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Thermal expansion investigation of iron rich glass-ceramic

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Abstract

A theoretical procedure was developed with the aim of obtaining an estimation of the crystallisation fraction in glass-ceramics by means of thermal expansion measurements. The theoretical model was applied to the crystallisation of an iron rich glass composition yielding magnetite and pyroxene as crystalline phases.

The crystallisation mechanism was investigated by means of DTA, XRD, FTIR, TEM; the thermal expansion by Differential Dilatometer. A relationship between the weight fraction of crystal phase and the linear thermal expansion coefficient was obtained. The values of the fraction of crystal phase, evaluated by means of dilatometric measurements, showed a good agreement with the results obtained by means of density variation and XRD analyses.

The crystallisation kinetic of the iron rich glass, at 630 and 700 °C, was also investigated by dilatometry and the variation of CTE as a function of the crystallisation time explained in terms of increasing of the apparent viscosity of the residual glass.

Keywords: Thermal expansion; Glass-ceramic

1. Introduction

Glass-ceramics are polycrystalline materials obtained by the crystallisation of high viscous glass-forming melts with appropriate compositions. Their properties basically depend on the kind and percentage of the crystal phase formed and on the composition of the residual glass. During the crystallisation process, the parent glass is transformed into a new material with different and sometimes outstanding properties as compared to the parent glass. The property modification depends on the degree of crystallisation in such a way that, in some cases, it might be used as an indicator of the transformation or as an estimate of the degree of crystallisation.

As proposed by Winkelmann and Schott, the physical properties of glasses, such as density, mechanical strength, thermal expansion, electrical conductivity and opacity, can be predicted by using the additive rule and the weight fraction of the constituent oxides.[1,2] The thermal expansion, in particular, is an important property of the materials since it affects many fields of application. The dilatometry is the technique utilised to investigate the thermal expansion and to evaluate the glass transition temperature, the solid state transformations and contraction during sintering of ceramics samples. By means of a dilatometer, the variation of linear dimension of a material as a function of a thermal cycle can be observed and measured.

As the thermal expansion coefficient, CTE, of a glass depends on the asymmetry of the amplitude of thermal vibrations, it decreases as the rigidity of the glass network increases. Modifying cations decrease the rigidity of the glass network by introducing non-bridging oxygen ions and therefore increase the CTE of the glass. The variation of the thermal expansion of the glass is proportional to the amount of the additives; if the change in the CTE of the glass, $\Delta\alpha$, caused, by an additive i, is divided for its amount, the thermal expansion prefactor for that additive, α_i is obtained. As a result of the crystallisation process, depending on the kind and fraction of crystal phase and on the composition of the residual glass, a modification of the CTE is obtained. Since the thermal expansion coefficient depends on the fraction of crystal phase formed during crystallisation, the relation between these two properties can be investigated.

Kingery evaluated the CTE of composites as the weight average of each phase CTE, density and bulk modulus.[3] Rapp investigated the correlation between percent crystallinity and CTE in Li_2O–Al_2O_3–SiO_2 glass-ceramics.[4] Freiman and Hench showed that in Li_2O–$2SiO_2$ the degree of crystallisation may be estimated from the variation of the CTE of the material.[5] In all these investigations, homogeneous crystallisation took place,

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i.e. the parent glass and the crystal phase formed had the same composition.

In most of the glass-ceramic forming systems, however, the parent glass and the crystal phases have different compositions and the CTE of the residual glass varies with the degree of crystallisation.

In this work, the relation between the weight fraction of crystallisation, w, and the CTE, α, has been investigated in an iron rich glass composition by means of differential dilatometer, XRD and FTIR techniques.

2. Theoretical approach

The additive rule of the physical properties was applied to the thermal expansion coefficient (CTE) of an iron rich glass composition. The CTE of the glass can be evaluated from the weighted sum of the empirically determined prefactors, α_i, of each oxides i constituting the glass. Winkelmann & Schott, English & Turner determined the thermal expansion prefactors when the weighted sum is expressed in terms of weight fraction of the oxides. Appen determined the thermal expansion prefactors of the oxides constituting the glasses when the weighted sum is expressed in terms of molar fraction of the oxides.[1–6]

Glass-ceramics may be considered as composite materials made up of a crystal phase and a residual glass. When the formed crystal phase and the parent glass have different compositions, the residual glass composition varies with the degree of crystallisation. Since only a fraction, w, of the parent glass is transformed into a crystal phase, it can be assumed that the parent glass, g0, consists of two glasses forming an ideal solution[7]: a glassy phase, gt, with the same composition as the crystal phase which is going to be formed, and a residual glass, gr. As a result of the crystallisation process, the fraction gr does not change, while gt is transformed into the crystal phase c.

