Sintering of glasses in the system RO–Al₂O₃–BaO–SiO₂ (R=Ca, Mg, Zn) studied by hot-stage microscopy

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Abstract

Glass–ceramics for sealing solid oxide fuel cells (SOFCs) were developed by sintering and crystallization of the powdered glass seal. The non-isothermal sintering kinetics and crystallization kinetics were studied for four glasses in the system 50SiO₂/(45–x)BaO·xRO·5Al₂O₃ (R = Ca, Mg, Zn and x = 0, 15) (mol%). Hot-stage microscopy (HSM) and differential thermal analysis (DTA) measurements demonstrated that it is possible to first sinter and then crystallize these glasses obtaining glass–ceramic seals with thermal expansion coefficients in the range 9–12 x 10⁻⁶ K⁻¹.

The non-isothermal sintering kinetics was analyzed by computer simulations using a previously reported model of sintering for polydispersed glass powders which takes into account the particle size distribution, surface energy and viscosity. Good agreement was found between the measured kinetics with HSM and the calculated kinetics for all glasses.

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1. Introduction

In planar solid oxide fuel cells (SOFCs), gas-tight seals must be applied along the edges of each cell and between the fuel cells stack and the gas manifolds in order to prevent gas mixing during operation. The sealing material has to fulfil strict requirements, including an operating temperature of around 850 °C and a mean-life of 5 years.

Other main requirements are: gas tightness, high stability to the fuel and cell components, electrically insulating (ρ ≥ 10⁴ Ω cm), a thermal expansion coefficient (α) of ~ 9–12 x 10⁻⁶ K⁻¹, a viscosity of 10⁶–10⁹ dPa s at the sealing temperature and ≥ 10¹⁰ dPa s at the working temperature, and good adherence to the components (mainly stainless steel, zirconia and Ni/YSZ).

From consideration of these conditions, glass–ceramics seem the most appropriate materials for sealing SOFCs [1]. Sealings are usually applied on the surfaces (stainless steel) to be sealed using powder glass mixed with a binder. The glass–ceramic formation involves the sintering of glass powders, followed by crystallization at a higher temperature. Crystallization is needed to increase the seal viscosity and improve the chemical and mechanical properties of the sealant, which has to maintain the bulk stability and not flow during operation at high temperatures.

Sintering and crystallization processes can occur consecutively or simultaneously. If crystallization occurs before sintering is completed, the viscosity increases sharply and sintering stops. Under these conditions, a porous glass–ceramic or ceramic material is produced. The sintering stage should be completed before crystallization takes place. Final dense and low porosity materials are needed for obtaining a gas-tight glass–ceramic seal [2].

Hot-stage microscopy (HSM) is considered a suitable experimental technique to study sintering phenomena in glasses. Not only qualitative observations but also quantitative studies of sintering kinetics can be undertaken with this technique [3,4]. Likewise, differential thermal analysis (DTA) is a very useful tool for studying the crystallization process of a glass. Thus, a combination of HSM and DTA represents a simple and fast method for...
describing the sintering/crystallization process of different glass compositions.

In the present study, four barium silica based compositions have been studied in the system RO–Al2O3–BaO–SiO2 (R = Ca, Mg or Zn), which are promising candidates for sealing SOFCs [5]. The objective of this work was to explore the sintering/crystallization process of these glasses, as well as the thermal properties, the viscosity and the melting behaviour.

The Clusters model of non-isothermal sintering [6–8] was used to compute the sintering kinetics of the glass powders, which helps to clarify the effect of particle size distribution of the powder, surface energy and viscosity on the sintering kinetics.

2. Experimental

2.1. Glass compositions

The compositions in the system 50SiO2–(45 – x)BaO·xRO·5Al2O3 (R = Ca, Mg, Zn and x = 0, 15) (mol%) were prepared from reagent-grade BaCO3, CaCO3, MgCO3, ZnO, Al2O3 and SiO2 sand. Table 1 summarizes the different glass compositions. The thoroughly mixed batches were melted using porcelain crucibles at 1550 °C for 2 h in a gas furnace. The melts were poured onto brass moulds at room temperature obtaining homogeneous, bubble-free and transparent bulk glasses that were subsequently annealed at a temperature close to the glass transition temperature (Tg).

