



## Effects of lanthanum oxide on the properties of barium-free alkaline-earth borosilicate sealant glass



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### ABSTRACT

We have explored the effects of lanthanum oxide ( $\text{La}_2\text{O}_3$ ) on the properties of barium-free  $\text{SrO-CaO-ZnO-B}_2\text{O}_3\text{-SiO}_2$  glass system varying its content from 0 to 6 mol%. The coefficient of thermal expansion and glass transition temperature of the glasses are found to be in the ranges  $10.6\text{--}10.8 \times 10^{-6}/\text{K}$  (50–600 °C) and 650–690 °C respectively. Differential scanning calorimetric studies revealed an increase in crystallization peak temperature and thermal stability of the glasses up to 4 mol% and then decrease on further addition. A monotonic increase in characteristic shrinkage temperature of glass powder compact is observed on addition of  $\text{La}_2\text{O}_3$  as revealed in the heating stage microscopic study. X-ray diffraction studies revealed reduced crystallization peak intensity in  $\text{La}_2\text{O}_3$  added glasses. Fourier transformed infrared spectra disclosed that the addition of  $\text{La}_2\text{O}_3$  stabilized the glass structure by reducing the number of non-bridging oxygens. Vickers micro hardness of the glasses varied in the range 2.6–5.6 GPa. Scanning electron microscopy revealed the formation of particulate nature of microstructures in parent glass which is not observed in the  $\text{La}_2\text{O}_3$  added glasses. Activation energy of crystallization has increased from 331 to 361 kJ/mol determined by Kissinger and Augis–Bennett models. Above properties of these glasses clearly advocate their applicability as solid oxide fuel cell sealants.

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### 1. Introduction

Solid oxide fuel cell (SOFC) is a source of renewable energy which produces electrical energy from the chemical energy of incoming fuel by means of an electrochemical reaction. Sealing the cathode from oxidant inlet and outlet, and the anode from fuel inlet and outlet is prerequisite for SOFC operation [1]. Keeping in mind the effects on environment, long term durability and low cost of fabrication, most of the SOFCs are operated in the temperature range of 700 to 1000 °C which is termed as intermediate temperature SOFCs (IT-SOFC) [2,3]. An electrical insulating nature and composition based tailorable property have made glass as the most befitting candidate for SOFC sealant.

Extensive work has been done by various research groups in the  $\text{BaO-CaO-Al}_2\text{O}_3\text{-SiO}_2$  (BCAS) glass system [4–10]. Although these glass sealants possessed high coefficient of thermal expansion (CTE) and low glass transition temperature ( $T_g$ ), but formation of high CTE ( $16\text{--}18 \times 10^{-6}/\text{K}$ ) phase,  $\text{BaCrO}_4$  as a result of chemical interaction with the Cr-rich interconnect used in IT-SOFCs caused spallation of the glass ceramic from the sealing interface and finally mechanical stack failure. In order to avoid this chromia reaction problem associated with the barium containing glass ceramics a few researchers has developed BaO-free alkaline-earth borate, silicate and borosilicate glasses [11]. A group of researchers has developed and worked extensively on the  $\text{SrO-CaO-ZnO-Al}_2\text{O}_3\text{-TiO}_2\text{-B}_2\text{O}_3\text{-SiO}_2$  glass system using  $\text{MnO}_2$

and  $\text{Cr}_2\text{O}_3$  as additives according to the properties tuned/processed for SOFC application [12]. These glasses have been investigated in terms of their thermal and mechanical stability, chemical compatibility and crystallization kinetics [13]. Information on this type of glasses is as follows. Reis and Brow [12] has reported that incorporation of ZnO in addition to SrO and CaO has brought down the sealing temperature of the SOFC stack by reducing the glass transition ( $T_g$ ) and deformation temperature ( $T_d$ ) of the glasses while maintaining an appreciable CTE match with the adjoining SOFC components. Formation of consistent crystallization phase and less apparent Cr-rich layer at the metal-glass interface has lead to considerable thermal cycle stability of these glasses. Zhang et al. [14] has studied crystallization kinetics in the glass with composition  $19.2\text{CaO-18.5SrO-13.2ZnO-1.9B}_2\text{O}_3\text{-2.9Al}_2\text{O}_3\text{-2.0TiO}_2\text{-42.2SiO}_2$  (mol%). They found variation in activation energy of crystallization with change in glass particle size and concluded that surface crystallization is the dominant crystallization mechanism for this glass, particularly for small particle size. Ojha et al. [15] has studied the effect of accelerated devitrification on thermo-physical properties of  $25.7\text{SrO-4.1La}_2\text{O}_3\text{-13.1Al}_2\text{O}_3\text{-12.8 B}_2\text{O}_3\text{-44.3 SiO}_2$  (mol%) glass and reported that evolution of hexacelsian phase from the initial hours of sintering; however, lanthanum silicate phase appeared after longer hours of sintering. They observed that formation of hexacelsian phase increased the CTE of glass ceramic and formation of lanthanum silicate phase reduced the CTE of the glass ceramic. Chen et al. [16] has studied the physical and crystallization properties of  $\text{Co}^{2+}$  doped  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$  glasses with various  $\text{La}_2\text{O}_3$  additions (0–10 wt%). They reported that  $\text{La}_2\text{O}_3$  hardly influence the nucleation and crystallization processes of