With this assumption, the additive law can be adopted to evaluate the CTE of the initial glass;[1,2] the following expression applies:

$$\alpha_{g0} = w\alpha_{gt} + (1-w)\alpha_{gr} \tag{1}$$

where w, weight fraction of the glass gt; $\alpha_{gt} = \sum x_i\alpha_i$; $\alpha_{gr} = \sum x_j\alpha_j$, x, molar fraction, i, oxide components of the glass generating the crystal phase, j, oxide components staying in the residual glass.

During the crystallisation heat treatment, the parent glass, g0, is transformed into the glass-ceramics, gc; the glass, gt, becomes the crystal phase, c, and its weight fraction, w, becomes the fraction of the crystal phase. Eq. (1) can be written as:

$$\alpha_{gc} = w\alpha_{c} + (1-w)\alpha_{gr} \tag{2}$$

The combination of Eqs. (1) and (2) yields the relation between the crystal phase fraction w and the thermal expansion coefficients:

$$w = \frac{\alpha_{gc} - \alpha_{g0}}{\alpha_c - \alpha_{gt}} \tag{3}$$

In Eq. (3), α_c, α_{gt} and α_{g0} are constants, therefore the crystal fraction is a linear function of the CTE of the glass-ceramic.

Since the crystals are randomly dispersed in the glassy matrix, the linear α_c of a crystal phase in a glass-ceramic can be assumed as 1/3 of its volumetric CTE.

When several crystalline phases are formed and their weight fraction, w_{ci}, is known, α_c and α_{gt} in Eq. (3) become, respectively:

$$\alpha_c = \sum w_{ci}\alpha_{ci} \quad \text{and} \quad \alpha_{gt} = \sum w_{ci}\alpha_{gti}$$

where:

- w_{ci} is the ratio between the mass of the crystalline phase i and the whole mass of the crystalline phases;
- α_{ci} is the CTE of the crystalline phase i;
- α_{gti} is the CTE of the glass with the same composition of the crystalline phase i.

3. Experimental

The iron rich glass composition investigated in the present study was obtained by mixing different industrial residues and raw materials in a ratio defined according to the glass-forming region for the systems SiO_2–Fe_2O_3–(CaO,MgO).[7] The investigated iron rich glass had the following composition in oxides wt%: SiO_2: 52.9, Al_2O_3: 4.1, Na_2O: 6.4, K_2O: 1.1, MgO: 1.8, CaO: 5.2, PbO:1.7, ZnO: 2.7, Fe_2O_3: 24.1, determined by means of an X-ray Fluorescence Xepos Spectro instrument.

Fusion was carried out in corundum crucibles by means of an electric furnace in the 1400–1450 °C temperature range. The melt was quenched in a 15 cm × 15 cm stainless-steel mould.

Thermal analysis of the glass was carried out on bulk samples, in air at 10 °C/min, by means of a Netzsch STA mod. 409 apparatus. Glass-ceramics were obtained by means of a controlled crystallisation of the glass, by proper thermal cycles.[7]

The formed crystalline phase fractions were determined by XRD technique, using a Philips-1830 apparatus and Cu Kα radiation. The ratio between the different crystalline phases was obtained by comparing the intensities of the major peaks. The parent glass and the heat-treated samples were investigated by

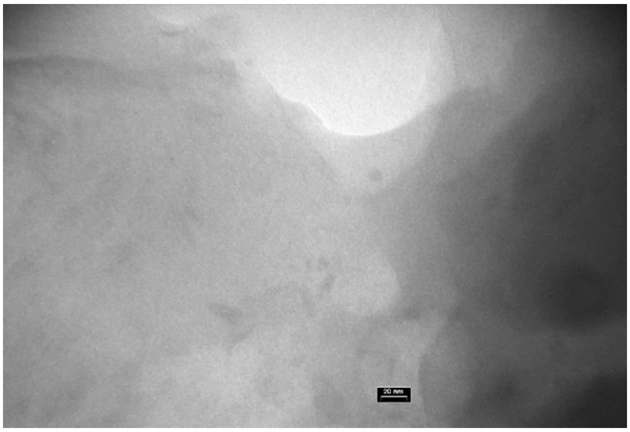

Fig. 1. TEM image of the parent glass (265 k×, bar 20 nm).

