

Alumina and zirconia as inhibitors of crystallization during sintering of borosilicate glasses

M. Jesus Pascual, Luis Pascual and Alicia Durán

Instituto de Cerámica y Vidrio (CSIC), Arganda del Rey, Madrid (Spain)

Peter Wange and Christian Rüssel

Otto-Schott-Institut für Glaschemie, Friedrich-Schiller-Universität Jena, Jena (Germany)

The glass composition (in mol%) $16 \text{ Na}_2\text{O} \cdot 24 \text{ B}_2\text{O}_3 \cdot 60 \text{ SiO}_2$ has suitable viscosity and dilatometric properties to be used as sealing material for the gas manifolds of molten carbonate fuel cells (MCFC). Nevertheless, quartz crystallization takes place during sintering of the borosilicate glass powder at temperatures between 600 and 700 °C. The quartz crystallization leads to the formation of pores and a variation in the thermal expansion coefficient; both giving rise to defects and tensions in the seal.

In this work, the possibility of inhibition of quartz crystallization by substituting Al_2O_3 or ZrO_2 for 2 or 5 mol% of SiO_2 is described. The thermal properties and the viscosity-temperature curve of the new compositions, especially those containing alumina do not differ much from the original glass.

1. Introduction

Molten carbonate fuel cells (MCFC) are made up of a stack whose lateral faces are closed by the gas manifold plates. The tightness of the cell is obtained by means of a seal located between the dielectric isolator of the manifold, an alumina frame, and the stack [1]. The seal must be mainly joined to the alumina frame. Glasses have a series of advantages for this application. A glass is a nonporous material that softens at high temperature and fits to the profile of the elements to be sealed ensuring a hermetic close. The viscosity and thermal expansion coefficient can be adjusted by varying the chemical composition. The most difficult requirement is a high chemical resistance in molten carbonates due to the incompatibility of properties.

A borosilicate glass with adequate thermal and chemical properties has been developed for this application [2 and 3], but it crystallizes during sintering at temperatures close to the working temperature of the cell (650 °C) [4].

Jean and Gupta [5 to 8] developed a method to inhibit the crystallization of cristobalite during the sintering of borosilicate Pyrex[®] glass powder between 700 and 1000 °C. According to these authors, the kinetics of

transport of alkaline ions is the controlling step in the crystallization reaction. As a solution, they propose the deviation of the flux of alkaline ions towards centres of the glass network in which their presence does not provoke nucleation and crystal growth. In any case, the transport rate must be greater than the nucleation rate of cristobalite. These points of the glass network polarize the flux of alkaline ions occupied by cations. Moreover, according to the random network model of glass structure, network formers with a valence number of three (M^{3+}) and tetrahedrally co-ordinated with oxygen may act as crystallization inhibitors. As a consequence, the negative charge created by the substitution of M^{3+} for Si^{4+} in the glass network provides an electrochemical potential for alkali ions (M^+) to segregate to M^{3+} in order to maintain electroneutrality at the local level. To verify the above hypothesis, a wide variety of oxides including trivalent metal ions such as Al_2O_3 , Ga_2O_3 , Y_2O_3 , La_2O_3 and Sc_2O_3 were chosen and separately added to Pyrex[®] borosilicate glass during sintering [9]. However, only Al_2O_3 and Ga_2O_3 prevented the cristobalite formation as indicated by X-ray diffraction, electron microscopy and thermal expansion measurements.

Other glass components, such as MgO , ZnO , TiO_2 or ZrO_2 , may also decrease the tendency to crystallization. Furthermore, the addition especially of ZrO_2 should improve the corrosion resistance in alkaline media [10].

