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PAPER

Sintering behavior of lanthanide-containing glass-ceramic sealants for solid oxide fuel cells

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This article reports on the influence of different lanthanides (La, Nd, Gd and Yb) on sintering behavior of alkaline-earth aluminosilicate glass-ceramic sealants for their application in solid oxide fuel cells (SOFCs). All the glasses have been prepared by the melt-quench technique. The *in situ* follow up of sintering behavior of glass powders has been done by a high temperature-environmental scanning electron microscope (HT-ESEM) and a hot-stage microscope (HSM) while the crystalline phase evolution and assemblage have been analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). All the glass compositions exhibit a glass-in-glass phase separation followed by two stage sintering resulting in well sintered glass powder compacts after heat treatment at 850 °C for 1 h. Diopside (CaMgSi₂O₆) based phases constituted the major crystalline part in glass-ceramics followed by some minor phases. The increase in lanthanide content in glasses suppressed their tendency towards devitrification, thus resulting in glass-ceramics with a high amount of residual glassy phase (50-96 wt%) which is expected to facilitate their self-healing behavior during SOFC operation. The electrical conductivity of the investigated glass-ceramics varied between (1.19 and 7.33) $\times 10^{-7}$ S cm⁻¹ (750–800 $^{\circ}$ C) while the coefficient of thermal expansion (CTE) varied between (9.4 and 11.2) $\times 10^{-6}$ K⁻¹ (200–700 $^{\circ}$ C). Further experimentation with respect to the long term thermal and chemical stability of residual glassy phase under SOFC operation conditions along with high temperature viscosity measurements will be required in order to elucidate the potential of these glass-ceramics as self-healing sealants.

1. Introduction

Sealing technology is an important issue with respect to the successful development and commercialization of various high temperature electrochemical devices that function by maintaining two separate gaseous streams and causing reactions to occur at the surfaces of conductive layers of adjacent components. Typical examples of such electrochemical devices include solid oxide fuel cells (SOFCs), solid oxide electrolyzer cells (SOECs), syngas membrane reactors, oxygen generators, *etc.*

One type of electrochemical device which has received, and continues to receive, considerable attention is SOFC. SOFC functions due to an oxygen ion gradient that develops across a solid–electrolyte membrane when one side is exposed to an oxygen-rich environment and the other side to a reducing gas. In order to maintain this gradient, and thereby maximize the performance of the device, the electrolyte and the joint that seals this membrane to the device chassis must be hermetic. Although these basic concepts of SOFC technology have been known for many years, these energy conversion devices have not yet proven their economic viability. One of the most arduous steps towards commercialization of SOFC is the development of a hermetic seal between the ceramic and metallic components such that the resulting joint remains rugged and stable over the lifetime of the stack. The metal–ceramic seals, in particular, pose a significant challenge because of their severe functional requirements as well as difficulty in selection of material and associated processing optimization.

The majority of SOFC seal development has focused on bonded, rigid seals, primarily glasses and glass-ceramics, which essentially "glue" the stack components together. The glass seals are designed to soften, and flow above the SOFC operating temperature to provide hermetic seals by mechanical/ chemical bonding. On cooling back down to operating temperature, the glass crystallizes to form a rigid, bonded seal. A principal advantage of glass seals is that the glass composition can be tailored to optimize the properties like CTE, mechanical strength, electrical resistance, *etc.* The importance of glass/glass-ceramic seals in different technological

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applications can be realized from the fact that apart from a significant number of research articles and patents that have been published on this subject so far, the last 5 to 6 years have witnessed seven review articles dedicated to sealing technology and glass/glass-ceramic sealing, mainly highlighting different issues related to sealing in SOFC.¹⁻⁷

Sintering behavior plays a crucial role in seal development for SOFC because glass is usually applied on the surface (ceramic or metallic) to be sealed using glass powder mixed with a binder which undergoes sintering before the formation of a continuous phase of glass-ceramic. In general, two different trends can be observed related to the sintering and crystallization behavior of the glasses: (i) the onset of crystallization (T_c) occurs after the final sintering stage. Thus, under such circumstances, sintering and crystallization are independent processes and the resultant glass-ceramic is well sintered and mechanically strong (desired trait for a suitable SOFC seal). (ii) T_c appears before maximum density has been reached. In this case, the crystallization process starts before complete densification, thus preventing further sintering and resulting in a mechanically weak glass-ceramic. The present study is dedicated towards investigating the influence of lanthanides (La³⁺, Nd³⁺, Gd³⁺, and Yb³⁺) on sintering behavior of glass-ceramicseals for SOFC. The lanthanides have the ability to alter the properties of glass/glass-ceramic seals by tailoring their viscosity and CTE.8 However, literature survey reveals that apart from La₂O₃, no other rare-earth oxide has been given its due importance in designing glass seals.⁵

Also, this topic is of interest for the researchers working in the area of nuclear waste immobilization as lanthanides can act as surrogates for actinides in glass-ceramics which are being considered as potential host materials for nuclear wastes.⁹⁻¹¹ In particular, an extensive effort is being made in USA to develop glass-ceramics capable of immobilizing alkali/alkaline-earth metals along with lanthanides and transition metal fission products that will be generated during uranium extraction (UREX⁺) aqueous separation type process.¹² Therefore, results obtained from this study are expected to shed some light on the influence of lanthanides on thermal properties of glasses and resultant glass-ceramics which are important for nuclear waste immobilization.

2. Experimental

2.1 Glass design and synthesis

A total of 12 glasses with different lanthanide concentrations were designed and synthesized in the primary crystallization field of diopside (CaMgSi₂O₆) with their theoretical compositions: Ca_{0.7}Sr_{0.3}Mg_{0.9}Al_{0.1}RE_{0.1}Si_{1.9}O₆; Ca_{0.7}Sr_{0.3}Mg_{0.85}Al_{0.1}RE_{0.2}Si_{1.85}O₆ and Ca_{0.7}Sr_{0.3}Mg_{0.8}Al_{0.1}RE_{0.3}Si_{1.8}O₆, where RE: La, Nd, Gd and Yb. Also a rare-earth free glass with composition Ca_{0.7}Sr_{0.3}Mg_{0.95}Al_{0.1}Si_{1.95}O₆ was synthesized in order to understand the influence of rare-earth oxides on different properties of glasses. The glass compositions were designed free from BaO in order to minimize the possibility of any detrimental chemical interactions between seal and metallic interconnect as well as to avoid the formation of monoclinic celsian in the glass-ceramic.⁵ Further, Al₂O₃ was added in relatively

small amounts so as to control the devitrification behavior of glasses¹³ while 2 wt% B₂O₃ was added to all the glass compositions to tailor their flow behavior.⁶ The partial substitution of SiO₂ and MgO with lanthanides (Si⁴⁺ + Mg²⁺ \leftrightarrow 2 Ln³⁺) has been made considering the fact that both silica and magnesia tend to decrease the CTE and increase the viscosity of glasses which might affect the flow as well as joining behavior of glass seals to SOFC components. Table 1 presents the detailed compositions of all the investigated glasses.

