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Thermal expansion behaviour of glass ceramics derived from prophyric sands [1]

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Abstract

The thermal expansion curves are reported for "as-quenched" and "heat-treated" glasses obtained by adding MgO (8–16%) and TiO_2 (4%) to porphyric sands of composition: $SiO_2 = 72.40\%$; $Al_2O_3 = 13.85\%$; $K_2O = 4.60\%$; $Na_2O = 3.00\%$; $Fe_2O_3 = 2.15\%$; $CaO = 1.30\%$; $MgO = 0.84\%$; $TiO_2 = 0.20\%$; loss on calcination = 2.06%.

The variations in the glass transition temperature T_g, the thermal expansion coefficient α, and the dialatometric softening temperature M_g, are discussed. The experimental results can be explained by assuming that Na_2O, K_2O and CaO (all or a part of them) segregate preferentially with respect to MgO into the titania-rich phase. Diffusion appears to fall as the MgO content is increased.

INTRODUCTION

The dimensional changes that occur when the temperature is raised are of great technological importance [1]. Resistance to thermal shock depends on the thermal expansion coefficient α. When two materials are bonded together, a close matching of their α values is needed. The thermal expansion behaviour is strongly dependent on the structure and composition of the phases present in the material and, therefore, on the heat treatment schedule [1, 2].

Porphyric sands ($SiO_2 = 72.40\%$; $Al_2O_3 = 13.85\%$; $K_2O = 4.60\%$; $Na_2O = 3.00\%$; $Fe_2O_3 = 2.15\%$; $CaO = 1.30\%$; $MgO = 0.84\%$; $TiO_2 = 0.20\%$; loss on calcination = 2.06%) have been melted together with MgO and TiO_2 to make glass ceramics. It is known that TiO_2 favours glass in glass phase separation and, hence, enhances the devitrification process [1]. The effect of the heat treatment schedule on the thermal expansion

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characteristics has been studied and, to explain the experimental results, hypotheses are proposed concerning the phase separation chemistry of this system which is compositionally very complex.

EXPERIMENTAL

Mixtures (40 g) of the porphyric sands (composition above), $MgCO_3$ and TiO_2 were melted for 5 h at 1450°C in an electric oven. The melts were cooled rapidly to 500°C, and then slowly to room temperature. The glasses obtained have the following compositions (wt.%): Glass **a**: $Fe_2O_3 = 1.94$; $Na_2O = 2.70$; $K_2O = 4.14$; $CaO = 1.17$; $MgO = 8.09$; $Al_2O_3 = 12.48$; $SiO_2 = 65.23$; $TiO_2 = 4.25$. Glass **b**: $Fe_2O_3 = 1.88$; $Na_2O = 2.63$; $K_2O = 4.03$; $CaO = 1.14$; $MgO = 10.51$; $Al_2O_3 = 12.13$; $SiO_2 = 63.43$; $TiO_2 = 4.25$. Glass **c**: $Fe_2O_3 = 1.78$; $Na_2O = 2.48$; $K_2O = 3.80$; $CaO = 1.08$; $MgO = 15.34$; $Al_2O_3 = 11.45$; $SiO_2 = 59.84$; $TiO_2 = 4.23$.

They mainly differ in MgO content which falls in the range 8–15%.

Thermal expansion curves have been recorded by means of a Linseis L75 thermodilatometer, using a quartz tube and a heating rate $\beta = 5°C\ min^{-1}$. The samples were 5–10 mm long, 5 mm × 5 mm in cross section. The thermal expansion coefficient was evaluated in the temperature range 20–600°C.