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Table 1. Compositions of the borosilicate glasses studied

glass	composition in mol%
B	16Na ₂ O·24B ₂ O ₃ ·60SiO ₂
A2	2Al ₂ O ₃ ·16Na ₂ O·24B ₂ O ₃ ·58SiO ₂
A5	5Al ₂ O ₃ ·16Na ₂ O·24B ₂ O ₃ ·55SiO ₂
Z2	2ZrO ₂ ·16Na ₂ O·24B ₂ O ₃ ·58SiO ₂
Z5	5ZrO ₂ ·16Na ₂ O·24B ₂ O ₃ ·55SiO ₂

The objective of this work is to inhibit the crystallization of quartz during sintering of a special borosilicate glass which is a candidate for sealing MCFC. Here, the viscosity as well as thermal properties, such as the thermal expansion coefficient, should be maintained. For this purpose, up to 5% Al₂O₃ or ZrO₂ were added to the borosilicate glass.

2. Experimental procedure

Compositions containing Al₂O₃ and ZrO₂ were prepared substituting for 2 and 5 mol% SiO₂ from the base glass (B) 16 Na₂O · 24 B₂O₃ · 60 SiO₂ (in mol%). The glasses were prepared from quartz, vitreous B₂O₃ and Al₂O₃, ZrO₂ and Na₂CO₃, reactants quality. Once homogenized, the vitrifiable mixture was introduced in a platinum crucible and heated at 1000 °C for 2 or 3 h. After calcination, the glasses were melted in an electrical furnace at 1500 °C for 1 h in air. The compositions of the five borosilicate glasses studied are presented in table 1.

The dilatometric curves of the glasses were recorded using a differential dilatometer Netzsch Gerätebau model 402 EP (Germany) with a Netzsch programme model 410 and silica support. The heating rate in all cases was 5 K/min from room temperature up to the softening temperature. Prismatic samples were employed with ≈ 1 cm length.

The glass viscosity between 10⁸ to 10¹³ dPa s was measured by fibre elongation method employing a Haake viscometer with a sensor system ME 1700 (Germany). The samples were prepared following the standard DIN 52 312, part 3 [11], and the tests were performed according to ISO 7884-3 [12]. The viscosity data were fitted to the Vogel-Fulcher-Tammann (VFT) equation employing a regressive calculus.

A transmission electron microscope HITACHI H-7000 (Japan) has been employed to study phase separation in the borosilicate glasses. The micrographs were obtained from carbon replica from fresh fracture and etched with HF (5 vol.%) for 20 s.

The glasses were milled in dry conditions employing an agate mill. The powder was sieved and fractions with medium particle size around 10 μm were obtained. Samples were prepared from the powdered glass by iso-

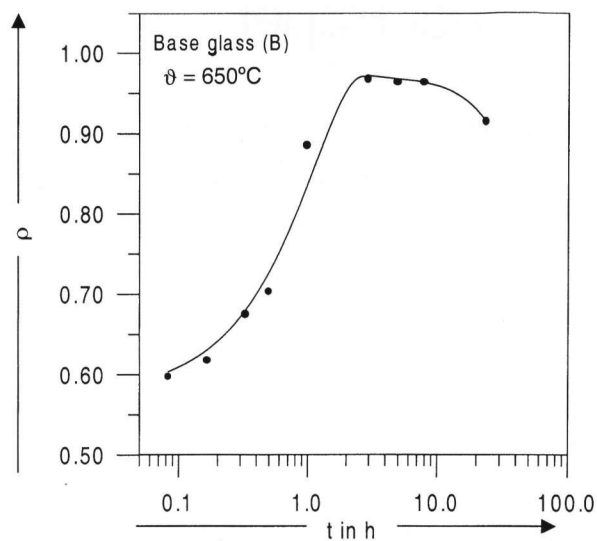


Figure 1. Relative density of powder samples of base glass (B) at 650 °C as a function of annealing time.

static pressure at 200 MPa during one minute and their apparent density was measured by the Archimedes method employing mercury. The initial relative density of the samples is approximately equal to 0.60±0.02. The samples were isothermally treated at 625, 650 and 675 °C during 24 h and the sintering stage was evaluated through the density change. The formation of crystalline phases was determined by X-ray diffraction (XRD) employing a Siemens diffractometer model D5000, with a generator KRISTALLOFLEX 710 (Germany).

