication at home on issues relevant for fostering children appreciation of learning at school.

#### large audience activities

- Summer (secondary) school (25 h lab work)
- Chemistry Olympiads (53 Basic and 51 Secondary Schools)
- Ca. 5 newspaper articles
- 1 radio interview







## about CICECO | 15



#### scientific highlights

i) Miniaturized prototype for pH sensing in the pH range 5-7.5, constructed from a photoluminescent Eu<sup>3+</sup> metal-organic framework containing two different Eu<sup>3+</sup> sites;

ii) First extended system where framework embedded  $Eu^{3+}$ -O- $Eu^{3+}$  dimers behave like a molecule, exhibiting a unique emission signature and one of the longest  ${}^{5}D_{0}$  lifetimes so far observed for  $Eu^{3+}$  in solids;

iii) A ligand-assisted rational design was used to process the Ln<sup>3+</sup>containing organic-inorganic hybrids displaying the highest emission quantum yield (0.60±0.06) reported so far;

iv) The role of oxygen moieties at graphene surface on gold nucleation and growth has been investigated and the derived platforms were investigated as SERS substrates;

v) Heteroepitaxial growth of MFI zeolites over titanosilicate molecular sieves;

vi) The influence of step sites in the molecular mechanism of the water gas shift reaction catalyzed by copper was investigated;

vii) The key role of the surface membrane in why gastropod nacre grows in towers was explained.



figure: TEM image of polystyrene nanocomposites containing Au/TOA/OA *in Langmuir 2010, 26 (13), 11470-11412* 

### research team

on 31st december '1o

#### professors & lecturers

Ana Margarida M. V. Barros Timmons Ana Maria Vieira Silva Viana Cavaleiro Artur Jorge de Faria Ferreira Carlos Manuel Santos Silva Helena Isabel Seguro Nogueira Isabel Maria de Sousa Gonçalves João Carlos M. C. Gomes da Rocha José Joaquim Cristino Teixeira Dias Leonel Marques Vitorino Joaquim Luís António Ferreira M. Dias Carlos Maria Gracinda Ferreira da Silva Paulo Jorge Almeida Ribeiro Claro Tito da Silva Trindade

#### full time researchers

Ana Luísa Daniel da Silva Ana Rosa Silva Duarte Ananias Marques Fa Nian Shi Filipe Alexandre A. Paz José Richard B. Gomes Lianshe Fu Luís Miguel Monteiro Mafra Maria Rute A.S. Ferreira André Martyn Pillinger Nicola Alessandro Pinna Sérgio Manuel S. Pereira Zhi Lin

post-doctoral associates

Ana Catarina Costa Gomes Ana Sofia Madureira Bruno Ana Violeta O. M. Sousa Girão Angela Sofia dos Santos Pereira Bing Liu Cátia Andreia Silva Teixeira Filipa Lourosa Sousa Gianvito Caputo Guylhaine Emilie Clavel Hongzhou Lian José Alberto Pires Fernandes Mariana Isabel Rodrigues Sardo Mariela Martins Nolasco Patrícia Ferreira Lito Patricia Pereira Lima Paula Cristina Ramos Soares e Santos Reneé Eve Siegel Sérgio Miguel Santos Shiyong Yu Yinfeng Han

#### PhD students

Ana Luísa Carvalho Magalhães Andrea Pucci Bruno Manuel Henriques Simões Antunes Carlos António Delgado Sousa Brites Carlos Miguel Santos Vicente Catherine Marthe Dominique Marichy Filipe Miguel de A. M. Santos Julien Graffion Manuel António Martins da Silva Maria Isabel Gomes de Pinho Mengistie Leweyehu Debasu Patrícia dos Santos Neves Patrícia Rodrigues da Silva Sara Isabel Augusto Fateixa Sérgio Manuel Felipe Vilela Sónia Luzia Claro de Pinho Sónia Mafalda Ferreira Figueiredo Tatiana Amarante

#### **MSc students**

Ana Cristina Estrada M. G. Sousa Paula Alexandra Macedo Figueira Paula Cristina de Almeida Pinheiro Sónia Oliveira Pereira Tiago Luís da Costa Faria Vânia Patricia Castro Teixeira Freitas

#### other students

Ana Carolina Távora Loureiro **Daniel Ferreira Martins** Fabiana Neves Vieira Félix Marques Carreira Hélio Miguel Teixeira Albuquerque Hugo Miguel Amorim Barbosa Ines Sofia Moutinho Alves Joana Marcelino Pinheiro Júnior Andres Gomes Louro Luciana Carolina Lopes Ferreira Luis Manuel Cravo Pereira Marta Cristina Gomes Faria Patrão Nadine de Castro Coutinho Nuno Filipe Camarneiro Mendes Rita Paula Paiva Craveiro **Rita Pinheiro Lopes** Rute Catarina Batista Carvalho Duarte Sara Margarida Fernandes da Horta Simão Pedro Pereira Cardoso Teresa Margarida Mendes Mourão Tiago Belo Margues de Oliveira e Silva Valentina Rebuttini

#### collaborators

Adriano de Andrade Torrano Ana Catarina Dias Martins Coelho António Luciano Videira Chloé Montbabut Diogo Cerqueira Queirós Filipe Silva Gil Gonçalves Hermi Brito Hugo Jorge Ivo Sílva **Jkurt Wuthrich** Joana Filipa Brites Barata Joana Lia Cardoso de Sousa João Pina José Luis Cagide Fajín Karel Douglas Klika Lionnel Reis Xavier Manuel Ribeiro Carrott Marc-Georg Willinger Margarida Mano Moisés Luzia Gonçalves Pinto Oscar Malta Teresa Gaspar **Tiago Manuel Nunes Margues** 

#### activity report 2010

**Nanostructured Materials.** We report the fine-tuning of the relaxometry of  $g-Fe_2O_3@SiO_2$  core-shell nanoparticles by adjusting the thickness of the coated silica layer. It is clear that the coating thickness of  $g-Fe_2O_3@SiO_2$  nanoparticles has a significant impact on the r1 (at low B0 fields), r2, and r2 \* relaxivities of their aqueous suspensions. The silica layer is heterogeneous and has regions that are porous to water and others that are not. The viability and the mitochondrial dehydrogenase expression of the microglial cells are not sensitive to the vesicular load with these core-shell nanoparticles. The adequate silica shell thickness can therefore be tuned to allow for both a sufficiently high response as contrast agent, and adequate grafting of targeted biomolecules.

The anomalous thermalization in Gd<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> and Gd<sub>2</sub>O<sub>3</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> nanotubes, exhibiting up to one order of magnitude larger than previously reported for similar materials, have been reported. This anomalous thermalization induces unexpected energy transfer from Eu<sup>3+</sup> C<sub>2</sub> to S<sub>6</sub> crystallographic sites, at 11 K, and  ${}^{2}H_{11/2}$ -><sup>4</sup>I<sub>15/2</sub> Er<sup>3+</sup> upconversion emission; it is interpreted on the basis of the discretization of the phonon density of states, tuned by varying the annealing temperature (923–1123 K) in the synthesis procedure, and/or the Ln<sup>3+</sup> concentration (0.16–6.60%).

The work on ordered hybrid and doped nanostructures was further developed especially by targeting new nanostructured inorganic materials and new application such as Li ion batteries or biomedical applications. Various nanostructures (e.g. C and BN nanotubes) were "functionalized" with various metal oxides for application in various timely fields such as energy storage and gas sensing. Advanced structural characterization techniques were applied for a deep understanding of the structure-properties relation.

Hydrogel based nanocomposites comprising natural biopolymers and inorganic nanophases (Au nanostructures, magnetic nanoparticles) were prepared in the form of "bulk nanocomposites" and nanoparticulate systems (nanogels). The properties of these systems were investigated envisaging possible biomedical applications, namely for remotely controlled drug release.

We have developed a rigorous analysis model for the thermal conductivity of semiconductor nanostructures which takes into account the exact physical nature of the various acoustic and optical phonon mechanisms. Following the Callaway solution for the Boltzmann equation, where resistive and non-resistive phonon mechanisms are discriminated, we derived a formalism for the lattice thermal conductivity that takes into account the phonon incidence angles.

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The importance of all the mechanisms we have involved in the model is demonstrated clearly with reference to reported data regarding the isotopic composition effect in bulk Si and Si NW samples. Namely, our model accounts for previously unexplained experimental results regarding (i) the isotope composition effect on the thermal conductivity of bulk silicon (ii) the size effect individual Si NWs and (iii) the dramatic decrease in the thermal conductivity for rough Si NWs.

High quality  $AI_{(1-x)}I_{nx}N/GaN$  bilayers, grown by metal organic chemical vapor deposition (MOCVD), were characterized using structural and optical techniques.

Morphological uniform composites using miniemulsions of poly(*tert*-butyl acrylate) or poly(styrene) containing organically capped gold nanocrystals (NCs) have been prepared. The optical features of such hybrid structures are dominated by plasmonic effects and depend critically on the morphology of the resulting nanocomposite. In particular, we demonstrated the ability to tune the overall optical response in the visible spectral region by varying the Au NCs arrangement within the polymer matrix, and therefore the interparticle plasmon coupling, using Au NCs resulting from the same batch of synthesis. This is a consequence of two well-known effects on the optical properties of Au particles: the variation of the surrounding dielectric refractive index and interparticle plasmonic coupling.

The magnetic removal of Hg(II) from water has been assessed using silica coated magnetite particles. The magnetite particles were first prepared by hydrolysis of  $FeSO_4$  and their surfaces were modified with amorphous silica shells that were then functionalized with organic moieties containing terminal dithiocarbamate groups. Under the experimental conditions used, the materials reported here displayed high efficiency for Hg(II) uptake (74%).

Rheological and film properties research on polysaccharides showed that the pH and ionic conditions of the polysaccharide solutions strongly affects the stability of nanoparticles (NPs) which tend to aggregate as evidenced by Cryo-SEM. Consequently the properties of the ensuing NCs are compromised. In the case of films, the evaporation process seems to be the most critical factor for aggregation even upon surface modification of the fillers.

Studies using the Langmuir-Blodgett technique and phospholipids to assess the interactions of NPs with cell membrane models proved to be an interesting approach to understand interactions at the molecular level.

The polymerisation of PMMA chains from the surface of vertically aligned carbon nanotubes (VACNT) via ATRP yielded composites with higher compressive strength than the pristine VACNT forests as a result of the presence of the polymer chains. Furthermore, the honeycomb structure of the composite obtained may be promising for use as membranes for example. Encapsulation of SiO<sub>2</sub> fibbers and of Gd<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup>@SiO<sub>2</sub> by PAA-co-BA using a PAAmacroRAFT agent in solution was successful. Yet, further work is required to prepare these materials in aqueous media to yield anisotropic films.

*Layered Materials.* As part of an ongoing CICECO funded project entitled "Metal carbonyl intercalated anion exchangers as drug delivery systems", a series of molybdenum carbonyl complexes have been prepared and intercalated into layered double hydroxides (LDHs). For example, the complex  $[Mo(CO)_4(2,2'-bipyridine-5,5'-dicarboxylate)]$  was immobilised in Zn-Al-LDHs by ion-exchange methods. Although the structural integrity of the complex was retained upon intercalation, the resultant material suffered spontaneous release of CO over a period of several days.

Two new chiral metal organic frameworks, assembled from Y(III), Na(I), and chiral (tartaric acid) flexible-achiral rigid dicarboxylate ligands, were prepared. These luminescent materials were characterized by XRD and NMR and present layered structures whose three-dimensional stability is ensured by strong hydrogen bond interactions. They also have catalytic activity.

The thermal transformations of  $\gamma$ -titanium phosphate have been studied by thermal analyses, variable-temperature 2D <sup>31</sup>P-<sup>31</sup>P spin-exchange MAS NMR and synchrotron powder XRD. Vyazovkin's model-free kinetic algorithms have been applied to determine the apparent activation energy to both dehydration and dehydroxylation of g-titanium phosphate. Structural models for intermediate layered phases have been proposed.

**Mesoporous and microporous Materials.** Arenetricarbonyl complexes of the type  $-C_6H_4M(CO)_3-(M = Mo, Cr)$  were incorporated into crystal-like mesoporous phenylene-silica by liquid-phase deposition of  $M(CO)_6$ . The Mocontaining materials gave outstanding epoxide selectivity in the catalytic reaction of olefins with tert-butylhydroperoxide under quite mild reaction conditions. No metal leaching was detected and the catalytic reaction was heterogeneous in nature. The oxidation of (R)-(+)-limonene revealed an outstanding regioselectivity to the epoxidation of the endocyclic double bond.

The effect of several desilication experimental parameters (base concentration, temperature and time) on the characteristics of MOR zeolite was studied.

*Hybrid Materials.* The logarithmic time-dependence of the emitted relaxation energy of self-assembled alkylene/siloxane hybrid nanostructure upon heating/cooling cycles provided a fingerprint of emergent complex behaviour. A bpy-bridged silsesquioxane displaying an efficient and tuneable blue-to-green emission with the highest quantum yield value (0.22±0.02) reported so far for metal-free phosphors easily excited by commercial InGaN long-UV/blue LEDs was reported.

The Eu<sup>3+</sup> ions play a totally unparallel dual-role in the modulation of the morphology and size of bridged silsesquioxanes hybrids acting simultaneously as structure directing agents and structural probes to sense locally morphological alterations. Urea-based bis-silylated bpy organic–inorganic hybrids incorporating different Eu<sup>3+</sup>, Gd<sup>3+</sup>, and Tb<sup>3+</sup> were obtained by the sol–gel process. The emission color is easily tuned across the CIE diagram from the blue to the red, orange or green areas, depending on the lanthanide ion and on the excitation wavelength.

Di-ureasil hybrids containing different amounts of methacrylic acid modified zirconium tetrapropoxide nanoclusters incorporating  $EuCl_3$  and a  $\beta$ -diketonate complex were prepared. The nanoclusters incorporation enhances (30 %) the absolute emission quantum yield. All the above mentioned hybrids are white light emitters, presenting a host-related broad emission band superimposed on the  $Eu^{3+}$  intra-4f<sup>6</sup> transitions.

Three different types of photoluminescent hybrid materials containing Eu<sup>3+</sup> and Tb<sup>3+</sup>, chitosan, and silica have been prepared with different structural features. The different silica sources lead to diverse microstructures of hybrid materials, with silica being homogeneously dispersed in the chitosan materials, or forming a core-shell morphology.

We reported a new nanothermometer consisting of  $Eu^{3+}$  and  $Tb^{3+}$  complexes embedded into organic-inorganic hybrid nanoclusters (100-600 nm) formed by a maghemite magnetic core coated with a tetraethyl orthosilicate/aminopropyltriethoxysilane organosilica shell. The thermometer is self-referencing, allowing absolute measurements in the 10-350 K temperature range. Its temperature sensitivity is up to 4.9%/K, 1.5 times larger than the highest value reported previously for lanthanide-based temperature sensors, and it exhibits high photostability in long-term use. The nanoparticles changes it emission properties in a consistent way with the temperature making possible to predict the temperature by the analysis of the "colour" of the material. The tunability to the temperature working range is made by modifying the  $Eu^{3+}/Tb^{3+}$  ratio or by changing the host matrix.

Two kinds of bifunctional architectures combining the functions of paramagnetic nanoparticle and near infrared luminescent lanthanide complexes have been prepared. The resulting bifunctional nanocomposites exhibit superparamagnetic behaviour, high fluorescence intensity and color purity, and have potential applications in biological luminescent label.

Direct UV-laser writing was used to produce channel waveguides and Y-power splitters on thin films of di-ureasil organic-inorganic hybrid materials doped with methacrylic acid modified by zirconium tetrapropoxide. The incorporation of Rhodamine 6G into di-ureasils enabled the observation of efficient random laser behaviour. For the first time, we have introduced the use of hybrid multi-objective optimization in spectroscopic ellipsometry data analysis.



HRTEM image of [Tb(W<sub>5</sub>O<sub>18</sub>)<sub>2</sub>]/SiO<sub>2</sub> nanocomposite (from left-to-right): a) in dark field mode b) with overlapping of EDX mapping for Si (red) end W (green) c) with separated EDX mapping for Si d) with separated EDX mapping for W in J. Mater. Chem 2010, 20, 3313-3318

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*Crystal Engineering of Organic-Inorganic Hybrid Materials.* A microporous cationic lanthanide-organic framework,  $[Ce_2(pydc)_2(Hpydc)(H_2O)_2]CI \cdot (9+y)H_2O$  (where  $pydc^{2^-}$  is the diprotonated residue of 2,5-pyridinedicarboxylic acid), has been prepared under just 30 minutes (total reaction time) by applying microwave heating. This remarkable structure contains prominent channels (cross-section ca.  $12 \times 7 \text{ Å}^2$ ) which house disordered charge-balancing chloride anions and water molecules of crystallization. The BET surface area of the degassed material is 106 m<sup>2</sup>/g. Solvent exchange studies have been performed showing that water could be partially exchanged by chloroform or benzyl alcohol by crystal immersion at room temperature over a period of several days. The preparation of the known [Ce(Hpmd)(H<sub>2</sub>O)] framework (reported in a previous year) was also attempted by using microwave heating. A one-dimensional polymer formulated as [CeCl(mal)(H<sub>2</sub>O)<sub>3</sub>] (where mal- stands for malonate) was isolated instead and its crystal structure was studied using single-crystal X-ray diffraction.

Aqueous suspensions of layered microcrystalline powders of  $[Ln(H_2cmp)(H_2O)]$   $(H_2cmp = (carboxymethyl)iminodi(methylphosphonic acid), having a relatively wide crystallite distribution (from 400 nm to 1µm) were studied by relaxometry. The water 1H longitudinal <math>(r_1)$  and transverse  $(r_2)$  relaxivities were measured for aqueous suspensions of these materials containing distinct lanthanide ions. Compounds appear to be very efficient as potential MRI contrast agents for T<sub>2</sub>-weighted imaging, but not efficient for T<sub>1</sub>-weighted imaging, despite the presence of one water molecule in the inner-sphere of the coordination polyhedron.

The hydrothermal reaction between lanthanide nitrates and 2,3-pyrazinedicarboxylic acid led to a new series of two-dimensional (2D) lanthanide-organic frameworks:  $[Ln_2(2,3-pzdc)_2(ox)(H_2O)_2]n$  (where 2,3-pzdc2- = 2,3-pyrazinedicarboxylate,  $ox^{2^-}$  = oxalate and  $Ln^{3^+} = Ce^{3^+}$ ,  $Nd^{3^+}$ ,  $Sm^{3^+}$ ,  $Eu^{3^+}$ ,  $Gd^{3^+}$ ,  $Tb^{3^+}$  or  $Er^{3^+}$ ). Upon UV excitation at room temperature the organic ligands sensitize the luminescence of the Nd<sup>3+</sup>,  $Sm^{3^+}$ ,  $Eu^{3^+}$  and  $Tb^{3^+}$  ions, being more efficient for  $Eu^{3^+}$  and  $Tb^{3^+}$ . Lifetime values of 0.590±0.004 and 0.367±0.006 ms, and an absolute emission quantum yield of 0.13 were obtained for the  $Eu^{3^+}$  compound at 12 and 300 K, respectively.

Two new Mn(II) MOFs have been synthesized with molecular formula: 1 [Mn(H<sub>2</sub>O)<sub>2</sub>(HBTC) (H<sub>2</sub>O)] and 2 [Mn(H<sub>2</sub>O)<sub>2</sub>(4,4'-bipy)(HBTC)<sub>2</sub>] (H4,4'-bipy). 1 is composed of Mn–H<sub>2</sub>O–Mn 1D chains and further the chains are linked by HBTC ligands to form a 2D network in the ab plane; 2 is constructed by Mn–4,4'bipy–Mn 1D chains along the b direction with Mn ions coordinated to H2BTC and water as terminal ligands to form a 2D network. The magnetic properties have been studied. New chiral metal organic frameworks, assembled from Y(III), Na(I), and chiral, achiral rigid dicarboxylate ligands, formulated as [NaY(Tart)(BDC)(H<sub>2</sub>O)<sub>2</sub>] and [NaY(Tart)(biBDC)(H<sub>2</sub>O)<sub>2</sub>] were synthesized and showed that L-tartaric acid is a good flexible ligand which can induce chirality in new MOFs.

**Catalytic Materials**. Work has continued on the design, synthesis and structural elucidation of novel catalysts containing the cis-dioxomolybdenum(VI) unit,  $MOO_2^{2+}$ . During efforts to coordinate pyridine to the molybdenum centre, the salts ( $C_5H_6N$ )<sub>3</sub>[MoCl<sub>4</sub>O<sub>2</sub>]Cl and ( $C_5H_6N$ )<sub>4</sub>[Mo<sub>2</sub>Cl<sub>2</sub>O<sub>5</sub>(SO<sub>4</sub>)<sub>2</sub>] were isolated and their crystal structures determined. A detailed crystallographic study was also carried out for the tetramethylammonium salts ( $MMe_4$ )<sub>2</sub>[MO<sub>2</sub>(Hdhb)<sub>2</sub>].nH<sub>2</sub>O (M = Mo, W; Hdhb = monoprotonated form of 2,3- or 3,4-dihydroxybenzoic acid). In other work, the complexes [MoO<sub>2</sub>Cl<sub>2</sub>(bipy]] (bipy = 2,2'-bipyridine) and [MoO<sub>2</sub>Cl(HC(bim)<sub>3</sub>)]Y (Y = Cl, BF4, PF6; HC(bim)<sup>3</sup> = tris(benzimidazolyl)methane) were prepared and examined as catalysts for the epoxidation of cis-cyclooctene at 55 °C with tetr-butylhydroperoxide (TBHP) as the oxidant. During the catalytic reaction the bipy complex transforms into the molybdenum oxide/bipyridine hybrid materials [MoO<sub>3</sub>(bipy)] when the oxidant is TBHP/decane and {[MoO<sub>3</sub>(bipy)][MoO<sub>3</sub>(H<sub>2</sub>O)]]<sub>n</sub> when the oxidant is TBHP/water. The crystal structure of the latter material (determined from synchrotron X-ray powder diffraction data) is composed of two distinct neutral one-dimensional polymers, which are interconnected by OH•••O hydrogen-bonding interactions. An alternative preparation of [MoO<sub>3</sub>(bipy)] (in quantitative yield) consists of the oxidative decarbonylation of the complex cis-[Mo(CO)<sub>4</sub>(bipy)] with TBHP at room temperature. A similar treatment of cis-[Mo(CO)<sub>4</sub>(di-t-Bu-bipy)] (di-t-Bu-bipy = 4,4'-di-tert-butyl-2,2'-bipyridine) led to the isolation of oble polynuclear complex [Mo<sub>8</sub>O<sub>24</sub>(di-t-Bubipy)<sub>4</sub>] with a structure containing a central Mo<sub>4</sub>(m<sub>3</sub>-O)<sub>4</sub> cubane. Several other types of molybdenum carbonyl complexes were examined as catalyst precursors in the epoxidation of olefins, namely the tricarbonyl complex CpMo(CO)<sub>3</sub>CH<sub>3</sub> and the dicarbonyl complexes Cp'Mo(CO)<sub>2</sub>(h<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>) [Cp' = h<sup>5</sup>-C<sub>5</sub>H<sub>5</sub> (Cp), h<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Me, h<sup>5</sup>-

**Polyoxometalates.** Photoluminescent lanthanopolyoxotungstate core/shell nanoparticles were prepared by the encapsulation of lanthanide-containing polyoxometalates (POMs) with amorphous silica shells. Photoluminescence studies show that there is efficient emission from the POM located inside the SiO<sub>2</sub> shells, through excitation paths that involve O/Eu/Tb and O/W ligand-to-metal charge transfer. Excitation of the POM containing europium(III) may be tuned towards longer wavelengths via an antenna effect, by coordination of an organic ligand such as 3-hydroxypicolinate.

