

# Investigation properties of BaO/RO-Al<sub>2</sub>O<sub>3</sub>-R<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass-ceramic sealants for solid oxide fuel cell

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**Abstract** Glass-ceramics are commonly used as sealing materials for planar solid oxide fuel cells (SOFCs). The major requirements of stack and module builders for these materials are the stability of the coefficient of thermal expansion (CTE), the excellent bonding (sticking) behaviour and the absence of volatile ingredients, which can lead to changes of the material properties and the sealing ability. In this study, the thermal stability of glasses in the BaO-Al<sub>2</sub>O<sub>3</sub>-La<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system was investigated, to develop a suitable sealing glass for planar solid oxide fuel cell operating at 800–850°C. The developed glasses were characterised through measurement of different properties, coefficient of thermal expansion (CTE), glass transition temperature ( $T_g$ ), dilatometric softening temperature ( $T_d$ ), crystallisation behaviour during prolonged heat-treatment, density etc. At a target operating temperature of 750°C, the long-term coefficient of thermal expansion (CTE) of one particular composition (G4) was found to be particularly stable, due to devitrification to a mixture of glasses and ceramic phases.

**Keywords** Glass-ceramic · Solid oxide fuel cell · Thermal expansion · Glass sealant · Crystallisation

## Introduction

Solid oxide fuel cell (SOFC) is an energy conversion device that converts chemical energy of a fuel (such as hydrogen and methane) into electricity through a series of electrochemical reactions; no combustion process is involved. As a result, fuel cell efficiencies are not limited by Carnot efficiencies. This system produces electricity by the electrochemical reaction between a fuel and an oxidant [1–3]. Solid oxide fuel cells are being developed for a broad range of applications including portable electronic devices, automobiles, power generation, aeronautics etc. The salient features of SOFC are all solid construction and high temperature electrochemical reaction-based operation, resulting in clean and efficient power generation from a variety of fuels. There are two different designs of SOFCs, tubular and planar, and are currently under development. The planar SOFCs (pSOFC) are mostly preferred due to several advantages such as simple manufacturing and relatively short current path resulting in higher power density and efficiency. In the main structure of a fuel cell, the device consists of an anode electrode (exposed to fuel), an electrolyte and a cathode electrode (exposed to oxidant). The repeating unit of a planar solid oxide fuel cell is formed by anode-electrolyte-cathode and interconnects [2, 4]. However, planar SOFCs require hermetic seals to separate and contain fuel and oxidant within the cell and to bond cell components together [4–6]. The sealants for planar SOFCs must meet some important requirements: they have to be hermetic in order to prevent mixing of the fuel and oxidant and should have a thermal expansion coefficient close to those of the interconnect and the electrolyte. Moreover, the sealant must be mechanically and thermochemically stable in both oxidising and wet-reducing environments at 800 °C

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**Table 1** Chemical compositions of the developed glasses

Code	Chemical composition (wt%)							
	BaO	CaO	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	La <sub>2</sub> O <sub>3</sub>	Nd <sub>2</sub> O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>
G1 <sup>a</sup>	45–50	–	7–10	12–15	17–20	12–15	–	–
G2	35–40	10–15	7–10	12–15	17–20	12–15	–	–
G3	45–50	–	7–10	12–15	17–20	5–8	5–8	–
G4	45–50	–	7–10	12–15	17–20	–	–	12–15

<sup>a</sup> This composition is selected from literature as standard of this system [12]

and must not undergo any reaction with the other cell components [6]. There are generally two types of seals for pSOFC stacks: compressive seals and rigid seals [7, 8]. Compressive seals suffer from problems of oxide scaling and chemical stability in addition to the drawback of an externally applied force [2, 3, 9]. Rigid seals are therefore more popular energy than compressive seals. Among the rigid seals developed, glasses and glass-ceramics are the most promising ones to be used in pSOFC systems. Glass or glass-ceramic may offer best perspectives as seal for planar system SOFCs because of the inertness to oxidising and reducing conditions, as well as thermal and mechanical stability [6, 10]. By carefully choosing the glass composition, glasses and glass-ceramics meet, in principle, most of the requirements of an ideal sealant. Glass-ceramics, which can be prepared by controlled sintering and crystallisation of glasses, possess superior mechanical properties and higher viscosity at the SOFC operating temperature than those of glasses. Sohn et al. [7] investigated the thermal stability of SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>-BaO-Al<sub>2</sub>O<sub>3</sub> glass and chemical compatibility with electrolyte (8YSZ). They found that the TEC (thermal expansion coefficient) values of their glasses decreased with the formation of celsian.