3. Results and discussion

3.1 Sintering of base glass (B)

Figure 1 presents the relative density, ρ , of different B glass samples sintered at 650 °C as a function of time. The sintering is complete ($\rho = 0.98$) after two hours. From this time, longer treatments lead to a density decrease due to crystallization processes.

The XRD analysis (figure 2) of a sample treated for 24 h at 650 °C indicates the presence of α -quartz. The density of α -quartz (2.65 g/cm³) is greater than the density of the glass (2.46 g/cm³), but crystallization implicates a volume decrease of 15% producing the opening of porosity and decreasing the relative density. The α -quartz crystallization is expected because of the location of B glass composition in the phase diagram of the system Na₂O–B₂O₃–SiO₂ [13]. Figure 2 also shows the diffractograms for samples treated at 625, 650 and 675 °C for 24 h. The growing of the quartz peaks indicates the increase of crystallization rate with temperature, justifying the faster decrease of density at these temperatures.

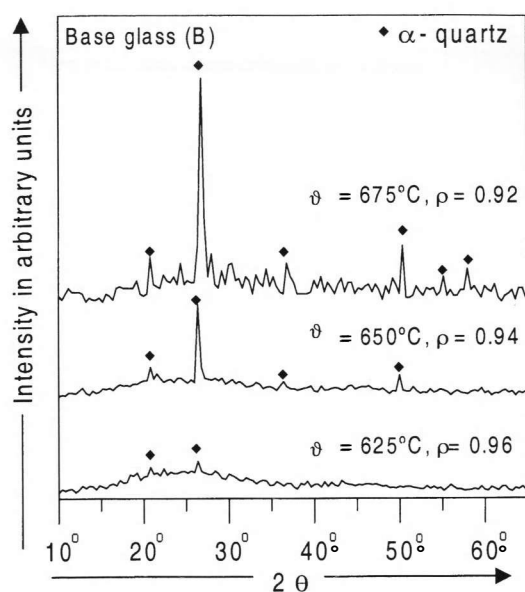
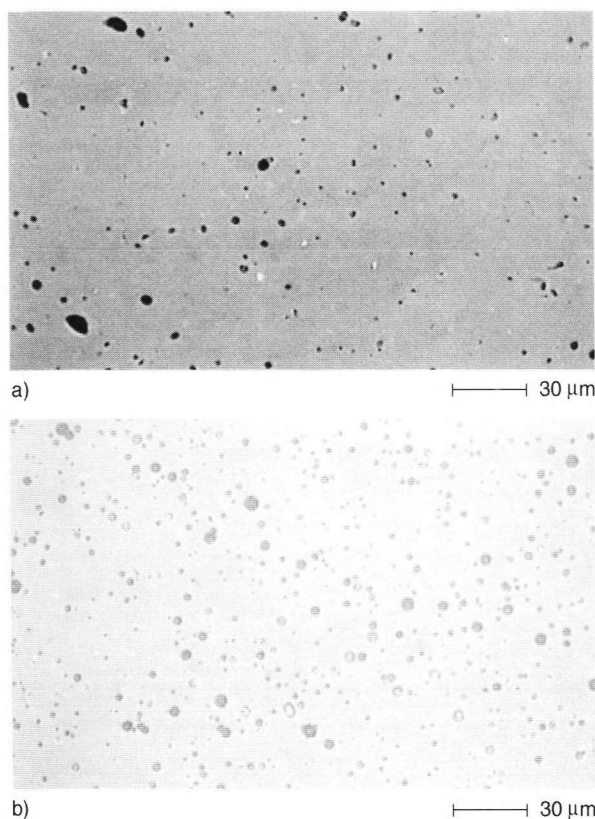


Figure 2. XRD patterns of powder samples of base glass (B) treated at 625, 650 and 675 °C for 24 h and the relative densities reached.