Hybrid compounds with POMS and organic moieties have been prepared. The work on compounds with parent Keggin anions and L-arginine was published. The study on compounds with transition-metal monosubstituted Keggin-type polyoxotungstates and different cations was pursued. Crystal structures of some compounds were determined.

Polyoxotungstates in the catalytic oxidation of organic compounds have been investgated and the oxidation of ethylbenzene and related compounds, with  $H_2O_2$ , in homogeneous conditions has been reported. EIS was used to assess the properties of different modified electrodes with POMs. Electrodeposition of PEDOT was used to prepare electrodes modified with silicotungstates, and the electrochemistry of the immobilized hybrids was assessed.

**Non-aqueous Chemistry Applied to Atomic Layer Deposition.** Non-aqueous sol-gel approaches applied to the atomic layer deposition technique were further investigated and new materials have been deposited on different substrates targeting application in the field of photonics, and environment (e.g. gas sensing).

Adsorption, Surface and Inclusion Phenomena. Sr adsorption on silicon surfaces has attracted considerable attention due to the possibility of growing  $SrTiO_3$  high-k dielectric layers on top of silicon. This is one of the main contenders to replace  $SiO_2$  in sub-32 nm gate length complementary metal oxide semiconductor technology. We have calculated the potential-energy surface (PES) for Sr adsorption on Si(111)-7x7 within density-functional theory. The main diffusion paths and corresponding energy barriers are determined for a Sr atom on reconstructed Si(111) surface. It was found that Sr thermal motion alone cannot account for the apparently noisy STM image patches. The origin of the peculiar intensity distribution in those images is due to charge transfer from the Sr atom to Si adatoms in the 7x7 reconstruction. Thus, electronic effects complement the picture and enable to understand the observations. With this knowledge in hand, the contradiction between experimental apparently noisy STM image patches and calculated PES for other adsorbates is readily explained.

Preparation of AOT-D<sub>2</sub>O-decane water-in-oil (W/O) microemulsions with unsubstituted and methylated cyclodextrins. Record of Dynamic Laser Scattering experiments with the prepared microemulsions, to obtain and interpret the reversed micelle sizes distribution. During September 2010, a new experiment proposal was prepared and submitted to Laboratoire Leon Brillouin to obtain Small Angle Neutron Scattering (SANS) data of the above mentioned microemulsions.

**Structural Elucidation of Functional Compounds.** X-ray diffraction techniques (powder and single-crystal) have been employed for the elucidation of complex structures of functional materials or compounds. The domino Michael-Michael-aldol reaction from (E,E)-1,5-diarylpenta-2,4-dien-1-one with nitromethane afforded novel pentassubstituted cyclohexane chiral derivatives. Chiral new compounds were also obtained (in high yields) from the asymmetric organocatalytic additions of malononitrile and nitromethaneto (E,E)-1,5-diarylpenta-2,4-dien-1-ones. The absolute structural configuration of all these compounds was unequivocally attained from detailed single-crystal X-ray diffraction studies. The structural details of chiral aminophosphonic molecules, having great potential to be employed in the synthesis of metal-organic frameworks, have also been elucidated, in particular (R)-(1-ammoniopropyl)phosphonate and (R)-(1-ammonioethyl)phosphonate.

**Computer Aided Characterization of Materials' Structure and Properties.** Particular attention has been given to the description of materials from combining computational modelling with spectroscopic 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 pursued. An example of the use of computational and vibrational spectroscopic data in the elucidation of the crystal structure of a molecular crystal without strong hydrogen bonds was provided with the study of 4-dimethylaminobenzaldehyde. Comparison of observed and calculated spectra presents strog evidence for the hydrogen-bond contact between a methyl group and the carbonyl oxygen atom.

The MD simulations are being employed in the study of the structure of ionic liquids (ILs) and of their interaction with solutes (e.g. sulfonated compounds), in close collaboration with on-going experimental work in CICECO and with a private company. Additionally, MD simulations together with docking calculations are also being developed on interaction of inhibitors with cysteine proteases of P. falciparum with the ultimate goal of designing more effective antimalarials. The latter work is being carried out with close collaboration with experimental groups in Portugal and abroad.

Density functional theory (DFT) calculations were combined with a periodic slab approach in the study of the dissociation of water catalyzed by planar and stepped transition metal surfaces, the bottleneck reaction in the water gas shift reaction (WGSR). As a result, a reactivity scale was proposed. Importantly, an useful Brønsted-Evans-Polanyi (BEP) relationship has been introduced for the first time in the literature. Surprisingly, a new descriptor, i.e., the interaction energy of oxygen adatoms (a species that is not present in the WGSR) was proposed and validated, which allows the screening of a large number of metallic (and bimetallic, work in progress) systems in a simple way.

More recently, van der Waals corrected DFT approaches are being strongly used in calculations involving the interaction of small gaseous species with porous materials containing Si atoms. The idea is to develop potentials that can be combined with classical simulations in the calculation of properties such as adsorption isotherms. The goal is to design in silico new materials that can be good adsorbents or that can be used in gas separation. These works are being heavily funded by FCT.



group coordinator: Paula Vilarinho (paula.vilarinho@ua.pt)

#### scientific highlights

i) Fabrication of BaxSr<sub>1-x</sub>TiO<sub>3</sub> thin films at 120 °C on flexible polymeric Kapton films.

ii) Synthesis of the novel porous  ${\rm BaTiO}_3$  ferroelectric films and particulates.

iii) Identification of high effective piezoelectric coefficient values in self-assembled diphenylalanine peptide nanotubes.

iv) Polarization switching kinetics of ferroelectric polymer nanomesas fabricated by self-organization from Langmuir–Blodgett.

v) Modelling of the effect of the annealing rate on the crystallization of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>.

#### research team

on 31<sup>st</sup> december '1o

#### professors & lecturers

Ana Maria de Oliveira Rocha Senos Isabel Margarida Miranda Salvado Maria Elisabete Jorge Vieira Costa Paula Maria Lousada S. Vilarinho Pedro Manuel Lima Q. Mantas Victor Ferreira

#### full time researchers

Aiying Wu Aleksey Yaremchenko Andrei Kholkin Paula Celeste da Silva Ferreira Rob Pullar

#### post-doctoral associates

Alejandro Heredia Barbero Indrani Coondoo Sudheendran Kooriyattil Xiaodong Zhang

#### **PhD students**

Ana Luísa Carvalho Magalhães Andrea Pucci Bruno Manuel Henriques Simões Antunes Carlos António Delgado Sousa Brites Carlos Miguel Santos Vicente Catherine Marthe Dominique Marichy Filipe Miguel de A. M. Santos Julien Graffion Manuel António Martins da Silva Maria Isabel Gomes de Pinho Mengistie Leweyehu Debasu Patrícia dos Santos Neves Patrícia Rodrigues da Silva Sara Isabel Augusto Fateixa Sérgio Manuel Felipe Vilela Sónia Luzia Claro de Pinho Sónia Mafalda Ferreira Figueiredo Tatiana Amarante

#### **MSc students**

Ana Cristina Estrada M. G. Sousa Paula Alexandra Macedo Figueira Paula Cristina de Almeida Pinheiro Sónia Oliveira Pereira Tiago Luís da Costa Faria Vânia Patricia Castro Teixeira Freitas

#### other students

Ana Carolina Távora Loureiro Daniel Ferreira Martins Fabiana Neves Vieira Félix Marques Carreira Hélio Miguel Teixeira Albuquerque Hugo Miguel Amorim Barbosa Ines Sofia Moutinho Alves Joana Marcelino Pinheiro Júnior Andres Gomes Louro Luciana Carolina Lopes Ferreira Luis Manuel Cravo Pereira Marta Cristina Gomes Faria Patrão Nadine de Castro Coutinho Nuno Filipe Camarneiro Mendes Rita Paula Paiva Craveiro Rita Pinheiro Lopes Rute Catarina Batista Carvalho Duarte Sara Margarida Fernandes da Horta Simão Pedro Pereira Cardoso Teresa Margarida Mendes Mourão Tiago Belo Marques de Oliveira e Silva Valentina Rebuttini

#### collaborators

Adriano de Andrade Torrano Ana Catarina Dias Martins Coelho António Luciano Videira Chloé Montbabut Diogo Cerqueira Queirós Filipe Silva Gil Gonçalves Hermi Brito Hugo Jorge Ivo Sílva **Jkurt Wuthrich** Joana Filipa Brites Barata Joana Lia Cardoso de Sousa João Pina José Luis Cagide Fajín Karel Douglas Klika Lionnel Reis Xavier Manuel Ribeiro Carrott Marc-Georg Willinger Margarida Mano Moisés Luzia Gonçalves Pinto Oscar Malta Teresa Gaspar **Tiago Manuel Nunes Margues** 

#### activity report 2010

*High Frequency Dielectric Materials:* TiTe<sub>3</sub>O<sub>8</sub> powders were synthesized via solid-state-reaction at 620°C. Thick films of TiTe<sub>3</sub>O<sub>8</sub> were fabricated by EPD on Pt coated Si-substrate. The effect of different suspension media and additives was studied. The stability of the suspension was analysed by zeta potential measurements. It was verified that acetone as disperse media with the addition of triethanolamine (TEA) is very effective in the EPD of TiTe<sub>3</sub>O<sub>8</sub> powders. Under these conditions high quality green thick films were prepared. Without the addition of TEA, the stability of the suspension is decreased and the quality of the film is deteriorated in relation to the films prepared from the suspension with TEA. TiTe<sub>3</sub>O<sub>8</sub> films derived from the acetone suspension with TEA can be sintered at 700° for 5h. The permittivity and loss tan of ceramics and films are ~60 and 0.007, measured at 100KHz.

*Ferroelectric Ceramics and Ferroelectric Fibers, Single Crystals and Films:* Studies on the preparation and properties of Aurivillius oxides (AO) thin films with n>=5 were initiated. The studied compositions included  $Sr_{n-3}Bi_4TinO_{3n+3}$  with n=5,6 (SBTi 5 and SBTi 6). A chemical solution deposition (CSD) method starting from organic precursor solutions was developed. Experimental variables respecting either precursor solution (chemical composition, concentration, additives, viscosity, etc) either heat treatment schedule (annealing temperature and time) were manipulated for achieving uniform thin films of the desired perovskite composition with improved dielectric and ferroelectric properties. The electrical properties study revealed that the increase of the number of pseudo-perovskite layers (n) from 5 to 6 is accompanied by a decrease of polarization and dielectric permittivity. The preparation of the AO thin film compositions by rf magnetron sputtering was also initiated. The required ceramic targets were firstly prepared by uniaxially pressing ceramic powders having the  $Sr_{n-3}Bi_4TinO_{3n+3}$  (n=6) nominal composition. The variation of experimental conditions including Argon:Oxygen ratio and RF power was carried out aiming to establish an adequate schedule of deposition parameters for achieving SBTi6 uniform thin films. This work is still at an incipient stage and is to be continued.

The study of the processing and properties (mechanical and electrical) of lead free potassium niobate (K0.5Na0.5NbO3 (KNN))-based polycrystalline materials and single crystals was initiated. KNN single crystals were successfully grown by a high temperature flux method. Two different fluxes were used and their effects on the obtained crystals were assessed. It was observed that in spite of the similar properties of the obtained crystals (same yellowish color and transparency and equivalent sizes, 4.5x 4mm and 3x3.2mm) the addition of boron oxide to the flux allowed to decrease the maximum temperature for crystal growth. Some studies are now in progress in order to optimize the flux composition for obtaining larger crystals of high quality for characterization and texturing studies. The studies on KNN ceramics were focused on Mn doped KNN, namely on the site occupancy in KNN lattice. Mn doped KNN ceramics on A and B site were prepared by solid-state route under different sintering temperatures. Main results obtained until now revealed that the B site solubility limit is larger than that observed for A site. Mn helped to reduce the sintering temperature while ensuring a high densification of B-site doped KNN. Other benefits of B-site doping include the decrease of leakage current and the improvement of remanent polarisation. These studies will be continued in order to get deeper understanding of Mn role on KNN A and B site. The BaFe<sub>12</sub>O<sub>19</sub>–BaTiO<sub>3</sub> composite ferroelectric/ferromagnetic ceramics were prepared by conventional solid-state sintering technique. The magnetic properties are consistent with the ratio of the magnetic phase present but ferroelectric properties are degraded due to a sufficiently high degree of conductivity in the ceramics. Magnetoelectric coupling was observed at a local level by means of the scanning probe microscopy (SPM). Piezoresponse and magnetic force modes of SPM were both utilized to assess strain-mediated magnetoelectric coupling between neighbouring grains. The observed variation in the magnetic signal after the electrical poling with SPM was attested to the changes in the magnetic interactions and magnetic anisotropy leading to broadening of the magnetic domain wall.

For thick films the required high sintering temperatures present a challenge for processing functional oxides on base metal substrates. In our study it was shown that it is possible to adapt well-known ceramic processing strategies to the fabrication of thick lead zirconate titanate (PZT) films on Cu with useful ferroelectric properties. PZT powders with optimized particle sizes were used to fabricate thick films by electrophoretic deposition in combination with a post-deposition isostatic pressing step. This approach to maximize green packing is sufficient to dramatically lower the required sintering temperatures. 25 micron thick PZT films on Cu sintered at 900°C have a dielectric permittivity of 585, a loss tangent at 10 kHz of 0.03, a remanent polarization of 19 micro coulomb per square centimer and a coercive field of 22 kV cm-1. This significant improvement in the dielectric response opens the possibility of using thick PZT films on Cu for a wide range of devices where cost, yield and reliability are concerns.

Epitaxial Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub> (NBT) thin films presenting various thicknesses were grown by pulsed laser deposition on epitaxial (100) platinum bottom layers supported by (100) MgO single crystal substrates. X-ray diffraction data indicated that all NBT layers are single-phased and that (100) - oriented NBT crystallites are predominant. Further x-ray investigations revealed a pronounced asymmetry of the (100) NBT reflection. The analysis of the asymmetrical broadening of the reciprocal lattice point suggests a variation in the chemical composition across the samples thickness, in agreement with comparative Rutherford backscattering Spectroscopy.

A well-defined shape of the polarization-electric field hysteresis loops was recorded, and a vertical drift of the loops was systematically observed, originating from the very asymmetric conduction of the Pt/NBT/Pt capacitors at different polarities. The nanoscale electrical properties of the thinnest film have been characterized by both tunneling atomic force microscopy (TUNA) and piezoforce microscopy (PFM). PFM data showed that most of the grains seem to be constituted of single ferroelectric domains.

Incipient Ferroelectrics: SrTiO<sub>3</sub> : Mn ceramics, prepared according to the chemical formulae SrTi<sub>1-</sub> yMn<sub>y</sub>O<sub>3</sub> and SrT<sub>1-y</sub>Mn<sub>y</sub>O<sub>3</sub>, were studied by Fourier transform infrared and time-domain terahertz spectroscopy in the temperature range of 10–300 K to support the incorporation of Mn ions into the perovskite lattice of  $SrTiO_3$ , and to ascertain their different lattice site locations. The polar soft mode of the incipient ferroelectric SrTiO<sub>3</sub> is found to be hardened in the whole temperature range by the substitution of Mn ions on Ti sites, and only in the low-temperature range by the Sr site substitution. Activation of the mode, associated with the R point condensation of the Brillouin zone due to the doubling of the unit cell by antiphase rotations of the Ooctahedra below the structural transition temperature Ta, shows that the substitution of Mn ions on the Sr sites increases Ta, whereas the Ti-site substitution suppresses Ta with respect to the undoped SrTiO<sub>3</sub>. The coordination of Mn in doped SrTiO<sub>3</sub> ceramics having nominal compositions  $SrTi_{0.98}Mn_{0.02}O_3$  and  $Sr_{0.98}Mn_{0.02}TiO_3$  was analyzed using x-ray absorption fine structure XAFS measurements. As expected,  $Mn^{4+}$  substitution for Ti<sup>4+</sup> leads to Mn occupancy of the octahedral B - sites of ABO<sub>3</sub> perovskite lattice with a Mn–O bond distance of 1.902 Å compared to 1.953 Å for Ti–O and no significant local distortions around the Mn atoms. In contrast, for the composition  $Sr_{0.98}Mn_{0.02}TiO_3$ , Mn segregates to both the A -sites as Mn<sup>2+</sup> and the B – sites predominantly as Mn<sup>4+</sup>. Extended XAFS confirms strong 0.77 Å" displacements of Mn<sup>2+</sup> cations off the ideal A - site positions along <001> directions with a significant distortion of several coordination shells around the dopant atoms. The present XAFS study, conduceted within a collaboration with NIST (USA) resolved the ambiguity regarding the Mn coordination in SrTiO<sub>3</sub>: Our results confirmed that Mn substitution for Sr promotes Mn occupancy of the A -sites in the host SrTiO<sub>3</sub> lattice.

figure:

SEM photographs of scaffolds with varying bioactive glass contents (0, 10, 30 and 50 wt.%) and different quenching times (30, 60, 120 and 180 min) in Acta Biomaterialia 6 (2010) 3611-3620



Voltage dependence of dielectric constant of ferroelectrics and low dielectric loss of incipient ferroelectrics make them attractive for tuning elements in microwave circuits. In this work, the field dependence of the low-temperature dielectric permittivity and polarization of Mg-doped SrTiO<sub>3</sub> films was studied. Incorporation of Mg on both Sr and Ti sites decreases the permittivity and relative tunability of sol-gel derived SrTiO<sub>3</sub> films, whereas polarization is reduced by Ti site substitution only. The losses of the studied films are 0.012, decreasing at low temperatures down to 0.001 when Ti is substituted by 5% of Mg.

In ceramics of KTaO<sub>3</sub> doped with 3 mole-% of Mn it was observed that the dielectric response is dominated by the polydispersive behavior of  $Mn^{2+}$  centered polar regions, whereas the magnetic and magnetoelectric behaviors reflect an intimate coupling between A-site substituted  $Mn^{2+}$  ions and minute amounts of  $Mn_3O_4$  precipitates mediated by the polar host material. This becomes apparent by the common onset at Tc  $-_42$  K of the ordering of ferrimagnetic Mn<sub>3</sub>O<sub>4</sub> and of a spin cluster glass, which is characterized by memory and rejuvenation effects. The composite magnetic system exposed to external magnetic and electric dc fields shows large 3rd order magnetoelectric susceptibility with a sharp anomaly at Tc and 1/T2 dependence as T -> 0.

Nanoscale properties of ferroelectrics and related materials: Mapping polarization disorder in PLZT ceramics: Relaxors constitute a large class of ferroelectrics where disorder is introduced by doping with ions of different size and valence, in order to maximize their useful properties in a broad temperature range. Polarization disorder in relaxors is typically studied by dielectric and scattering techniques that do not allow direct mapping of relaxor parameters, such as correlation length or width of the relaxation time spectrum. In this paper, we introduce a novel method based on measurements of local vibrations by Piezoresponse Force Microscopy (PFM) that detects nanoscale polarization on the relaxor surface. Random polarization patterns are then analyzed via local Fast

Fourier Transform (FFT) and the FFT PFM parameters, such as amplitude, correlation radius and width of the spectrum of spatial correlations, are mapped along with the conventional topography. The results are tested with transparent (Pb,La)(Zr,Ti)O<sub>3</sub> ceramics where local disorder is due to doping with La<sup>3+</sup>.

Real space mapping of polarization dynamics in PMN-PT crystals: Polarization switching in ergodic relaxor and ferroelectric phases in the  $PbMg_{1/3}Nb_{2/3}O_3$ - $PbTiO_3$  (PMN-10%PT) system is studied using piezoresponse force microscopy, single point electromechanical relaxation measurements, and voltage spectroscopy mapping. The dependence of relaxation behavior on voltage pulse amplitude and time is found to follow a universal logarithmic behaviour with a nearly constant slope. This behavior is indicative of the progressive population of slow relaxation states, as opposed to a linear relaxation in the presence of a broad relaxation time distribution.

The role of relaxation behavior, ferroelectric nonlinearity, and the spatial inhomogeneity of the tip field on hysteresis loop behavior is analyzed in detail. The hysteresis loops for ergodic PMN-10%PT are shown to be kinetically limited, while in PMN with larger PT content, true ferroelectric hysteresis loops with low nucleation biases are observed.