Yang et al. [11] investigated the chemical interactions of SiO<sub>2</sub>-CaO-B<sub>2</sub>O<sub>3</sub>-BaO-Al<sub>2</sub>O<sub>3</sub>-based sealing glasses with oxidation-resistant alloys. They found that the formation of BaCrO<sub>4</sub> led to the physical separation of the sealing glass from the interconnect alloys due to high thermal expansion mismatch. There are still some problems in improving the high temperature resistance of glass-ceramic materials. This area is still open for research for

new investigations for fuel cell sealant applications. In order to improve the high temperature properties and solve the problem of mismatch thermal expansion coefficient, this study is worked out. The purpose of this study is to investigate properties of different compositions of BaO/RO-Al<sub>2</sub>O<sub>3</sub>-R<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass-ceramic in comparison to those of the literature.

## Methods and procedures

Different chemical compositions of the glasses studied during the present work are given in Table 1. To prepare a suitable glass-sealing composition, B<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> were chosen as glass formers wherein B<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> ratio was kept at around 0.69. Other ingredients such as BaO were added to increase the CTE, La<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub> to control the viscosity and Al<sub>2</sub>O<sub>3</sub> to prevent rapid crystallisation during heat-treatment as well as to control the surface tension of the glass. Anode-supported bilayers, consisting of NiO/5YSZ (zirconia stabilised with 5 mol% yttria) as the anode and 8YSZ as the electrolyte, and thin gage stainless steel (FeCrAlY ferritic alloys) (Crofer 22 APU) were chosen as model substrates in this study.

## Glass preparation

The thoroughly mixed batches were taken in an alumina crucible and melted in an electric furnace (Protherm, PLF 160/30) at 1400 °C for 2 h. To obtain the glass, the melts were quenched by pouring into cooled water. It was rinsed with acetone to remove impurity and then dried at 80 °C for 2 h. The dried glass frit was milled in a ball mill below 100-µm particle size. These amorphous glasses were called as GX (X is changed from 1 to 4). Starting composition and code of samples were given in Table 1. G1 is a standard composition which is selected from literature [12].

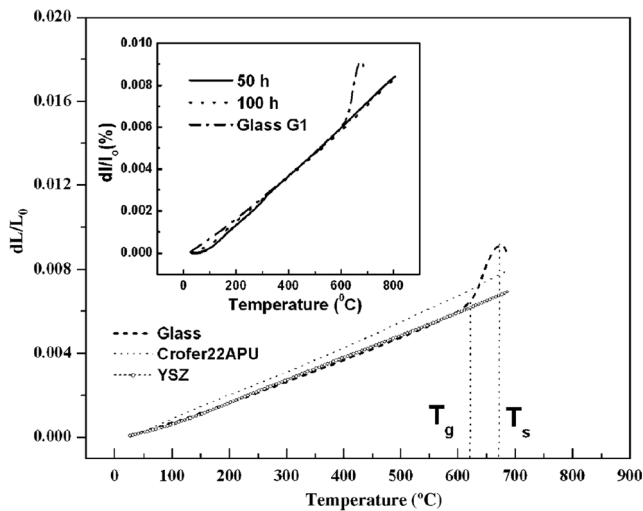
## Glass-ceramic preparation

The prepared glass powders were mixed with 3 wt% polyethylene glycol (PEG) solution as a binder and then uniaxially pressed into discs with 40 mm in diameter under 30 MPa pressure. Five tablets were prepared for each composition.