The glasses were ground using an agate mill and sieved with a 20-μm mesh. The particle size distribution of the glass powders was determined by laser scattering with a Mastersizer S instrument (Malvern Instruments).

2.2. Thermal characterization

The thermal properties (glass transition temperature (Tg), dilatometric softening temperature (Td) and the coefficient of thermal expansion (α)) of the bulk glasses and final glass–ceramics were measured in air with a Netzsch dilatometer and a heating rate of 5 K min−1. The samples, cylinder-shaped, ≈ 3 mm in height and placed on a 10 × 15 × 1 mm alumina (>99.5 wt.% Al2O3) support, were prepared with cold-pressed glass powder with a particle size <20 μm. The temperature was measured with a Pt/Rh (6/30) thermocouple contacted under the alumina support.

The temperatures corresponding to the characteristic viscosity points (first shrinkage, maximum shrinkage, softening, half ball and flow) were obtained from the photomicrographs taken during the hot-stage microscopy experiment following Scholze’s definition and [9].

The first shrinkage viscosity value was corrected for the particle size, considering the following reasoning. In a sintering experiment, at the first shrinkage temperature, necks are formed among the smallest particles. This sintering stage is described by the Frenkel model (Eq. (1)):

\[
d\left(\frac{\Delta L}{L_0}\right) = \frac{3\gamma v}{8\eta(T)r_{\text{min}}} dt
\]

where \(L_0\) is the sample’s original length, \(\Delta L\) the linear shrinkage after a sintering time \(t\), \(\eta(T)\) the temperature-dependent shear viscosity, \(\gamma\) the glass–vapor surface energy (whose temperature dependence is minimal), \(r_{\text{min}}\) the smallest particle radius and \(\nu\) the volume fraction of particles with \(r_{\text{min}}\).

If the sintering is made at a constant heating rate, and we are interested in the arbitrarily chosen, first 5 per thousand linear shrinkage, then:

\[
\left.\frac{\Delta L}{L_0}\right|_{T_0.005} = \frac{3\gamma v}{8\eta_{\text{min}}} \int_{T_{FS}}^{T_0.005} dT' \frac{dT'}{\eta(T')}
\]

where \(T_{FS}\) is the temperature for which the linear shrinkage of the sample is 0.005, \(T_0.005\) is the first temperature at which shrinkage starts and \(q\) is the heating rate.

If the temperature interval is sufficiently small, it is reasonable to define an average viscosity value, \(\bar{\eta}\), for the temperature interval, \(T_0.005 - T_{FS}\). Then:

\[
0.005 = \frac{3\gamma v \Delta T}{8\eta_{\text{min}} q} \quad \bar{\eta} = \frac{3\gamma v \Delta T}{8\eta_{\text{min}} 0.005}
\]

where \(\Delta T = (T_{FS} - T_{0.005})\) and, according to its definition, \(\bar{\eta}\) is assigned to a temperature \(\bar{T} = T_{FS} + \frac{\Delta T}{2}\), since we can consider a linear behavior of viscosity with temperature in such a short interval.

Thus, for a given glass powder compact, the value of \(\gamma\) is determined by its chemical composition, \(r_{\text{min}}\) can be deter-
mined by standard measurement techniques, $q$ is an experimental variable which can be varied as desired and $\Delta T$ can be determined from the shrinkage record, for example, by hot-stage microscopy, of a sintering experiment.

Simultaneously, thermal analyses TG-DTA were performed with an EXSTAR 6300 (Seiko) equipment on glass powder samples ($\phi < 20 \text{ m} \mu$) employing a heating rate of 5 K min$^{-1}$. $\alpha$-$Al_2O_3$ calculated at 1200 °C was used as inert reference.

2.3. Sintering and crystallization

Glass powders were isostatically pressed (200 MPa during 1 min) to cylindrical green samples of 1 cm in height and 0.6 cm in diameter.