Piezoresponse Force Microscopy of ZnO films: Zinc oxide (ZnO) thin films were grown on uncoated and zinc-coated Corning glass substrates by pulsed-laser deposition (PLD). X-ray diffraction measurements revealed that the as-deposited films are polycrystalline having preferential orientation along the [0002] and [10-111] directions. Transmittance spectroscopy verified that the as deposited films are transparent with a direct bandgap of about 3.28 eV at room temperature. Piezoresponse imaging and local hysteresis loop acquisition were performed to characterize the piezoelectric and possible ferroelectric properties of the films. The out-of-plane (effective longitudinal piezocoefficient) and in-plane (effective shear piezocoefficient) coefficients were estimated from the local piezoresponse based on the comparison with LiNbO<sub>3</sub> single crystals. Measurements of all three components of piezoresponse (one longitudinal and two shear signals) allowed constructing piezoelectric maps for polycrystalline ZnO and to relate the variation of piezoelectric properties to the crystallographic and grain structure of the films. A shifted piezoresponse hysteresis loop under high voltages hints at the possible pseudoferroelectricity.

Ferroelectric phase transition in PMN-PT ceramics: The spontaneous transition between the ferroelectric and relaxor states was investigated in 0.86PbMg<sub>1/3</sub>Nb<sub>2/3</sub>O<sub>3</sub>–0.14PbTiO<sub>3</sub> ceramics using piezoresponse force microscopy Macroscopically, the transition from the ferroelectric to relaxor phases manifests itself by an anomaly in the temperature dependences of the dielectric permittivity and by a sharp decline of the remanent polarization. Alternatively, PFM reveals a decay of the ferroelectric micron-size domains at the macroscopic Curie temperature, Tc. Simultaneously, smaller domains of submicron sizes are observed at temperatures appreciably above Tc, being concentrated near grain boundaries. It is argued that the particular mechanical and electrical conditions at the grain boundaries promote nucleation of the ferroelectric phase. Characterization of PZT films on polymer substrates: This work analyzes the processing of Pb(Zr,Ti)O<sub>3</sub> (PZT) thin films directly on coppercoated polymer films. PZT thin film deposition was performed onto the metalized Kapton® films using a single RF plasma jet. In order to reduce the interaction of PZT and Cu during the initial growth stage, an ultrathin amorphous TiO<sub>2-x</sub> seeding layer was sputter-deposited prior to PZT deposition. The film texture was a mixture of (111)-oriented perovskite nanocrystals, rutile and pyrochlore. Topography and piezoelectric in-plane and out-of-plane response of the films were self-polarized with polarization pointing at the surface of the sample. Polarization was switchable and a piezoelectric hysteresis was obtained.

**Nanoscale and Nanostructured Materials:** Within the on going studies on bottom up approaches to prepare barium titanate, the effect of poly(acrylic acid) (PAA), poly(vinylpyrrolidone) (PVP), sodium dodecylsulfate (SDS), hydroxypropylmethylcellulose (HPMC), and D-fructose additives on the growth of BaTiO<sub>3</sub> particles by aqueous synthesis is studied. Through different mechanisms, all the tested additives influenced the growth of BaTiO<sub>3</sub>. For high concentrations, PAA adsorbed on specific crystallographic faces changing the growth kinetics and inducing the oriented attachment of the particles acting as a crystal growth modifier. PVP, SDS, and HPMC behave as growth inhibitors rather than crystal habit modifiers, and barium titanate crystals as small as 26 nm were obtained. D-Fructose appeared to increase the activation energy for barium titanate nucleation when the additive concentration increases. The present study gives new insights into how additives control barium titanate particle growth in aqueous media.

The influence of the neutralization process after hydrothermal synthesis on the structure and morphology of titanate nanotubes was investigated by X-ray diffraction, high-resolution transmission electron microscopy and Raman spectroscopy. Well formed nanotubes were obtained during the hydrothermal treatment of anatase in highly alkaline conditions. Synthesis at 150 °C led to the formation of layered titanate structure with the general formula  $Na_{2-x}H_xTi_2O_55$ -1.8H<sub>2</sub>O, where x depends on pH. The tubular morphology is not dependent on the Na+/H+ ion exchange reaction.









#### **3** research group magnetostructural and multiferroic modulation of correlated electron materials group coordinator: Vitor Amaral (vamaral@ua.pt)

#### scientific highlights

i) Observation of bias-induced phase transition to ferroelectric state in charge-ordered and magnetic manganites;

ii) Development of a nanometric luminescent ferrofluid;

iii) Development of a method to correctly calculate the magnetic entropy change in first-order phase transitions;

iv) Development of a method to produce ultrathin metallic oxygen barrier diffusion applied to Si-based components and microelectronics devices

#### research team

on 31st december '10

#### professors & lecturers Armando António C.S. Lourenço

Armando Antonio C.S. Lourenço Joaquim Manuel Vieira Vitor Brás Sequeira Amaral

**full time researchers** Andrei Kholkin Nuno João Silva

#### post-doctoral associates Alejandro Heredia Barbero João Cunha de Sequeira Amaral Neeraj Panwar Radheshyam Rai Soma Das Vladimir Bystrov Xiaodong Zhang

**PhD students** 

Carlos António Delgado Sousa Brites João Nuno Santos Gonçalves Li Jian Marco António Batista Peres **MSc students** Abel Eduardo Silva Fenta Fábio Gabriel Nazário Figueiras

#### other students

Eric David Bosne Inês Monteiro de Sena S Carvalho Narciso Alexandre Gouveia Soares Rui Pedro Gonçalves Lopes Samuel Coutinho dos Santos

**collaborators** Mário de Sousa Reis Júnior Mohamed Karmaoui

#### activity report 2010

#### Strongly Correlated Electron Systems: Theory and Experiment

a) Multifunctional/multiscale phenomena in mixed valence colossal magnetoresistive and multiferroic oxides. The role of magneto-structural-electronic coupling is studied in a multiscale approach, from atomic ordering and nanoscopic phase separation phenomena to macroscopic phase transition effects. Techniques range from nuclear probe hyperfine measurements, scanning piezoresponse and magnetic force microscopies, Raman spectroscopy, neutron and X-ray diffraction to macroscopic electric and magnetic (SQUID and VSM) measurements. Studies on multiferroic hexagonal manganites:  $REMnO_3$  (RE=Er, Lu, Eu). Competition of orders and doping effects: Non-stoichiometric nano powder samples LuMn<sub>1-z</sub>O<sub>3-δ</sub> showed that intrinsic multiferroics based on the RMnO<sub>3</sub> ferroelectric hexagonal manganites, which exhibit ferroelectric (FE) and antiferromagnetic (AFM) order in the same phase can be modified by selective nonstoichiometry doping (cationic vacancies), generating a limited amount of Mn<sup>4+</sup> ions within the structure that breaks the AFM spin frustration geometry, promoting a partial ferromagnetic state, while keeping ferroelectic proprieties, which are more interesting for multiferroic development. Detailed studies of the Raman spectra were started: on the single phase LuMnO<sub>3</sub> sample a shift in the temperature dependence of the A1 mode frequency correlated with phonon anomalies across the magnetic phase transition near 90 K was found.

The study of the role of microstructure on magnetic properties of LFZ-grown manganite oriented ceramics and single crystals (La-CaMnO<sub>3</sub>) was continued.

Studies on multiferroic ferrites:

The studies of doped BiFeO<sub>3</sub> expanding previous work on Gd doping to Sm and Dy doping led to the observation of polar-nonpolar phase transition on doping of BiFeO<sub>3</sub> and phase coexistence advantageous for magnetoelectric coupling. The investigation of polycrystalline Bi<sub>1-x</sub>R<sub>x</sub>FeO<sub>3</sub> (R=Sm, Dy, 0.1<x<0.2) samples was performed by X-ray diffraction, piezoresponse force microscopy and SQUID-magnetometry techniques. Rare-earth substitutions cause the transformation of R3c structure typical of BiFeO<sub>3</sub> to yield polar orthorhombic phases with 2ax2 2ax 2a and 2ax2ax 2a superlattices (a is the parameter of the cubic perovskite subcell). **Sm-doping:** increasing samarium content induces a polar-to-nonpolar phase transition near x = 0.2. Within the polar region,

increasing samarium content induces a polar-to-nonpolar phase transition near x = 0.2. Within the polar region, a rhombohedral and two orthorhombic modifications of  $Bi_{1-x}Sm_xFeO_3$  were found. The appearance of spontaneous magnetization was significantly enhanced upon the composition-driven transition from a rhombohedral to an orthorhombic phase. **Dy-doping**: a similar composition-driven rhombohedral-to-orthorhombic R3c->Pnma phase transition at x=0.15 was observed correlated to changes in ferroelectric and magnetic properties. Both structural phases were found to coexist in a broad concentration range. Piezoresponse force microscopy found suppression of the parent ferroelectric phase upon dysprosium substitution. Magnetometric study confirmed that the A-site doping induces appearance of a weak ferromagnetic behavior.

#### Multiferroic composites:

Besides single phase multiferroics which unfortunately are inherently very difficult to produce and rarely present optimized properties near room temperature. To circumvent those problems and allow the tuning of properties, we study magnetoelectric coupling in two-phase solid-solution or composite ceramics based on ferrites (BiFeO<sub>3</sub> or hexagonal BaFe<sub>12</sub>O<sub>19</sub>) or manganites (La-BaMnO<sub>3</sub> or La-SrMnO<sub>3</sub>) with ferroelectrics such as BaTiO<sub>3</sub> or LuMnO<sub>3</sub>.

**BiFeO**<sub>3</sub>-based solid solutions: Solid solutions of Bi<sub>1-x-y</sub>Gd<sub>x</sub>Ba<sub>y</sub>Fe<sub>1-y</sub>Ti<sub>y</sub>O<sub>3</sub> were prepared via solid-state reaction method with the aim to obtain magnetoelectric coupling (i.e., linear relation between magnetization and electric field) at room temperature. Optimum calcination and sintering strategies for obtaining pure perovskite phase, high density ceramics and homogeneous microstructures were determined. Studied samples of composition x = 0.1 and y = 0.1, 0.2, and 0.3 are tetragonal at room temperature. The maximum ferroelectric transition temperature (T<sub>c</sub>) of this system was 150–170°C with the dielectric constant peak of 2300 at 100 kHz for y = 0.1. Above T<sub>c</sub> the dielectric constant is decreasing up to a certain temperature and then increasing with temperature similar to that observed in other perovskites due to chemical inhomogeneities in both A and B sites of the ABO<sub>3</sub> cell. The variation of ferroelectric and magnetic properties was followed by piezoresponse force microscopy and vibrating sample magnetometer, respectively. Well-saturated piezoelectric loops were observed for all compositions indicating room temperature ferroelectricity.

 $BaFe_{12}O_{19}$ — $BaTiO_3$  composite ferroelectric/ferromagnetic ceramics: samples were prepared by conventional solid-state sintering technique. The magnetic properties are consistent with the ratio of the magnetic phase present but ferroelectric properties are degraded due to a sufficiently high degree of conductivity in the ceramics. Magnetoelectric coupling was observed at a local level by means of the scanning probe microscopy (SPM). Piezoresponse and magnetic force modes of SPM were both utilized to assess strain-mediated magnetoelectric coupling between neighbouring grains. The observed variation in the magnetic signal after the electrical poling with SPM was attested to the changes in the magnetic interactions and magnetic anisotropy leading to broadening of the magnetic domain wall.

#### Nano-Powder ferroelectric/ferromagnetic Composites:

The composite bulk samples feat the intended quality objectives in terms of phase composition and purity, with high degree of homogeneity. SEM images in the prepared systems confirm compact grain packaging and size distribution around the 50 nm scale.





40 μm



*Manganite composites*  $LuMnO_3 + La_{0.7}Sr_{0.3}MnO_3$ : This nano-powder system combining ferromagnetic rhombohedric  $La_{0.07}Sr_{0.3}MnO_3$  and ferroelectric hexagonal LuMnO<sub>3</sub> (at room temperature) takes advantage of the immiscibility of the two structural/compositional phases; the conditions for forming intimate mechanical contact between phases are implemented by spontaneous segregation mechanisms from precursors in solution, afterward controlling the nucleation and particles size by thermal treatments. Magnetoelectric effect (ME) measurements performed in sample Lu78-LSM, confirm the effective (mechanical and eventually chemical) connection between the two different phases giving rise to a magnetoelectric effect at room temperature reaching ~150 mV/m.Oe under 1 Tesla bias field and 105 Hz 10 Oe a.c. field. The observation of new active Raman modes not present in the pure phases at the composites Lu78-LSM and Lu89-LSM suggests the presence of new atomic arrangements structures having a strong non-centro-symmetric geometry. These are interpreted as resulting from the formation of a perfusion of O4Mn—O—MnO5 (Octahedra connecting bipyramid) molecular arrangements along the grain boundaries. Besides configuring new polaronic states and extending accessible angles for the Mn<sup>3+</sup>—O<sup>2-</sup>—Mn<sup>4+</sup> transfer integral, such metastable structures also suggest a high multiferroic functional potential.

Manganite/Titanate composites BaTiO<sub>3</sub> +  $La_{0.7}Ba_{0.3}MnO_3$ : Bulk composites based in perovskites materials: ferroelectric BaTiO<sub>3</sub> and ferromagnetic  $La_{0.7}Ba_{0.3}MnO_3$  may take advantage of some expected degree of miscibility to ensure better interface connection of the functional grains. In order to prevent excessive diffusion of atomic species between the two phases and avoid chemical reaction of spurious phases, gentle mechanical mixture and hot pressing of the independent powders was used. The observed FM character of the BaTiO<sub>3</sub> phase grain boundaries enables to establish an additional and direct coupling route with the magnetic moment orientation of neighbouring  $La_{0.7}Ba_{0.3}MnO_3$  phase grains, besides the strictive interaction between the two phases. This explains the observation of anomalies on the electrical resistivity of the LBM phase at the structural/ferroelectric transition temperatures of BTO. Direct ME measurements of the sample BTO78-LBM sample show that the structural transitions of the magnetic phase at ~350 K results in a inversion of ME coefficient behavior

b) Ferroelectricity driven by magnetic order or charge/orbital order and bias-induced phase transitions. One of the proposed driving mechanisms for ferroelectricity in multiferroics is the occurrence of charge and orbital ordering that break inversion symmetry. Half-doped charge ordering manganite systems, like  $(Pr_{1-x}Ca_{xx})MnO_3$  or  $La_{1-x}Ca_xMnO_3$  near x<sup>-0.5</sup> Ca content, were set forth in the literature as prototype systems for induced electronic ferroelectricity mechanism, associated with the appearance of site- and bond-centered orbital ordering (bond dimerization) or spin dimerization, respectively. However, the finite conductivity of these systems hinders an observation of possible macroscopic polarization study as direct proof of ferroelectricity. Considering that the polarization can exist in nanoscale volumes, we used local-probe techniques like the Piezoresponse Force Microscopy (PFM) for studying local electrical and electromechanical properties of manganites. This technique allows measurements of local hysteresis loops at the resolution of 10 nm level by detection of local piezoelectric deformation induced by an external electric field. Our previous results in  $La_{0.89}Sr_{0.11}MnO_3$  were extended to  $(Pr_{1-x}Ca_x)MnO_3$  and  $La_{0.5}Ca_{0.5}MnO_3$  systems (single crystals or polycrystalline) where a clear bias-induced piezocontrast and local hysteresis loops could be investigated providing evidence of the existence of a locally induced polar state with ferroelectric response even above the charge order transition. The microscopic mechanisms associated with these bias-induced modifications, which may be associated to the presence of nanoscopic CO regions, are interpreted in terms of a charge doping process, according to the bias polarity dependence, and of the role of charge/ionic or oxygen vacancies motion mechanisms. The different time-scales associated with piezoelectric (electronic) deformations and with ionic electrodiffusion in the materials are key points discussed to elucidate the possible electrochemical strain effects

The possibility of producing single domain electronic phase transitions opens a new pathway to achieve spatially localized multiferroic studies (electronic reconstruction and phase control at interfaces) and widens the possibilities of high density applications, by the ability to create artificial multiferroic materials for memory cells.

#### c) Studies on multiferroic thin films and heterostructures.

Shape-memory alloys/piezoelectric oxides heterostructures:

The study of ferromagnetic Ni-Mn-Ga thin films deposited at low temperature (400°C) by rf magnetron sputtering using co-deposition of two targets Ni50Mn50 and Ni50Ga50 was continued, by finding appropriate thermodynamic conditions to deposit Ni-Mn-Ga magnetic phase on sapphire (0001), MgO (001), SrTiO<sub>3</sub> (100) and Si (100) substrates. Curie temperature ~ 330K, with well-defined hysteresis loops, low coercivity (~ 100 Oe) and a saturation magnetization of ~ 200 emu/cc was obtained without the need

loops, low coercivity (~ 100 Oe) and a saturation magnetization of ~ 200 emu/cc was obtained without the need for post-deposition annealing or further thermal treatment. With the deposition on active ferroelectric PMN-PT (100) substrates we achieved the preparation of multiferroic heterostructures, with effective magnetoelectric coupling between the Ni-Mn-Ga thin film as ferromagnetic material and PMN-PT as piezoelectric coupling between Ni-Mn-Ga thin film as ferromagnetic film was confirmed by the presence of the piezoelectric substrate (ferroelectric) after the deposition of the ferromagnetic film was confirmed by the presence of the hysteresis loop. The room temperature ME measurementson the Ni-Mn-Ga/PMN-PT multiferroic heterostructures gave measured maximum induced magnetoelectric voltage ~3.2 mV/cmOe for films deposited at substrate temperature of 370-400°C. These low values as compared to other systems are thought to be due to partially crystalline nature of the Ni-Mn-Ga film. However, these values will enhance near the magnetic transition temperatures which, for these films, is above room temperature, and will be studied later.

#### Ferromagnetic Manganite Ferroelectric Titanate thin film heterostructures:

In parallel to the study of bulk composites, thin film heterostructures consisting of one BaTiO<sub>3</sub> titanate layer (14 or 34 nm) within two La<sub>0.7</sub>Ba<sub>0.3</sub>MnO<sub>3</sub> manganite layers (3-30 nm bottom and 30-100 nm top) were deposited by magnetron sputtering on sapphire (0001), MgO (001), SrTiO<sub>3</sub> (100) and Si (100) substrates. For comparison, single phase films with similar thicknesses (20-100 nm) were also deposited. The structural analysis confirms that both materials grow well oriented (or even epitaxially). Magnetic measurements confirm a ferromagnetic behaviour on the thin films and heterostructures. The saturation of magnetization is between 383 to 842 emu/cm<sup>3</sup> at 50 K, and 8 to 152 emu/cm<sup>3</sup> at 300 K. Measurements of resistance versus temperature on the heterostructures, which measure the top manganite layer, present hysteresis thermal loops around 180 K when the middle BTO layer has a structural transition from rhombohedral to orthorhombic, confirming the good structural coupling through the interface. Also AFM and PFM measurements confirm the piezoelectric and ferroelectric behaviour of BTO. Further studies are envisaged to have a more detailed knowledge of the influence of deposition conditions, layer thickness and interface quality on the properties.

#### d) Theoretical and experimental study of magnetic systems and phase transitions with multiple order parameters. Magnetic studies and modelling of physical properties in the vicinity of phase transitions:

Studies are undertaken, using Landau theory and mean field approaches to provide a systematic understanding of coupled magnetic, structural and electric order parameters, including systems with chemical or structural disorder. A novel scaling approach was improved, reaching a quantitative estimate of relevant parameters; it was applied to the study of the critical exponents and magnetic scaling function. Measurements on ferromagnets (pure Ni and Gd) were used to quantitatively compare with the calculations from renormalization group results. A program to fit or simulate the magnetic behaviour of inhomogeneous magnetic systems, within the mean-field approximation, was developed, and applied to ferromagnetic manganites with critical temperature distribution, due to chemical dispersion of dopants.

Experimental studies under high magnetic field (24 T) were done in the Grenoble High Magnetic Field Laboratory on magnetic alloys with large magnetostructural coupling (MnAs, Gd-Si-Ge) in the vicinity of the high temperature (>250K) structural and magnetic transitions; an analysis of the nature of the critical points of the phase diagram is developed.

#### Thermodynamic theory of magnetoelectric effect in nanostructures:

A nonlinear thermodynamic theory is developed for the strain-mediated direct ME effect displayed by ferroelectric-ferromagnetic nanostructures, resulting from transmission of magnetic-field-induced deformations of a thick ferromagnetic substrate to a thin ferroelectric overlayer, where the polarization changes due to lattice strains. The strain-dependent polarization and permittivity of an epitaxial nanolayer (few tens of nm thick) were calculated using the thermodynamic theory of single-domain ferroelectric films. The substrate magnetostrictive deformations are described phenomenologically, taking into account their nonlinear variation with magnetic field. The calculations show that ME polarization and voltage coefficients strongly depend on the initial strain state of the film. For BaTiO<sub>3</sub> and PbTiO<sub>3</sub> films deposited on  $Co_{0.8}Zn_{0.2}Fe_2O_4$ , the out-of-plane polarization and related ME coefficients are calculated numerically as a function of magnetic field parallel to the interface. For films stabilized in the monoclinic phase, this transverse ME response depends on the orientation of magnetic field relative to their in-plane crystallographic axes. The longitudinal ME coefficient is also evaluated and, for a substrate geometry minimizing the demagnetizing field, predicted to be comparable to the transverse one. For BaTiO<sub>3</sub> and PbTiO<sub>3</sub> films deposited on Terfenol-D, the calculations yield high ME polarization coefficients 10<sup>-7</sup> s/m and giant ME voltage coefficients 50 V/cmOe.

Competing ground states in low-doped  $La_{0.95}Sr_{0.05}MnO_{3+\delta}$  manganites: Doping of antiferromagnetic LaMnO<sub>3</sub> with divalent ions leads to the appearance of ferromagnetism associated with Mn mixed valence and double exchange interactions. For low doping competing magnetic ground state result in inhomogeneous behavior. We study the structural and magnetic properties of crystalline nonstoichiometric granular La<sub>0.95</sub>Sr<sub>0.05</sub>MnO<sub>3+8</sub> system prepared by a chemical route, through SEM, HRTEM, dc magnetization and magnetic relaxation studies. The extrinsically introduced nonstoichiometry and the distribution of Mn<sup>3+</sup>/Mn<sup>4+</sup> in the system successfully gives an evolution of disordered ferromagnetic ordering in a wide temperature ranges, with two main peaks in the distribution.