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$\text{Co}^{2+}$ -doped  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$  glasses when used <5 wt.%, while the nucleation of the glass was hindered and  $\text{MgAl}_2\text{O}_4$  spinel could not be formed with the  $\text{La}_2\text{O}_3$  content greater than 5 wt.%. Goel et al. [17] has studied the effect of  $\text{La}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{B}_2\text{O}_3$  substitution on structural, thermal and chemical properties of diopside based glass-ceramic sealants for SOFC. Sohn et al. [18] investigated glasses in  $\text{BaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$  system using additives  $\text{La}_2\text{O}_3$ ,  $\text{ZrO}_2$  and  $\text{NiO}$ . Their studies revealed that CTE of the glasses increased with the addition of  $\text{La}_2\text{O}_3$  or  $\text{NiO}$  but decreased with the addition of  $\text{ZrO}_2$  and the fluidity of the glass was more strongly influenced by the  $\text{B}_2\text{O}_3/\text{SiO}_2$  ratio rather than by the type or amount of additives.

Various researchers have demonstrated that lanthanum oxide controls the viscosity (flow ability), CTE of the silicate glass and glass ceramic [19–22]. The control on viscosity helps the sealant to maintain necessary fluidity after softening as well as the required mechanical rigidity after ceramization. In addition to these, minimized CTE mismatch of the glass ceramic sealant with the fuel cell components leads to long term stability and thermal cyclability of the stack. The oxidation kinetics (of Cr diffusion) of the Crofer22APU interconnect material can be reduced by modifying the glass composition adding oxides of reactive elements, like La, Ce and Y. Further it is also reported that rare-earth elements are also added to optimize the alloying elements of interconnects to get the desired oxide coating which is responsible for electron conduction capacity of the materials [23]. All these facts establish to believe that the addition of  $\text{La}_2\text{O}_3$  in the glass composition is advantageous for its SOFC sealant application. Although a few reports of studies on  $\text{SrO-CaO-ZnO-B}_2\text{O}_3\text{-SiO}_2$  (SCZBS) glass system are available in the literature, a detailed study on different glass properties upon addition of  $\text{La}_2\text{O}_3$  in this glass system has not been reported till now.

In view of the above, the objective of this work is to investigate the role of  $\text{La}_2\text{O}_3$  on different glass properties of the barium-free SCZBS glass system. A comprehensive study of these glasses has been done in details in terms of their thermal, structural, microstructural and mechanical properties by varying  $\text{La}_2\text{O}_3$  content (0–6 mol%) with respect to their application as SOFC sealant. The crystallization kinetics of the glasses has also been studied applying two different models.

## 2. Experimental procedure

### 2.1. Preparation of precursor glass

Four glasses having composition  $(25 - x/2)\text{SrO} - (25 - x/2)\text{CaO} - 5\text{ZnO} - 5\text{B}_2\text{O}_3 - 40\text{SiO}_2 - x\text{La}_2\text{O}_3$  (mol%), where,  $x = 0, 2, 4, 6$  were prepared following the conventional melt-quench technique. 100 g of homogeneous batch mixture of pure raw materials of  $\text{CaCO}_3$  (98%, Extra pure; Loba Chemie, Mumbai, India),  $\text{SrCO}_3$  (99%, Extra pure; Loba Chemie, Mumbai, India),  $\text{ZnO}$  (GR, 99%; Loba Chemie, Mumbai, India),  $\text{H}_3\text{BO}_3$  (GR, 99.5%; Loba Chemie, Mumbai, India),  $\text{SiO}_2$  (99.8%; Sipur A1 Bremtheler Quartzitwerk, Usingen, Germany) and  $\text{La}_2\text{O}_3$  (99.99%, Alfa Aesar, Lancashire, UK) was melted in a 100 ml platinum crucible at 1500 °C for 2 h in air with intermittent stirring. The molten glasses were quenched on a preheated iron mold. The obtained bulk glasses were immediately annealed at 600 °C for 2 h. The glass compositions are presented in Table 1. Cylindrical samples ( $\varphi = 6$  mm,  $L = 25$  mm) were prepared from these glasses for dilatometric experiment. The remaining glasses were pulverized in a mortar grinder