Homogeneous mixtures of batches (~100 g) in accordance with glass compositions presented in Table 1 were prepared by ball milling of powders of SiO₂ (purity >99.5%), CaCO₃ (>99.5%), Al₂O₃ (Sigma Aldrich, \geq 98%), H₃BO₃ (Merck, 99.8%), MgCO₃ (BDH chemicals, UK, >99%), SrCO₃ (Sigma Aldrich, 99+%), La₂O₃ (Sigma Aldrich, 99.9%), Nd₂O₃ (Sigma Aldrich, 99.9%), Gd₂O₃ (Sigma Aldrich, 99.9%), and Yb₂O₃ (Sigma Aldrich, 99.9%). The glass batches were calcined at 1150 °C for 3 h and then melted in Pt crucibles at 1550 °C for 1 h, in air.

Glasses in bulk form were produced by pouring the melts on preheated bronze molds followed by annealing at 550 °C for 1 h while glass frits were obtained by quenching of glass melts in cold water. The frits were dried and then milled in a high-speed agate mill resulting in fine glass powders with mean particle sizes of 10– 20 μ m (determined by a light scattering technique; Coulter LS 230, Beckman Coulter, Fullerton, CA; Fraunhofer optical model). The chemical composition of some of the as synthesized glasses was analyzed by inductive coupled plasma-optical emission spectroscopy (ICP-OES; Jobin Yvon, JY 70 plus, France) in order to observe the differences between the designed and as synthesized glass compositions.

 Table 1
 Glass compositions (RE refers to lanthanide cation present in the glass)

Glass		MgO	CaO	SrO	SiO_2	Al_2O_3	B_2O_3	RE ₂ O ₃
RE-0	wt%	16.25	16.66	13.20	49.73	2.16	2.0	
	mol%	23.64	17.42	7.47	48.54	1.24	1.68	
La-0.1	wt%	14.68	15.89	12.58	46.20	2.06	2.0	6.59
	mol%	22.66	17.63	7.55	47.85	1.26	1.79	1.26
La-0.2	wt%	13.25	15.18	12.02	42.98	1.97	2.0	12.60
	mol%	21.66	17.84	7.64	47.14	1.27	1.89	2.55
La-0.3	wt%	11.94	14.53	11.51	40.04	1.89	2.0	18.10
	mol%	20.63	18.05	7.74	46.42	1.29	2.00	3.87
Nd-0.1	wt%	14.65	15.85	12.55	46.09	2.06	2.0	6.79
	mol%	22.67	17.63	7.55	47.84	1.26	1.79	1.26
Nd-0.2	wt%	13.19	15.12	11.97	42.80	1.96	2.0	12.96
	mol%	21.66	17.84	7.64	47.14	1.27	1.90	2.55
Nd-0.3	wt%	11.87	14.45	11.44	39.80	1.88	2.0	18.58
	mol%	20.63	18.05	7.73	46.41	1.29	2.01	3.87
Gd-0.1	wt%	14.57	15.77	12.49	45.85	2.05	2.0	7.28
	mol%	22.66	17.63	7.55	47.84	1.26	1.80	1.26
Gd-0.2	wt%	13.06	14.96	11.85	42.37	1.94	2.0	13.82
	mol%	21.66	17.83	7.64	47.13	1.27	1.92	2.55
Gd-0.3	wt%	11.69	14.24	11.28	39.22	1.85	2.0	19.72
	mol%	20.62	18.05	7.74	46.40	1.29	2.04	3.87
Yb-0.1	wt%	14.48	15.67	12.41	45.55	2.03	2.0	7.86
	mol%	22.66	17.63	7.55	47.83	1.26	1.81	1.26
Yb-0.2	wt%	12.90	14.78	11.71	41.85	1.92	2.0	14.84
	mol%	21.65	17.83	7.64	47.12	1.27	1.94	2.55
Yb-0.3	wt%	11.49	13.99	11.08	38.55	1.82	2.0	21.07
	mol%	20.61	18.04	7.73	46.39	1.29	2.08	3.87

2.2 Dilatometry

Dilatometry measurements were done on prismatic samples with a cross-section of $4 \times 5 \text{ mm}^2$ (Bahr Thermo Analyse DIL 801 L, Hüllhorst, Germany). The glasses were analyzed at a heating rate of 2 K min⁻¹ while glass-ceramics were analyzed at 5 K min⁻¹. The dilatometry measurements were made on a minimum of 3 samples from each composition and the standard deviation for the reported values of CTE is in the range $\pm 0.1 \times 10^{-6} \text{ K}^{-1}$.

2.3 Differential thermal analysis (DTA)

The differential thermal analysis (DTA, SetaramLabsys, Setaram Instrumentation, Caluire, France) of glass powders was carried out in air from room temperature to 1000 °C at 5 K min⁻¹. The glass powders (mean particle size: 10–20 μ m) weighing 50 mg were contained in an alumina crucible and the reference material was α -alumina powder. The standard deviation reported for the values of characteristic temperatures as obtained from DTA is in the range of ± 5 °C.

2.4 In situ-hot stage scanning electron microscopy

(ESEM, Environmental scanning electron microscopy FEIXL30, Eindhoven, Netherlands), with an in situ heating stage, was employed to shed some more light on the sintering behavior of glasses. Due to the highly expensive and time consuming nature of this study, three glasses with similar lanthanide content (Nd-0.2, Gd-0.2 and Yb-0.2) were selected for this analysis. Small amounts of glass powder were introduced in a MgO crucible plated with Pt (platinum plating is used to connect electrically the inside of the crucible to the SEM, so that a potential can be applied to the inside of the crucible). Since the glass grains were large enough to be manipulated with tweezers, a few grains were arranged in contacting pairs so as to facilitate the formation of necks during sintering. Observations were made in environmental mode with a water vapor pressure of 2 Torr. The samples were heated to 500 °C at 30 K min⁻¹, and then until 1000 °C at 10 K min⁻¹ (with several pauses to take pictures at different temperatures). The formation of a neck between two glass particles was followed as a function of temperature.