Figures 3a and b. Photographs of reflection optical microscopy of base glass (B) sintered at 650 °C for a) 5 h and b) 24 h.

Figures 3a and b present the densification degree for B samples treated for 5 and 24 h, respectively. Figure 3b shows the generation of new porosity during the quartz crystallization that provokes a decrease in the relative density values.

At 650 °C, the growth rate of quartz crystals is low enough to allow sintering by viscous flow. After thermal treatment longer than 10 h at this temperature, the size of the crystals is large enough to provoke the formation of pores and a decrease in density (figure 1). The crystallization of the seal can also affect other properties such as viscosity, thermal expansion coefficient and, as observed, may lead to the formation of pores. All these problems affect the mechanical and thermal stability of the seal.

3.2 Al₂O₃ and ZrO₂ as inhibitors of quartz crystallization

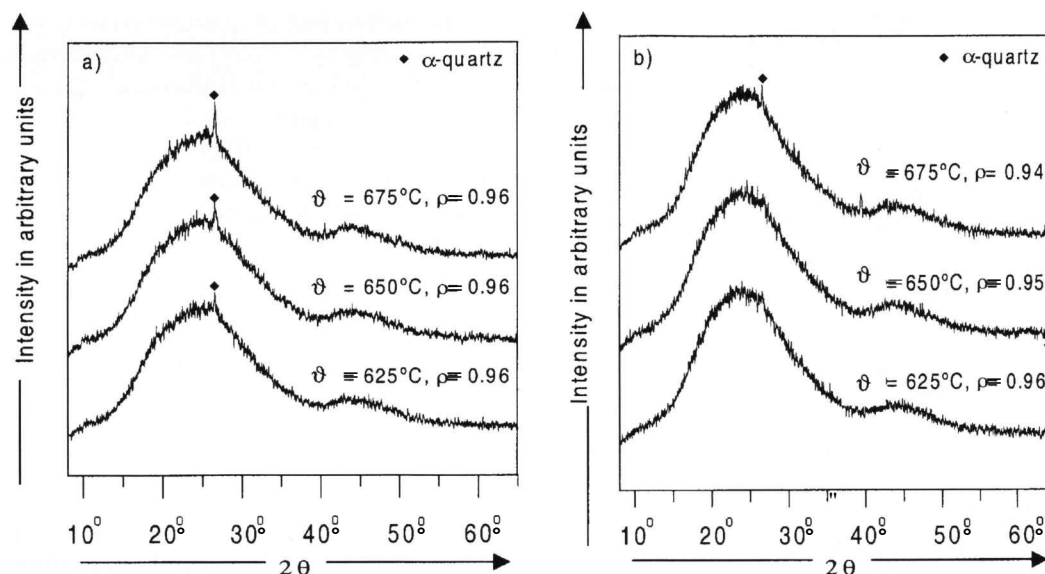
Figures 4a and b show the influence of the substitution of Al₂O₃ for 2 and 5 mol% SiO₂ for on the crystallization of quartz for samples treated at 625, 650 and 675 °C for 24 h together with the relative density reached. In comparison to the base glass composition, the reflections caused by quartz are much less intense in these samples. Crystallization of α-quartz is not at all observed for the glass with 5 % Al₂O₃ (within the XRD detection level), with the exception of samples thermally treated at 675 °C.

Inhibition of the quartz crystallization is not observed for samples with 2 % ZrO₂ thermally treated at 675 °C, however, inhibition is observed for samples with 2 and 5 % ZrO₂ after thermal treatment at 625 and 650 °C (see figures 5a and b). The effect of ZrO₂ is smaller than that of alumina, according to the tetravalent character of the Zr⁴⁺ ion. The decrease in the tendency to crystallization observed for the sample with 5 % ZrO₂ should be due to an increase in the viscosity rather than to the affinity of Zr⁴⁺ for alkaline ions. This is demonstrated by the crystallization taking place at temperatures higher than 650 °C, because here, the viscosity is lower than that of the base glass composition.

