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Sintering and crystallization of SrO-CaO-B_2O_3-SiO_2 glass-ceramics with different TiO_2 contents

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ABSTRACT

Glass and glass-ceramics (GCs) of the CaO-SrO-B_2O_3-TiO_2-SiO_2 system are promising candidates as sealants for solid oxide fuel cells (SOFCs), mainly because of the possibility of the formation of Sr_2SiO_4 and $Sr(TiO_3)$ as crystalline phases, which minimizes the interfacial reaction between the interconnection elements and the sealant. Four glass compositions of this system, with different TiO_2 content, were obtained. The crystalline phases formed after crystallization were identified by X-ray diffraction (XRD). Combining Differential Scanning Calorimetry (DSC) and Optical Microscopy (OM), it was found that the overall activation energy for crystallization did not change with TiO_2 content. The predominant crystallization mechanism is controlled by the surface, and the growth of the crystalline layer is governed by diffusion. The sintering behavior was investigated by DSC and Hot Stage Microscopy (HSM). All glass compositions exhibited a single-stage shrinkage behavior, but those with a larger amount of TiO_2 showed high sinterability. The measured coefficient of thermal expansion (CTE) varied from $10.2 \times 10^{-6} K^{-1}$ (100–550 °C) in the glass to $13.9 \times 10^{-6} K^{-1}$ (100–550 °C) in the GCs, which is in good agreement with the typical CTE of SOFC components. These consistent values of the CTE and good sintering behavior allow us to propose that the glass composition with a higher percentage of titanium is a promising candidate for further experimentation and development as a sealant material.

1. Introduction

Solid oxide fuel cells (SOFCs) are electrochemical devices that convert chemical energy into electrical energy with high efficiency at high temperatures. Each cell consists of an electrolyte integrated with a porous anode and cathode [1,2], whereas an SOFC assemblage comprises individual cells connected with the interconnect components, which transport the electronic current between the unit cells and the external circuit. The interconnection components are exposed to reducing or oxidizing atmospheres because the fuel (hydrogen or hydrocarbons) is oxidized at the anode, while the oxidant (air or oxygen) is reduced at the cathode. Among the various existing SOFC designs, intermediate temperature solid oxide fuel cells (IT-SOFCs) operate at temperatures between 600 and 1000 °C and allow the use of ferritic stainless steels as interconnect components [3–5]. Nevertheless, the development of a hermetic seal is important because it can prevent mixing of fuel and oxidant into the fuel cell, and it keeps the cell components together [6–10].

Therefore, the development of a sealant for SOFC applications must meet several crucial requirements, e.g., (i) the sealants must have a coefficient of thermal expansion (CTE) similar to that of the cell's other components (i.e., cathode, anode and interconnection components) in general in the range of $(9–13) \times 10^{-6} K^{-1}$[11,12]; (ii) good mechanical properties [13]; (iii) the material must be an electrical insulator (electrical resistance $> 2\,k\Omega\,cm$), to avoid parallel currents [14]; and (iv) be chemically compatible with other fuel cell components [6], while minimizing thermal stresses during high-temperature operations [9,15]. These requirements constitute a major challenge.

Several studies have shown that glass and glass-ceramic (GC) materials are promising candidates for sealant applications, mainly due to the possibility of tailoring the chemical composition [6,9,16]. In the case of an IT-SOFC, the interfacial reaction between glass-ceramic

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sealants and ferritic interconnects results in the formation of chromate phases, e.g., $BaCrO_4$ and $SrCrO_4$, leading to a weak adherence and a possible physical separation between the sealant and the interconnect alloy [4,6,17–21].

Zhang et al. [20] and Chen et al. [21] recently demonstrated that glasses and glass-ceramics of the $CaO{\cdot}SrO{\cdot}B_2O_3{\cdot}SiO_2$ (CSrBS) system doped with TiO_2 (2–8 mol%) are potential candidates for sealant applications due to the precipitation of Sr_2SiO_4 and $Sr(TiO_3)$, which minimizes the interfacial reaction between the sealant and the component alloys of the IT-SOFC. Additionally, its CTE values closely match those of the interconnect elements (e.g., $9.8 \times 10^{-6}\,K^{-1}$, GC, to $11.3 \times 10^{-6}\,K^{-1}$, glass). However, the sinterability and crystallization kinetics of these glasses were not yet investigated. The knowledge of glass sinterability and crystallization kinetics are crucial for predicting the sealing ability of the glass powders to ceramic or metallic surfaces [22], since grained glass samples devitrify more easily than bulk glass samples and the corresponding glass-ceramic materials can be obtained through a process of simultaneous amorphous state sintering and crystallization. Moreover, the effect of TiO_2 on the crystallization kinetics was not yet investigated.

Other very important point of view to be analyzed is that the glass sealant must be resistant against the crystallization during the cells operation to avoid thermal and mechanical stresses [21]. In fact, these authors analyzed the glass stability against crystallization during heating using the relation $T_x - T_g$, where T_x and T_g are the onset of the crystallization peak and the glass transition temperatures, respectively. Nevertheless, Nascimento et al. [23] pointed out that the glass stability is more precisely evaluated by the parameters that also take into account the melting or liquidus temperature, such as $K_H = (T_x - T_g)/(T_m - T_x)$, $K_W = (T_x - T_g)/T_m$ and $K_{LL} = T_x/(T_g + T_m)$, where T_m means melting or liquidus temperature [24].