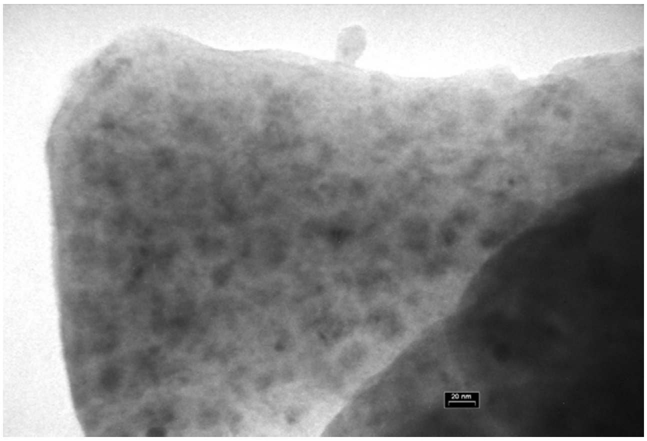

Fig. 2. TEM image of the sample heated at 630 °C/2 h (265 k×, bar 20 nm).

means of FTIR, in transmission mode and KBr medium, using a Nicolet Nexus apparatus. A Philips CM 200 Transmission Electron Microscopy, TEM, operating at 200 keV was employed to investigate the micro-structure of the glass and glass-ceramics. The thermal expansion as a function of temperature was measured by means of a Differential Dilatometer Netzsch mod. 402 using 5 mm × 5 mm × 25 mm samples, at a heating rate of 3 °C/min and alumina as reference. The density was measured by means of a Micromeritics Accupyc 1330 He-pycnometer.

4. Results and discussion

Fig. 1 is the TEM image at 265 k× magnification of the parent glass showing an amorphous and homogeneous glassy phase. This visual evidence was confirmed by the electron scattering image. Fig. 2 shows the glass at 265 k× heat treated at 630 °C for 2 h; the presence of two phases, in the approximate ratio of 1:1, is clearly noticeable. Fig. 3 shows the TEM images at 700 k× of the samples heat treated for 2 h at 630 and 700 °C; in the same figure, the corresponding XRD spectra are reported for comparison.

The TEM picture of the sample heat treated at 630 °C for 2 h shows the presence of two phases that can be ascribed to a liquid–liquid immiscibility and to the beginning of crystallisation, as shown by the XRD spectrum, where the magnetite formation is visible. In the sample b, heat treated at 700 °C for 2 h, two crystalline phases are clearly distinguishable and the corresponding XRD spectrum highlights the presence of magnetite and pyroxene.

In order to clarify the crystallisation behaviour of the iron rich glass, FTIR experiments were carried out on the parent glass and the heat-treated samples. The FTIR spectra of the parent glass and the heat-treated samples at 630 and 700 °C for 2 h are reported in Fig. 4.

In the parent glass the maximum of absorbance, relative to the Si–O–Si asymmetric stretching vibration, is centred at a