2.5 Hot stage microscopy (HSM)

The sintering behavior of the glass powders was also investigated by using a hot-stage microscope (HSM). A side-view HSM EM 201 equipped with an image analysis system and electrical furnace 1750/15 Leica was used. The microscope projects the image of the sample through a quartz window and onto the recording device. The computerized image analysis system automatically records and analyses the geometry changes of the sample during heating. The measurements were conducted in air with a heating rate of 5 K min⁻¹. The cylindrical shaped samples with height and diameter of ~ 3 mm were prepared by coldpressing the glass powders and were placed on an alumina support. The temperature was measured with a Pt/Rh (6/30) thermocouple contacted under the alumina support. The temperatures corresponding to the characteristic viscosity points were obtained from the photographs taken during the hot-stage microscopy experiment following ref. 14. The standard deviation

reported for the values of characteristic temperatures as obtained from HSM is in the range of ± 10 °C.

2.6 Crystalline phase assemblage in sintered glass-ceramics

The circular disc shaped pellets with 20 mm diameter and \sim 3 mm thickness were prepared from glass powders by uniaxial pressing (80 MPa) and were sintered under non-isothermal conditions at 850 °C for 1 h at a slow heating rate of 2 K min⁻¹. The amorphous nature of glasses and qualitative along with quantitative analysis of crystalline phases in the glass-ceramics (crushed to particle size <63 µm) were made by X-ray diffraction (XRD) analysis using a conventional Bragg-Brentano diffractometer (Philips PW 3710, Eindhoven, The Netherlands) with Ni-filtered Cu- K_{α} radiation. The quantitative phase analysis of glass-ceramics was made by the combined Rietveld-R.I.R (reference intensity ratio) method. A 10 wt% of corundum (NIST SRM 676a) was added to all the glassceramic samples as an internal standard. The mixtures, ground in an agate mortar, were side loaded in an aluminium flat holder in order to minimize the preferred orientation problems. Data were recorded in 2θ range = 5–115° (step size 0.02° and 25 s of counting time for each step). The phase fractions were extracted by Rietveld-R.I.R refinements, using Diffrac^{plus} TOPAS (Bruker AXS).

Microstructural observations were done on polished glassceramic samples (chemically etched by immersion in 2 vol% HF solution for 2 min) by field emission-scanning electron microscopy (FE-SEM; SU-70, Hitachi).

2.7 Linear shrinkage measurements

The linear shrinkage during sintering was calculated from the difference of the diameter between the green and the sintered pellets. The mean values and the standard deviations presented for linear shrinkage have been obtained from (at least) 5 different samples.

2.8 Electrical conductivity of glass-ceramics

The total conductivity was studied by the AC impedance spectroscopy (Impedance analyzer Biological Model VMP3, 40 Hz–1 MHz) using dense disk-shaped samples (sintered at 850 °C for 1 h) with porous Pt electrodes and Pt current collectors, in atmospheric air. In the course of impedance measurements, the magnitude of AC voltage was fixed at 1.00 V.

3. Results

3.1 Glass forming ability

For all the investigated compositions, melting at 1550 $^{\circ}$ C for 1 h was sufficient to obtain bubble-free, homogeneous transparent

 $\label{eq:composition} \begin{array}{l} \mbox{Table 2} & \mbox{Glass composition (wt\%) of some glasses as determined by ICP-OES analysis} \end{array}$

Glass	MgO	CaO	SrO	SiO ₂	Al_2O_3	B_2O_3	RE ₂ O ₃
RE-0 La-0.2 Nd-0.2 Gd-0.2 Vb 0.2	15.25 12.06 11.27 11.41	16.49 15.30 15.67 15.29	13.94 12.67 14.03 13.39	50.42 43.10 42.79 42.32 41.71	2.36 2.06 2.12 2.08	1.55 1.88 1.85 1.79	12.93 12.28 13.73 15.68

glasses. Table 2 presents the experimental compositions for some of the glasses as determined by ICP-OES analysis. Negligible changes were observed in the chemical composition of the glasses after melting the glass batch as 1550 °C. The absence of crystalline inclusions was confirmed by XRD analysis (Fig. 1). Although it has been reported that the upper limit of the amount of rare-earth oxides that can be incorporated into the aluminosilicate glasses decreases in accordance with lanthanide contraction,15 no such concern was observed in the present study, possibly because the concentrations of rare-earth oxides used are lower in comparison to those used by Makishima et al.¹⁵ With respect to the color of glasses, all the glasses except those containing Nd were colorless. Nd-containing glasses exhibited bluepurple coloration characteristic of Nd³⁺ (4f³) ion f-f transitions: this is the most stable oxidation state of neodymium.¹¹ Also, according to Loiseau et al.11 the colorless state of Gd and Yb containing glasses refers to the occurrence of the most stable trivalent oxidation state for these ions under normal conditions in air: Gd³⁺ (4f⁷) ions absorb in the ultra-violet range, whereas Yb³⁺ (4f¹³) ions absorb in the near infrared range. It is noteworthy that the formation of Yb2+ is possible only in glasses melted under reducing conditions and this would have been responsible for strong absorption band in the short wavelengths due to allowed f-d transitions.

3.2 Coefficient of thermal expansion

Tailoring the CTE is one of the most crucial aspects of glass seal design as it should match with the CTE values of other SOFC components, especially, ceramic based electrolyte and metallic interconnect. Since both tensile (when CTE of component is higher than that for glass seal) and compressive (when CTE of component is lower than that for glass seal) stresses are possible at the interface, the CTE mismatch between seal and component should not exceed $1 \times 10^{-6} \text{ K}^{-1}$. In general, a CTE varying between (9 and 12) $\times 10^{-6} \text{ K}^{-1}$ is considered desirable for a stable



Fig. 1 X-ray diffractograms of as synthesized glasses depicting their amorphous nature.

glass/glass-ceramic sealant for SOFC application.⁴ Table 3 presents the CTE values for all the investigated glasses and glass-ceramics (after sintering at 850 °C for 1 h). All the studied glasses exhibited their CTE in the range (9–10.5) \times 10⁻⁶ K⁻¹ while the CTE of glass-ceramics varied between (9.4 and 11.1) \times 10⁻⁶ K⁻¹ which is desirable for their application as a sealing material in SOFC.