Based on the above, the purposes of this work are: (i) to investigate the effect of TiO_2 in the sinterability of glasses doped with different TiO_2 contents; (ii) to assess the crystalline phases precipitated; (iii) to identify the predominant crystallization mechanisms of these glasses by Differential Scanning Calorimetry (DSC); and (iv) to analyze the effect of TiO_2 on the glass stability and the crystallization mechanism. In order to do this, four glass compositions of the CSrBS system doped with different TiO_2 contents (1, 2, 3 and 4 mol%) were prepared. The crystalline phases of the corresponding GCs were then identified in order to confirm the presence of Sr_2SiO_4 and $Sr(TiO_3)$ phases. Also, the CTE values of each parent glass and corresponding GCs were determined to ascertain their compatibility with the interconnect elements of the IT-SOFCs.

2. Experimental procedures

2.1. Glass synthesis

Four glass compositions of the $(26 - 0.25x)CaO\ (26 - 0.25x)SrO\ (4 - 0.05x)B_2O_3\ xTiO_2\ (44 - 0.45x)SiO_2$ (with $x = 1, 2, 3$ and 4 mol %) system were obtained and referred as T_1, T_2, T_3 and T_4, respectively. The reagents grade alkaline earth carbonates, boric acid, SiO_2, and TiO_2 were mixed and placed in a platinum crucible for melting at 1500 °C for 1 h. Then, each liquid was quenched in air onto a steel plate and remelted three times to prevent the formation of bubbles and streaks. In the last re-melting, the liquids were pressed between two stainless steel plates (splat-cooling) and annealed at 50 °C below the corresponding glass transition temperature (T_g-50 °C) to avoid residual stresses. The Chemical composition was determined using a MagiX Super Q version 3.0 Phillips X-ray fluorescence spectrometer (Philips, The Netherlands), equipped with IQ+ analytical software used for semi-quantitative analysis. Calibration curves were prepared from standards of certified composition of natural and synthetic calcium phosphates and calcium silicates. The sample preparation was performed by melting of 0.3 g of each sample and 5.5 g of $Li_2B_4O_7$ in a Pt/Au crucible and casting into pearl form in a special controlled furnace Perl'X3 (Philips). The nominal and experimental compositions in mol% are presented in Table 1.

Table 1
Nominal and experimental compositions (mol%) of the T_1, T_2, T_3 and T_4 glasses.

Glasses	CaO	SrO	B_2O_3	TiO_2	SiO_2	Impurities
Nominal composition						
T_1	25.75	25.75	3.95	1.00	43.55	–
T_2	25.50	25.50	3.90	2.00	43.10	–
T_3	25.25	25.25	3.85	3.00	42.65	–
T_4	25.00	25.00	3.80	4.00	42.20	–
Chemical analysis[a]						
T_1	24.71 (5)	21.95 (1)	3.36 (3)	1.03 (4)	46.72 (9)	2.21 (1)
T_2	24.06 (3)	24.21 (8)	3.83 (2)	1.91 (4)	45.97 (6)	n.d[a]
T_3	24.35 (9)	23.46 (2)	3.71 (7)	3.02 (3)	45.46 (9)	n.d[a]
T_4	24.59 (9)	21.45 (5)	3.58 (7)	4.27 (8)	43.88 (5)	2.20 (2)

[a] Uncertainties of the last digit in parentheses. n.d.: below the limit of determination of the analytical method.

2.2. DSC analysis

DSC experiments were performed to infer the glass-stability and the non-isothermal crystallization kinetics of each glass. All experiments were performed in an NETZSCH STA 449C thermal analyzer using platinum crucibles under air atmosphere. For this purpose, monolithic glass samples (3.0 × 3.0 × 2.5 mm) of each composition were heated from room temperature until the corresponding liquidus or melting temperature using different rates ($\phi = 5$, 10, 15 and 20 °C/min). From these DSC data, the onset values of T_g, T_x and T_m were estimated and the glass stability of each glass was calculated using the equations proposed by Hrüby (K_H), Weinberg, (K_W) and Lu and Liu (K_{LL}): $K_H = (T_x - T_g)/(T_m - T_x)$, $K_W = (T_x - T_g)/T_m$ and $K_{LL} = T_x/(T_g + T_m)$ [24].

To estimate the sinterability parameter for each vitreous composition, DSC experiments were also performed for powdered glass samples (< 43 μm) at the same heating rate (10 °C/min) and temperature range (room temperature until 1400 °C).

The Avrami coefficient, n, and the activation energies for overall crystallization, E, were calculated from the Ozawa [25–27] and Matusita & Sakka equations [26,28] given by Eqs. (1) and (2), respectively:

$$-n = \left.\frac{\ln(-\ln(1-\chi))}{\ln\phi}\right|_T \tag{1}$$

$$\ln\left(\frac{\phi^n}{T_P^2}\right) = \frac{mE}{RT_P} + cte \tag{2}$$

In these relations, χ is the crystallized fraction at a given temperature, m is the crystal growth dimensionality, while T_p and R are the crystallization peak temperature and the gas constant, respectively.

It should be remembered that the DSC data must be analyzed assuming two different scenarios: (1) that crystal growth occurs at a fixed number of nuclei or surface crystallization; (2) that further nuclei are formed during the DSC measurement. For both cases, the Matusita & Sakka equation (Eq. (2)) can be used to estimate the activation energy for crystallization, which includes the nucleation and crystal growth phenomena. In the former, one has $n = m$. When there is a significant nucleation, $n = m + 1$.

2.3. Dilatometric behavior

The CTE and softening temperature (T_d) were measured for each bulk glass sample (11 × 5 × 3 mm) and the corresponding glass-ceramics. To obtain glass-ceramics for CTE measurements, cylindrical pellets with 2.5 cm in diameter of glass powder (< 43 μm) were uniaxially pressured and partially crystallized upon a single heat treatment at 850 °C with different dwelling times (20, 60 and 100 h). CTE was