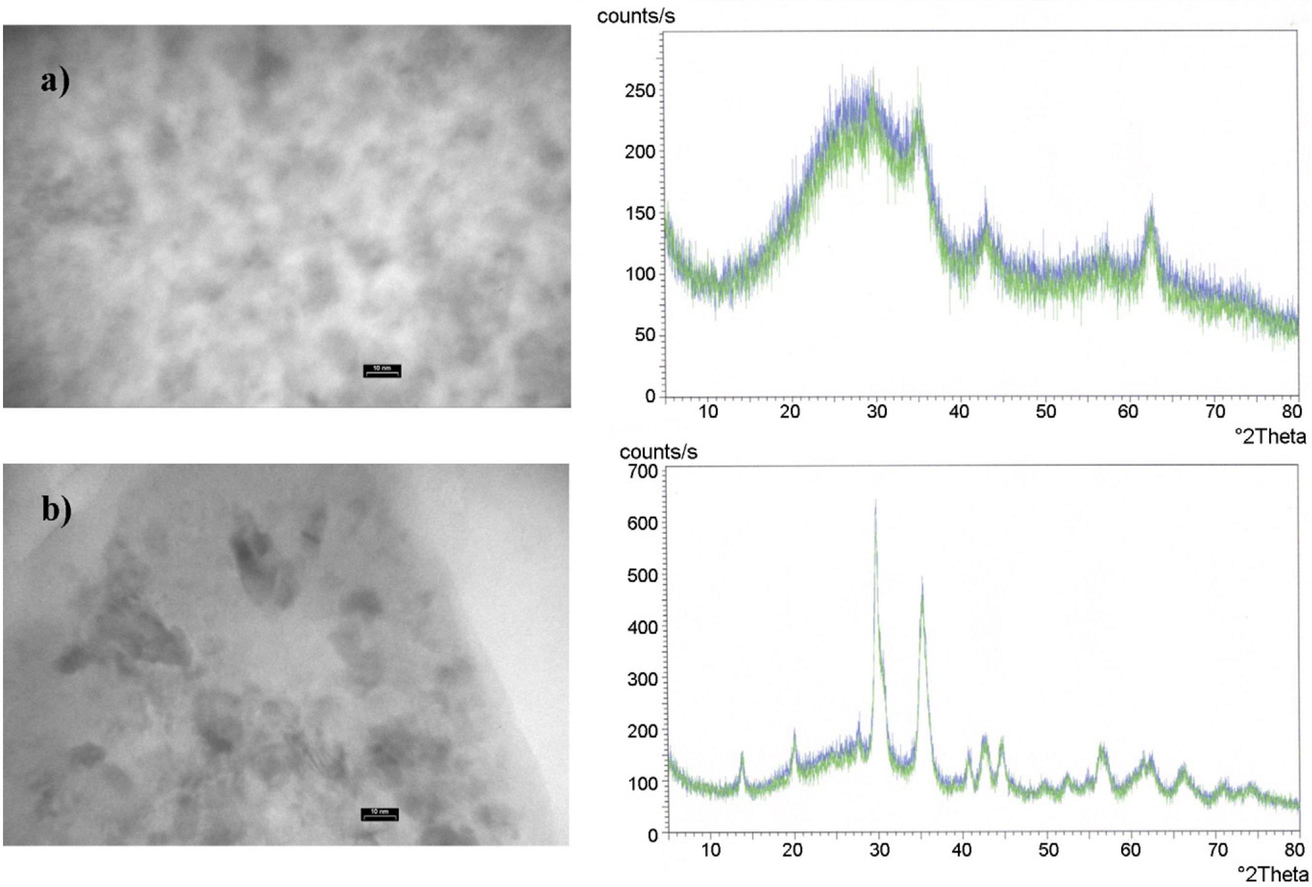

Fig. 3. TEM images (700 k×, bar 10 nm) and corresponding XRD spectra of heat-treated samples (a) 630 °C, 2 h and (b) 700 °C, 2 h.

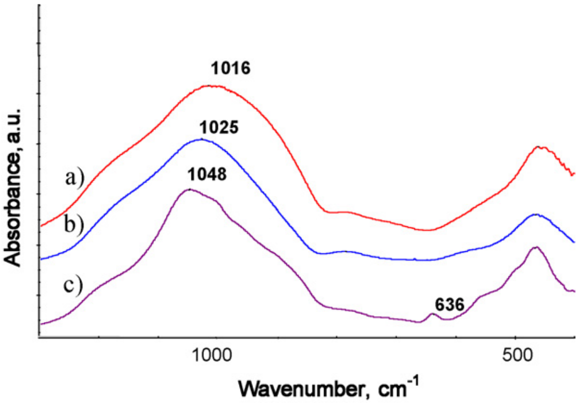

Fig. 4. FTIR spectra of: (a) parent glass, (b) 630 ht sample and (c) 700 ht sample.

wavenumber of 1016 cm^{-1}; the spectrum of the sample treated at 630 °C shows a positive shift of 10 cm^{-1} of the Si–O–Si asymmetric stretching highlighting a rearrangement of the silica network. The spectrum of the sample treated at 700 °C shows a positive shift of 30 cm^{-1} of the Si–O–Si asymmetric stretching and a peak at 638 cm^{-1} highlighting the presence of pyroxene and magnetite in a not defined proportion due to the overlapping of the wavenumbers of these crystalline phases.