The introduction of 1.26 mol% of rare-earth oxides in glasses led to an increase in the CTE of glasses except for glass La-0.1 which has a CTE value similar to that for parent glass RE-0. Further, all the glasses containing La, Nd, Gd, and Yb exhibited an almost similar trend as their CTE values decreased with increase in lanthanide concentration from 1.26 mol% to 2.55 mol % and then increased with increasing lanthanide content to 3.87 mol%. At any particular concentration of lanthanides, CTE of glasses was lowest for La containing glass compositions and the highest for Yb-containing glasses (except for glass Yb-0.2). These results are in contradiction with those reported for rareearth containing aluminosilicate glasses¹⁶ and soda-lime-silica¹⁷ glasses where CTE values have been shown to decrease linearly with the ionic field strength of the rare-earth ions (lanthanide contraction). This may be attributed to the compositional complexity of the investigated glasses which consequentially affects their atomic and molecular structure and might lead to a variety of phenomena depending upon the nature and amount of lanthanides (i.e. lanthanide clustering, or network modifying effect/charge compensating effect),16-21 thus affecting their thermal expansion behavior. For example, in alkali/alkalineearth silicates, the addition of lanthanides beyond a certain amount leads to the phenomenon of concentration quenching and phase separation. However, incorporating Al₂O₃ in these glasses has been shown to increase the solubility limit of lanthanides, thus allowing the homogeneous dissolution of rareearth oxides in amounts much higher than otherwise possible.²² Therefore, a detailed structural evaluation of these glasses depicting the silicon, aluminium and boron coordination along with the local structural environment of various lanthanide cations is required in order to provide a reasonable justification for their thermal expansion behavior.

With respect to the CTE variation for glass-ceramics, their thermal expansion behavior depends on the nature and amount of crystalline phase present in the glass-ceramic system. As will

Table 3 CTE (\times 10^{-6} $K^{-1})$ of glasses (200–500 °C) and glass-ceramics (200–700 °C)

Label	Glass	Glass-ceramic
RE-0	9.46	10.85
La-0.1	9.46	10.84
La-0.2	9.03	10.42
La-0.3	9.71	11.09
Nd-0.1	9.65	10.83
Nd-0.2	9.41	11.12
Nd-0.3	9.79	10.48
Gd-0.1	9.65	10.32
Gd-0.2	9.32	10.38
Gd-0.3	10.06	9.38
Yb-0.1	10.21	10.50
Yb-0.2	9.09	10.06
Yb-0.3	10.01	9.79

be discussed in Section 3.4, diopside-based crystalline phases comprise majority of the crystalline content in the investigated glass-ceramics. It has been shown previously that mono-mineral glass-ceramics containing augite (Al-containing diopside) as the only crystalline phase exhibit a CTE value of $\sim 9.5 \times 10^{-6} \text{ K}^{-1.23}$ Since the glass compositions being investigated in the present study also comprise Sr2+ and RE3+ ions, an increase in the CTE of resultant glass-ceramics is therefore inevitable. It is noteworthy that in a crystallized glass seal, the CTE of glass-ceramic decides the stability and hermeticity of the join between metal-ceramic or ceramic-ceramic components of SOFC as the glass seal is prone to crystallize during joining. In the present case, considering the CTE value of ceramic electrolyte (i.e. 8YSZ) to be $\sim 10 \times 10^{-6} \text{ K}^{-122}$ and for metallic interconnect (Crofer22 APU; Sanergy HT) varying between (11 and 12) $\times 10^{-6}$ K⁻¹, the glassceramic compositions with their CTE values $\geq 10.5 \times 10^{-6} \text{ K}^{-1}$ should be suitable for rigid glass-ceramic seals. However, long term thermal stability of these glass-ceramics is yet to be investigated.

3.3 Sintering behavior of glass powders

3.3.1 In situ hot-stage scanning electron microscopy. Fig. 2, 3 and 4 present the SEM images of the glasses Nd-0.2, Gd-0.2 and Yb-0.2, respectively, at temperatures varying between 600 and 750 °C. As per the observations made in HT-ESEM, the glass particles started to move and rotate in the temperature range of 500-600 °C without depicting any changes in their morphology. A gradual increase in temperature to 620-630 °C led to the slight softening of the glass particles (typically characterized by a smoothening of their edges). This temperature range is almost equivalent to the softening point of glasses as observed from thermal expansion curves of the investigated glasses. A dwell for 5-7 min at this stage initiated the neck formation between the particles (i.e. beginning of sintering). A further increase in temperature to 640-650 °C led to the growth in neck formation among the glass particles resulting in a string of particles. The neck formation was observed to shift towards higher temperature with a decrease in ionic radii of lanthanide cation. In the temperature interval of 650-670 °C, the as formed string of particles merges into a single droplet of glass. Beyond this point, the apparition of very light, rounded shadows (darker areas) on

the surface of glass droplets might suggest an amorphous phase separation. This phenomenon was observed in the case of glass Yb-0.2 at 680 °C (Fig. 4) while glass Nd-0.2 exhibited phase separation at comparatively higher temperature *i.e.* 720 °C (not shown). A macroscopic shrinkage is observed around 750 °C.

3.3.2 HSM-DTA. Fig. 5 presents the data as obtained from DTA and HSM ($\beta = 5 \text{ K min}^{-1}$) pertaining to sintering and devitrification behavior of glasses that allow observation of the following trends:

(i) Fig. 5a-e present the variation in the relative area obtained from the HSM measurement and differential temperature (from DTA) with respect to temperature for glass RE-0 (Fig. 5a), La-0.3 (Fig. 5b), Nd-0.3 (Fig. 5c), Gd-0.2 (Fig. 5d) and Yb-0.2 (Fig. 5e), respectively. The DTA thermographs of all the thirteen glasses exhibited a single crystallization exothermic curve. This signifies that the glass-ceramic is formed as a result of either single phase crystallization or an almost simultaneous precipitation of different crystalline phases.