RESULTS AND DISCUSSION

Thermal expansion curves were recorded for as-quenched samples and for samples heat-treated for 1 h in the temperature range 800–1000°C. Figure 1 shows the thermal expansion curve of as-quenched glass **a**, which

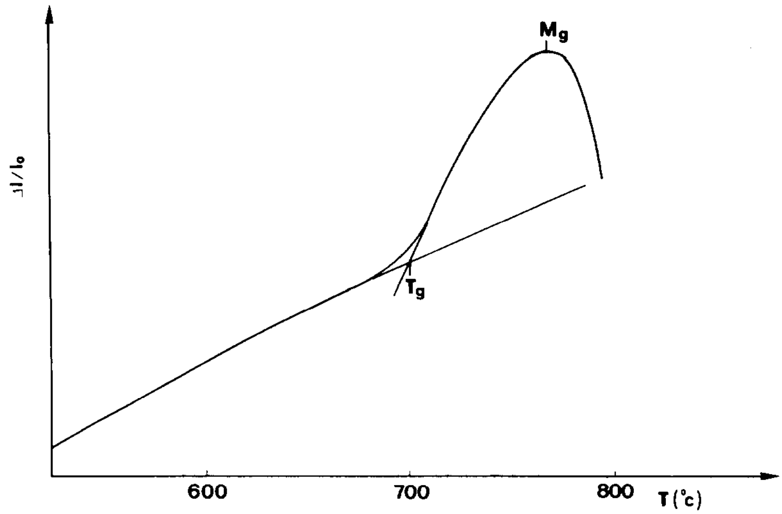

Fig. 1. Representative thermal expansion curve: as-quenched glass **a**.

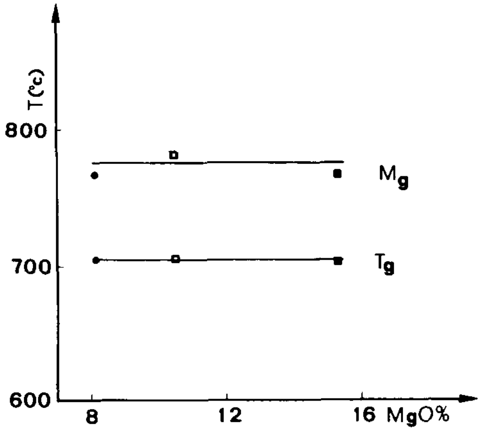

Fig. 2. T_g and M_g of as-quenched samples plotted against composition.

is representative of the behaviour of all the samples. A slope change is observed in the glass transition range; this is believed to be due to the release of the blocked vibrational states [1]. The temperature of the maximum of the curve is the softening temperature M_g: the apparent contraction is due to local deformation under the action of the small force necessary to keep the measuring device in contact with the specimen [1,3].

In Fig. 2, the T_g and M_g values of as-quenched glasses are reported as a function of the composition, expressed with respect to MgO%. Figure 3 gives the T_g values for samples heat-treated for 1 h, as a function of the thermal treatment temperature. As can be seen, heat treating has a much greater effect on T_g (variations of up to 60°C) than the change in MgO

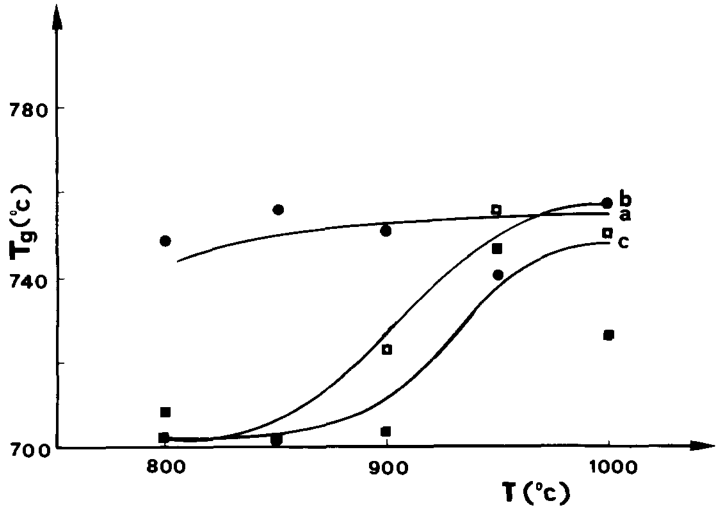

Fig. 3. T_g versus heat treatment temperature (1 h): ●, glass **a**; □, glass **b**; ■, glass **c**.