These samples were heat-treated in an electrical furnace in air at 900 °C up to 24 h following the same conditions with that of the DTA and HSM measurements. Samples were extracted at different temperatures during the heating ramp and after different periods at 900 °C.

The density of the green and treated samples was measured by the Archimedes method in Hg.

The treated samples were studied by X-ray diffraction (XRD) with a Siemens D5000 diffractometer.

3. The clusters model of sintering

The method used for computing the sintering kinetics is the Clusters model for sintering, previously discussed in Ref. [6]. A summary of this model for non-isothermal sintering of polydispersed particles with concurrent crystallization is given in Ref. [7]. Only the main equations useful to this work are presented, considering that no crystallization takes place during sintering, as experimentally proved.

In a non-isothermal process, the time, $t$, may be treated as a temperature dependent variable, $dt = dT/q$, where $q$ is a constant heating rate.

For an isotropic, non-isothermal process in the early stages of sintering, in which the relative density of the glass compact is smaller than 80% (the Frenkel stage), the sintering kinetics (for each particle radius $r$) is given by:

$$\rho_F = \rho_0 \left( 1 - 3\gamma \rho_F \frac{1}{8qr} \int_{T_g}^T \frac{1}{\eta(T')} dT' \right)^3$$

where $\rho_0$ is the initial green density, $\gamma$ the surface liquid-vapor energy and the index $F$ indicates “Frenkel stage”. In Eq. (4), $x_f$ is the glassy surface fraction of the particles (the fraction of particle surface that is not crystallized or covered with inclusions) and $p_F$ is a packing factor: the average number of necks each particle develops at the Frenkel stage divided by 6 (6 is the number of necks of an hypothetical cubic array). In this work, we take $x_f = 1$ since we are dealing with a clean non-crystallized particle surface, and $p_F = 4/6$ since the relative green densities of the compacts are low, around 0.47–0.5. For more details about $x_f$ and $\rho_0$, see Ref. [8].

The corresponding Mackenzie–Shuttleworth (MS) expression [7] is given in Eq. (5):

$$\rho_{MS}(r, T) = \rho_0 + (1 - \rho_0) \left( \frac{3\gamma x_f}{2\rho_0 q} \right) \times \int_{T_g}^T \frac{1}{\eta(T')} \frac{1}{q_r} \frac{d\rho}{dT'} dT'$$

In Eq. (5), $d_0$ is the radius of the pores which form during sintering of the particles with size, $r$. The other quantities

**Table 2** Dilatometric properties of bulk original glasses and final glass–ceramics

<table>
<thead>
<tr>
<th>Glass</th>
<th>$T_g$ (°C)</th>
<th>$T_d$ (°C)</th>
<th>$x_{50-700}$ (× 10$^6$ K$^{-1}$)</th>
<th>$x_{50-700}$ (× 10$^6$ K$^{-1}$), Glass–ceramic</th>
</tr>
</thead>
<tbody>
<tr>
<td>V1–Ca</td>
<td>716 ± 2</td>
<td>767 ± 5</td>
<td>10.2 ± 0.1</td>
<td>9.7 ± 0.1</td>
</tr>
<tr>
<td>V2–Mg</td>
<td>719 ± 2</td>
<td>763 ± 5</td>
<td>8.3 ± 0.1</td>
<td>9.6 ± 0.1</td>
</tr>
<tr>
<td>V3–Zn</td>
<td>692 ± 2</td>
<td>743 ± 5</td>
<td>10.6 ± 0.1</td>
<td>9.7 ± 0.1</td>
</tr>
<tr>
<td>V4</td>
<td>709 ± 2</td>
<td>754 ± 5</td>
<td>10.7 ± 0.1</td>
<td>13.2 ± 0.1</td>
</tr>
</tbody>
</table>

Fig. 1. Particle size distribution of the powder samples.

Fig. 2. Viscosity–temperature curve for the four studied glasses obtained from HSM measurements.
were defined above. As detailed in Ref. [7], Eq. (5) slightly underestimates the sintering kinetics in the MS regime.