**Table 2** Physical and thermal properties of developed glasses

Code	T <sub>g</sub> (°C)	T <sub>c</sub> (°C)	Density (g/cm <sup>3</sup> )	CTE * 10 <sup>-6</sup> /K	(Heat-treated at 800 °C for 24 h)
G1 <sup>a</sup>	693	742	3.37	8.35	9.54
G2	705	768	3.16	7.88	8.33
G3	690	752	3.36	8.06	–
G4	713	770	3.43	8.33	8.27

<sup>a</sup> This composition is selected from literature as standard of this system [12]



**Fig. 1** Comparison of thermal expansion for G1 glass (–) and glass-ceramics (sintered at 800 °C for 50 and 100 h) with YSZ and Crofer 22 APU (metallic interconnect) [12]

**Characterisation**

*Thermal analysis*

Crystallisation capacity of glass-ceramics, glass transition ( $T_g$ ), crystallisation ( $T_c$ ) and melting ( $T_m$ ) temperatures was determined by differential thermal analyser (DTA, Netzsch STA 409 DTA PC). The milled frit with particle size under 63  $\mu\text{m}$  was used for thermal analysis.

Coefficient of thermal expansion (CTE) of glass powder was measured by a dilatometer (Netzsch DIL 402 PC) characterisation. Sample was uniaxially pressed into a bar with dimensions of 25 × 10 × 4 mm. They were analysed with 10°/min heating rate by subtracting to 1400 °C. In order to

show the changes in CTEs (coefficients of thermal expansion), values of the glass-ceramics dilatometric measurements were also performed on the rectangular (25 × 10 × 4 mm) bulk samples sintered heating to 850 °C with a heating rate 10 °C/min.

*Phase characterisation*

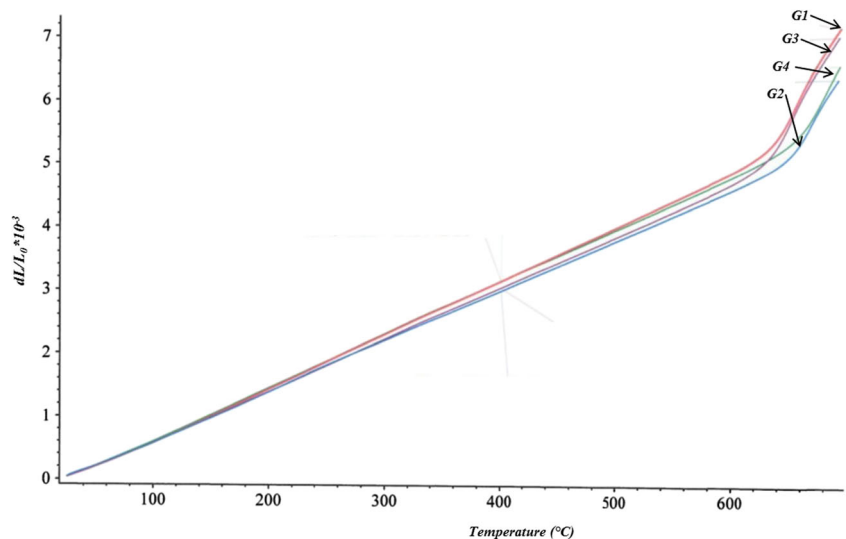
In order to explore the evolution process of crystalline phases, the green discs were heat-treated at 800 °C for different durations of 12 and 24 h with heating rate of 10 °C/min. The heat-treated pellets were analysed using an X-ray diffractometer (Rigaku Rint 2000) with  $\text{CuK}\alpha_1$  ( $\lambda = 1.5056 \text{ \AA}$ ) radiation at 40 kV and 40 mA, with  $2\Phi = 10\text{--}60^\circ$  and  $2^\circ/\text{minute}$  to confirm the amorphous nature (as-prepared glass) and to identify the crystalline phases (heat-treated glass).