content has on the T_g of the as-quenched samples. The results can be explained by remembering that titanium dioxide is reported to be a nucleating agent. Separation plays an important role in the controlled crystallization of titania-containing glasses [1]. Although TiO_2 is soluble in a wide range of molten glasses, on cooling and subsequent reheating, separation of a titania-rich phase is reported to occur. It is reported that TiO_2 does not separate out as a pure compound [1]. In titania-nucleated $MgO–Al_2O_3–SiO_2$ glasses, magnesium titanate $MgO \cdot TiO_2$ crystals form. In a previous work [4], it was demonstrated that separation occurs in the studied glasses and that devitrification in the temperature range 800–1000°C gives rise to the formation of TiO_2 and $MgSiO_3$ crystalline phases; the experimental results also indicated that only a small fraction, if any, of the added MgO segregates into the titania-rich phase. The studied system is very rich in CaO, Na_2O and K_2O which are reported to be network-modifier oxides; these weaken the glassy network and decrease T_g [1, 2]. The reported results, together with those of Figs 2 and 3, can be explained by the preferential segregation of CaO, Na_2O and K_2O (all or a part of them), with respect to MgO, into the titania-rich phase. The same hypothesis was applied to explain the devitrification behaviour of the same glasses on quenching or subsequent reheating [5]. The curves drawn in Fig. 3, which roughly interpolate the experimental data, suggest the general trends: the largest T_g increases, at all temperatures, are recorded for the lowest MgO%. The proposed hypothesis implies that diffusion decreases as the MgO content is increased, so that smaller increases in T_g are progressively recorded.

Figure 4 reports the thermal expansion coefficients for samples heat-treated in the temperature range 800–1000°C as a function of the heat

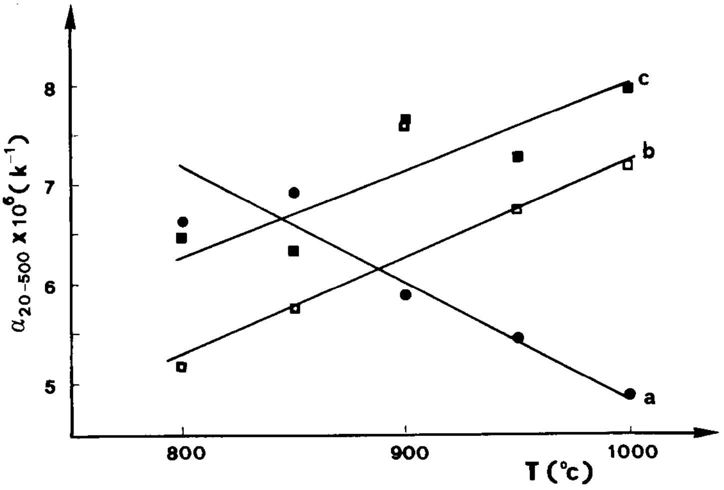

Fig. 4. α versus the heat-treatment temperature (1 h); symbols as in Fig. 3.

treatment temperature. The decreasing trend of devitrified glass **a** contrasts with the increasing trends of devitrified glasses **b** and **c**. A thermal expansion coefficient of $\alpha = 8 \times 10^{-6}\,°C^{-1}$ [1] has been reported in the temperature range 100–200°C for the clinoenstatite $MgO \cdot SiO_2$ which forms in this system in the temperature range 800–1000°C [4,6]; this is larger than the values of all the studied devitrified glasses. It is well known that the addition of alkaline and alkaline earth oxides to silicates causes α to increase [2]. Therefore in the studied system, the proposed hypothesis would suggest two competing effects: α increase due to formation of $MgSiO_3$; and α decrease because the primary glassy phase is depleted of CaO, Na_2O, K_2O and MgO due to $MgSiO_3$ formation and diffusion into the secondary glassy phase. In the case of glasses **b** and **c**, the first effect appears to be dominant. However, effect 2) appears to be dominant in glass **a**. In fact, glass **a** has a lower MgO content so that lower amounts of magnesium silicate can be formed [4,6] and, according to the interpretation of the T_g diagram, greater amounts of CaO, Na_2O and K_2O (all or some of them) segregate into the titania-rich phase.