(Retsch, Model RM 200) using yttria stabilized zirconia jar and pestle. All the powders were granulated with 2 wt.% polyvinyl alcohol (PVA) solution and powder compacts (PCs) of required dimensions were prepared by uniaxial hydraulic press (applying hand pressure). These pellets were heated to 400 °C at 2 °C/min for binder burn-off, kept there for 2 h followed by heating to 800 and 900 °C for 2 h before cooling them to room temperature. These powder compacts of the glasses were heat-treated at 800 and 900 °C for 2 h and labeled as PC8 and PC9 respectively preceded by the glass identity for the sake of convenience (e.g. L-0PC8 and L-0PC9).

### 2.2. Characterization

The glass sealants are applied in the form of paste at the edges of the individual cells and at the electrolyte to interconnect joints in the stack. Therefore to investigate the applicability of the prepared glasses in SOFCs, the glasses were powdered and the characterization of powder compacts of required dimension was carried out along with the following characteristic investigation tools of precursor glasses.

Differential scanning calorimetry of the glass powders ( $\approx 55$  mg) were carried out in nitrogen atmosphere from room temperature to 1000 °C at heating rate 10 °C/min with the help of a DSC instrument (Model STA 449 C; NETZSCH-Gerätebau GmbH, Selb, Germany) to determine the glass transition temperature ( $T_g$ ) and crystallization peak temperature ( $T_c$ ) with a measurement error of  $\pm 1$  °C. Crystallization kinetics was studied at four different heating rates such as 5, 10, 15 and 20 °C/min. The glass transition temperature ( $T_g$ ), dilatometric softening temperature ( $T_d$ ) were determined with a measurement error of  $\pm 1$  °C using a horizontal loading dilatometer (Model DIL 402 PC; NETZSCH-Gerätebau GmbH, Selb, Germany) using cylindrical samples ( $\varphi = 6$  mm,  $L = 25$  mm). The CTE of the glass and heat-treated PCs were also determined with a measurement error of  $\pm 0.1$  using the above instrument. The X-ray diffraction of the glasses and heat-treated PCs were investigated using a XPERT-PRO MPD diffractometer (PANalytical, Almelo, Netherlands). The source of X-ray used was Ni filtered  $\text{CuK}\alpha$  ( $\lambda = 1.5406$  Å) irradiated at 40 kV and 40 mA. The scan range was 5°–90° with a step size of 0.05°. Microstructural studies of the heat-treated samples were done using scanning electron microscope (Model S430i, LEO, CEA, USA). For this purpose the heat-treated and polished PCs were etched with 2 vol.% HF aqueous solution for 5 min. The infrared transmittance spectra of glasses were recorded in the wave number range 400–1600  $\text{cm}^{-1}$  with the help of Fourier transformed infrared spectrometer (Model 1600 Series; Perkin-Elmer Corporation, Norwalk, CT, USA) with a resolution of  $\pm 2$   $\text{cm}^{-1}$ . The degree of shrinkage and sintering behavior of the glasses were investigated at a heating rate of 10 °C/min with the help of heating stage microscope (Misura 3HSM; Expert System Solutions, Italy). Samples of dimension (2 mm  $\times$  2 mm  $\times$  3.5 mm) were placed on an alumina support contacted underneath with platinum thermocouples. The change in geometry of the samples with increasing temperature was photographed using the image analysis system of the instrument synchronized with the programming schedule of the furnace. The HSM software calculates the percentage of decrease in height, width and area of the sample images with respect to the initial sample dimensions. The characteristic temperatures (e.g. first shrinkage, maximum shrinkage, sphere, hemisphere and melting) were determined with a measurement error of  $\pm 1$  °C. The Vickers micro hardness of all the polished heat-treated PCs were determined with a measurement error of  $\pm 3\%$  using (Clemex CMT, Longueuil, Canada) instrument equipped with a conical indenter. Average of 10 indentations was measured for all the samples applying 300 gf load for 10 s. Hardness was calculated using the following standard equation for Vickers geometry.

$$H_v = 1.8544 \left( P/d^2 \right) \quad (1)$$

**Table 1**

Chemical composition of the investigated glasses.

Glass identity	Composition (mol %)					
	SrO	CaO	ZnO	$\text{B}_2\text{O}_3$	$\text{SiO}_2$	$\text{La}_2\text{O}_3$
L-0	25	25	5	5	40	0
L-2	24	24	5	5	40	2
L-4	23	23	5	5	40	4
L-6	22	22	5	5	40	6

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