For a polydispersed compact with a volume fraction, $v_r$, of spherical particles of radius, $r$, the following expression holds for the densification kinetics at a given heating rate (Clusters model [6,7]):

$$q(T) = \sum_r [q_F(r, T) \theta_F(T_{0.8} - T) + q_{MS}(a_0(r), T) \theta_{MS}(T - T_{0.8})] v_r \xi_r \quad (6)$$

Eq. (6) sums up the relative density $\rho(r, T)$ for each particle size, $r$, as a function of temperature, $T$. During the Frenkel stage of sintering, $\rho_F(r, T) < 0.8$ and $\rho_F(r, T)$ is calculated using the Frenkel equation (Eq. (4)). Later, at $\rho(r, T) > 0.8$, $\rho_{MS}(r, T)$ is calculated by the Mackenzie–Shuttleworth model (Eq. (5)). For each cluster, the transition from the Frenkel regime to the MS regime is made using the temperature step functions, $\theta_F(T_{0.8} - T)$ and $\theta_{MS}(T - T_{0.8})$, whose values switch between 1 and 0 at $T = T_{0.8}$, when $\rho_F(r, T_{0.8}) = 0.8$ is reached. Thus, $\theta_F(T_{0.8} - T) = 1$ and $\theta_{MS}(T - T_{0.8}) = 0$ for $T < T_{0.8}$, and $\theta_F(T_{0.8} - T) = 0$ and $\theta_{MS}(T - T_{0.8}) = 1$ for $T > T_{0.8}$.

The pore radius $a_0(r)$ in Eq. (6) is calculated by our algorithm to ensure a continuous $\rho(r, T)$ function at $T = T_{0.8}$ for each particle size. The adjustment is achieved by first computing $t_{0.8}$ with Eq. (4), then calculating $a_0(r)$ with Eq. (5) at $T = T_{0.8}$. With this model, it is possible to predict the densification kinetics ($\rho(T)$) at any chosen temperature for a given heating rate.

Although the particle size distribution is wide (see Fig. 1), $n_r = 1$ (the neck-forming ability of each particle, can be calculated from the particle size distribution, as discussed in Refs. [6,7]), gave the best fit of calculations to experimental data. The effect of $n_r$ on the sintering kinetics is overlapped with the effect of the particle shape and of the particle packing. Although it has been investigated in the past, still remains to be an open problem.

In this work, the Clusters model is applied to the sintering data obtained by HSM for the first time. Only a small quantity of sample is needed for this treatment. The results are compared with the density of samples densified in an electrical furnace for which one sample is necessary for each thermal treatment.

<table>
<thead>
<tr>
<th>Glass</th>
<th>$A$</th>
<th>$B$</th>
<th>$T_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>V1–Ca</td>
<td>1.26</td>
<td>1547</td>
<td>880</td>
</tr>
<tr>
<td>V2–Mg</td>
<td>0.73</td>
<td>2017</td>
<td>848</td>
</tr>
<tr>
<td>V3–Zn</td>
<td>1.75</td>
<td>1219</td>
<td>891</td>
</tr>
<tr>
<td>V4</td>
<td>−0.023</td>
<td>2855</td>
<td>769</td>
</tr>
</tbody>
</table>

Table 3 Constants of VFT equation for glasses in Fig. 2

Fig. 3. (a) Variation in area and height of powder samples of V1–Ca during the HSM measurement. (b) Photomicrographs of the shape sample evolution associated to (a).
The relative density variation in the HSM experiments was calculated taking into account the area and the height shrinkage as recorded by the image recording device.

4. Results and discussion

All melted glasses displayed a broad amorphous XRD profile.

The particle size distribution of the glass powders shows bimodal distributions with maxima around 10 and 0.4 μm for the four studied glasses.

The dilatometric data obtained for the bulk glasses and the glass–ceramics obtained on sintering the glass powders at 900 °C during 10 h are shown in Table 2.