In Fig. 5, the softening temperatures M_g for samples heat-treated for the same time (1 h) are reported as a function of the thermal treatment temperature. It is known that the refractory properties are strongly dependent on the level of crystallinity. In order to explain the results, M_g values are plotted in Fig. 6 as a function of the crystallinity percentage $C\%$ developed after the indicated thermal treatments. The values of $C\%$ were taken from ref. 6. While the values for glasses **b** and **c** can be interpolated by the same curve, the data for glass **a** appear to need a different interpolating curve: if a comparison is made at the same $C\%$, M_g values of glass **a** appear to be larger than those of **b** and **c**. In the light of the

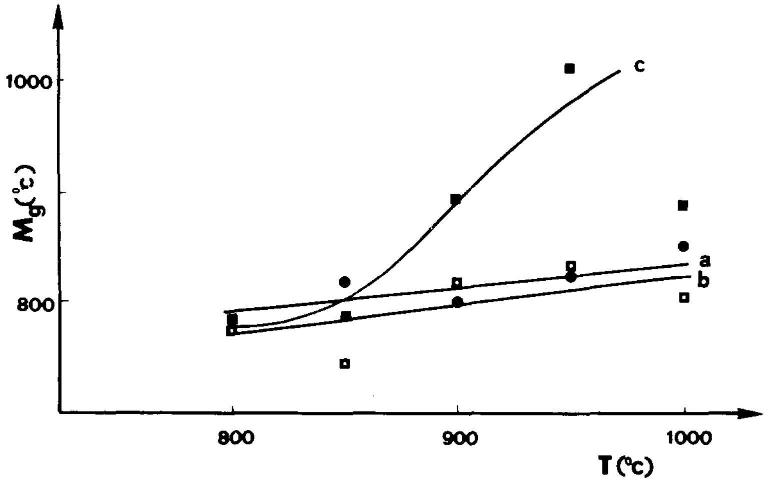

Fig. 5. M_g versus the heat-treatment temperature (1 h); symbols as in Fig. 3.

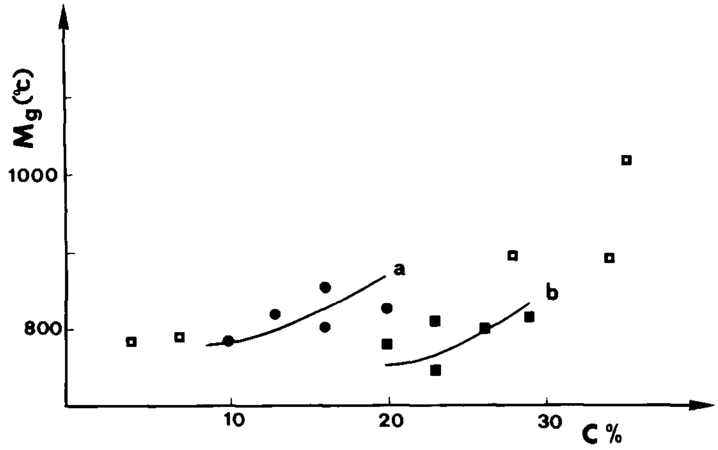

Fig. 6. M_g versus crystallization degree; ●, glass **a**; ■, glass **b**; □, glass **c**.

proposed hypothesis, this could be ascribed to the greater refractory nature of the glassy phase, which is more rapidly depleted of the network-modifier oxides.

CONCLUSIONS

The thermal expansion behaviour of the studied glass ceramics derived from porphyric sands can be explained from the fact that Na_2O, CaO and K_2O (all or part of them) segregate into the titania-rich phase.

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