#### Magnetocaloric Effect and Magnetic cooling: Experimental and Theoretical work

a) The investigation of materials with magneto-structural coupling for applications in magnetic refrigeration, particularly near room temperature was continued on further (Mn<sub>1-x</sub>M<sub>x</sub>)As (M=Cu,Cr,Fe x<0.02) samples to assess the role of phase mixing in magnetic first-order phase transition kinetics: a combined study of Calorimetry, XRD (micrometer coherence), Magnetic Force Microscopy (100 nm range), hyperfine and magnetic measurements are undertaken. b) Magnetic and Magnetocaloric studies are undertaken in Eu and Er doped La-Ca/Sr manganite fibers prepared by laser floating zone. The chemical and structural tuning of the effects is studied and compared with other preparation routes.

c) A new set-up to measure the magnetocaloric effect using the direct method was developed. The system uses a thermocouple and an infrared sensor to measure the adiabatic temperature change when a magnetic field (in the range 0-1Tesla) is varied. The use of the infrared sensor allows the measurement without physical contact to the sample. The measurements have a resolution better than 0,1 K and can be made as fast as 10 measurements per second. A sample holder with a Peltier heater/cooler allows measurements to be performed in the range 270-340K, necessary for the study of materials for application at room temperature. The system was used to study the effect in gadolinium and ferromagnetic manganities.

d) The characterization of magnetic properties of thermoelectric Bi-Co oxide materials prepared by laser-floating zone was initiated, aiming at a deeper understanding of coexisting phases and material homogeneity.

#### Hyperfine Interactions and First-principles Calculation (DFT) of Properties of Materials.

a) Hyperfine studies using implanted radioactive isotopes at ISOLDE-CERN.

Two international projects in CERN leaded by our group were started in 2009 and continued in 2010 (IS487: Study of Local Correlations of Magnetic and Multiferroic Compounds and I81: Radioactive probe studies of coordination mechanisms of heavy metal ions from natural waters to functionalized magnetic nanoparticles). A new project was started I87 in 2010: (New insights in Metal-Oxide junctions for nano-electronic applications). Hyperfine techniques (Perturbed angular correlation spectroscopy), addressing charge/orbital order and electronic phase segregated systems; measurements of electric field gradient and hyperfine magnetic field in oxides and magnetic semiconductors for structural, electronic polarization and magnetic field studies. Samples include multiferroic and ferromagnetic manganites (RMnO<sub>3</sub>), chromites (MCrO<sub>2</sub>) and nickelites (RNiO<sub>3</sub>), as well as MnAs, in broad temperature range (10-1000K). Studies on polaron dynamics and percolative effects in lightly doped ferromagnetic insulator manganites. Effect of charge/orbital ordering and local electrical polarization on hyperfine measurements.

#### b) Complementary calculation of electronic structure using ab-initio DFT methods:

Comprehensive study of role of defects, and local lattice distortions on the hyperfine parameters, electronic charge distribution and states. A new line of studies was started with the use of the program VASP that allows the simultaneous calculation of hyperfine properties (electric field gradient EFG) and electric polarization (with the quantum Berry phase approach). This ab-initio study allowed to establish for the first time a firm theoretical basis of the relation between the EFG and the polarization that was reported since early experiments on ferroelectric materials using hyperfine interactions techniques (Mössbauer, NMR, PAC, NQR).

The analysis of the two quantities from density functional theory has already been applied to a series of multiferroic and ferroelectric compounds.

#### c) Biophysics and nanoparticle systems:

Hyperfine studies on nanoparticle systems for heavy ion removal from waste water applications were continued using other nanoparticles sizes and experimental conditions. The study of the lattice location of Hg<sup>2+</sup> ions in the several steps of the cations uptake by magnetite nanoparticles, modified at the surface with amorphous SiO<sub>2</sub> and functionalized by grafting dithiocarbamate groups to the particles surface was improved.

## Thin Film and Structures Preparation Studies with RF sputtering deposition.

Deposition optimization studies of several types of materials on different substrates and different thermodynamic conditions were pursued. The studies include thorough investigation of structural XRD, (including grazing incidence and HRXRD), SEM, TEM and scanning probe microscopies. The substrate-induced lattice distortion effects and anisotropy towards the growth of (multi) functional thin films and heterostructures were analysed.

-La-Ba manganites with highest Tc, above room temperature -BaTiO<sub>3</sub> ferroelectic perovskites and multilayer heterostructures, with multiferroic behaviour.



figure: Scanning electron micrograph of the studied La<sub>0.7</sub>Ba<sub>0.15</sub>Sr<sub>0.15</sub>MnO<sub>3</sub> compound. *in Materials Chemistry and Physics 120* (2010) 468-471

(high k-oxide materials, as HfO<sub>2</sub>). These studies are complemented by electric and hyperfine (Hf PAC) studies of the Hf oxide layers

Advanced Multifunctional Materials

-Metallic and oxide buffer layers for oxide/oxide multilayered structures and silicon/oxide for electronic applications

Magnetic nanoparticles, molecular systems and composites relevant for bio-medical applications (e.g. Fe oxidesbased systems). The main topics are the study of key parameters that control the magnetic properties (superparamagnetism, anisotropy) and its relation with structure/disorder.

We have successfully synthesized and studied iron-based magnetic nanoparticles and luminescent molecular complexes inside organic-inorganic hybrid matrices, which are dispersible in water and act as nanometric luminescent thermometers with superior performance.

We investigated the structural and magnetic properties of nanoparticles, nanoparticles/polymers and nanoparticles/organic-inorganic hybrids under extreme conditions such as high pressure and high magnetic fields, in order to access basic problems as the origin of the uncompensated moment in antiferromagnetic nanoparticles. The antiferromagnetic component and crystal field effects on magnetic properties and magneto-structural coupling in iron oxide nanoparticles (maghemite, magnetite and ferritin) were further studied, improving the understanding on coercivity and loop shifts observed.

 $CoFe_2O_4$  nanoparticles were prepared by Co-precipitation method. The particles are then modified with a hydrophilic, biocompatible, and biodegradable coating of N-phosphonomethyl iminodiacetic acid (PMIDA). Then folic acid functional molecule is coupled to prepare the system for targeting and intracellular drug-delivering. Magnetic measurements in the initial state show superparamagnetic behaviour at room temperature, with a decreasing trend of saturation magnetization with increasing grain size, limiting the precipitation time to a maximum of 1 hour in 70C. Magnetorelaxometry properties of these nanoparticles (for T2 contrast enhancement in vitro) were started in collaboration Biochemistry Department at University of Coimbra.



#### scientific highlights

i) Development of (Ce,Pr)O<sub>2</sub>-based mixed conductors with the highest known levels of mixed conductivity in fluorite materials;

ii) Demonstration of proton and mixed conductivity in a novel material type (Ba<sub>4</sub>Nb<sub>2</sub>O<sub>9</sub>) and their correlations with structural features and stability limits;

iii) Interpretation for limitations of mixed transport properties in  $Sr_3La(Fe,AI)_3O_{10-\delta}$  based on consistent spectroscopic studies and computer modelling.

## research team

on 31st december '10

#### professors & lecturers

Fernando Manuel Bico Marques João Carlos de Castro Abrantes Jorge Ribeiro Frade José Maria da Fonte Ferreira

**full time researchers** Filipe Miguel H. Lebre R. Figueiredo Vladislav Kharton Yevgeniy Naumovich **post-doctoral associates** Andrei Kovalevsky

#### **PhD students**

Ana Brandão Eddy Michael Pedro Domingues Maria Adelaide Cotovio Salvador Nuno Miguel Dias Vitorino Vladislav Kolotygin

MSc students Ana Inês Batista Lourenço Rondão João Ricardo Santos Pereira

#### other students José Filipe Pinto Monteiro Teresa Isabel Galinho de Carvalho Túlio Bruno Barbosa Sandoval

collaborators

Aliaksandr Shaula Dmitry Khalyavin Ekaterina Tsipis José António Perez de la Torre Ludwig Gauckler Mikhail Patrakeev

#### activity report 2010

#### Materials for High Temperature Electrochemical Applications

Activities included work on solid electrolytes and corresponding electrodes for solid oxide fuel cells and other solid state electrochemical devices or systems. This included a variety of solid electrotytes based on zirconia, ceria, lanthanum silicate, barium zirconate, and less common materials such as LaNbO<sub>4</sub>-based scheelite, and a-Ba<sub>4</sub>M<sub>2</sub>O<sub>9</sub>, M=Nb,Ta,.. with Sr<sub>4</sub>Ru<sub>2</sub>O<sub>9</sub>-type structure and nanostrured ceria-carbonate composites. Two-step sintering was used as an alternative method to obtain ceria-based electrolytes Ce<sub>1-x</sub>M<sub>x</sub>O<sub>2-x/2</sub>, M=Y, Gd; this yielded gas tight ceramics with sub-micrometer grain sizes, especially with further doping with Ga<sub>2</sub>O<sub>3</sub>. One also analysed the impact on bulk and grain boundary properties. A different study addressed the onset of mixed transport properties of CSO and used this information to predict effects on ceria-based SOFC under fuel cell operating conditions; this included predictions for the dependence of open cell voltage on the degree of fuel conversion at the anode.

One developed pseudo-binary phase diagrams to analyze the thermodynamic stability of perovskite materials in contact with CO<sub>2</sub>, water vapour or other gases, including the impact of reducing atmospheres on promising materials for solid state electrochemical applications. These diagrams were suitable guidelines to analyse the stability of Ba(Zr,Pr,Y)O<sub>3- $\delta$ </sub> in contact with different atmospheres, as expected for fuel conversion. YSZ based films were sputtered onto La<sub>10-x</sub>(Si,Al)O<sub>27-y</sub> solid electrolytes, as prospective buffer layer to overcome undue interaction between those silicate based electrolytes for SOFCs and prospective electrode materials. These buffer layers were nanocrystalline and played a key role on electrochemical fuel conversion.

It was demonstrated that addition of Sr contributed to retain the scheelite phase in La<sub>1-x</sub>Sr<sub>x</sub>Nb<sub>1-y</sub>V<sub>y</sub>O<sub>4- $\delta$ </sub>, enhances its low-temperature proton conductivity, and avoids thermomechanical risks related to structural changes and corresponding strain/stress effects. On also analyzed effects of changes in the atmosphere on transport properties and onset of secondary phases, with emphasis on (La,Sr)VO<sub>3</sub>. Phase transition in  $Ba_4M_2O_9$  (with M=Nb,Ta) were studied in detail, including temperature dependent

structural refinement, for their prospective impact on hydration and impact on protonic and oxygen ion conductivities.

Composite electrolytes based on samaria-doped ceria and Na/Li carbonates were prepared and characterized to confirm homogeneous distribution of the nanostructured CSO phase and alkali carbonates. These composites show impressive grain in electrical conductivity, clearly deviating from classical electrolytes.

Alternative structure types have been analysed for alternative mixed conducting oxygen or air electrodes. Structural changes in materials based on YBaCo<sub>4</sub>O<sub>7</sub> were revised with emphasis on effects of composition on bond-valence, and their impact on phase transformations and on oxygen storage ability. Important structural effects on oxygen nonstoichiometry, thermochenmical expansion, and high-temperature electrical properties were also observed for layered NdBaCo<sub>2</sub>O<sub>5+ $\delta$ </sub> and SmBaCo<sub>2</sub>O<sub>5+ $\delta$ </sub>. It was confirmed that layered structures usually show much lower chemical expansion than corresponding materials with perovskite-type structure.

 $Sr_3Fe_{2-x}Mo_xO_{5\pm\delta}$  were prepared and characterized as prospective anode materials for lanthanum gallate-based electrolytes. This study was based on evaluation of oxygen nonstoichiometry, chemical expansion, mixed conductivity, and their dependence on composition and structure.

Aluminosilicate glass-ceramic were prepared and characterized for applications as sealants for SOFC. The study also include the dependence of electrical conductivity on composition, and thermal expansion, to assess impact on losses and compatibility with other cell components such as YSZ electrolyte and interconnector alloys.

#### Microstructural eEfects

One used strontium titanate thick films to analyze correlations between impedance spectra of bulk ceramics and in-plane configurations; this also emphasizes common misunderstandings concerning analysis of microstructural contributions, and also the risks of non-negligible contributions by the substrate. YSZ+TZP composites were designed to analyze space charge effects at heterogeneous interfaces and

microstructural effects on transport properties of 2-phase materials. This work also showed important synergetic effects on mechanical properties which exceed simple linear dependence on the fractions of constituent phases.

*Mixed Conductors and Catalysts for Oxygen Separation or Partial Oxidation of Hydrocarbons* One continued previous work on perovskite-type  $SrFe_{0.7}AI_{0.3}O_{3-\delta}$  and  $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ , and corresponding 2-phase composites ( $SrFeO_{3-\delta}$ )<sub>0.7</sub>( $SrAI_2O_4$ )<sub>0.3</sub> and ( $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ )<sub>0.7</sub>( $SrAI_2O_4$ )<sub>0.3</sub>. In addition to mixed transport properties and their dependence on composition and structural features, one analysed thermochemical expansion, and their dependence on composition and structural features are divised to the properties and their dependence on composition and structural features. and expected constraints imposed by changes in working conditions or under high gradients of chemical potential. Mixed conducting membranes have been assessed for potential application in oxygen permeable membrane for CO<sub>2</sub> capture in a natural gas-fired power plant, including transient behavior. This analysis integrates information on selected mixed conducting materials and process conditions to assess effects on efficiency, thermochemical constraints, etc..

Atomic scale analysis of oxygen ionic transport in La<sub>2</sub>NiO<sub>4</sub>-based materials was performed by computer simulation, employing static lattice and molecular dynamics (MD); this allowed identification of anion migration pathways, energetic parameters and effects of the transition metal dopants on oxygen ion transport in La<sub>2</sub>Ni(M)O<sub>4</sub>+delta (M = Fe, Co, Cu).

#### Materials for Other Electrochemical Processes

One confirmed the enhanced performance of oxygen electrodes in the presence of hematite suspensions, for a variety of metallic electrodes based on the Ni-Co-B system. Materials in the system  $FeO_{x-1}AI_2O_3$  have been prepared and characterized as potential electrode materials for pyroelectrolysis.

#### Materials for Heat/cold Storage and Conversion

One developed very stable and converging methods to analyze the kinetics of solidification of phase change materials (PCM) was analyzed for combined heat conduction in the PCM and container wall, and convection in the cold fluid. These methods were based on combined analytical transformation of the relevant heat transfer balances, and computing codes with self adjusted mesh scaling.



### scientific highlights

ii) A new generation of hybrid sol-gel coatings doped with ceria nanoparticles or with different organic inhibitors was developed for active corrosion protection of aluminum alloys;

ii) New smart self-healing coatings based on layered double hydroxide (LDH) nanocontainers loaded with organic inhibitors were developed;

iii) Anodic coatings on titanium and aluminium were deposited using high-voltage powerful discharge technique for the first time:

iv) Nanocrystalline diamond (NCD) coatings were demonstrated to provide a suitable surface for cell attachment, spreading and proliferation;

v) Water lubricated NCD/NCD tribosystems confirmed to have very high film delamination loads (85 N) and very low friction coefficient values ( $\mu$ =0.02 to 0.05) combined with a high wear resistance (10-9 mm<sup>3</sup>.N<sup>-1</sup>.m<sup>-1</sup>);

vi) NCD coated bits presented a superior excel behaviour in bone drilling when compared to steel conventional ones;

vii) In situ TEM study of the effect of an encapsulated alloy in the mechanical behaviour of filled turbostratic carbon nanotubes, providing the first experimental evidence for potential nanomechanics control of these nanostructures;

viii) Composites prepared from WC powders sputter-coated with stainless steel were shown to possess higher fracture toughness versus hardness values, when compared with identical composites conventionally prepared.



Picture of painted electrogalvanised steel with two artificial defects after 8 days of exposure to 5 mM NaCl (a); SVET maps of the ionic currents in solution measured in the xz plane, normal to the surface, and in the xy plane, parallel to the surface (b); distribution of Zn<sup>2+</sup> (c). Maps in xy plane were taken at 100 mm above the surface and the scanned area corresponded to the area of figure (a).

in Electrochemistry Communications 12 (2010) 394-397

on 31<sup>st</sup> december '10

**professors & lecturers** Augusto Luís Barros Lopes José Maria da Fonte Ferreira Rui Ramos Ferreira e Silva

**full time researchers** Filipe José Alves de Oliveira Mikhail Zheludkevich Pedro Miguel FJ da Costa

#### post-doctoral associates

Andrei Salak António Alexandre Cunha Bastos Ashutosh Goel Joao André da Costa Tedim Margarida Isabel dos Santos Amaral Miguel Ângelo da Costa Neto Silvar Kallip

#### PhD students

Aleksey Lisenkov Diogo Miguel Rodrigues M. Mata Eduardo Luís Trindade da Silva Ermelinda da Conceição P. Salgueiredo Kiril Yasakau Olga Karavai Pedro Miguel B. Sousa Ramalhete Raquel João Fialho Antunes Susana Maria Baptista Pereira Ferreira

#### **MSc students**

Alena Kuznetsova Filipe de Sousa Pires Luís Miguel Quaresma Mohammadmehdi Shabani

#### other students

Frederico Calheiros Maia Jorge Augusto Oliveira Carneiro Luís Miguel Cardoso Vilhena P. Silva Tiago Filipe Vieira da Silva Tiago Heinrich Vilas Hol

#### collaborators

Alexandre José de Sousa da C. Pires Cristina M. Silva Fernandes Dilshat Tulyaganov Emmanuel Francisco C. Chimamkpam Flávia Aparecida de Almeida João Miguel Maia Carrapichano Joaquim Manuel da Graça Sacramento Mário Guerreiro Silva Ferreira Paulo Barreto Cachim Susana Maria Henriques Olhero Venkatachalam Rajendran

# activity report 2010

#### Carbon Based Materials (CVD Diamond Coatings and Carbon Nanotubes):

The main achievements of 2010 research on carbon nanotubes (CNTs) and carbon nanofibers (CNFs) are here summarized:

A strategic partnership was established between the University of Aveiro and the IFW-Dresden. This was supported by the award of a short term visiting research fellowship from the Gulbenkian Foundation, an Alexander von Humboldt Experienced Researcher Fellowship and a Memorandum of Understanding between the two institutions.
A comprehensive study of the wet-chemical etching treatments for nickel foils and the growth parameters using the HFCVD technique was published in Carbon journal. It was shown that well-shaped, nano-sized Ni protrusions are required to achieve high yield growth. Good correlation was seen between the statistical distributions of the protrusion size and the CNF diameters depicting sp/df ratios close to unity
Another article was published in Carbon showed how to produce stacked-cup CNTs over silica.

Another article was published in Carbon showed how to produce stacked-cup CNTs over silica.
 Three articles were published on the ZnS@CNT system. The first one highlighted the difficulty of extracting mechanical properties by solely imaging the nanostructures in a transmission electron microscope (TEM). Next, imaging the chemical oxidation of a single hybrid CNT inside a TEM was reported, providing the missing proof that the Kirkendall effect is behind the nanocable-to-nanotube transformation seen in these materials. The third article, in Pure App. Chem., was a brief review of the work published so far on the ZnS@CNT system.

- A bibliometric study of the carbon nanotubes (CNTs) field in Portugal showed that a stronger effort is necessary to catch up with the international scientific community in this area. The work on micro- and nanocrystalline diamond (MCD, NCD) coatings also continued during 2010:

- A new surface pre-treatment protocol was proposed for CVD diamond by hot-filament technique (HFCVD). It consisted in four steps (mirror-like polishing;  $CF_4$  plasma etching; amorphous carbon layer deposition; diamond powder seeding), demonstrating to provide high adhesion levels (no delamination under Brale indentation at 900 N).



SEM images illustrating representative CNFs morphologies for several growth runs (temperature/pressure/foil). Below each image is the corresponding diameter size distribution. (a) 650/5/C1; (b) 650/5/C2; (c) 650/5/C3; (d) 650/10/C1; (e) 650/10/C2; (f) 650/10/C3; (g) 800/5/C1; (h) 800/5/C3. in Carbon 48 (2010) 2839-2854

figure:

Number of CNFs
Erosion tests on NCD were performed being relevant not only for the evaluation of the erosive wear resistance, anticipating applications where coated materials are exposed to particle impacts, but also as a way to evaluate their adhesion to the substrates. CF<sub>4</sub> plasma pre-treated substrates yielded a three-fold increase in delamination time comparing to untreated specimens leading to improved adhesion levels.
Boron-doped nanocrystalline diamond (B-NCD) films were grown by HFCVD on very sharp tungsten tips obtained

- Boron-doped nanocrystalline diamond (B-NCD) films were grown by HFCVD on very sharp tungsten tips obtained by electrochemical etching tungsten wires. The cyclic voltammetry showed a stable behavior with a wide electrochemical window of ~2.25 V in a 0.05 M NaCl solution proving the applicability of the developed UME for localized electroanalytical studies in biomedical and corrosion applications.

## **Protective Coatings for Metallic Materials:**

The main research activity related to the surface protection technologies and development of new nanostructured delivery systems in 2010 can be summarized to the following main topics:

- Several new nano-/micro-containers of corrosion inhibitors were developed based on hydroxoapatite microparticles and Layered Double Hydroxides (LDH). Both types of nanocontainers demonstrated sensitivity to corrosion related triggers such as pH and concentration of the corrosive ions.

- Combination of LDH-nanocontainers loaded with different corrosion inhibitors was found to have synergistic anticorrosion effect and can be used as a tool for designing new protective self-healing coatings. The fundamental studies on the structure and release kinetics of inhibitor-loaded LDH nanocontainers was performed. - The electrochemical co-deposition of Al–Ce metallic protective coating with active inhibiting effect was performed for the first time using an ionic liquid as an electrolyte. Cerium was introduced into the aluminium coating as a potential corrosion inhibitor which can be liberated during sacrificial dissolution of the galvanic layer deposited on the alloy surface.