All glasses present an adequate thermal expansion coefficient ($\alpha$) for application in SOFCs, with the exception of MgO (V2–Mg), which has a slightly lower value. The $\alpha$ of the original glasses and the resulting glass–ceramics are quite similar, except for the ternary glass, which is a necessary condition to obtain materials with good mechanical stability.

The dilatometry of crystallized samples treated up to 1000 °C showed neither $T_d$ nor $T_g$, indicating that the samples were highly crystalline.

Fig. 2 presents the viscosity of the four glasses as a function of temperature. The experimental points, derived from HSM images following Ref. [9], are situated between log $\eta$ values of 12 and 3 with $\eta$ in dPa s. The viscosity curve $\eta(T)$ is described by the Vogel–Fulcher–Tamman (VFT) equation:

$$\log \eta = A + \frac{B}{T - T_0}$$

(7)

Table 3 shows the VFT constants for each glass.

A smooth variation of the viscosity with temperature, i.e., low fragility, is one of the most important conditions for obtaining a good seal. Fig. 2 shows that viscosity varies between $10^6$ and $10^9$ dPa s, in the sealing range (800–900 °C). Thus, all the glasses accomplish the $\eta$ requirements for sealing.

From a typical thermogram of a glass composition, it is possible to identify the glass transition temperature ($T_g$) as an inflexion point, the exothermic crystallization peak ($T_C$) and the endothermic melting peak ($T_m$). The last peak may or may not be present depending on the final temperature of the experiment, but was not observed in the present experiments.

![Fig. 2](image)

**Fig. 2.** (a) Variation in area and height of powder samples of V3–Zn during the HSM measurement. (b) Photomicrographs of the shape sample evolution associated to (a).
It is useful to compare DTA and HSM results in the same temperature range, which reveals how the composition affects sintering and devitrification phenomena. Two different trends are normally exhibited by this procedure. In the first case, the beginning of crystallization ($T_X$) occurs after the final sintering stage (MS). Thus, sintering and crystallization are independent processes. In other glasses, $T_X$ (or $T_C$) falls before maximum density has been reached. In this case, the crystallization process starts before complete densification, thereby preventing further sintering.

DTA and HSM results for V1–Ca and V3–Zn are shown as examples in Figs. 3a and 4a, respectively, in which the decrease in the area and height of the samples as a function of the temperature may be observed. The glass transition temperature $T_g$ and crystallization temperature $T_C$ of the glasses obtained by DTA measurements are indicated in the figures. Figs. 3b and 4b show the corresponding evolution of the shape of the samples presented in Figs. 3a and 4b.

Table 4 summarizes the temperature values at which initial shrinkage, maximum shrinkage, softening and flow take place for the different glasses obtained by HSM measurements, and $T_g$ and $T_C$ obtained by DTA results.

Figs. 3a and 4a indicate that complete densification takes place before the crystallization temperature. Considerable expansion (~30%) is observed in samples V1–Ca and V2–Mg glasses in the temperature range in which crystallization takes place (850–1000 °C). This is an undesirable effect for sealing (Fig. 3a). The expansion observed for glasses V3–Zn and V4 is smaller (Fig. 4a).

Larger pressed samples ($d=1\,\text{cm}$, $h=1\,\text{cm}$) were treated with the same thermal schedule (at 5 K min$^{-1}$) and extracted at different temperatures during the heating ramp and after different lengths of time at 900 °C. Density and X-ray diffraction patterns of the samples are discussed below.

Fig. 5 shows the X-ray diffraction pattern of powder pressed samples of V4 glass (bulk glass density 3.92 g/cm$^3$). Crystallization is not detectable at temperatures below 900 °C. Barium silicate (BaSiO$_3$) ($d=4.44$ g/cm$^3$) is the main crystalline phase, with BaAl$_2$Si$_2$O$_8$ ($d=3.29$ g/cm$^3$) also present. Maximum densification is reached for V4 glass at 900 °C (relative density = 0.99), but after 24 h at this temperature, expansion takes place and the relative density decreases (0.83). Crystallization of the BaAl$_2$Si$_2$O$_8$ with
lower density than the bulk glass and/or gas evolution during crystallization could produce this expansion. Similar behaviour was observed for the Ca-containing glass.