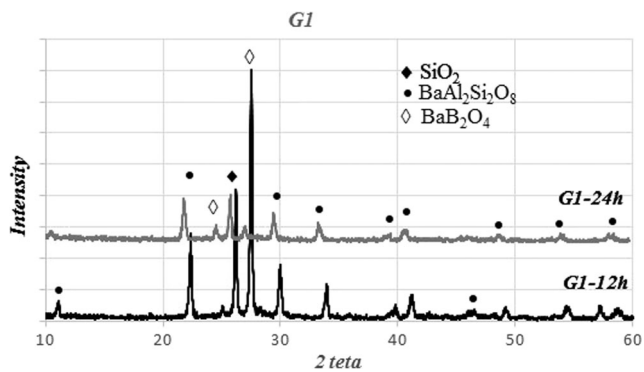
**Results and discussion**

**Physical properties of developed glasses**

The physical properties of each glass are almost identical for all the developed composition. G1 and G3 samples have similar densities ( $\sim 3.37 \text{ g/cm}^3$ ), whereas G2 has the lowest (Table 2). These differences are directly related with the starting composition of glasses. The G2 has CaO, which is not in other composition, and due to low decomposition temperature of this material, the density of G2 is the lowest. On the other hand, G1 and G3 have a similar amount starting raw and main difference is the amount of rare earths ( $\text{La}_2\text{O}_3$  and/or  $\text{Nd}_2\text{O}_3$ ) in the composition. Melting temperature and molecular weight of these rare earths are similar (2315–2233 °C and

**Fig. 2** Thermal expansion behaviour of all glasses





**Fig. 3** XRD pattern of G1 glass-ceramic heat-treated at 800 °C for 12 and 24 h

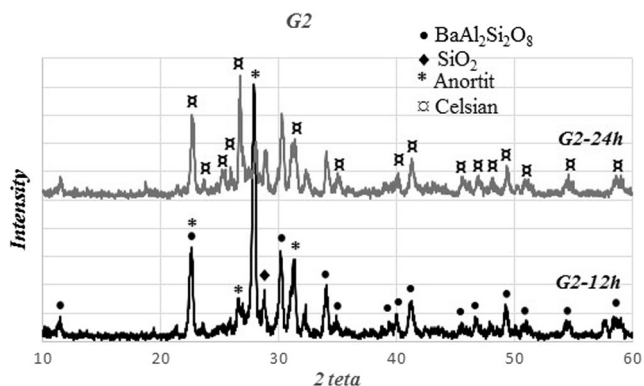
6.51–7.24 g/cm<sup>3</sup>, respectively); therefore, these results are expected for these compositions. However, G4 glass-ceramic has the highest density (~3.43 g/cm<sup>3</sup>) due to the different rare earths used in the composition. Y<sub>2</sub>O<sub>3</sub> has more refractory properties compared with those of other rare earths ( $T_{\text{melting}}$  is 2425 °C), whereas its molecular weight is lower (225 g/mol) than that of others (La<sub>2</sub>O<sub>3</sub> and Nd<sub>2</sub>O<sub>3</sub> have 325.805 and 336.48 g/mol, respectively). Therefore, in the same ratio, the amount of Y<sub>2</sub>O<sub>3</sub> is higher than that of La<sub>2</sub>O<sub>3</sub> and/or Nd<sub>2</sub>O<sub>3</sub> in the composition. And the amount of liquid phase will be higher than that of other composition to increasing sintering behaviour of system. These reasons explain why the G4 has the highest  $T_g$ ,  $T_c$  and density. Due to the similar physical and thermal properties to G1, G4 was found to be very promising. Hence, this particular glass composition has been referred extensively in this study.

The  $T_g$  values for the developed glasses lie within the temperature range 620–645 °C, which is below the SOFC operating temperature (800 °C). The CTE values of all these glasses ( $\sim(7.88$  to  $8.35) \times 10^{-6}/\text{K}$ ) from room temperature to  $T_g$  are in the same range as those of other cell components, zirconia electrolyte in particular [13]. According to results