- New protective sol-gel nanocomposite coatings were developed for corrosion protection of magnesium alloys. It was demonstrated that addition of corrosion inhibitors can significantly suppress the corrosion activity in the micro-defects of the coatings on Mg.

- New approaches for localized electrochemical measurements of corrosion-related processes were developed. Two novel microelectrodes for potentiometric and amperometric detection of the active species in micro-confined environments were reported. A multielectrode cell for screening of corrosion inhibitors for multi-material combinations was also created.

## Advanced Ceramics and Other Hard Materials:

Processing and characterization of advanced ceramics and cermet materials was accomplished on several themes: - Studies on the effect of ageing time on the stability of aqueous Y-a-SiAION precursor powder suspensions demonstrated the feasibility of colloidal processing of such ceramics in aqueous medium. - A novel near-net shape route for consolidating complex-shaped ceramics, "hydrolysis induced aqueous gelcasting (GCHAS)" was developed by combining the synergetic effects of hydrolysis assisted solidification (HAS) and gelcasting (GC). - Cordierite ceramics both in bulk porous foam forms have also been prepared and the studies carried out included their complete characterization and modelling of the mechanical properties.

- Studies on dispersing Cu<sub>2</sub>O particles in aqueous suspensions were also continued aiming at developing metalceramic composites in the Al<sub>2</sub>O<sub>3</sub>/CuO-Al system by Al infiltration in Al<sub>2</sub>O<sub>3</sub>/CuO compacts. - The investigation on WC-Fe/Ni/Cr composites covered several aspects: (i) mechanical properties, namely hardness and toughness, in function of the binder amount, for conventional prepared and sputter coated composites; (ii) sintering kinetics using a homemade dilatometry; (iii) exploitation of the hot explosive compaction technique.





## scientific highlights

i) Design of green products and search for new functionalities;

ii) Valorisation of secondary raw materials, some of them toxic, through its use in the preparation of inorganic ceramic pigments;

iii) Development of traditional ceramic products that show new functionalities. These include decontamination of aerial pollutants (NOx, SOx, etc), decolouration of dyes and wastewaters, antimicrobial and self cleaning effects. The deposition of active layers in the surface of ceramic tiles and AI sheets, by expedite and easy controllable techniques (e.g. jet spray, and screen printing) seems to be a viable way to assure those requirements. Porcelain tiles having anti-microbial action, high chemical resistance, and anti-stains characteristics, were also developed in collaboration with a local producer;

iv) Sustainable Built Environment is particularly appealing area for partnership with the Habitat cluster companies and also municipalities, that face tricky questions regarding wastes and its managing in their daily activity. This attempt has been coordinated by the Sustainable Construction Platform (www.centrohabitat.net).



**figure:** Scanning electron micrographs of C1 tiles, fired at 950 and 1050 °C. *in Applied Clay Science 48 (2010) 552-560* 

# on 31<sup>st</sup> december '10

**professors & lecturers** Ana Maria Bastos Costa Segadães João António Labrincha Batista José Maria da Fonte Ferreira Victor Miguel C. Sousa Ferreira

**full time researchers** Maria Paula Da Silva Seabra Rob Pullar post-doctoral associates Luciano Senff

**PhD students** Maria Arlete Carneiro R Carvalho Rajamma Rejini

**MSc students** Bruno Joel Simões Gonçalves João Paulo Gonçalves Tarelho Maria Manuela Portela Marques Patrícia Margarida Vaz Lobo Regina Célia Espinosa Modolo **other students** Sandra Manuel Simaria de O.Lucas Walid Hajjaji

**collaborators** José Miguel Morais Ferraz Manuel Joaquim P. Marques Ribeiro

# activity report 2010

## Rationale

Earth's natural resources and the man-made environment are under intense pressures from growing population, urbanization, continuous expansion of the agriculture, transport and energy sectors, as well as climate variability and warming at local, regional and global scales. Europe needs to engage in a new sustainable relationship with the environment while improving competitiveness and strengthening European industry. The EU needs to strengthen its position in world markets for environmental technologies. Such technologies help deliver sustainable growth providing eco-efficient solutions to environmental problems at different scales and protecting our cultural heritage. Environmental requirements act as a stimulus for innovation and can provide business opportunities. European Technology Platforms on sustainable chemistry confirm the need for EU level action and their research agendas are taken into consideration in the activities below. Other Platforms (e.g. on Construction) partially deal with environmental technology issues and are taken into consideration as well. The activities of group 6 are included in the topics:

#### (a) Sustainable Management of Resources

Conservation and sustainable management of natural and man-made resources: waste management and prevention; soil protection, approaches against land degradation; sustainable management and planning of urban environment. The research activities carried out along the year of 2010 were according to the plan that has been proposed and included the reutilization of different types of glass wastes such as borosilicate glass from lab ware (a Master Thesis on this topic is underway), WEEE, CRT and fluorescent lamps glasses, for producing lightweight aggregates and foam materials by combining them with other kinds of industrial wastes.

A Vale I&DT project, RECON - Redução de Contaminantes no Fabrico do Bloco, was carried out with the company "R.M.C. – Revestimentos de Mármores Compactos, S.A.", aiming to identify the origin of metal contamination.

#### (b) Environmental technologies

Énvironmental technologies for prevention, mitigation, adaptation, remediation and restoration of the natural and man-made environment: related to soil, waste treatment, recycling, clean production processes, and protection of cultural heritage and of the built environment.

#### (c) Rehabilitation mortars for built heritage

The huge and special architectural heritage in Portugal from the beginning of the past century is characterized by the use of stone or adobe (mud sun-dried blocks), as structural material, with lime renders and mortars. Some of those buildings are situated in the city core and show different degradation degrees, promoted either by weathering in urban context, lack of maintenance, or the seaside proximity. To preserve this type of construction, a study was carried out in order to characterize renders, joint mortars and adobes, to know the composition and behaviour of each in the construction. For this purpose, samples were extracted from various locations of several buildings. The study of mineralogy was performed by X-ray diffraction (XRD), their thermal behaviour was obtained by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and these data were complemented by chemical analysis by x-ray fluorescence spectroscopy (XRF). The aggregate particle size distributions were obtained by dry sieving. Mechanical compressive strength (Rc) and capillarity performance were also evaluated. These studies have also been undertaken to support sustainable interventions, allowing the extraction of salts, the consolidation of renders and production of new compatible renders and mortars to substitute and refill the gaps capable of guaranteeing the integrity and prolonging the existence of this kind of architecture and building technique. The restoration and maintenance of old renders is one of the key aspects of correct rehabilitation practice. The ideal course of action is to replace the damaged material by a material with compatible characteristics. This work aims to analyze the effect of the maturation process on hardened state characteristics of hydrated powder lime mortars. The rheological characterization shows an air lime mortar thickening behaviour with the length of the test. The different mixes were subjected to a maturation process consisting on keeping them in the fresh state, covered with water, isolated from CO<sub>2</sub>, during seven days. The specimens and applications were prepared both with the non-matured and the matured mortars. Maturation seems to influence the hardened state characteristics causing a decrease in the capillary values, and an increase on the mechanical strength, which are more evident for mortars with higher binder contents.

A study on the effects of lightweight natural fillers, such as vermiculite and perlite, on the properties of a mixedbinder mortar based on a cement/lime/sand formulation with a typical ratio of 1:1:6 was also published. This kind of mortar may be used for indoor and outdoor rehabilitation purposes. Mortars with different contents of the abovementioned fillers were prepared and their effect on the fresh and hardened product characteristics was evaluated. In the fresh state condition, properties such as apparent density, air content and water retention ability were measured. In what concerns the hardened product characteristics, evaluation was based on the variations of mechanical properties, open porosity and capillarity. It is observed that both the content and the nature of the lightweight filler determine the final characteristics of the mortar. This is particularly enhanced, for instance, by the relationship between hardened product physical properties, microstructure and porosity distribution.

#### (d) Use of micro- and nanomaterials in mortars

The effect of curing conditions on the mechanical properties of mortars containing superabsorbent polymers (SAP) was studied. Curing temperature and relative humidity were varied from 20 to 40 °C and 30 to 95%, respectively, in mixes with different water/cement and cement/aggregate ratios. Tensile and compressive strength tests were performed at several ages. Weight loss over time was measured and related to curing conditions and strength. The addition of SAPs was found to effectively maintain cement-based mortar strength under extreme curing conditions.

Following this matter, the effect of fine aggregate particles on the rheological properties of high performance cement-based materials was assessed. The effect of narrow fractions of fine aggregate particles on the rheology of silica fume-modified low water cement systems was analyzed by means of a mortar rheometer. Yield stress and plastic viscosity were derived for time intervals between 10 and up to 150 min after water addition, and comparison with the slump value taken by the flow table test was done. It is concluded that the fine aggregate particles act as water fixation points in the diameter range of 75–1000 µm, via surface area, whereas for higher particle diameters the governing factor in terms of the resistance to flow may be related to other physical phenomena, such as the particle dimension and the resultant friction forces.

Moreover, the water requirement in order to give each system the same workability is performed by adjusting the water content on each system. Furthermore, a quantitative model is proposed to describe the characteristic initial torque peak and resistance to flow behaviour of high performance concrete, as function of the particle size of aggregate. The combined effect of silica fume and fine aggregate particles on the rheology parameters was discussed.

In terms of using nano and micro-materials in mortars, a study was performed on the effects of nanosilica (nS) and silica fume (SF) on rheology, flow table, compressive strength, water absorption, apparent porosity, unrestrained shrinkage and weight loss of mortars up to 28 days. Samples with nS (0–7 wt.%), SF (0–20 wt.%) and water/binder ratio (0.35–0.59), were investigated through factorial design experiments. Nanosilica with 7 wt.% showed a faster formation of structures during the rheological measurements. The structure formation influences more yield stress than plastic viscosity and the yield stress relates well with the spread on table. Compressive strength, water absorption and apparent porosity showed a lack of fit of second order of the model for the range interval studied. In addition, the variation of the unrestrained shrinkage and weight loss of mortars do not follow a linear regression model. The maximum unrestrained shrinkage increased 80% for nS mortars (7 days) and 54% (28 days) when compared to SF mortars in the same periods.

The effects of nanosilica (nS), microsilica (silica fume, SF) and their simultaneous use (nSzSF) was evaluated on both the microstructure of cement pastes and the mechanical properties of mortars. After water curing at 21°C for 7, 28 and 90 days, samples with water/binder w/b ratio of 0.35 were characterized by thermo gravimetric analysis, X-ray diffraction, scanning electron microscopy and compressive strength test. Single or mixed mineral additions did not generate "any" distinct hydration phases compared to the reference material without additives. A decrease in the calcium hydroxide contents in later curing ages indicated a pozzolanic effect of nS and SF. The chemical action promoted by nS together with the physical effect due to the small particle size distribution given by SF result in higher compressive strength and better hardened properties, suggesting the synergistic action of nSzSF compared with single additions.

This work continued with the report of the effect of silica fume (SF), nanosilica (NS) and superplasticizer (SP) addition on the rheological behaviour of Portland cement pastes with different amounts of SF (0–10%), NS (1%) and SP (0–0.4%) and water to binder (W/B) ratio of 0.4. A rheometer with concentric cylinders geometry was used and the maximum shear rate of 100 s21 was applied. SP decreased the hysteresis area, while SF and NS increased it. Samples with NS showed high slopes in descending curves, while samples with SF and high dosages of SP showed lower values. In both cases, the Bingham model resulted in negative values for the yield stress, hence the Herschel–Buckley model was used instead. The spread values variation on flow table did not follow a linear regression model.

[at.%]	Co-Olivine	Co-Willemite
Si	12.55	14.93
Co	26.57	1.48
Zn	-	49.57
0	60.88	34.01
Total	100	100
Co/Si	2.12	0.10

figure: SEM/EDS characterisation of S2 based pigments. in Applied Clay Science 48 (2010) 552-560

## Running actions and future steps

## (i) Waste based inorganic pigments

Development of inorganic pigments complying with technological and environmental demands and incorporating alternative (and less expensive) raw materials. This alternative will help reduce the consumption of primary (scarce) resources.

Several industrial wastes have been investigated for this purpose, in particular metal-rich sludges: Al-rich sludge generated in the wastewater treatment unit of an anodizing or surface coating industrial plant; galvanizing sludge from the Cr/Ni plating process; sludge generated in the steel wiredraw process; foundry sand; etc ... Distinct pigment structures have been prepared, characterized and applied in colouring galzes and ceramic bodies: (a) Chrome-tin red malayaite Ca(Cr,Sn)SiO<sub>5</sub>; (2) Chrome-iron-nickel black spinel, (Fe,Ni)(Fe,Cr<sub>2</sub>O<sub>4</sub>; Novel blue pigment based on cobalt/nickel hibonite structure.

*(ii) New eco-friendly decontamination techniques* Use of advanced oxidative processes to remove resistant organic pollutants through their conversion into inorganic products (CO<sub>2</sub>, H<sub>2</sub>O, etc), with supported semiconducting layers (TiO<sub>2</sub> and ZnO). Ceramic and aluminium substrates had been tested and deposition conditions are under optimization.

#### (iii) Reuse of biomass fly ashes

Work was done on the characterization of the biomass fly ashes sourced from a thermal power plant and from a co-generation power plant located in Portugal, and the study of new cement formulations incorporated with the biomass fly ashes. The study includes a comparative analysis of the phase formation, setting and mechanical behaviour of the new cement-fly ash formulations based on these biomass fly ashes. Techniques such as X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), thermal gravimetric and differential thermal analysis (TG/DTA), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and environmental scanning electron spectroscopy (ESEM) were used to determine the structure and composition of the formulations.

## (iv) Sustainable mortars for rehabilitation

The work to be developed during 2011 is also focused in the fresh and hardened state behaviour of cement and lime based materials. Rheology of mortars and concrete incorporating nanomaterials and wastes such as biomass fly ash and others (paper pulp industry) will be studied and their impact on materials fresh and hardened state properties and their durability will be assessed.

Waste recycling and valorisation will be dealt in a perspective that allows creating solutions in construction materials and other products. The group is dealing with different types of wastes coming from different sources. Another important work in progress is the development of functional materials done through the incorporation in traditional formulations of wastes or micro- and nanomaterials.

In all these developments sustainability assessment of solutions and materials is under consideration trough the use of specific evaluation tools.





## scientific highlights

i) The use of the ionic liquid [EMIM][HSO4] instead of H<sub>2</sub>SO<sub>4</sub> was used with success for the conversion of pentoses and hexoses into furfural or 5-hydromethylfurfural;

ii) New polyesters of 2,5-furandicarboxylic acid (derived from renewable resources) with several diols were prepared. In particular, the ethylene glycol homologue, poly(ethylene 2,5-furanedicarboxylate) showed properties comparable to those of the basic polyester industrial counterpart, obtained with the aromatic analogue terephthalic acid, which is a petrochemical commodity;

iii) Novel transparent nanocomposite films were prepared from mixtures of chitosan and bacterial cellulose, following a simple and green method involving the dispersion of the bacterial cellulose nanofibrils in a chitosan solutions, followed by water casting;

iv) Cellulose/Ag nanocomposites, were prepared using two distinct cellulose substrates (vegetable and bacterial cellulose). Detailed studies of their antibacterial activity were carried out with several bacterial strains. Silver nanoparticles present in the cellulose fibers in concentrations as low as 5.0×10<sup>-4</sup> wt.% turned these nanocomposites into effective antibacterial materials;

v) lonic liquids with a basic character, suitable for the capture of acid gases such as  $CO_2$  were developed and studied. The mechanism of interaction between  $CO_2$  and the acetate ion was identified;

vi) Correlations for the thermophysical properties of ionic liquids allowing the design of new task specific ionic liquids using computer aided molecular design were proposed;

vii) The mechanism behind the salting-in/out of charged molecules in solution by salt ions was disclosed. The knowledge was used to study and develop new aqueous two-phase systems for the extraction and purification of biomolecules.

#### research team on 31st december '10

## professors & lecturers

Ana Maria Xavier Armando Jorge Domingues Silvestre Carlos Manuel Santos Šilva **Carlos Pascoal Neto** Dmitry Victorovitch Evtyugin Francisco Avelino da Silva Freitas João Manuel Costa AP Coutinho José António da Purificação Martins José Joaquim Costa Cruz Pinto Luísa Alexandra Seuanes Serafim Leal Maria Inês Purcell Portugal Branco

#### full time researchers

Alessandro Gandini Anabela Tavares Aguiar Valente Carmen Sofia da Rocha Freire Barros

#### post-doctoral associates

Ana Teresa Ribeiro Daniel Luis Abreu Fernandes Eduardo Luís Gomes Oliveira **Eliane Trovati** Juan José Villaverde Mella Luciana Isabel Nabais Tomé Márcia Carvalho Neves Natércia da Conceição Tomé Martins Sérgio Nuno Martins Lima Sidhpuria Bhikhubhai Kalpeshkumar Susana Cristina de Matos Fernandes Zélia Velez

**PhD students** 

Ana Luísa Carvalho Magalhães Ana Patrícia dos Santos Marques Ana Rute Marques Ferreira Carla Andreia Cunha Vilela Catarina Maia Seco Seiça Neves Catarina Ralheta Graça Raquel Veiga Vaz Helena Wedin João Lima

Jorge Fernando Brandão Pereira Maria Jorge Pratas de Melo Pinto Maria Margarida Feitor P. M. Antunes Paula Andreia Fernandes de Sousa Pedro Emanuel Garcia Loureiro Pedro Jorge Marques de Carvalho Ricardo João Borges Pinto Rui Alberto Magueta da Silva Samuel Venancio de Sousa Freitas Sónia Andreia Oliveira Santos Sónia Patrícia Marques Ventura Susana Raquel de Sousa Pereira Tânia Almeida

#### **MSc students**

Ana Catarina Gil Martins Andreia Filipa B. Figueiredo dos Santos Ângela Guerra Carla Isabel Silva Ribeiro David Patinha Joana Leão Candeias Laura Felício Liliana Vieira Costa Martha Helga Freire Lopes Pedro Filipe Lopes Rua Roberto Carlos Gaspar Gomes Coelho Rui Miguel de Andrade Domingues Samuel Mineiro Inácio Sandra Pereira Magina Susana Cristina de M. Machado Leite Tâmara Isabel Barbosa da Silva Vania Manuela Mendes Dias Vera Susana Guimarães Abreu Cruz

#### other students

Ana Rita Ribeiro Teles Belinda Isabel Gomes Soares Carme Puig Catarina Daniela Goncalves Pinto Varanda Elisabete Valente da Costa Helena Isabel de Sousa Passos Joana Andreia Saraiva Mendes Joana Catarina P. da Costa Luzeiro Joel Ricardo Simões dos Santos José Pedro Salgado de Castro Aniceto Liliana Domingues Pedro Liliana Sofia Carvalho Tomé Marcos Andre Pinto de Carvalho Maria Sílvia Gomes de Sousa Marta Luísa Salsas Batista Nuno Pedro Domingues Loureiro Patrícia Ramos Ricardo Francisco Neto Rui de Figueiredo Duarte Sandra Lopes da Silva Sónia Oliveira Prozil

#### collaborators

Ana Ferro Ana Gisela Guedes Nunes da Cunha Ana Margarida Teixeira Ana Sofia Vila Mona Santiago Andrea Gabriela P. R. Figueiredo Andreas Bohn Conceição Fernandes Dora Salomé Correia Coelho Eliana Jerónimo Eurico Cabrita Flávio Gonzaga Castro Santos Silva **Helena Margues** Hossein Jalali Torshizi **Jacques Desbrieres** Joana de Oliveira Pais Joanna Krakowiak José Luís Santos Mara Guadalupe Freire Martins Maria Dolores das Dores Ramos Franco Moreira Maria Filomena Andrade de Freitas Mariana Belo Oliveira Marina da Conceição da Silva Matos Mohamed Belgacem Mónica Domingues Gomes Nuno Hélder da Cruz Simões Silva Olinda Guerreiro Paula Gomes Sílvia Carriço Monteiro Tiago Capote Umbelino Florêncio Infante Weidong Zhang Xavier Malcata



figure: Charge distribution for inorganic anions ordered from saltinginto salting-out effects. *in J.Phys. Chem. B Vol.114, no.5 (2010) 2004-2014* 

## activity report 2010

A) The implementation of the forest-based biorefinery, with focus on the characterization and extraction of valuable components from wood and bark, using benign extraction systems and the assessment of potential technologies for industrial implementation.

The development of new processes for the extraction and fractionation of the triterpenic fraction from eucalyptus bark was continued. This involved i) the fractionation using simple approaches as adequate pH control and salts precipitation, and ii) the use of supercritical CO<sub>2</sub> extraction/fractionation processes. The first approach has already bee extensively studied, and conditions to isolate fractions substantially enriched in these components were established. The use of supercritical extraction systems was started. The preliminary results obtained show an efficient extraction will require the use of co-solvents

The detailed study of the composition of phenolic fractions of eucalyptus bark, (which were previously shown to have promising tanning properties) was started and several fractions were isolated, and characterized in terms of total phenolics and antioxidant properties. The study will now involve the detailed LC-ESI/MS characterization of the extracts.

Lignosulphonates (LS) from acidic sulphite pulping were enzymatically oxidised to produce dyes. The oxidised LS showed good potential for use in natural surface modification of textile materials containing flavonoids. These findings have important practical implications for lignocellulosic fibre coloration, where new polymers can replace harsh chemicals in the textile industry.

## 40 | research group

The supercritical fluid extraction of grape seed oil has been carried out. Extracts obtained from both untreated and enzymatically pre-treated seed have been characterized in detail. The inhibitory capacity of the procyanidins fraction of the seeds has been measured upon the angiotensin converting enzyme I (responsible for high blood pressure).

The structural study on lignin, cellulose, hemicelluloses and pruine in grape skins and stalks was continued. The structure of glucuronoxylan from sisal fibres has been studied and the structural changes occurred during soda pulping and ECF/TCF bleaching was evaluated.

*B)* The development of novel polysaccharide based materials and composites, and the preparation of new cellulose-based functional materials bearing inorganic nanophases. The development and characterization of novel polymeric materials based on furan moieties.