(ii) The temperature of first shrinkage (T_{FS} ; log $\eta = 9.1 \pm 0.1$, η is viscosity; dPa s) as obtained from HSM (Fig. 6a) varied between 750 and 794 °C depending on the nature and amount of lanthanide content in glasses (Fig. 6).

(iii) Increasing La₂O₃ and Yb₂O₃ concentration in glasses showed a monotonic increase in $T_{\rm FS}$ (Fig. 6a and d) while glasses containing Nd₂O₃ and Gd₂O₃ exhibited a dip in their respective $T_{\rm FS}$ values for glasses Nd-0.1 and Gd-0.1 in comparison to rareearth free glass RE-0. A further increment in rare-earth content in Nd- and Gd-containing glasses shifted their $T_{\rm FS}$ temperature to higher side.

(iv) As is evident from Fig. 5a, rare-earth free glass RE-0 exhibited a single stage shrinkage behavior. Although a slight tendency towards exhibiting a two-stage sintering behavior can be seen in glass RE-0, it is not as evident as in the case of rareearth containing glasses.

(v) The two stage shrinkage behavior was observed for all the glasses as is evident from Fig. 5. The conclusion of first sintering stage is characterized with temperature of first maximum shrinkage ($T_{\rm MS1}$; log $\eta = 7.8 \pm 0.1$) while the end of second sintering stage is characterized with temperature of second maximum shrinkage ($T_{\rm MS2}$). Fig. 6 presents the variation in the values of $T_{\rm MS1}$ and $T_{\rm MS2}$ with respect to the lanthanide content in



Fig. 2 HT-ESEM images for glass Nd-0.2 obtained in situ during heat treatment of glass powder in the temperature range of 600-680 °C.



Fig. 3 HT-ESEM images for glass Gd-0.2 obtained in situ during heat treatment of glass powder in the temperature range of 600-720 °C.



Fig. 4 HT-ESEM images for glass Yb-0.2 obtained in situ during heat treatment of glass powder in the temperature range of 600-750 °C.

glasses. In all the glass compositions the $T_{MS1} < T_c$ (onset of crystallization) which demonstrates that sintering precedes crystallization in all the glasses (including RE-0) and, therefore, well sintered and mechanically strong glass powder compacts should be expected.

(vi) The value for $T_{\rm MS2}$ was higher than $T_{\rm c}$ in all the investigated glasses (Fig. 6) depicting that shrinkage continued in the glass powders even after onset of crystallization, possibly due to the presence of residual glassy phase in the glass-ceramic.

(vii) The values for T_p varied between 838 and 928 °C for Lacontaining glasses; 838–918 °C for Nd-containing glasses; 838– 931 °C for Gd-containing glasses and 838–935 °C for Yb-containing glasses. As is evident from Fig. 6, the lowest value of T_p was observed for glass RE-0 and the introduction of lanthanides (1.26 mol%) in this glass resulted in a considerable increase in peak temperature of crystallization. A further increase in lanthanide content in glasses (>1.26 mol%) did lead to an increase in their T_p ; however, this shift was less significant in comparison to that observed between glasses RE-0 and RE-0.1.

(viii) The value of sintering ability parameter $S_c (= T_c - T_{MS1})$ for the rare-earth free glass, RE-0 ($S_c = 17$), was considerably lower (~2 times) in comparison to its rare-earth containing counterparts (Fig. 5), thus depicting that addition of lanthanides (~1 mol% to 4 mol%) in aluminosilicate glasses enhances their sintering ability considerably.²⁴ In general, increasing the rare-earth content in glasses between 1 and 4 mol% (approximately) improved their sintering ability. Among all the lanthanide containing glasses, the lowest value of S_c was observed for glass Gd-0.2 ($S_c = 33$) while the highest was obtained for glass Yb-0.3 ($S_c = 56$).

(ix) In accordance with the results obtained from DTA and HSM, well sintered and dense glass powder compacts were obtained after sintering at 850 °C for 1 h. Table 4 presents the linear shrinkage values of all the thirteen glass powder compacts



Fig. 5 Comparison of DTA and HSM curves on the same temperature scale for glasses: (a) RE-0, (b) La-0.3, (c) Nd-0.3, (d) Gd-0.2, and (e) Yb-0.2 at a heating rate of 5 K min⁻¹.

after sintering them at 850 °C for 1 h. The values of linear shrinkage varied between 14% and 19% and confirm the good densification of glass powder compacts. Usually, glass powders in which crystallization precedes sintering result in porous and mechanically weak glass-ceramics exhibiting a small linear shrinkage value of 4 to 5% as has been reported in the case of enstatite (MgSiO₃) based glasses.¹³ The highest shrinkage was observed for composition La-0.1 (19%) while the lowest was observed for composition Gd-0.3 (14%).

(x) Fig. 7 and 8 present the photomicrographs of all the investigated glasses depicting the changes in geometric shape of the glasses with respect to temperature as obtained from HSM. The deformation temperature (temperature at which the first signs of softening are observed, generally shown by the disappearance or rounding of the small protrusions at the edges of the sample; $\log \eta = 7.8 \pm 0.1$) of all the glasses varied between 870 and 890 °C while sphere formation in almost all the glasses occurred at ~900 °C. This temperature

range (850–900 °C) is usually considered for joining of SOFC metallic/ceramic components by a glass/glass-ceramic sealant. In fact, attempts have been made to accomplish the joining of SOFC metallic interconnect with ceramic electrolyte at higher temperatures (950–1050 °C).^{25,26} However, sealing at temperatures >900 °C usually degrades the metallic interconnect and thus affects the performance of SOFC in a detrimental manner.²⁷

(xi) The half ball temperature (log $\eta = 4.1 \pm 0.1$) and flow temperature (log $\eta = 3.4 \pm 0.1$) for all the glasses varied between 1190–1260 °C and 1200–1270 °C, respectively (Fig. 7 and 8). The highest half ball and flow temperatures were observed for glass RE-0 depicting its highly refractory nature. However, introduction of lanthanide in glass RE-0 (0.05 Mg²⁺ + 0.05 Si⁴⁺ \leftrightarrow 0.1 RE³⁺) led to a significant decrease in both the temperature values (*i.e.* half ball and flow) irrespective of the nature of rare-earth cation. These results reflect the influence of rare-earth oxides on the viscosity of aluminosilicate glasses.