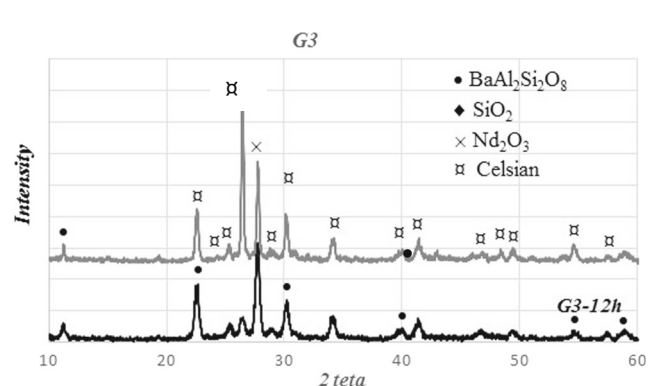
of G1 and G2, which indicate that  $T_g$  and  $T_{\text{sintering}}$  are almost independent of the change in BaO content under constant B<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> ratio (0.69), this results are in agreement with literature which are carried out in borosilicate glasses [6]. The results show that introduction of rare earth oxides increases the coefficient of thermal expansion and Nd<sub>2</sub>O<sub>3</sub> is an exception in viscosity. The glass transition temperature of BaO/RO-Al<sub>2</sub>O<sub>3</sub>-R<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass doped with rare earth oxides increases with increasing cationic field strength ( $r_{\text{cation}}/\text{values of cation}$ ) of corresponding rare earth ions [14]. G4 glass exhibited the highest CTE value of  $\sim 8.336 \times 10^{-6}/\text{K}$ . In this system, all the rare earths have the same charge (3<sup>+</sup>), whereas their cationic radius ( $r_{\text{cation}}$ ) is changing. Y<sup>3+</sup> has the lowest cationic radius in these three; therefore, its cationic field strength is highest in these cations. These results explain why G4 exhibited the highest CTE value.

A typical linear expansion curve for the same G1 glass is shown in Fig. 1 and compared with that of the CTE of YSZ and Crofer 22 APU [12]. The slope of the curve between  $T_g$  and  $T_d$  shows a dramatic increase in expansion just before the glass structure deforms by viscous flow. When fuel cell stacks are cooled to room temperature, stresses begin to develop as the temperature drops below  $T_g$  and with further decrease in temperature, the stress enhances significantly due to the thermal expansion mismatch. Therefore, to minimise the total stress produced, the  $T_g$  at which the viscosity equals to 1013 to 1013.6 dPas should be as low as practicable with adequate rigidity at the cell operating temperature of around 800 °C. Figure 1 also reveals that the difference in CTE values between the optimised glass G1 and YSZ electrolyte is small and exhibiting a thermal expansion mismatch.

The thermal expansion results of glasses are given in Fig. 2. According to these results, it is possible to conclude that G4, the best compositions in four, shows a similar behaviour to G1 and YSZ and Crofer 22 APU and is a good candidate for using in this application.