#### Novel Biomass-Derived Materials and Composites

The research on the development of novel functional materials based on polysaccharides, namely vegetable and bacterial cellulose, and chitosan was continued and strengthened.

Vegetable cellulose fibers modified with two perfluorinated reagents (trifluoropropanoyl chloride and pentaflourobenzoyl chloride) were tested in the preparation of new composites with one perfluorinated polymer matrix (poly(vinylidene fluoride-co-hexafluoroproplylene). The obtained materials were characterized in terms of their thermal and mechanical properties, morphology and dimensional stability (water uptake). The evaluation of the barrier properties of acylated cellulose membranes was also pursued, since it is a crucial parameter in several domains, such as in packaging applications. During this period, we focused mainly on the assessment of the dry and wet permeability of these materials to various gases.

Two novel strategies for the modification of cellulose fibers were also investigated during this year, viz the preparation of new organic –inorganic hybrid materials and of highly hydrophobic and lipophobic cellulose fibers by a straightforward gas-solid reaction. The preparation of the novel cellulose based class-II organic-inorganic hybrid materials involved the heterogeneous chemical modification of cellulose fibers with (3-isocyanatopropyl)triethoxysilane, followed by the acid hydrolysis (and condensation) of the appended siloxane moieties as such, and in the presence of either tetraethoxysilane or 1H,1H,2H,2H-perfluorodecyltriethoxysilane aiming to introduce different functionalities onto the fibers surface. The strategy of modification of cellulose fibers in the vapor state consisted on the reaction with gaseous trichloromethylsilane (TCMS). In both cases The characterization of the obtained materials involved FTIR-ATR and solid-state <sup>29</sup>Si NMR spectroscopy, scanning electron microscopy (SEM), X-ray diffration, thermogravimetry and contact angle measurements with different liquids.

New cellulose/silica hybrid (CSH) composites were prepared from bleached Eucalyptus globulus kraft pulp or primary treatment sludge cellulose fibers by a sol-gel method which aging was accomplished by hot pressing of pre-formed CSHs. The incorporation of a silica network in cellulosic materials increased significantly their dimensional stability during soaking in water, hydrophobicity, thermal stability and bending strength. The thermal conductivity of these hybrid materials is comparable to commercially available insulation foams. Similar approach was applied to produce hydrolysis lignin/silica hybris (LSH) composites. These were characterized by X-ray photoelectronic spectroscopy, FTIR and <sup>29</sup>Si and <sup>13</sup>C NMR and nitrogen sorption. The high bioremediation performance of the hybrid materials was proved by chemosorption of inorganic (Cu<sup>2+</sup>) and organic (2,4-dichlorophenoxyacetic acid) soil pollutants.

dichlorophenoxyacetic acid) soil pollutants. The studies on the coating of *E. globulus* paper sheets with chitosan and one water soluble chitosan derivative and mixtures of chitosan (and its derivative) and bacterial cellulose nanofibers were continued and optimized. The obtained coated materials were extensively characterized in terms of surface, mechanical and barrier properties. Moreover, the printability and aging of the coated papers were also assessed. The mixtures of chitosan (and one of its water-soluble derivative) with bacterial cellulose were also tested for the preparation of novel transparent nanocomposite films. The method consisted in the simple dispersion of the bacterial cellulose nanofibrils in the chitosan solutions, followed by water casting. The obtained materials were characterized by SEM, AFM, thermogravimetry, X-Ray Diffraction, Light Transmittance, DMA and mechanical essays. This strategy is particularly relevant because of its simplicity, green connotation and also because of the interesting properties of the obtained films.

Another research area was started during this year that consisted on the implementation of the production of bacterial cellulose in our laboratory. A pure *Acetobacter* strain was isolated from a commercial kombucha fermented tea sample and used on the production of bacterial cellulose under different culture conditions. In this context, bacterial cellulose membranes were investigated as substrates for the controlled release of model drugs. This preliminary study involved kinetic studies (followed by FTIR and UV-Vis) of the migration of lidocaine into wet, dry and lyophilised membranes and its subsequent release.

Research on novel nanocomposites based on cellulose and other polysaccharides incorporating nanostructured metals was pursued. New cellulose/Cu and cellulose/Fe (III) nanocomposites, involving plant and bacterial cellulose where prepared and characterized. The same approach was extrapolated to different metal alloys. Metal nanoparticles (Ag, Au) where successfully applied in the development of novel polymer nanocomposite films, using chitosan and chitosan derivatives as matrice. A new research line, dealing with the development of new nanofibrilated cellulose materials (NFC) was initiated. Ag/NFC and TiO<sub>2</sub>/Ag where prepared and its characterization was initiated.



#### figure:

Electrostatic potential mapped onto an electron density isosurface (ab initio MP2/cc-pVTZ(-f)) and estimated atomic point charges (ChelpG method) on (a) N-butylpyridinium, (b) N-butyl-2-methylpyridinium, (c) N-butyl-3-methylpyridinium, and (d) N-butyl-4-methylpyridinium cations. The values superimposed on selected atoms represent the corresponding atomic point-charge densities expressed in percentage of atomic charge units (acu %). The color code represents all gradations from low positive charge densities (cyan) to high positive charge densities (dark blue). Some atomic point charges of the aromatic carbon atoms are negative. in J. Phys. Chem. B, Vol114 No48 (2010) 15925-15934

### Polymers Derived from Renewable Resources

## Synthesis of polymeric materials based on the reversible Diels-Alder reaction

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. Particular attention was given to the preparation of AB (Meleimide-Furan) type monomers, in order to prepare intermediate structures that could be stored until polymerization. This involved the protection (through a Diels-Alder reaction) of the maleimide moiety with a volatile furan. Before polymerization, the volatile furan was removed through the retro-Diels-Alder reaction at high temperature, followed by the polymerization process, which took place as the temperature of the reaction medium decreased. The DA/retro-DA cycle was also applied to linear (AA+BB systems) and crosslinked (AA+B<sub>3</sub> system) polymers. These systems were analyzed in terms of the kinetics of the linear polymerization (based on preliminary studies on monofunctional model compounds) followed by UV and <sup>1</sup>H-NMR spectroscopy. This investigation is supported by a FCT project.

#### Synthesis of new polyesters based on 2,5-furandicarboxylic acid (FDCA)

New polyesters of FDCA with several diols (1,3-propanediol, 1,-2-propanediol, 1,4-benezenedimethanol isosorbide etc) were prepared, following polytransesterification and/or polycondensation approaches. The new materials were characterized in detail, and showed promising characteristics in terms of crystallinity and thermal properties (mp and Tg), comparable to those obtained for the polyesters obtained with the synthetic aromatic analog terephthalic acid.

Synthesis of polymers using monomers simulating lignin structural units Two different types of structures and hence two diffetent polymerization methods are at the basis of this doctorate study which aims at valorizing lignosulphonate fragments. The first topic concerns the radical and cationic polymerization of methoxy-substituted styrenes. The best results were obtained with cationic systems. The second topic deals with the polycondensation of differently substituted aromatic hydroxyacids, which provided highly stiff semicrystaline polyesters.

#### Synthesis of new polymeric materials from vegetal oils

The synthesis of new monomers derived from unsaturated fatty acids was started. During this period the synthesis of fatty acids vinyl esters was studied. The best results in terms of yields and selectivity were obtained by Iridiumcatalysed transvinylation of fatty acids with vinyl acetate. The vinyl esters were tested with success in radical polymerization/copolymerization with vinyl acetate and these materials tested in oxidative curing. A new research line was started involving the development of new chemical/biochemical tools to produce fatty acid hydroperoxides or other oxidised derivatives and their transformation into valuable products, namely new monomers for polymers synthesis.

#### Polyesters from Suberin

The development of new polyesters derived from suberin components was continued, involving the optimization of the polymerization conditions as well as the extension of these studies to birch outer bark suberin

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*C)* The conversion of biomass components into value added chemicals focusing on the development of: efficient catalytic conversion for the production of platform chemicals from polysaccharides; and biotechnological processes for the conversion of biomass components into fine chemicals and biofuels.

One of the areas of interest in G7 is the production of FUR and HMF from sugars and polysaccharides. The current approach uses sulphuric acid as acid catalyst for this conversion. G7 is actively investigating the use of ILs as alternative solvents and catalysts. In considering the potential of acid ILs to replace sulphuric acid in processes for the transformation of saccharides into furfural (FUR) or 5-hydromethylfurfural (HMF), it must be recalled that  $H_2SO_4$  is very hygroscopic and difficult to dry in vacuum, and when heated it emits highly toxic fumes, which include sulfur trioxide, leading to the accumulation of acidic waste. The dehydration of xylose and fructose and, on the other hand, the one-pot hydrolysis and dehydration of di/polysaccharides containing fructose units, in [EMIM][HSO\_4]/co-solvent gives fairly high yields (80-90%) of FUR and HMF, at 100 °C. Furthermore, better results were achieved with [EMIM][HSO\_4] (IL) than with aqueous  $H_2SO_4$ , under similar conditions. The IL can be recovered and reused without a significant drop in FUR yield in recycling runs. The use of [EMIM][HSO\_4] instead of  $H_2SO_4$  may allow process intensification with reuse of the acid IL.

Another aspect of interest is the valorization of spent sulphide liquor (SSL) to a second generation bioethanol. SSL contains dissolved sugars (40-45 g/L), mainly xylose, and around 10 g/L of acetic acid. Study on the bioethanol production by Pichia stipitis revealed that besides acetic acid Pichia stipitis is also inhibited by polyphenolics. Paecilomyces variotii can consume some inhibitory compounds and conversion to Single Cell Protein (SCP) is being optimised. Another research trend in the valorization of SSL is its biotransformation into biopolymers as polyhydroxyalkanoates (PHA) employing mixed cultures of microorganisms.

The kinetic study of the castor oil acetylation has been started, in order to be applied for the production of dielectric oils.

On the development of analytical techniques to support these studies the advanced 2D NMR techniques were applied for the first time for the analysis of muconic acid type structures (MATS) in oxidised lignins. This allowed the reliable assignment of MATS signals thus providing a methodology for detection and distinguishing of MATS from structurally similar moieties. 13C NMR and advanced 2D NMR techniques were combined with specific 13C-enrichement of lignin model polymers (DHP) to avoid the signal-overlap problems and aiding in definitive signal assignments. This allowed a new database for the lignin signals assignment. The work was initiated for application of advanced mass spectrometry techniques (ESI-MS/MS and ESI-MSn) for the study of minor functionalities in hemicelluloses. The application of new electronic tongue (ET) multisensor system for the real-time monitoring of polyoxometalates (POM) re-oxidation with laccase and molecular oxygen has been accomplished. New methodology to assess the chromophores in bleached pulps employing micro UV-Raman spectroscopy has been developed.

#### D) Development of new separation processes applied to the biorefinery.

G7 is actively investigating the development of new separation processes based on ionic liquids for the extraction of biomolecules or the enhanced separation of biorefinery products using a greener approach. For that purpose ILs have been studied for the formation of aqueous two-phase systems (ATPS). The effect of the inorganic salts on the solubility of ionic liquids in aqueous solutions was investigated and the mechanisms responsible for the salting-in/out of the IIs were identified. An extensive study of the IL cation and anion on the ATPS formation was developed allowing the design of ATPS with defined characteristics. The extraction of biomolecules such as aminoacids, food dyes, proteins and other biomolecules were carried with success. The IL based ATPS present larger partition coefficients and lower viscosities than the conventional polymer based ATPS allowing for a faster mass transfer and easier phase manipulation.

The use of ILs for the purification of biogas and syngas by the removal of the acid gases ( $CO_2$  and  $H_2S$ ) has been extensively studied. The  $CO_2$  solubility in a large number of ionic liquids was measured and the mechanism of  $CO_2$  solubility on ionic liquids was disclosed. A general correlation allowing the design of ILs for enhanced  $CO_2$ solubility was developed. The study of the  $CH_4$  solubility was started aiming at understanding the methane solubility in ILs and develop ILs with optimized selectivities for biogas purification.

solubility in ILs and develop ILs with optimized selectivities for biogas purification. We have also been developing the CPA-EoS for the description of the phase equilibria relevant for biodiesel purification. The current version of the CPA is now able to describe the VLE and LLE, in binary or higher order systems, containing short chain alcohols, water, glycerol, fatty acids and fatty acid esters. It is shown that this model is far more accurate and possesses predictive capabilities than current models implemented in process simulators such as ASPEN.

The separation of alcohol-water or organic acids-water systems, common in biorefinery processes, using extractive or azeotrópico distillation involving the use of ILs or other solvents is being under research. Concerning Liquid-liquid extractions work on the dynamics of liquid-liquid dispersions in chemical processing is being continued. Another type of separation processes under study uses membranes. On this subject we are carrying the dynamic characterization of new inorganic membranes. The experimental set-up necessary for the measurement of pure gas permeances is already installed. Assays of pure gas permeation at constant temperature and at programmed temperature have been carried out, and new models for the representation and interpretation of transport mechanism across membranes have been proposed and validated with data from literature.



## scientific highlights

i) Spray-dried hydroxyapatite-5-Fluorouracil (Hap/5FU) granules as drug delivery systems;

ii) Confirmation that porosity of glass/PLLA composite scaffolds for bone tissue engineering applications, developed by TIPS, can be tailored by simply controlling the glass filler solubility without the use of toxic surfactants (patent);

iii) In silico research of synthetic receptors for medicinal applications;

iv) The protocol for cell metabonomics was developed to ensure reproducibility in cell/drug studies;

v) Insight into human fetal metabolism under conditions of prenatal disorders/disease: use of NMR-metabonomics for diagnosis, follow-up and prognosis;

vi) Insights into lung cancer metabolism and demonstration of the use of NMR-metabonomics in monitoring and diagnosing cancer;

vii) Study of the interaction mechanisms between DNA quadruplexes and antitumor complexes using computational methods;

viii) Investigation of the diffusion and transport of drugs across membranes using molecular dynamics approaches.



#### figure:

SEM microstructures of porous HAp scaffold (up) SEM microstructures of porous b-TCP scaffold (down) *in J.Mater. Sci.: Mater. Med 21 (2010) 2955-2969* 

## research team

on 31st december '10

#### professors & lecturers

Ana Maria Pissarra Coelho Gil Brian James Goodfellow José Maria da Fonte Ferreira Maria Clara Ferreira Magalhães Maria Elisabete Jorge Vieira Costa Maria Helena F. Vaz Fernandes Isabel Margarida Miranda Salvado Maria de Lourdes Gomes Pereira Maria Margarida Tavares L. Almeida Teresa Margarida dos Santos Victor Manuel Sousa Félix **full time researchers** Iola Melissa Fernandes Duarte Paula Cristina F. Silva Brandão

#### post-doctoral associates

İsabel Alexandra Fernandes Lemos Paulo Jorge Costa Sandra Cristina de Almeida Pina Sílvia Cristina Ferreira de Carvalho

#### **PhD students**

Ana Isabel Ferreira Franco Vicente Avito Hernâni dos Santos Rebelo Catarina Ferreira dos Santos Cláudia Manuela Mesquita da Rocha Erika Judith Cardoso Rodrigues Davim Gonçalo Miguel Gomes Graça Hugo Alexandre G. Rocha Fernandes Inês Dias Lamego Ishu Kansal Joana Teixeira A. Gomes Marques João Miguel da Cruz M. A. Caio Miguel Maurício Machado dos Santos Natália Braz Barroca Paula Maria da Costa Torres Poliana Pollizello Lopes Sílvia de Oliveira Diaz Susana Seabra Aveiro

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**MSc students** Jorge Louro Luís Igor Oliveira Marques Leonildo Delgado Liliana Sofia Oliveira Pires Raghu Raman Rajagopal

#### other students

Ana Isabel Martins Casal Ramos Carla Florbela Ferreira Pinto da Silva Claúdio Henrique dos Santos Diogo Figueiredo Pinho Joana Carolina Quintela Carrola Joana Isabel Monteiro Pinto Manuela Ermelinda Lopes do Lago Maria João Pinho Mota Sara Ferreira Carvalho

#### collaborators

Ana Filipa Ferreira Ladeirinha André Lopes Anjos L. Macedo Catarina Isabel de Oliveira Martins **Elisabeth Want** Elsa Maria Carvalheiro Dias Gloria C. Ferreira Isabel M.D. Jana Marrucho Ferreira Jean-Marc Moulis João Carlos Falcão Sardinha John Lindon (Prof.) José Galhardas Moura José Martinho Marques de Oliveira Dilshat Tulyaganov Emmanuel F. C. Chimamkpam Maria Manuela Abreu Venkatachalam Rajendran Sónia Marlene Rodrigues Oliveira Susana Santos Braga

## activity report 2010

**Biomaterials.** Within the theme of novel materials for regenerative medicine, novel glass compositions, glasscontainig composites and polymer-nanoparticles composites have been researched. Structural studies of Ti-Ca-P glasses gave a valuable contribution for the clarification of their degradation behaviour namely in biological environments. Raman and 31P MAS-NMR spectroscopic methods revealed the features of the internal structure of novel glasses with compositions xTi(65-x) P•35 Ca (x = 0–30 mol%). Replacing of typical P–O–P bonds by Ti–O–P bonds was detected for high Ti contents and mineralization in SBF and cytocompatibility was confirmed for these glass compositions. Powders of some of the new glasses were, for the first time, tested in Zebrafish, a model organism used in molecular genetics, to assess toxicological effects on embryo development. Glass and glass-ceramic scaffolds of the Si-Ca-P-B-Na system were produced by the salt-sintering method and the processing parameters optimized (particle size, heat treatment schedule).

The work carried out included the development of calcium phosphate powders doped with some elements that play essential roles in the physiological environment. Substitution of trace elements, such as Mg, Sr and Zn ions, into the structure of calcium phosphates was the subject of widespread investigation, because of their impending role in biological processes. A strontium- and magnesium- co-substituted b-tricalcium phosphate ( $\beta$ -TCP) was synthesized and characterized, this work comprising powder synthesis, crystalline phase transformations with heat, phase quantification and structural refinement of powders and cements determined through X-ray diffraction with Rietveld refinement, BET specific surface areas determination and particle size analysis, formulation of the cement pastes, study of the setting process and the characterization of the hardened cements for their physical/mechanical properties, the in vitro and in vivo performance. The doped β-TCP powders were used to prepare a-TCP-based and brushite-based bone cements. Their most salient features include good biocompatibility, excellent bioactivity, self-setting characteristics, low setting temperature, adequate stiffness, and easy shaping to accommodate any complicated geometry. They are commonly used in filling bone defects and trauma surgeries as mouldable paste-like bone substitute materials. Subtle differences in composition and structure of these materials may have a profound effect on their in vivo behavior. Other work studied the influence of Mg- and Srsubstitutions on injectability and mechanical performance of brushite-forming a-TCP cements and on the hydration kinetics. A noticeable dependence of injectability on the liquid-to powder ratio (LPR), smooth plots of extrusion force versus syringe plunger displacement and the absence of filter pressing effects were observed. For LPR values up to 0.36 ml g<sup>-1</sup>, the percentage of injectability was always higher and lower for Mg-containing cements and for Sr containing cements, respectively, while all the pastes could be fully injected for LPR > 0.36 ml g<sup>-1</sup>. The hardened cements exhibited relatively high wet compressive strength values (~17–25 MPa) being the Sr-and Mg-containing cements the strongest and the weakest, respectively, holding an interesting promise for uses in trauma surgery such as for filling bone defects and in minimally invasive techniques such as percutaneous vertebroplasty to fill lesions and strengthen the osteoporotic bone.

Other work evaluated the biological responses of brushite-forming Zn- and ZnSr-substituted b-tricalcium phosphate bone cements. Cell cultures were used to evaluate citotoxicity, bioactivity and biocompatibility of cements. The in vivo biocompatibility and cements resorption were evaluated using a pig model through histological and histomorphometric studies of decalcified sections. The results showed that the implanted cements are biocompatible and osteoconductive, without foreign body reaction. These properties make them good candidates for applications as bone substitutes.

Glass-ceramics in the diopside (CaMgSi<sub>2</sub>O<sub>6</sub>)-fluorapatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F)-wollastonite (CaSiO)<sub>3</sub>) system were proposed for restorative dental and bone implant materials. The influence of varying SiO<sub>2</sub>/CaO and CaF<sub>2</sub>/P<sub>2</sub>O<sub>5</sub> molar ratios on the structure and thermal behaviour of glass compositions in the CaO-MgO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>-Na<sub>2</sub>O-CaF<sub>2</sub> system was studied by hot-stage microscopy and differential thermal analysis. An increase in CaO/SiO<sub>2</sub> ratio degraded the sinterability of the glass powder compacts, resulting in the formation of akermanite as the major crystalline phase, while an increase in P<sub>2</sub>O<sub>5</sub>/CaF<sub>2</sub> ratio improved the sintering behaviour of the glass-ceramics.

Strongly adherent (~75 MPa) bioactive glass films were deposited on Ti substrates by radiofrequency magnetron sputtering at low temperature (150°C) under different working atmospheres: Ar 100%, Ar + 7%O<sub>2</sub>, and Ar + 20%O<sub>2</sub>. The effects of atmosphere composition on bioactivity revealed that the best biomineralization capability, expressed by the thickest chemically grown carbonated hydroxyapatite layer, was obtained for the bioglass coating sputtered in a reactive atmosphere with 7% O<sub>2</sub>. On the other hand, the influence of argon pressure (0.2 Pa, 0.3 Pa and 0.4 Pa) used during deposition on the short-range structure and biomineralization potential of the bioglass coatings was also studied in another paper. The thickness of the chemically grown hydroxyapatite layers was more than twice greater for the BG films deposited at the highest working pressure, in comparison to those grown on the films obtained at lower working pressures. The results were explained based on structural and compositional considerations. Two licence agreements were established with two Portuguese companies dealing with the production of biomaterials, one with AGORAMAT – Produção de Materiais Cerâmicos, Lda., and another with CERAMED – Cerâmicos para aplicações médicas Lda.

Additional work revealed that the thermal stability of TEOS-PDMS hybrid materials can be increased by small additions of zirconium. Hybrid materials containing gelatin as the organic part and calcium phosphate silicate/wollastonite as the inorganic part were successfully synthesized and shown to form an apatite layer after immersion in simulated body fluid. Silica hybrid biomaterials containing gelatin and methylmetacrilate found application as carriers for immobilization of cells with nitrilase activity.