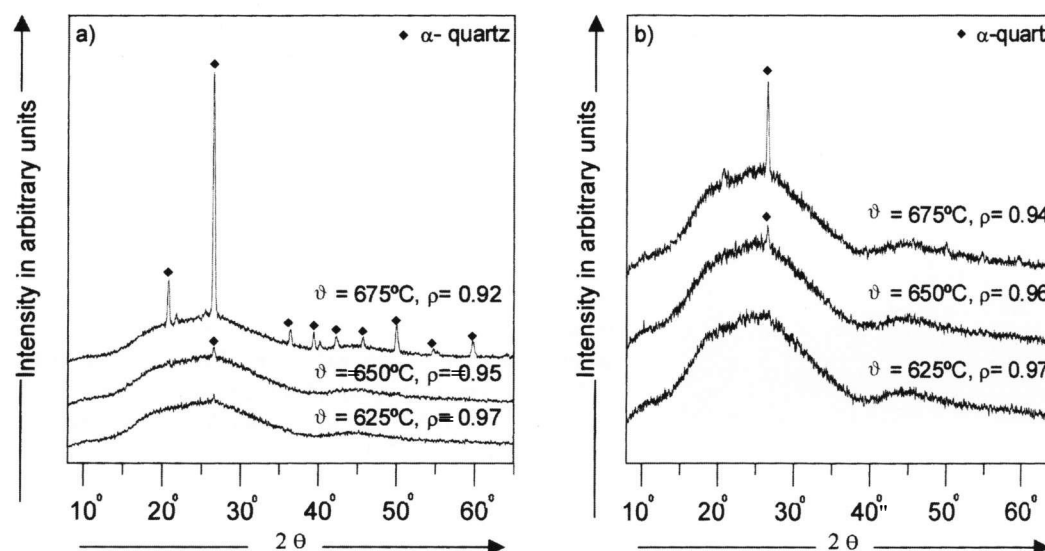
From these results, it can be deduced that substitutions of 2 and 5 % Al₂O₃ or 5 % ZrO₂ for SiO₂ inhibit the quartz crystallization at 650 °C, the working temperature of the cell. In order to select the most suitable inhibitor, the viscosity and dilatometric properties of the glasses have been studied.

3.3 Viscosity

In order to seal the gas manifolds of MCFC, it is necessary that the viscoplastic range of the glass is within the temperature range from 650 to 750 °C. Therefore, the viscosity in this range must be between $\lg \eta$ (dPa s) = 6 and $\lg \eta$ (dPa s) = 10. Viscosities larger than $\lg \eta$ (dPa s) = 10 at 650 °C would hinder the seal formation. If the glass viscosity were below $\lg \eta$ (dPa s) = 6, fluency could occur and the glass could be thrown out of the



Figures 4a and b. XRD patterns of a) A2 and b) A5 glass samples treated at 625, 650 and 675°C for 24 h and the relative densities reached.



Figures 5a and b. XRD patterns of a) Z2 and b) Z5 glass samples treated at 625, 650 and 675°C for 24 h and the relative densities reached.

alumina frame due to the big overpressures in the manifolds. This fact is specially important considering that during the start-up of the cell, temperature peaks up to 750°C can be reached.

Figure 6 presents the viscosity data for glasses containing Al_2O_3 . By contrast to borosilicate glasses of the Pyrex® type, Al^{3+} ions act as modifiers when added to the base glass composition. Thus, the increase in the concentration of nonbridging oxygens and the formation of AlO_6 octahedra leads to a decrease in viscosity. From these data, it can be deduced that a substitution of Al_2O_3 for 5% SiO_2 in the base glass provokes a decrease of viscosity $\lg \eta$ (dPa s) = 7.5 to 10, ϑ = 650 to 580°C. This may restrict its application for sealing MCFC.