Fig. 6 The variation in different thermal parameters for glasses obtained from DTA and HSM with respect to (a) La_2O_3 , (b) Nd_2O_3 , (c) Gd_2O_3 , and (d) Yb_2O_3 content in glasses. The error bars have been masked by the data points.

Table 4 Linear shrinkage of glass powder compacts after sintering at 850 $^{\circ}\mathrm{C}$ for 1 h

Composition	Shrinkage (%)
RE-0	18.55 ± 0.12
La-0.1	19.17 ± 0.06
La-0.2	17.63 ± 0.11
La-0.3	17.36 ± 0.07
Nd-0.1	18.68 ± 0.08
Nd-0.2	17.54 ± 0.08
Nd-0.3	17.02 ± 0.14
Gd-0.1	17.94 ± 0.13
Gd-0.2	16.62 ± 0.19
Gd-0.3	14.34 ± 0.20
Yb-0.1	19.10 ± 0.02
Yb-0.2	17.83 ± 0.19
Yb-0.3	17.50 ± 0.14

3.4 Crystalline phase evolution

Fig. 9 presents the X-ray diffractograms of the sintered glassceramics while Table 5 presents the quantitative analysis of the crystalline phases present in all the investigated glass-ceramics as obtained from XRD analysis adjoined with Rietveld-R.I.R technique. Fig. 10 shows the fit of a measured XRD pattern of a sintered glass-ceramic RE-0 by using the TOPAS software. The fitting to the measured X-ray diagram has been performed by a least-square calculation. The calculated diagram (Fig. 9) is based on crystallographic structure models, which also take into account specific instrument and sample effects. The parameters of this model have been refined simultaneously using leastsquares methods in order to obtain the best fit to all measured data. By least-squares refinement, a so-called figure-of-merit function R has been defined, which describes the residual (agreement) between observed and calculated data.²⁸ The R factors show the mean deviation in accordance with the model used in per cent. The values of R factor (not shown) as obtained in the present investigation are well within the limits of experimental accuracy. The difference plot in Fig. 10 does not show any significant misfits. The differences between the main peaks of augite, Sr-diopside and corundum are caused by adjustment difficulties based on the crystallinity of the phases.

Sr-containing diopside (Ca_{0.8}Sr_{0.2}MgSi₂O₆; ICSD: 68178) crystallized as the primary phase in all the glass-ceramics followed by an Al-containing diopside [augite; (Ca(Mg_{0.70}Al_{0.30})-(Si_{1,70}Al_{0,30})O₆); ICSD: 62547] as the second most dominant crystalline phase except for compositions La-0.2 and Yb-0.2 (Table 5). While augite dominated the crystalline phase assemblage of glass-ceramic La-0.2 followed by Sr-diopside as the secondary phase, Yb-containing keivyite (Yb₂Si₂O₇; ICSD: 65363) crystallized as the primary phase in composition Yb-0.2 followed by augite and Sr-diopside as the secondary phases. Some other alkaline earth silicate based crystalline phases including Ca₂SiO₄ (ICSD: 39124), CaSrSiO₄ (ICSD: 20544), akermanite (Ca2MgSi2O7; ICSD: 50066) and low-quartz (SiO2; ICSD: 75657) crystallized as minor phases in the glass-ceramics as presented in Table 5. Increasing lanthanide content in glasses (in particular glasses containing Gd and Yb) retarded their tendency towards devitrification as is evident from Table 5. The residual amorphous content in glass-ceramics is highest for glassceramics Gd-0.3 (96 wt%) and Yb-0.3 (96 wt%).

SEM images of the glass-ceramics as presented in Fig. 10 are in good agreement with the DTA-HSM and XRD data. Fig. 11a-c present the SEM images of glass-ceramics La-0.1, La-0.2 and



Fig. 7 HSM images of rare-earth free glass (RE-0) along with La₂O₃ and Nd₂O₃ containing glass powder compacts on alumina substrates at various stages of heating cycle.

La-0.3, respectively, depicting their good densification as well as crystalline/amorphous microstructure. In accordance with the XRD data, Fig. 11d presents the SEM image of glass-ceramic Gd-0.1 depicting its high crystallinity with Fig. 11e exhibiting the disc shaped morphology of the crystals typical for diopside based crystalline phases.²⁹ On the other hand, Fig. 11f presents the microstructure typical for an amorphous phase, thus confirming the presence of negligible amount of crystallinity as revealed by XRD. The high amount of residual glassy phase along with the flow behavior of these compositions as exhibited by XRD and HSM, respectively, makes the investigated glasses as potential candidates for self-healing glass-ceramic seals.

3.5 Electrical conductivity of glass-ceramics

Fig. 12 presents the variation in the electrical conductivity (σ) of glass-ceramics with respect to temperature. The conductivity of all the glass-ceramics varied between (1.19 and 7.33) × 10⁻⁷ S cm⁻¹ (750–800 °C). The electrical conductivity of the glass-ceramics increased with increasing temperature due to the higher

diffusion of network modifying cations. In order for a material to qualify for sealing application in SOFC, it should behave as an electrical insulator with its total electrical conductivity lower than 10^{-5} S cm⁻¹ so as to avoid parasitic currents which decrease the efficiency of the system. The electrical conductivity of investigated glass compositions is considerably lower in comparison to its desired value which makes them suitable material for sealing. Further, the electrical conductivity was observed to increase with increasing lanthanide content in glassceramics as is evident from Fig. 11. Also, decreasing ionic radii (increasing ionic field strength) of lanthanide cations decreased the total electrical conductivity of the glass-ceramics as La containing glass-ceramics exhibited the highest electrical conductivity while the lowest conductivity was observed for Yb-containing glass-ceramics.

The electrical conductivity of a seal glass depends on the glass network formers, modifiers and intermediates. Although a lot of literature has been published with reference to the role of various glass components on their electrical conductivity, the additive effect is still uncertain because of the different roles played by



Fig. 8 HSM images of Gd₂O₃ and Yb₂O₃ containing glass powder compacts on alumina substrates at various stages of heating cycle.