Development of potential drug delivery systems entailed the development of porous calcium phosphate granules for bone regeneration and controlled drug (Levofloxacina) release in situ. In addition, the development of porous HAp and b-TCP scaffolds processed by starch consolidation in combination with the foaming method was carried out. The ability of these scaffolds to release drugs suitably for osteomyelitis was studied in vitro. The results of the study indicated that HAp exhibited better drug release profile than b-TCP when drug was used alone indicating the high influence of the carrier material. However, this restriction got relaxed when a bilayered scaffold was formed using chitosan along with the drug. SEM studies along with EDAX on the drug-chitosan bilayered scaffold showed closest apposition of this combination to the calcium phosphate surface. Other work dealt with glass/PMMA composites for bone cements of improved bonding capability were loaded with medicals (anti-inflammatory, antibiotics) and analysed in terms of their drug delivery response. Finally, newly developed chemically derivatized carrageenan-based nanoparticles were studied in terms of their controlled release properties in relation to model drugs.



#### figure:

Snapshots of  $(H_6L^1A)^{i+}$  assembled entities taken at 10.5 ns of MD simulation for btc<sup>3-</sup> anion (left), tph<sup>2-</sup> (centre) and iph<sup>2-</sup> (right). Only the closest solvent molecules within 8 A distance from  $(H_6L1)^{6+}$  are shown. Atom colour scheme used as given in Fig. 4 apart of the carbon atoms of MeOH molecules, which are drawn in light blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article). *in Tetrahedron 66 (2010) 8714-8721* 

**Bio-Inorganic Systems and Toxicity Studies.** Several chromium compounds with biologically relevant functions were studied due to a current important controversy about their essentiality. In addition, Cr(VI), a proved strong carcinogenic, was studied on mice sperm in order to evaluate Cr(VI) reduction effects on the spermatogenic cycle. Other metal-based mixtures were also assayed in vivo in small rodents in order to evaluate adverse effects on relevant organs such as kidneys.

Ongoing work on ruthenium trithiacyclononane (9aneS<sub>3</sub>) complexes for antimicrobial, antifungal or antitumoral action has led to the isolation of [Ru(9aneS<sub>3</sub>)(2,2'-bipyridine)Cl][NO<sub>3</sub>] and progress is being made in obtaining anticandida complexes, by incorporation of bisimidazole and carvacrol.Further work was carried out Ru(II) complexes bearing organic ligands used as models of natural products (eg lapachol), have continued to be studied (main characterisation by 1H and 13C NMR).

In addition, modification of the properties of metal complexes by molecular encapsulation using cyclodextrins, in particular concerning catalytic, cytotoxic and enzyme mimicking functions, was reviewed in the form of a book chapter.

Artificial Receptors for Pharmaceutical and Environmental Applications. The application of computational methods (quantum chemical calculations, molecular mechanics (MM) and molecular dynamics (MD) simulations) in the comprehension of the association processes between synthetic receptors and several substrates or between drugs and proteins are the research activities of the Molecular Modeling group. Studies were performed on the ability of two heteroditopic calix[4]diquinone receptors to transport a KCl ion-pair and a dopamine zwitterion (a very important neurotransmitter) through a water-chloroform interface finding that the transport free energy barriers are lower when the receptors are used. A molecular modeling study on the binding properties of murine (mHBP) and human (hHBP) p22HBP protein (heme-binding protein) with four tetrapyrrole ring systems: iron protoporphyrin IX (HEMIN), protoporphyrin IX (PPIX), coproporphyrin III (CPIII), and coproporphyrin I (CPI) was also performed. The relative binding affinities predicted by our computational study were found to be similar to those observed experimentally and the protein-tetrapyrrole complexes are stabilized by non-bonded interactions between the tetrapyrrole propionate groups and basic residues of the protein, and by the preferential solvation of the complex compared to the unbound components. A MD/MM study followed by Density Functional Theory (DFT) calculations was undertaken in order to understand the formation of a pseudorotaxane trough cooperative halogen and hydrogen bonds using a 2-bromo-functionalised imidazolium derivative. The term halogen bond describes the interaction of a halogen atom (X) in a molecule (R-X), with a negative site on another molecule (B), i.e. an R-X•••B interaction. The association of CI- by rotaxanes possessing a pyridinium ring revealed to be influenced by the macrocyclic cavity size.

Molecular dynamics (MD) simulations showed that methyl group in the pyridinium ring can only occupy the same plane as the macrocycle polyether chain in the largest macrocycle, which increases its stability. The MD simulations also showed that the  $H_2PO_4$ - and  $CH_3COO$ - anions, due to their biggest size, are located outside the rotaxanes cavity. The group activity also included experimental studies on supramolecular anion associations, which were carried out primarily by single crystal X-ray diffraction (XRD). The XRD was also used for the structure determination of several macrocyclic and organometallic complexes.

In terms of environmentally relevant applications, novel potential molecular biomarkers were tested in fish and mollusc species (comet assay, cytochrome P450 1A1 gene expression) and a study of the soil, plant water interactions in contaminated mine sites, was carried out as well as the study of processes to control elemental bioavailability.

Analytical Tools on Biological Systems. NMR-based Metabonomics has been extensively applied to different disease processes, as well as to the study of cellular metabolism in situations of stress. In relation to disease research, lung cancer has been one of the main subjects investigated. Metabolic signatures of this disease have been uncovered in tissues and biofluids, paving the way to formulate new pathophysiological hypotheses and to develop new diagnostic tools based on metabolite profiling. In particular, multivariate modelling of urine and plasma data allowed good discrimination between patients and healthy controls, thus showing the potential of this approach for the minimally invasive detection and monitoring of the disease. In prenatal health, NMR and MS characterization of biofluids was carried for the identification of early markers of pregnancy pathologies. A complete metabolite profiling of human amniotic fluid was achieved and ongoing work focuses on urine and plasma analysis, all biofluids having shown to contain early indicators of conditions diagnosed or occurring later in pregnancy.

We have also investigated the response of human cells (osteosarcoma and lung cell lines) to different external stimuli, namely a chemotherapy drug (cisplatin) and radiation exposure. This work allowed metabolic changes to be followed, as a function of different variables (such as drug concentration and exposure time) and correlated to various cellular biochemical processes. Furthermore, NMR metabolic profiling of control and mistranslating yeasts was continued. Extraction methods were optimized and growth curves profiled. A sideline of the Metabonomics work relates to food quality control, aiming at establishing solid links with some sectors of the food industry (e.g. beer and wine). In this respect, NMR metabonomics was employed for studying vine plant diseases and NMR and GC-MS models were built for rapid beer aging monitoring, in tandem with sensorial analysis.

In terms of biomolecular structure characterization, experimental studies of mHBP-PPIX and mHBP-hemin systems (wild type and mutants), using fluorescence quenching and NMR chemical shift mapping, were carried out and compared with theoretical studies. All mutants show similar binding constants to wild type mHBP. Functional studies of mHBP were continued using novel siRNA based methodologies in collaboration with CEA (Grenoble, France). New clones for hSOUL were used to obtain new NMR data for structure determination in solution. Results suggest that hSOUL does not bind heme. Using this clone a crystal structure of hSOUL was obtained to 3.3 A resolution. The structure was found to be similar to mHBP.

associated laboratory centre for research in ceramics and composite materials





# **PhD theses**

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figure: SEM microstructures of screen printed films fired at 1300 .C (left) and 1400 .C (right). *in Journal of European Ceramic Society 30 (2010) 221-225* 

# patents patents international national

Matriz orgánica-inorgánica luminiscente, procedimiento para su obtención y termómetro molecular luminiscente basado en dicha matriz.

Carlos LD, Amaral V, Lima PP, Brites CDS, Palácio F, Millán A, Silva NJO.

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Ion-selective solid contact microelectrode and its production method. Lamaka SV, Zheludkevich ML, Ferreira MGS. WÓ/2010/076717.

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Método de preparação de suportes porosos compósitos de base polimérica para aplicação em engenharias de tecidos Fernandes MHFV, Vilarinho PMLS, Daniel-da-Silva AL, Barroca

NB 22-01-2010. PT 104136.

Processo de encapsulamento de aluminatos luminescentes de berílio, magnésio, cálcio, estrôncio ou bário dopados com cério (III) encapsulados com TiO2 e as suas respectivas utilizações. Zurba NK, Ferreira JMF. PT 104801. 29-10-2010

Pasta dental luminescente antibacteriana à base de aluminatos de berílio, magnésio, cálcio, estrôncio ou bário dopados com cério (III) encapsulados com TiO<sub>2</sub>. Zurba NK, Ferreira JMF. PT 105395.

Método ultra-sónico de fabricação de nanoarames, nanofios, nanohastes e/ou nanobastões luminescentes de aluminatos dopados com cério (III) e co-dopados com outros iões Lantanídeos. Zurba NK, Ferreira JMF. PT 105107.

Processo de obtenção de grés porcelânico com acção antimicrobiana Seabra MP, Grave LC, Labrincha JÁ. PT 105240.

Pastas celulósicas modificadas, método de preparação por processamento por alta pressão e respectivas aplicações. Evtuguin DV, Saraiva JMA, Figueiredo dos Santos AFB. PT 105422.

# **Projects finished during '1o**

NMP3-CT-2007-SSA 032308 NANOCOFC - Nanotechnologies and Nanosciences, Knowledge Based Multifunctional Materials, New Production Processes and Devices Principal Researcher: Fernando Manuel Bico Marques Status: Participante Beginning Date: 01-11-2006 / 36 Months Funding: European Commission / UA Value: 32.650,00 STREP 033410 MATSILC-Novel materials for silicate based fuel cells Principal Researcher: Jorge Frade Status: Participante Beginning Date: 01-12-2006 / 36 Months Funding: EC-6º PROGRAMA QUADRO/ UA Value: 252.000,00

NMP3-CT-2005-011783 MULTIPROTECT - Advanced Environmentally Friendly Multifunctional Corrosion Protection by Nanotechnology Principal Researcher: Mikhail Zheludkevich Status: Participante Beginning Date: 01-03-2005 / 48 Months Funding: European Commission / UA Value: 282.203,00

> EuropeAid/120707/C/SER/Br nº PAIIPME-ATI-POA2-022 Principal Researcher: Rui Ramos Ferreira e Silva Status: Beginning Date: 01-02-2009 / 2 Months Funding: PAIIPME , Brasil / UA Value: 11.340,00

> EuropeAid/120707/C/SER/Br nº PAIIPME-ATI-POA2-050 Principal Researcher: Rui Ramos Ferreira e Silva Status: Beginning Date: 2009 / Months Funding: PAIIPME, Brasil / UA Value: 5.410,00

POCI/CTM/60064/2004 ELECTROPOLYMERIZED COATING USED AS PRE-TREATMENTS FOR ALUMINIUM ALLOYS Principal Researcher: Mário Guerreiro da Silva Ferreira Status: Participante Beginning Date: 15-07-2005 / 36 Months Funding: FCT / UA Value: 17.276,00

PTDC/FIS/65233/2006 Ternary and quaternary nitride alloys for lattice matched heterostructures: novel materials for high efficiency field effect transistors and optoelectronic devices Principal Researcher: Sérgio Manuel Sousa Pereira Status: Participant Beginning Date: 01-04-2007 | 36 Months Funding: FCT | UA Value (€): 59.520,00

> PTDC/EQU-ERQ/66045/2006 Use of membrane reactores in the water-gas shift reaction Principal Researcher: Zhi Lin Status: Participant Beginning Date: 01-09-2007 | 36 Months Funding: FCT | UA Value (€): 25.919,00

PTDC/CTM/65667/2006 Synthesis and characterization of multiferroic nanostructures synthetised via novel non-aqueous sol-gel routes Principal Researcher: Nicola Allessandro Pinna Status: Proponent Beginning Date: 01-11-2007 | 36 Months Funding: FCT | UA Value (€): 151.000,00

PTDC/CTM/73243/2006 Nanostructured Photoluminescent rare-earth nanotubes and microporous silicates Principal Researcher: João Carlos Matias Celestino Gomes da Rocha Status: Proponent Beginning Date: 01-12-2007 | 36 Months Funding: FCT | UA Value (€): 60.456,00

# international projects


PTDC/QUI/71198/2006 Ansa-bridged organorhenium(VII) oxides and their application as homogeneous and heterogeneous catalysts Principal Researcher: Isabel Maria Sousa Gonçalves Status: Proponent Beginning Date: 01-01-2008 | 36 Months Funding: FCT | UA Value (€): 42.372,00

PTDC/QUI/65805/2006 Water nanodrops in microporouse and inorganic-organic hybrid materials Principal Researcher: João Carlos Matias Celestino Gomes da Rocha Status: Proponent Beginning Date: 01-01-2008 | 36 Months Funding: FCT | UA Value (€): 61.000,00

PTDC/CTM/72093/2006 Self-patternable organic/inorganic hybrids for low cost integrated optics devices Principal Researcher: Maria Rute de Amorim e Sá Ferreira André Status: Proponent Beginning Date: 01-01-2008 | 36 Months Funding: FCT | UA Value (€): 74.746,00

PTDC/QUI/67712/2006 Nanochemistry of magnetic/luminescent composites for in vitro medical diagnosis applications Principal Researcher: Tito da Silva Trindade Status: Proponent Beginning Date: 01-01-2008 | 36 Months Funding: FCT | UA Value (€): 40.900,00

PTDC/CTM/73643/2006 Developing Novel Microporous Powders and Membranes Principal Researcher: Zhi Lin Status: Proponent Beginning Date: 01-02-2008 | 36 Months Funding: FCT | UA Value (€): 78.000,00

POCI/CTM/55648/2004 PERIODIC MESOPOROUS ORGANIC-INORGANIC HYBRIDS Principal researcher: Paula Celeste da Silva Ferreira Status: Proponente Beginning Date: 01-05-2006/ 36 Months Funding: FCT / UA value (€): 55.000,00

A-14/07 Principal Researcher: Maria Helena Figueira Vaz Fernandes Status: Participante Beginning Date: october 2006/ 48 Months Funding: CRUP/ UA Value: 2.500,00

Programa PESSOA Luso-Frances Functional studies of the SOUL/ HBP family of heme.binding proteins Principal Researcher: Brian James Goodfellow Status: Proponente Beginning Date: 01-01-2008/ 36 Months Funding: FCT/ UA Value: 6.000,00

CIMAGO 14/06 Principal Researcher: Iola Melissa Fernandes Duarte Status: Proponente Beginning Date: 01-09-2006/ 36 Months Funding: CIMAGO/ UA Value: 5.000,00

Estudo sobre o melhoramento da interacção tinta/papel na impressão offset e ink/jet Principal Researcher: Dmitry Victorovitch Evtyugin Status: Participante Beginning Date: 01-07-2007/ 24 Months Funding: RAIZ - Instituto de Investigação da Floresta e Papel/ UA Value: 25.000,00

### other national

Produção de biocompósitos de valor acrescentado a partir do engaço e do folhelho da uva Principal Researcher: Dmitry Victorovitch Evtyugin Status: Participante Beginning Date: 01-04-2009 / 9 Months Funding: TAVFER/ UA Value: 13.200,00

# **Projects in progress during '11**

Marie Curie FP7-PEOPLE-2009-RG-256509 Oxalkanes - Sustainable catalytic oxidation of alkanes, FP7 Marie Curie Reintegration grant Principal Researcher: Ana Rosa Silva Status: Proponent Beginning Date: 01-04-2010 | 24 Months Funding: EU | UA Value (€): 45.000,00

> ENERMATaa Principal Researcher: João Rocha Status: Participant Beginning Date: 11-01-2010 | 24 Months Funding: EU | UA Value (€): 498.709,45

INTAS-05-1000008-8091 Polarization-driven self-assemply of organics and biomaterials using ultrathin ferroelectric polymers Principal Researcher: Andrei Kholkin Status: Proponente Beginning Date: 01-11-2006/ 30 Months Funding: INTAS/ UA Value: 16.000,00

NMP3-CT-2006-32616 MULTICERAL-Multifunctional Ceramics Layers with High Electro-magnetoelastic couplin in complex geometries Principal Researcher: Andrei Kholkin Status: Proponente Beginning Date: 01-11-2006/36 Months Funding: FP7 - European Commission/ UA Value: 263.000,00

> IP515960 ULCOS- Ultra Low CO2 Steelmaking Principal Researcher: Jorge Frade Status: Participante Beginning Date: 31-10-2004 / 70 Months Funding: European Commission / UA Value: 415.000,00

NMR3-LA-2008-214261 Multi-level protection of materials for vehicles by 'Smart' nanocontainers (MUST) Principal Researcher: Mikhail Zheludkevich Status: Participante Beginning Date: 01-06-2008 / 48 Months Funding: European Commission / UA Value: 824.769,00

RFSR-CT-2008-00028 Prediction of the kinetics of self-repaired of forming induced defects on thin functional primers for advances automotive applications (KINSREP) Principal Researcher: Mikhail Zheludkevich Status: Participante Beginning Date: 01-07-2008 / 36 Months Funding: European Commission / UA Value: 160.341,00

CP-IP 228589-2 AFORE – Forest Biorefinery: Added Value Chemicals and Polymers by new integrated separation, fractionation and upgrading technologies Principal Researcher: Armando Silvestre Status: Participante Beginning Date: September 2009/ 48 Months Funding: FP-7/ UA Value: 674.687,00

> 228802 SUNPAP - Scale-up of Nanoparticles in Modern Papermarking Principal Researcher: Carlos de Pascoal Neto Status: Participante Beginning Date: June 2009/ 36 Months Funding: FP7/ UA Value: 226.000,00 B5–1000/03/000339 DOLCETA - Development of on-line consumer education tools for adults Principal Researcher: Maria Clara Ferreira Magalhães Status: Participante Beginning Date: December 2003

Funding: European Commission/ UA Value: 120.000,00

# international projects

PTDC/CTM/64357/2006 NOVEL LAYERED FERRITE MATERIALS WITH MIXED IONIC-ELECTRONIC CONDUCTIVITY FOR APPLICATIONS IN ALTERNATIVE ENERGY SOURCES Principal Researcher: Vladislav Kharton Status: Participant Beginning Date: 01-01-2008 / 36 Months Funding: FCT/ UA Value: 76.760,00

PTDC/CTM/098486/2008 Nanocell Principal Researcher: Fernando Manuel Bico Marques Status: Proponente Beginning Date: 01-01-2010 / 36 Months Funding: FCT/ UA Value: 122.000.00

PTDC/CTM/098361/2008 Nanotubes and Nanowires based hybrid nanostructures Principal Researcher: Nicola Allessandro Pinna Status: Participant Beginning Date: 01-04-2010 | 36 Months Funding: FCT | UA Value (€): 180.000,00

NANO/NMed-SD/0140/200 Integrated lab on chip platforms for medical diagnosis Principal Researcher: Tito da Silva Trindade Status: Participant Beginning Date: 01-08-2009 | 24 Months Funding: FCT/CSIC | UA Value (€): 20.040,00

PTDC/QUI/64770/2006 Catalytic oxidation reactions by transition metal complexes confined into mesoporous structured solids Principal Researcher: Ana Rosa Silva Status: Proponent Beginning Date: 01-02-2009 | 36 Months Funding: FCT | UA Value (€): 64.638,00

PTDC/QUI/65142/2006 Recycling antimalarials: rational design of novel 8-aminoquinoline analogues with gametocytocidal and blood-schizontocidal activity Principal Researcher: José Richard Batista Gomes Status: Participant Beginning Date: 01-01-2009 | 36 Months Funding: FCT | UA Value (€): 0,00

PTDC/CTM/65718/2006 Fabrication of ordered mesoporous carbon networks for catalysts support Principal Researcher: José Richard Batista Gomes Status: Participant Beginning Date: 02-01-2008 | 36 Months Funding: FCT | UA Value (€): 0,00

PTDC/QUI-QUI/100998/2008 Development of high-resolution 1H solid-state NMR methods and applications on materials and molecules of biological interest Principal Researcher: Luís Miguel Monteiro Mafra Status: Participant Beginning Date: 01-01-2010 | 36 Months Funding: FCT | UA Value (€): 97.368,00

PTDC/EQU-EQU/099423/2008 Intelligent Design of Mesoporous Organosilicas for Adsorptive Separation Processes Principal Researcher: José Richard Batista Gomes Status: Participant Beginning Date: 01-01-2010 | 36 Months Funding: FCT | UA Value (€): 68.232,00

PTDC/QUI-QUI/098098/2008 Nano-sized Functional Metal-Organic Frameworks Based on Lanthanide Polyphosphonates Principal Researcher: Filipe Alexandre Almeida Paz Status: Proponent Beginning Date: 01-01-2010 | 36 Months Funding: FCT | UA Value (€): 148.620,00

PTDC/CTM/108975/2008 Preparation and photoluminescence features of white-emitting single-phased phosphors for light emitting diodes Principal Researcher: Lianshe Fu Status: Proponent Beginning Date: 01-01-2010 | 36 Months Funding: FCT | UA Value (€): 63.760,00