For the Ca containing glass (bulk glass density = 3.57 g/cm³), crystallization is delayed with respect to glass V4, taking place only after 5 h at 900 °C crystallization starts to be detected. Similar results have been obtained with magnesium (3.64 g/cm³) and zinc (3.74 g/cm³), although in the last case, BaZnSiO₄ crystallization is already detected once 900 °C is reached.

Fig. 6 shows the crystalline phases appearing for each glass composition after 24 h at 900 °C. In Ca- and Mg-containing glasses, Ba₅Si₈O₂₁ (d = 3.92 g/cm³) and BaAl₂Si₂O₈ (d = 3.29 g/cm³) are the main phases. The low density of the former phase together with gas evolution during crystallization may be responsible for the large expansion observed by HSM at temperatures around 900 °C. The maximum relative density reached at 900 °C was 0.99, decreasing to 0.51 after 24 h at this temperature. For Mg-containing glass, similar behaviour is observed.

The glass with Zn contains BaZnSiO₄ (d = 4.71 g/cm³) as the main phase and BaAl₂Si₂O₈. The maximum relative density reached at 900 °C for this glass was 0.97, with only slight expansion observed after 24 h at this temperature (relative density = 0.90).

With the aim of clarifying the role of each parameter (particle size distribution, surface energy and viscosity) on the non-isothermal sintering kinetics, the experimental results were analyzed by computer simulations using the Clusters model of sintering [6–8].

The measured values of the viscosity and particle size distribution were used for each glass. Surface energy values were calculated using partial molar surface energy values according to Abbe [10]. As indicated by the DTA analyses, crystallization takes place at temperatures above the maxi-

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Fig. 6. XRD patterns of the four studied glasses after 24 h at 900 °C.

Fig. 7. Relative density as a function of temperature treatment for V1–Ca glass comparing density obtained by HSM (measured), density of bigger treated samples (sequential) and the simulated density by Cluster model (calculated).
mum shrinkage temperatures and does not affect the sintering kinetics. In the simulations, the particle surface was considered 100% glassy ($x_f = 1$, i.e., there are no crystals or foreign dust on the particles surface). The average number of neighbours per particle was taken as 4 due to the low green density [8].

Figs. 7 and 8 show the comparison of the experimental density results obtained from HSM (measured) and the larger samples (sequential) and the simulated results (calculated). The final densities of the HSM experiments were obtained from initial relative density values between 0.46 and 0.48; the densification was calculated using the height and width of the samples as a function of the temperature, the width was calculated from the area and height (Figs. 3a and 4a). The initial green density of the pressed samples is 0.67–0.70. Figs. 7 and 8 indicate that a good agreement was found between measured and calculated kinetics for all glasses.

Only a small quantity of glass was required to carry out HSM densification experiments compared to the experiments with larger samples. In addition, the Cluster model has been proved for the first time to be suitable for analysing HSM measurements. Hence, a simple HSM experiment and the use of the Cluster model permits the behaviour at different sintering conditions of heating rate, particle size, viscosity, etc., to be analyzed, considerably reducing the experimental work.

5. Conclusions

New glass ceramics in the system BaO–RO–SiO$_2$ ($R = Ca, Mg and Zn$) with 5 mol% Al$_2$O$_3$ were investigated for sealing SOFCs. The studied glasses presented good dilatometric and viscosity properties for this application. Crystallization of barium silicate phases takes place. The thermal expansion coefficients of glass ceramics are similar to those of the original glasses, thus ensuring good mechanical stability.

When using a heating ramp simulating an SOFC start up, the sintering of glass powders is completed before crystallization. Consequently, good sealing and dense final glass ceramics can be obtained. Ca and Mg glasses exhibited undesirable expansion during the crystallization process. The Zn containing glass best fits the sealing requirements.

Simple HSM experiments and the Cluster model can be used to analyse the behaviour of samples at different conditions of heating rate, sintering time, particle size, viscosity, etc., thereby considerably reducing the experimental work.

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