Figure 7 shows the viscosity values for glasses containing ZrO_2 . In this case, an increase of viscosity is expected since the substitution of other oxides with the same valence for SiO_2 implicates the increase of viscosity according to the order of their coordination demands imposed by the increasing ionic radius. Nevertheless, the glass with 5% ZrO_2 presents a viscosity lower than that of the glass with 2% ZrO_2 and very similar to the base glass. Possibly, this is due to phase separation phenomena well known for borosilicate glasses containing ZrO_2 . This phase separation usually occurs in form of droplets, enriched in ZrO_2 . The result is a glass matrix with a smaller ZrO_2 concentration and, hence, with lower viscosity. Figure 8 shows the structure of a Z5 glass sample thermally treated at 625°C for 5 h. The micrograph pre-

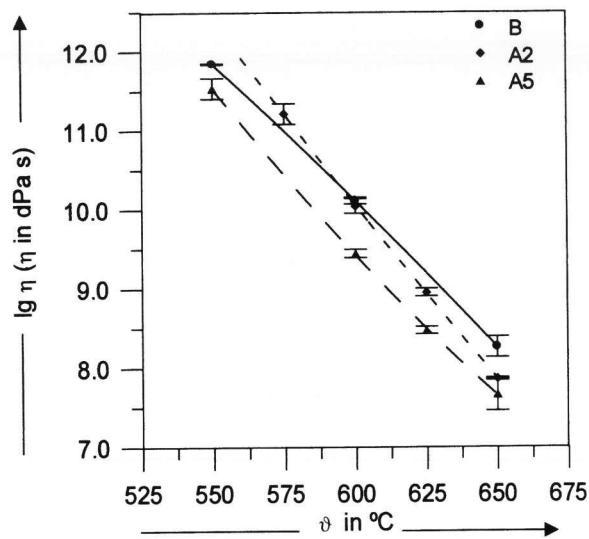


Figure 6. Viscosity-temperature curves within the viscoplastic range for various Al_2O_3 -containing glasses obtained from the fibre elongation method; lines: fit to Vogel-Fulcher-Tammann equation.

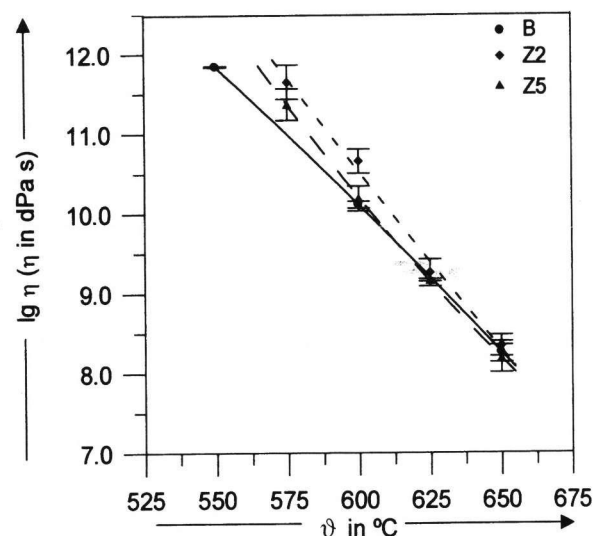


Figure 7. Viscosity-temperature curves within the viscoplastic range for various ZrO_2 -containing glasses obtained from the fibre elongation method; lines: fit to Vogel-Fulcher-Tammann equation.

sents phase separation with the formation of a droplet phase which is in good agreement with that exposed above.