Fig. 9 X-ray diffractograms of glass powder compacts after sintering at 850 °C for 1 h.

these ions in varying concentrations. In particular, there is a considerable dearth of data on the effect of rare-earth cations on the electrical conductivity of glasses/glass-ceramics. As a rule of thumb, it is generally accepted that the electrical conductivity should increase with decreasing ionic radii (i.e. La-containing glasses should exhibit lower electrical conductivity in comparison to Yb containing glasses).⁴ However, it should be noted that this rule might not stand valid in glasses with high compositional complexity, as has been seen in the present study. Therefore, a detailed structural evaluation of the investigated glass system is required with special emphasis on their tendency towards glassin-glass phase separation and lanthanide clustering as both of these phenomena control the electrical conductivity in glasses to a greater extent. Further, it should be noted that in a glassceramic system, the electrical conductivity is decided by the nature and amount of crystalline phase formed along with the chemical composition of residual glassy matrix.⁴

4. Discussion

The sintering and crystallization processes play an important role in determining the properties and applications of glass–ceramic sealants for SOFC. For example, an installation process for the Siemens-SOFC stack required that the sealing glass be partially viscous at 950 $^{\circ}$ C for 2 to 3 h to allow small displacements of the

 Table 5
 Quantitative crystalline phase analysis of glass-ceramics from Rietveld-R.I.R. analysis (wt%)

	Amorphous	Augite (78-1392)	Sr-diopside (80-386)	Diopside (78-1390)	Akermanite (35-592)	CaSrSiO ₄ (72-2260)	Ca ₂ SiO ₄ (23-1042)	Quartz (82-1563)	Keivyite (Yb) (37-458)
RE-0	52 43	23.86	23 71						
La-0.1	53.43		46.57						
La-0.2	55.48	26.32		18.20					
La-0.3	56.78	8.50	16.74		0.00	16.44	1.55		
Nd-0.1	48.89	10.68	40.43		_	_	_		
Nd-0.2	54.09	1.47	44.44						
Nd-0.3	68.14		27.74		2.00	2.12			
Gd-0.1	31.53	7.27	58.85					2.35	
Gd -0.2	86.24	0.00	13.43					0.33	
Gd -0.3	96.19	0.00	3.81						
Yb-0.1	52.86	17.73	29.41	_	_				
Yb -0.2	56.70	12.56	6.76	_	_				23.99
Yb -0.3	95.97		4.03	_	_				





Fig. 10 Observed (red), calculated (blue), and difference curves from the Rietveld refinement of glass-ceramic RE-0 after sintering at 850 °C for 1 h.

single stack elements after joining at 1000 °C.³⁰ This can be achieved by using a slowly crystallizing glass. Therefore, sintering stage should be completed before significant crystallization occurs in order to get a fully dense material suitable for SOFC seal. Uncontrolled crystallization during the initial sintering process can lead to the formation of a porous sealing layer that can adversely affect the SOFC operation.

During the sintering of a glass-powder compact with a size distribution of glass particles, small particles get sintered first as shown by Prado *et al.*³¹ Thus, sintering kinetics at first shrinkage is dominated by the neck formation among smallest particles by viscous flow and is best described by the Frenkel model of sintering.³² Maximum shrinkage is reached when larger pores (pores formed from cavities among larger particles) have disappeared due to viscous flow that reduces their radii with time. This region of sintering kinetics may be described by the Mackenzie–Shuttleworth model of sintering.³³ However, various physical processes (entrapped insoluble gases and crystallization) occurring at the very end of the sintering process might affect the densification kinetics.

In accordance with the above discussed theory, the following sintering and devitrification stages were observed in the present study with an increment in temperature: (i) the initiation of sintering took place with neck formation in the temperature range of 620–650 $^{\circ}$ C followed by the formation of a string of particles which further converted into a single glass droplet with



Fig. 11 SEM images of polished and chemically etched (2 vol% HF) glass-ceramics (a) La-0.1; (b) La-02; (c) La-0.3; (d) Gd-0.1; (e) Gd-0.1; (f) Gd-0.2, after sintering at 850 °C for 1 h.

increasing temperature; (ii) the glass droplet exhibited glass-inglass phase separation whose tendency increased with decreasing ionic radii of lanthanide cation; (iii) macroscopic shrinkage as observed under HT-ESEM which is the temperature range of first shrinkage ($T_{\rm FS}$) as detected by HSM; (iv) two-step sintering behavior (as observed in HSM) most probably due to the presence of glass-in-glass phase separation; and (v) onset of crystallization ($T_{\rm c}$) after the termination of first sintering step ($T_{\rm MS1}$), thus resulting in well sintered and dense glass powder compacts.

Liquid–liquid phase separation is a well-known and common phenomenon in silicate liquids, and can be observed in highsilica regions of many alkaline-earth silicate glass systems, at temperatures either above or below the liquidus.^{34,35} Adding a few mole percent of Al₂O₃ inhibits the phase separation to a significant extent in these glasses but still the nano-sized domains which are rich either in silica or in alkaline-earth



Fig. 12 Total electrical conductivity (σ) of dense glass-ceramics in air in the temperature range of 625–800 °C: (a) La-, (b) Nd-, (c) Gd, (d) Yb-containing glass-ceramics.

aluminosilicate do exist.³⁴ According to De Veckey et al.,³⁶ in glasses located in CaO-MgO-Al₂O₃-SiO₂ system, phase separation is caused by segregation of calcium and magnesium ions. It is probably due to this reason that a single stage sintering behavior has been observed for glass RE-0. However, addition of lanthanides in the glasses shifted the sintering behavior from one-stage to two-stage owing to the phase separation induced by them as has also been explained by McGahay and Tomozawa²² on the basis of theory of corresponding states. Also, the temperature values obtained from HSM are considerably higher than those obtained from in situ HT-ESEM (Fig. 2-4) for the initiation of sintering. This discrepancy can be explained on the basis of different magnifications of the two instruments being used to study the sintering behavior of these glasses. While the sintering behavior of glass powders in ESEM has been observed at a magnification of 3000×, the magnification for the lens being used in HSM is $\sim 10 \times$. Therefore, although the sintering in glass powders starts at considerably lower temperatures as has been observed by HT-ESEM (Fig. 2-4), it can be observed in HSM only at higher temperatures in terms of total area shrinkage (Fig. 5).