### national projects

Híbridos Orgânicos-Inorgânicos com Propriedades de Emissão Optimizadas para Aplicação na Nova Geração de Comunicações Ópticas Principal Researcher: Luís António Ferreira Martins Dias Carlos Status: Proponent Beginning Date: 01-03-2010 | 36 Months Funding: FCT | UA Value (€): 77.878,00 PTDC/CTM/101453/2008 Novel light emitting heterostructures with plasmonic coupling to metal nanocrystals Principal Researcher: Sérgio Manuel Sousa Pereira Status: Proponent Beginning Date: 01-01-2010 | 36 Months Funding: FCT | UA Value (€): 95.000,00 PTDC/FIS/100448/2008 Free-charge carrier properties and doping mechanisms of InN-based materials Principal Researcher: Sérgio Manuel Sousa Pereira Status: Participant Beginning Date: 01-01-2010 | 36 Months Funding: FCT | UA Value (€): 21.720,00 PTDC/QUI-QUI/098892/2008 Study of intermolecular interactions in alternative solvents: A NMR based contribution to sustainable chemistry Principal Researcher: Luís Mafra Status: Participant Beginning Date: 01 -01-2010 | 36 Months Funding: FCT | UA Value (€): 0,00 PTDC/FIS/104310/2008 High-pressure synthesis and structure determination of novel nanostructured materials Principal Researcher: Leonel Marques Vitorino Joaquim Status: Proponent Beginning Date: 01-05-2010 | 36 Months Funding: FCT | UA Value (€): 163.000,00 PTDC/QUI/65647/2006 Novas matrizes sólidas quelantes com hidroxipirimidinonas imobilizadas para aplicações ambientais e biológicas Principal Researcher: João Carlos Matias Celestino Gomes da Rocha Status: Participant Beginning Date: 01-12-2008 | 36 Months Funding: FCT | UA Value (€): 9.300,00 RNRMN Rede Nacional de Ressonância Magnética Nuclear Principal Researcher: João Carlos Matias Celestino Gomes da Rocha Status: Participant Beginning Date: 01-01-2010 | 36 Months Funding: FCT | UA Value (€): 209.364,00 FCT/CHINA-2010/2012 Síntese de Peneiros Moleculares com Volume Grande do Poro e suas Propriedades como Armazenadores de Hidrogénio Principal Researcher: Zhi Lin Status: Proponent Beginning Date: 01-07-2010 | 36 Months Funding: FCT | UA Value (€): 22.380,00 **EULANEST Network** Magnetotransduction: development of magnetic nanoparticles-viral vector complexes for therapeutic gene delivery in the senile brain Principal Researcher: Tito da Silva Trindade Status: Participant Beginning Date: 25-06-2010 | 24 Months Funding: FCT | UA Value (€): 39.900,00 PTDC/CTM-NAN/112168/2009 Modelação de complexos de lantanídeos a emitir no visível para aplicação em Díodos Orgânicos Emissores de Luz - Vermelho. Verde e Azul: uma metodologia computacional e experimental Principal Researcher: Mariela Nolasco Status: Participant Beginning Date: 01-02-2011 | 24 Months Funding: FCT | UA Value (€): 62.526,00 PTDC/CTM-BPC/112774/2009

Deposição Bio-inspirada de um Biomineral sobre Biopolímeros e sobre Híbridos de Biopolímero/siloxano para Aplicações Biomédicas Principal Researcher: Luís António Ferreira Martins Dias Carlos Status: Proponent Beginning Date: 01-01-2011 | 36 Months Funding: FCT | UA Value (€): 22.668,00

PTDC/CTM/101324/2008

PTDC/CTM-NAN/110776/2009 Hierarchical Nanostructures for Lithium-Ion Batteries Principal Researcher: Nicola Allessandro Pinna Status: Participant Beginning Date: 01-01-2011 | 36 Months Funding: FCT | UA Value (€): 148.415,00

PTDC/QUI-QUI/109914/2009 Theoretical study of silicate chemistry in the synthesis of nanoporous materials Principal Researcher: José Richard Batista Gomes Status: Proponent Beginning Date: 01-02-2011 | 36 Months Funding: FCT | UA Value (€): 54.402,00

PTDC/CTM/71643/2006 Novel Aurivillus oxides for microelectronic applications Principal Researcher: Andrei Kholkin Status: Participante Beginning Date: 16-02-2008/ 36 Months Funding: FCT/ UA Value: 72.000,00

PTDC/CTM/68614/2006 Shear-induced solidification studies on polymers and polymer-clay nanocomposites Principal Researcher: Andrei Kholkin Status: Participante Beginning Date: 02-01-2008/ 36 Months Funding: FCT/ UA Value: 20.000,00

Nano/Nmed-SD/0156/2007 Smart joint implants using bionanocomposites Principal Researcher: Andrei Kholkin Status: Participante Beginning Date: 01-10-2009/ 24 Months Funding: FCT/ UA Value: 65.000,00

PTDC/CTM/81442/2006 Origin of polar state in relaxors via Scanning Probe Microscopy Principal Researcher: Andrei Kholkin Status: Proponente Beginning Date: 15-05-2007/ 36 Months Funding: FCT/ UA Value: 119.724,00

PTDC/CTM/73367/2006 Colossal permittivity perovskite films by chemical solution deposition methods for microelectronic and sensor applications Principal researcher: Alying Wu Status: Proponente Beginning Date: 01-03-2008 / 36 Months Funding: FCT/ UA value (€): 85.000,00

PTDC/QUI/72584/2006 Photocatalytic reduction of carbon dioxide into valuable hydrocarbon products Principal researcher: Paula Celeste da Silva Ferreira Status: Proponente Beginning Date: 01-01-2008/ 36 Months Funding: FCT/ UA value (€): 41.200,00

PTDC/CTM/71643/2006 Novel Aurivillius Oxides for microelectronic applications Principal researcher: Maria Elisabete Jorge Vieira Costa Status: Proponente Beginning Date: 01-02-2008/ 36 Months Funding: FCT/ UA value (€): 72.000,00

PTDC/CTM/64805/2006 Statics and dynamics of hight polarizable ultra-thin films and nano-layered superlattices Principal researcher: Paula Maria Lousada Silveirinha Vilarinho Status: Participante Beginning Date: February 2008/ 36 Months Funding: FCT/ UA value (€): 44.663,00

PTDC/CTM/67575/2006 PROCESSING AND CHARACTERIZATION OF MULTIFERROIC CERAMICS FOR SENSOR AND ACTUACTOR APPLICATIONS Principal researcher: Paula Maria Lousada Silveirinha Vilarinho Status: Participante Beginning Date: 02-01-2008/ 36 Months Funding: FCT/ UA value (€): 25.001,00 PTDC/EQU-EQU/099423/2008 Intelligent Design of Mesoporous Organosilicas for Adsorptive Separation Processes Principal researcher: José Richard Batista Gomes Status: Participante Beginning Date: 01-01-2010 / 36 Months Funding: FCT/ UA value (€): 68.232,00

> PTDC/CTM/98130/2008 Design of multifunctional films from porous thin films Principal researcher: Paula Celeste da Silva Ferreira Status: Proponente Beginning Date: 01-01-2010/ 36 Months Funding: FCT/ UA value (€): 100.000,00

NANO-NMed-SP/0156/2007 Smart joint implants using bionanocomposites – SIMBIO Principal researcher: Paula Maria Lousada Silveirinha Vilarinho Status: Participante Beginning Date : 01-03-2009/ 35 Months Funding: FCT/ UA value (€):

PTDC/CTM/104186/2008 Ferroelectric - carbon nanotube (CNT) composites towards the fabrication of advanced functional devices Principal researcher: Paula Maria Lousada Silveirinha Vilarinho Status: Proponente Beginning Date : 01-01-2010/ Months 36

PTDC/CTM/108319/2008 Low temperature synthesis of functional thin films towards compatibility with low cost substrates Principal researcher: Paula Maria Lousada Silveirinha Vilarinho Status: Proponente Beginning Date : 01-01-2010/ Months 36

> PTDC/CTM/100468/2008 Structural and chemical characterization at the nanometer scale Principal Researcher: Marc Willinger Status: Proponent Beginning Date: 01-03-2010 | 36 Months Funding: FCT | UA Value (€): 165.000,00

PTDC/CTM/099415/2008 Multiferroics and magnetoelectrics for spintronics: barriers and interfaces Principal Researcher: Vitor Brás de Sequeira Amaral Status: Participante Beginning Date: 01-02-2010/ 36 Months Funding: FCT/ UA Value: 43.680,00

PTDC/FIS/105416/2008 MULTIFOX: Nanometric Probing and Modification of Multiferroic Oxides Principal Researcher: Vitor Brás de Sequeira Amaral Status Proponente Beginning Date: 01-02-2010 / 36 Months Funding: FCT / UA Value: 109.512,00

CERN/FP/83643/2008 Research on Magnetic and Multiferroic Oxides using Radioactive Isotopes at ISOLDE-CERN Principal Researcher: Vitor Brás de Sequeira Amaral Status Proponente Beginning Date: 02-01-2009 / 12 Months Funding: FCT / UA Value: 20.988.00

CERN/FP/109357/2009 Research on Magnetic and Multiferroic Materials using Radioactive Isotopes at ISOLDE-CERN Principal Researcher: Vitor Brás de Sequeira Amaral Status Proponente Beginning Date: 01-02-2010 / 12 Months Funding: FCT / UA Value: 17.216,00

> CERN/FP/109325/2009 Local probe studies on Metal/Oxide junctions Principal Researcher: Armando António C. S. Lourenço Status: Participante Beginning Date: 01-01-2010/ 12 Months Funding: FCT / UA Value: 2.520,00

IS-487 Study of Local Correlations of Magnetic and Multiferroic Compounds Principal Researcher: Vitor Brás de Sequeira Amaral Status: Proponente Beginning Date: 01-01-2009 / 36 Months I-81

Radioactive probe studies of coordination mechanisms of heavy metal ions from natural waters to functionalized magnetic nanoparticles Principal Researcher: Vitor Brás de Sequeira Amaral Status: Proponente Beginning Date: 01-01-2009 / 36 Months Funding: FCT/ UA Value:

NANO/NMed-AT/0042/2007 Avanço na área de entrega de fármacos: terapias dirigidas combinadas no tratamento do cancro da mama e leucemia (a rede Onco TargetNanoMed) Principal Researcher: Joaquim Vieira Status: Participante Beginning date: 01-07-2009 / 24 Months Funding: FCT /UA Value: 14.000,00

RME – REDE/1509/RME/2005 Rede Nacional de Microscopia Electrónica Principal Researcher: Joaquim Vieira Status: Proponente Beginning date: 01-01-2009/ 36 Months Funding: FCT /UA Value: 622.661,73

PTDC/CTM/66041/2006 Sensing the micro-distribution of chemical species in solution close to the active metal Principal Researcher: António Alexandre da Cunha Bastos Status: Proponente Beginning Date: 01-01-2008 / 36 Months Funding: FCT / UA Value: 82.425,00

PTDC/CTM/72223/2006 Anodic films on light metals obtained by novel high-voltage pulsed anodizing technique Principal Researcher: Mário Guerreiro da Silva Ferreira Status: Proponente Beginning Date: 01-01-2008 / 36 Months Funding: FCT / UA Value: 107.202,00

PTDC/CTM/65632/2006 Self-healing protective coating with 'intelligent' nanoreservoirs of corrosion inhibitors Principal Researcher: Mikhail Zheludkevich Status: Proponente Beginning Date: 01-03-2008 / 36 Months Funding: FCT / UA Value: 82.600,00

PTDC/CTM/66195/2006 Designing ultra-fine textured microstructures by laser floating zone – LaFlorZone Principal Researcher: Rui Ramos Ferreira e Silva Status: Participante Beginning Date: 01-01-2008 / 36 Months Funding: FCT / UA Value: 115.697,00

PTDC/EME-TME/100689/2008 Principal Researcher: Filipe Oliveira Status: Participante Beginning Date: 01-03-2010 / 36 Months Funding: FCT / UA Value: 124.999,00

COLL-CT-2006 030338 ADOPTIC ADOPTIC - ADDITIVE OPTIMISATION FOR IMPROVED CERAMICS Principal Researcher: José Maria da Fonte Ferreira Status: Participant Beginning Date: 01-09-2006/ 36 Months Funding: European Commission/ UA Value: 74.040,13

PTDC/CTM/66302/2006 DEVELOPMENT OF A SELF-FLOW REFRACTORY CASTABLE WITHOUT CEMENT FOR MONOLITHIC APPLICATIONS Principal Researcher: Ana Maria Segadães Status: Participante Beginning Date: 07-01-2007/ 36 Months Funding: FCT/ UA Value: 7.500,00

PTDC/CTM/72318/2006 Ecopigments - Development of novel inorganic pigments from industrial wastes Principal Researcher: João António Labrincha Batista Status: Proponente Beginning Date: 01-01-2008/ 36 Months Funding: FCT/ UA Value: 62.880,00

PTDC/ECM/72104/2006 Study of functional mortars for a sustainable construction Principal Researcher: Victor Miguel de Sousa Ferreira Status: Proponente Beginning Date: 01-01-2007/ 36 Months Funding: FCT/ UA Value: 81.600,00

PTDC/CTM/65243/2006 EXREACT - Mitigação de reacções deletérias expansivas internas em estruturas de betão Principal Researcher: João António Labrincha Batista Status: Participante Beginning Date: 01-01-2008/ 36 Months Funding: FCT/ UA Value: 16.800,00

> PTDC/ECM /102154/2008 Principal Researcher: Victor Miguel de Sousa Ferreira Beginning Date: 01-01-2010 / 36 Months Funding: FCT/ UA Value: 23.400,00

> PTDC/ECM /100234/2008 Principal Researcher: Victor Miguel de Sousa Ferreira Beginning Date: 01-02-2010 / 36 Months Funding: FCT/ UA Value: 63.876,00

> > FCT/CNPq – biénio 2009-2010 Principal Researcher: Ana Maria Segadães Status: Proponente Beginning Date: 01-09-2009 / 24 Months Funding: FCT/ UA Value: 9.000,00

PTDC/CTM/102141/2008 Novos Vidros e compósitos vidro/ nanoparticulas cerâmicas sintetizáveis a baixas temperaturas Principal Researcher: Maria Helena Figueira Vaz Fernandes Status: Participante Beginning Date: 01-01-2010/ 36 Months Funding: FCT/ UA Value: 37.057,00

PTDC/QUI/68472/2006 Controlled chemical modification of polysaccharides for the development of novel materials/ Modificação químicas controlada de polissacarídeos para o desenvolvimento de novos materiais Principal Researcher: Carmen Sofia da Rocha Freire Barros Status: Participante Beginning Date: 01-01-2008 / 36 Months Funding: FCT/ UA Value: 69.300,00

> PTDC/CTM/68614/2006 Shear Induced solidification studies in polymers and nanocomposites Principal Researcher: José Martins Status: Proponente Beginning Date: June 2008 / 36 Months Funding: FCT/ UA Value: 12.931,00

PTDC/EQU-EQU/100476/2008 Síntese e Caracterização de Novas Membranas de Niobiossilicatos e Titanosilicatos Microporosos e sua Aplicação na Separação de Misturas Contendo Hidrogénio Principal Researcher: Carlos Manuel Santos da Silva Status: Proponente Beginning Date: 2010/ 36 Months Funding: FCT/ UA Value: 48.800,00

> PTDC/CTM/67444/2006 Reversible Diels-Alder furan click chemistry at the service of novel functional materials based on renewable resources Principal Researcher: Alessandro Gandini Status: Proponente Beginning Date: 01-01-2009/ 36 Months Funding: FCT/ UA Value: 73.440,00

PTDC/CTM/71491/2006 OLIVEPOL – Espumas de Poliuretano e Compósitos Termoplásticos baseados em caroço de azeitona oxipropilado. Principal Researcher: Alessandro Gandini Status: Participante Beginning Date: January 2009/ 35 Months Funding: FCT/ UA Value: 28.960,00

> PTDC/QUI/101058/2008 Development of new polyesters derived from 2,5-furandicarboxylic acid Principal Researcher: Armando Silvestre Status: Proponente Beginning Date: 01-01-2010 / 36 Months Funding: FCT/ UA Value: 88.458,00

PTDC/AAC-AMB/101050/2008 Biopolymers production as a new concept on wastewater treatment - POLIBIO Principal Researcher: Luísa Alexandra Seuanes Serafim Leal Status: Participante Beginning Date: 01-01-2010 / 36 Months Funding: FCT/ UA Value: 152.976,00

PTDC/AAC-AMB/100790/2008 MICROBIAL CONTRIBUTION TO THE VALORIZATION OF WASTE/BY-PRODUCTS FROM BIOFUELS PRODUCTION Principal Researcher: Luísa Alexandra Seuanes Serafim Leal Status: Participante Beginning Date: 01-02-2010 / 36 Months Funding: FCT/ UA Value: 0,00

PTDC/AGR-AAM/104911/2008 Principal Researcher: Dmitry Victorovitch Evtyugin Status: Participante Beginning Date: 01-01-2010 / 48 Months Funding: FCT/ UA Value: 67.728,00

PTDC/QUI-QUI/100044/2008 Principal Researcher: Dmitry Victorovitch Evtyugin Status: Participante Beginning Date: 01-01-2010 / 48 Months Funding: FCT/ UA Value: 127.332,00

PTDC/EQU-FTT/102166/2008 Sweetening of natural gas using ionic liquids Principal Researcher: João Manuel da Costa e Araújo Pereira Coutinho Status: Proponente Beginning Date: 01-01-2010 / 36 Months Funding: FCT/ UA Value: 78.000,00

PTDC/QUI/72903/2008 Anchoring Basic Parameters for Fundamental Predictive Models in Liquid Salt Systems Principal Researcher: João Manuel da Costa e Araújo Pereira Coutinho Status: Proponente Beginning Date: 01-01-2009/ 36 Months Funding: FCT/ UA Value: 76.388,00

PTDC/EQU-FTT/65252/2006 Vapour Liquid Equilibrium of Pure Ionic Liquids and their Mixtures with Organic Solvent Principal Researcher: João Manuel da Costa e Araújo Pereira Coutinho Status: Proponente Beginning Date: 01-10-2007/ 36 Months Funding: FCT/ UA Value: 104.970,00

ERA-IB/BIO/0001/2008-ERA-NOEL Novel Enzyme Tools for Production of Functional Oleochemicals from unsaturated lipids (ERA-NOEL) Principal Researcher: Armando Silvestre Status: Participante Beginning Date: March 2009/ 36 Months Funding: ERA-NET/FCT/ UA Value: 129.943,00

PTDC/QUI/66523/2006 A Nuclear Magnetic Resonance (NMR)-based metabonomic study of health disorders of foetus and mother during pregnancy: towards biochemical characterisation and early diagnostics Principal Researcher: Ana Maria Pissarra Coelho Gil Status: Participante Beginning Date: 15-01-2008/ 36 Months Funding: FCT/ UA Value: 64.960,00

PTDC/QUI/64203/2006 Structural and functional studies of the soul/hbp family of heme-binding proteins Principal Researcher: Brian James Goodfellow Status: Proponente Beginning Date: 01-01-2008/ 36 Months 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 Principal Researcher: Iola Melissa Fernandes Duarte Status: Proponente Beginning Date: 15-01-2008/ 36 Months Funding: FCT/ UA Value: 59.200,00

PTDC/SAU-BEB/66896/2006 Implantable scaffolds for local osteo-sarcoma chemotherapy Principal Researcher: Rui Nunes Correia Status: Proponente Beginning Date: 01-09-2007/ 36 Months PTDC/QUI/68582/2006 Molecular design of novel aza-bridged calixarene receptors for medicinal chemistry: encapsulation of lanthanide ions and resolution of racemic druas Principal Researcher: Vitor Manuel Sousa Félix Status: Proponente Beginning Date: 01-01-2008/ 36 Months Funding: FCT/ UA Value: 24.060,00 PTDC/QUI-QUI/101022/2008 Development of azacalix(hetero) arene transporters for mediated anionic flux across membranes: a novel approach for studying ionic passive diffusion Principal Researcher: Vitor Manuel Sousa Félix Status: Proponente Beginning Date: 2010/ 36 Months Funding: FCT/ UA Value: 61.060,00 PTDC/QUI/69302/2006 Principal Researcher: Susana Braga Status: Proponente Beginning Date: 25-07-2009/ 17 Months Funding: FCT/ UA Value: 32.956,00 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 Principal Researcher: José Maria da Fonte Ferreira Status: Proponent Beginning Date: 01-01-2005/ 36 Months Funding: FCT/ UA Value: 29.510,40 PTDC/CTM/73030/2006 Polarization-driven self-assembly of organic and biomaterials Principal Researcher: Andrei Kholkin Status: Proponente Beginning Date: 01-03-2008/ 36 Months Funding: FCT/ UA Value: 141.000,00 PTDC/CTM/69316/2006 Multiferroic, magnetoelectric and metallic micro and nanocomposites base don electroactive polymers Principal Researcher: Andrei Kholkin Status: Participante Beginning Date: 01-01-2009/ 36 Months Funding: FCT/ UA Value: 10.000,00 PTDC/FIS/108025/2008 NOLEAD: Novel lead-free ferroelectric films by PLD for optoelectronics Principal Researcher: Andrei Kholkin Status: Participante Beginning Date: 02-01-2010/ 36 Months Funding: FCT/ UA Value: 51.966,00

E-131/10 Nanomateriais multifuncionais com propriedades ópticas e magnéticas Principal Researcher: Luís António Ferreira Martins Dias Carlos Status: Proponent Beginning Date: 2010 | 12 Months Funding: CRUP | UA Value (€): 5.000,00

Designer catalytic materials for selective and greener tandem redox/coupling processes Principal Researcher: Ana Rosa Silva Status: Proponent Beginning Date: 01-03-2010 | 24 Months Funding: CRUP | UA Value (€): 5.000,00

Study of the constrained sintering of high Q low loss microwave dielectric thick films Principal researcher: Paula Maria Lousada Silveirinha Vilarinho Status: Participante Beginning Date : 01-01-2009/ 24 Months Funding: CRUP/ UA value (€): 2.500,00

Acção Integrada

## other national

Metal carbonyl intercalated anion exchangers as drug delivery systems Principal Researcher: Martyn Pillinger Status: Proponent Beginning Date: 01-03-2010 | 12 Months Funding: CICECO/ UA | UA Value (€): 15.000,00

Papéis de alto desempenho à impressão Principal Researcher: Dmitry Victorovitch Evtyugin Status: Participante Beginning Date: 01-10-2009 / 24 Months Funding: QREN / UA Value:189.676,00

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 Principal Researcher: Dmitry Victorovitch Evtyugin Status: Proponente Beginning Date: 01-09-2008/ 19 Months Funding: Sonae - Indústria de Revestimentos SA/ UA Value: 29.000,00

E-85/09

Prediction of wax precipitation in flow assurance: Identification of limitations of current models and their improvement Principal Researcher: João Manuel da Costa e Araújo Pereira Coutinho Status: Proponente Beginning Date: 01-01-2009 / 24 Months Funding: CRUP/ UA Value: 4.000,00

#### **Sponsors**