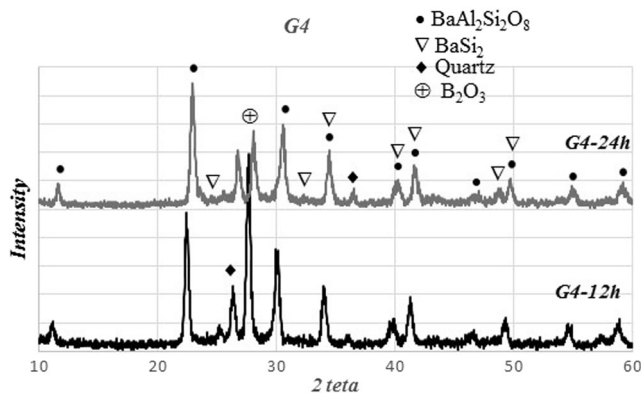


**Fig. 4** XRD pattern of G2 glass-ceramic heat-treated at 800 °C for 12 and 24 h



**Fig. 5** XRD pattern of G3 glass-ceramic heat-treated at 800 °C for 12 and 24 h





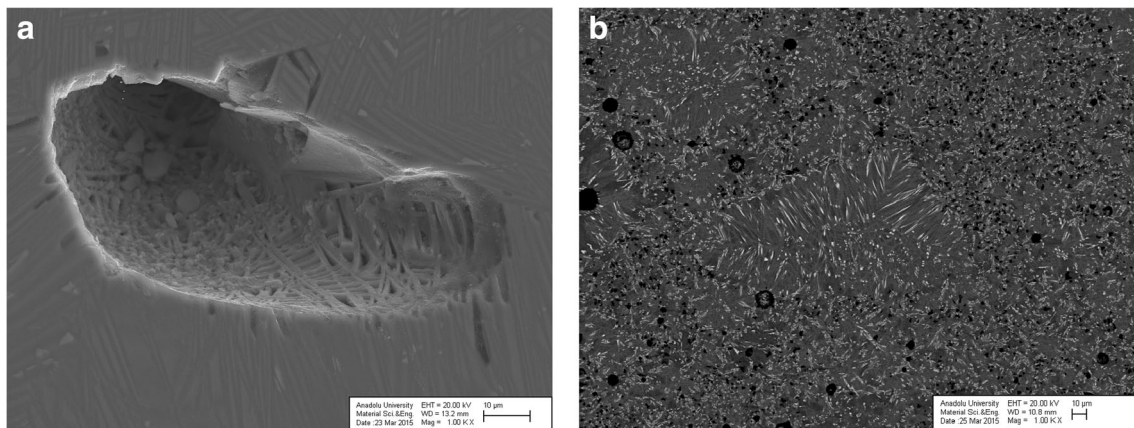
**Fig. 6** XRD pattern of G4 glass-ceramic heat-treated at 800 °C for 12 and 24 h

### Phase characterisation of glass-ceramics

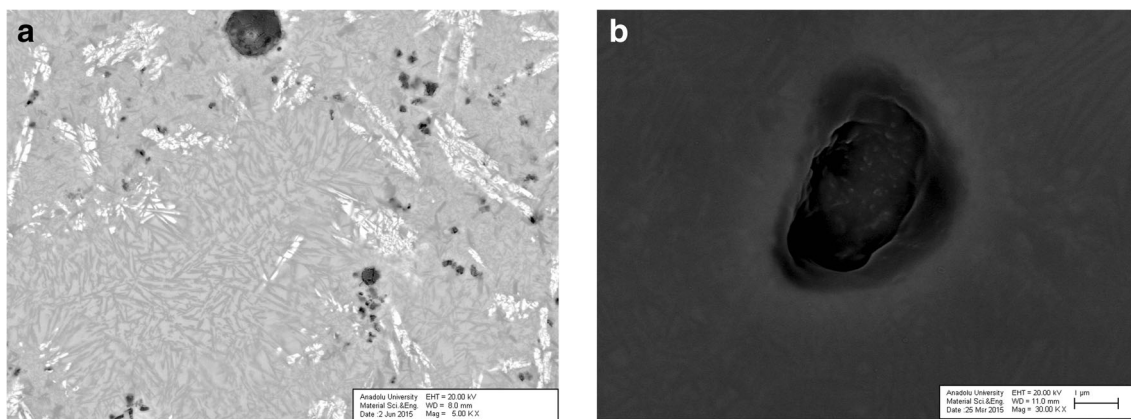
The X-ray diffraction analysis results of glass-ceramics, heat-treated at 800 °C for 12 and 24 h, are given in Figs. 3, 4, 5, and 6. The XRD analysis results show that the glass compacts sintered at 800 °C for 12 and 24 h have a crystalline structure. Figure 3 shows the XRD pattern of G1 glass-ceramics heat-treated at 800 °C for 12 and 24 h. The results show that two different morphologies of BAS glass phases are investigated as hexacelsian and celcian. As investigated by Ghosh et al., the high temperature phase, hexacelsian ( $\text{BaAl}_2\text{Si}_2\text{O}_8$ -JCPDS: 01-072-7502), forms metastable after heat-treatment at 800 °C for 12 h and always crystallises out first in these BAS glasses. When the glasses were heat-treated for longer period of time (24 h), the hexacelsian phase begins to transform to the monoclinic celcian phase ( $\text{BaAl}_2\text{SiO}_8$ -JCPDS: 01-077-0185) as the latter is thermodynamically stable below  $\sim 1590$  °C. The formation of celcian phase is, however, undesirable for SOFC sealing application as the same has a very low CTE of  $\sim 2.29 \times 10^{-6} \text{ K}^{-1}$  in between 30 and 1000 °C. The hexacelsian phase, on the contrary, has a relatively higher CTE value of