All the glass powders exhibited good sintering ability (as demonstrated by linear shrinkage data) resulting in well sintered glass-ceramics after heat treatment at 850 °C for 1 h with varying degrees of crystallinity. The influence of different lanthanides on sintering ability of investigated alkaline-earth aluminosilicate glasses has been elucidated by the sintering ability parameter ($S_c = T_c - T_{MS1}$). The parameter S_c is the measure of ability of sintering *versus* crystallization: the greater this difference, the more independent are the kinetics of both processes.²⁴ The variation in the S_c values with increasing rare-earth content in glasses as presented in Fig. 5 depicts that glass compositions Gd-0.3 and Yb-0.3 exhibit better sintering behavior ($S_c > 50$) among all the investigated glass compositions (Fig. 6d).

All the resultant glass-ceramics (except Gd-0.1) comprise \geq 50 wt% residual glassy phase along with appropriate flow behavior (Fig. 7 and 8), thus showing their ability to demonstrate self-

healing behavior at SOFC operation temperature (800-900 °C). In particular, the glass compositions La-0.1, La-0.2, Nd-0.1, Nd-0.2 are suitable for glass-ceramic sealing in SOFC mainly owing to their appropriate CTE values along with the absence of any undesired crystalline phases. Although RE-0 possesses similar traits, it does lack behind due to its high refractory nature. Also, the glass-ceramic compositions Gd-0.3 and Yb-0.3 might be considered as potential candidates for self-healing glass seals as they comprise >95 wt% residual glassy phase and are monomineral in nature (i.e. possess only one crystalline phase) which is a highly desirable feature for self-healing seals. The concept of self-healing glass seals can help alleviate some of the expansion mismatch and still be able to form a functioning seal between materials with significant mismatch by healing the cracks formed during thermal transients. Although good sintering ability, low devitrification tendency, appropriate thermal expansion, good flow behavior and low electrical conductivity make these glassceramics (in particular Gd-0.3 and Yb-0.3) to be potential candidates for self-healing glass seals in SOFC, glass-ceramics have to prove their efficacy during long term thermal treatments $(\sim 1000 \text{ h})$. The positive feature of these glass-ceramics is that they contain Sr-diopside as the only crystalline phase which possesses high CTE ($\sim 9 \times 10^{-6} \text{ K}^{-1}$) and does not exhibit polymorphism during long term heat treatments as is usually seen in the case of BaO-Al₂O₃-SiO₂ based glass seals (hexacelsian \rightarrow celsian).³⁷ Also, the absence of BaO from the glasses will ensure minimal interfacial reactions with metallic interconnect.38,39

We are in the process of investigating these glasses and glassceramics for their atomic and molecular structure along with their high temperature viscosity behavior and thermal stability during long term heat treatments. The results obtained from these studies will be published in our forthcoming articles.

From the standpoint of nuclear waste immobilization, the actinides Pu³⁺, Am³⁺ and Cm³⁺ (fission byproducts) can be simulated by Ce³⁺, Nd³⁺, Eu³⁺ and Gd³⁺ due to their close ionic radii. Moreover, Gd is a very efficient neutron poison and, therefore, could be advantageously incorporated in glassceramics.¹¹ Loiseau et al.^{10,11} have extensively investigated zirconolite (CaZrTi₂O₇) based glass-ceramics in the glass system SiO₂-Al₂O₃-CaO-ZrO₂-TiO₂ for this application; however, the lanthanide waste loading that has been achieved by them so far has not exceeded 10-11 wt%. Moreover, these glass-ceramics are highly refractory in nature which further raises concerns with handling and volatility of radioactive materials at high temperatures. On the other hand, the present glasses contain 18–21 wt% lanthanides and exhibit less refractory behavior and low melting temperatures in comparison to zirconolite glass-ceramics. Also, the performance of diopside based glasses/glass-ceramics from the perspective of a host for nuclear waste has been well demonstrated.40,41 However, further experimentation with respect to studying the thermal stability and crystallization kinetics of monolithic glasses is required to demonstrate the ability of these glasses as suitable materials for nuclear waste immobilization.

5. Conclusions

A detailed investigation dedicated towards evaluating the influence of lanthanides on sintering behavior of alkaline-earth aluminosilicate glass/glass-ceramics has been carried out with an aim to develop suitable glass-ceramic sealant for solid oxide fuel cells. Varying amounts (1.26–3.87 mol%) of different rare-earth oxides (La₂O₃, Nd₂O₃, Gd₂O₃ and Yb₂O₃) have been incorporated in glasses and their influence on thermal expansion, sintering behavior and electrical conductivity of glasses/glassceramics has been reported in the manuscript. A brief perspective for application of the studied glass system in nuclear waste immobilization has also been presented. The following conclusions can be drawn from the above discussed results:

(i) All the glasses exhibit CTE in the range of $(9-10.5) \times 10^{-6}$ K⁻¹ while the sintered glass-ceramics exhibit CTE in the range of $(9.8-11.12) \times 10^{-6}$ K⁻¹ which is appropriate for sealing applications in SOFC.

(ii) The sintering initiates in all the glasses in the temperature range of 620–650 °C followed by glass-in-glass phase separation, consequentially leading to a two stage sintering behavior.

(iii) Well sintered and dense glass-ceramics were obtained after sintering of glass powders at 850 °C for 1 with crystalline phase assemblage dominated primarily by diopside based crystalline phases.

(iv) The electrical conductivity of the investigated glassceramics varied between (1.19 and 7.33) $\times 10^{-7}$ S cm⁻¹ (750–800 °C). La-containing glass-ceramics exhibit highest electrical conductivity while Yb-containing glass-ceramics exhibited the lowest value.

(v) The as developed glass-ceramics possess a high amount of residual glassy phase (~30 to 96 wt%) along with appropriate flow behavior and CTE matching at SOFC operating temperatures (850–900 °C), thus making them suitable candidates for self-healing glass-ceramic seals for SOFC. In particular, glass-ceramics La-0.1, La-0.2, Nd-0.1 and Nd-0.2 are potential materials for sealing applications in SOFC. Also, glass-ceramics Gd-0.3 and Yb-0.3 demonstrate high sintering ability, monomineral crystalline phase assemblage and >95 wt% residual amorphous phase, thus making them suitable candidates for self-healing glass seals. However, further experimentation with respect to their thermal stability under long term testing is warranted in order to prove their efficacy.

(vi) With respect to nuclear waste immobilization, the studied glasses have the potential to host high-level nuclear wastes owing to their high lanthanide loading capacity, good glass forming ability and low tendency towards devitrification. However, further studies are required to elucidate and enhance their capability in terms of increased waste loading and high chemical durability.

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