3.4 Dilatometric properties

The materials to be sealed in the molten carbonate fuel cells are those constituting the gas manifold and the stack: alumina ($\alpha = 8 \times 10^{-6} \text{ K}^{-1}$) and stainless steel

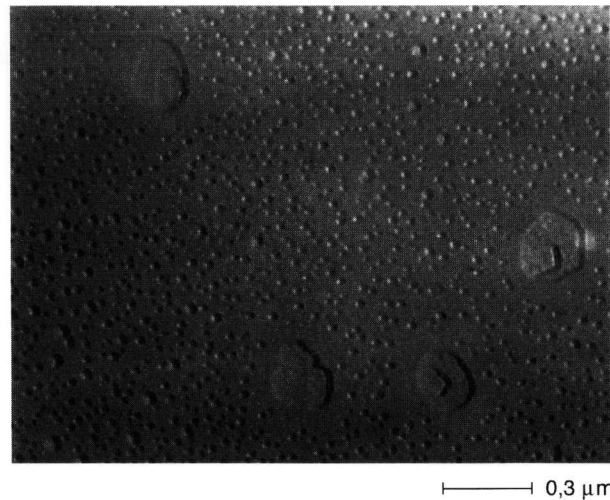


Figure 8. TEM micrograph of a Z5 glass sample treated at 625°C for 5 h (carbon replica).

Table 2. Glass transformation temperature, T_g , dilatometric softening point, T_d , and thermal expansion coefficient of the glasses studied

glass	T_g in $^\circ\text{C}$	T_d in $^\circ\text{C}$	$\alpha_{50-400} \cdot 10^6 \text{ K}^{-1}$
B	565	608	7.7
A2	554	612	8.3
A5	536	589	9.2
Z2	574	613	8.9
Z5	569	621	8.6

($\alpha = 14 \times 10^{-6} \text{ K}^{-1}$). The working principle is the adhesion of glass to the alumina frame and its sliding on the closing surface of the cell [14]. This principle has the advantage that the seal is joined to the alumina frame ensuring the close of the gas manifolds independent of the sliding during heating and working of the cell. The glass or glasses adapted to this application must have thermal expansion coefficients around $8 \times 10^{-6} \text{ K}^{-1}$ and softening temperatures between 550 and 625°C in order to provide a stable sealing with alumina at temperatures around the working temperature of the cell of 650°C .

The dilatometric properties of the glasses studied are presented in table 2. From the previously mentioned conditions, it can be deduced that the glass with 5% Al_2O_3 , and the glass with 2% ZrO_2 possess a too high thermal expansion coefficient, therefore glasses with 2% Al_2O_3 or 5% ZrO_2 seem to be more adequate.

The vitreous transformation temperature, T_g , decreases and the thermal expansion coefficient, α , increases with increasing the Al_2O_3 concentration since the substitution of Al_2O_3 for SiO_2 implicates a weakening of the glass network in these glasses. In contrast, the substitution of 2% ZrO_2 implicates the variation of properties in the opposite sense because of the stabilizing

effect of ZrO_2 . The glass with 5 % ZrO_2 presents similar properties than the base glass due to the phase separation process taking place in this composition resulting in a vitreous matrix poor in ZrO_2 with similar composition as the base glass and droplets of ZrO_2 -rich phase.

4. Conclusions

The substitution of 2 or 5 mol% Al_2O_3 or ZrO_2 for SiO_2 allows the inhibition of the crystallization of quartz during sintering of the glass with the basic composition (in mol%) $16 Na_2O \cdot 24 B_2O_3 \cdot 60 SiO_2$ at temperatures equal to or smaller than $650^\circ C$.

The compositions presenting dilatometric properties and viscosity similar to that of the base glass are those containing 2 % Al_2O_3 or 5 % ZrO_2 .

The composition with 5 % ZrO_2 is more adequate than the composition with Al_2O_3 for the application as sealant in MCFC since the former presents a too low viscosity value at $650^\circ C$ and would have a low resistance to the corrosion by molten carbonates.

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Contact:

Dr. M. J. Pascual Francisco
 Institute de Ceramica y Vidrio (CSIC)
 Antigua Ctra. de Valencia km 24,300
 28500 Arganda del Rey, Madrid
 (Spain)
 E-mail: mpascual@icv.csic.es