$\sim 8 \times 10^{-6} \text{ K}^{-1}$  within 30–1000 °C and is more compatible with the parent glasses compared to that of celcian in terms of CTE mismatch. Therefore, crystallisation of hexacelsian is always desirable in the preparation of glass sealant for SOFCs, whereas, rapid and progressive transformation from hexacelsian to celcian is considered undesirable [12]. Figure 3 shows that main phase in the structure is  $\text{BaAl}_2\text{Si}_2\text{O}_8$  (hexacelsian) (JCPDS: 00-028-0124). Additionally,  $\text{SiO}_2$  is observed as the secondary phase in this glass composition. This standard composition, chosen from literature, is in agreement with literature [12]. G2 glass composition, heat-treated for 12 h, analysis results show that it has  $\text{BaAl}_2\text{Si}_2\text{O}_8$  as main phase in its structure, whereas this phase transforms to celcian phase (JCPDS: 00-038-1450) after 24 h heat-treatment (Fig. 4). Additionally, it was observed that some amount of anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) is present due to  $\text{CaCO}_3$  in its starting composition. Fergus also investigated similar results in his study [9]. G3 glass analysis result is different from that of the others. This composition has  $\text{BaAl}_2\text{SiO}_4$  phase as main phase in the structure of heat-treated for 12 h. Additionally, it has a celcian morphology as the secondary phase. The transformation of hexacelsian to celcian is also observed in this sample after 24 h heat-treatment. Low amount of unreacted  $\text{Nd}_2\text{O}_3$  has also seen in the result (Fig. 5). The results of G4 sample are different from those of the others. It has  $\text{BaAl}_2\text{Si}_2\text{O}_8$  (hexacelsian) phase as the main phase in all conditions (12 and 24 h heat-treatment). Therefore, this composition is more suitable for SOFC sealing applications according to literature.

The polishing surface scanning electron microscopy (SEM) of samples is given in Figs. 7 and 8. Al matrix represents the hexacelsian phase as an elongated form in Fig. 6a for G1 sample. G2 sample has both phases as hexacelsian and celcian in its morphology (Fig. 7b). G3 sample has two different phases. The celcian phase is observed as grey, whereas hexacelsian phase as elongated form (white) in its structure



**Fig. 7** SEM micrographs of **a** G1 and **b** G2 samples heat-treated at 800 °C for 24 h



**Fig. 8** SEM micrographs of **a** G3 and **b** G4 samples heat-treated at 800 °C for 24 h

(Fig. 8a). As it is seen in Fig. 8b, G4 sample has a hexacelsian phase in its structure. All the microstructural results are in agreement with phases analysed of samples.

## Conclusion

BaO/RO-Al<sub>2</sub>O<sub>3</sub>-R<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass-ceramic system was investigated for application as potential SOFC sealants. In this study, as different from literature, dual and single rare earth addition was studied. The results showed that addition of La<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>-Nd<sub>2</sub>O<sub>3</sub> to composition affects the CTEs and transformation from hexacelsian to celsian phase. However, using of Nd<sub>2</sub>O<sub>3</sub> in composition (G4) helps to improve the CTE and prevent phase transformation during the heat-treatment process. According to results of reference [12], CTE of G4 was found to be well matched with the zirconia electrolyte, although there was less than 10% mismatch with the Crofer 22 APU (interconnect metal), which was within the tolerable limit for application as a sealing material. As a result of heat-treatment process, these glasses (G1, G2 and G3) were found to generate mainly two different polymorphs, celsian and hexacelsian, and also little amount of niobium, anorthite and boron oxide. Celsian phase is undesirable due to the high kinetic barrier associated with the transformation from hexacelsian to celsian. Therefore, G4 glass composition was observed as a good candidate due to prevention of this transformation and similar CTE value to that of SOFC.

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