By combining the results obtained by XRD and FTIR techniques and the images by TEM it appears that a liquid phase immiscibility takes place by heat treatment at 630 °C, yielding two glassy phases. One of them is richer in iron and leads to the formation of magnetite as primary crystalline phase. A liquid immiscibility in heating was proposed in a previous study.[8]

The DTA trace of the present glass composition, bulk samples heated at 10 °C/min in air, showed a glass transition temperature at 580 °C and an exothermic peak at about 765 °C corresponding to the crystallisation process. The XRD spectrum of the sample, heat treated at 700 °C for 2 h showed that pyroxene and magnetite are the main crystalline phases with an approximate ratio of 3:1, as obtained by comparing the intensity of the two major peaks. The crystallisation behaviour of iron rich glass-ceramics was subject of investigation in previous works.[7–12]

In Table 1, the CTE of some crystal phases, taken from literature, and the corresponding glasses calculated by Appen method (gt), are reported. Several CTE and thermal expansion prefactors calculation methods are present in literature; however, the Appen method was selected because it allows the possibility to calculate the CTE of a glass composition with high iron content.

Table 1
CTE of some typical crystal phases in glass-ceramics

	α_c	$\alpha_{gt\ Appen}$
Wollastonite—$CaO{\cdot}SiO_2$	10.8[a]	8.4
Anorthite—$CaO{\cdot}Al_2O_3{\cdot}2SiO_2$	4.5[a]	4.4
$Li_2O{\cdot}2SiO_2$	11[a]	11.53
Cordierite—$2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$	2.6[a]	2.77
Hematite—Fe_2O_3	7.93[b]	5.5
Magnetite—Fe_3O_4	6.86[b]	5.5
Diopside (D)—$Cao{\cdot}MgO{\cdot}2SiO_2$	9.26[b]	6.65
Hedenbergite (H)—$CaO{\cdot}FeO{\cdot}2SiO_2$	9.93[b]	6.52
Pyroxene solid solution—(D-H)	9.59[b]	6.58

[a] Linear CTE from Donald J. Mater. Sci. (reference no. [15]).

[b] 1/3 of volumetric CTE from Mineral Structure Data Bank-University of Colorado.

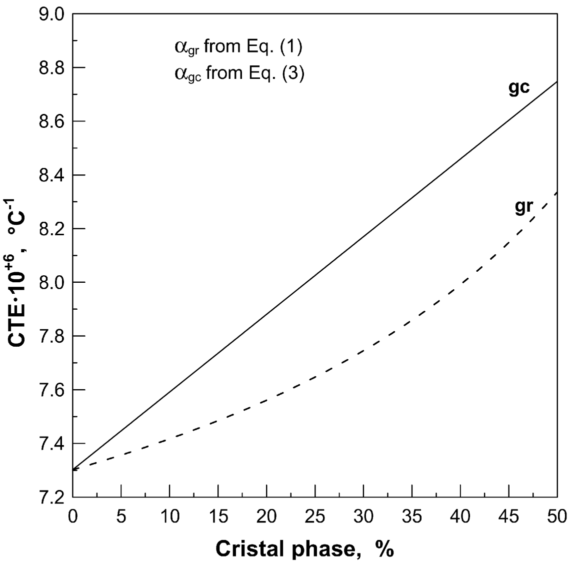

Fig. 5. Glass-ceramic, gc, and residual glass, gr, calculated CTE as a function of %crystal phase.

The dilatometric measurements carried out on the initial glass yielded an experimental CTE of $7.30 \times 10^{-6}\,°C^{-1}$ in the 20–300 °C and $7.72 \times 10^{-6}\,°C^{-1}$ in the 20–400 °C temperature ranges, with an associated error of $\pm 0.1 \times 10^{-6}$. The Appen method applied to the same glass composition yielded a calculated CTE of $7.61 \times 10^{-6}\,°C^{-1}$ in the 20–400 °C range, showing a very good agreement with the experimental values.

In Fig. 5, the CTE of the glass-ceramic (Eq. (3)) and the residual glass (Eq. (1)), for the investigated system are reported as a function of the percent of crystal phase. It can be observed that the CTE of the glass-ceramic increases with the crystallinity because both, the formed crystal phases and the residual glass, have a CTE higher than the parent glass. In fact, $\alpha_c = 9.16 \times 10^{-6}$ is higher than $\alpha_{g0} = 7.61 \times 10^{-6}$ and the residual glass is depleted of a glassy phase (gt) having a CTE lower than the parent glass ($\alpha_{gt} = 6.27 \times 10^{-6}$ compared to $\alpha_{g0} = 7.61 \times 10^{-6}$).

In a previous work,[7] the same oxide composition was investigated by means of density measurements. By assuming glass-ceramic as a composite material and the density as an additive property, a relation between the crystal phase percentage and the density was found. The method was then applied to the study of the crystallisation kinetic and the results were compared with the XRD method, showing an excellent concordance.

In the present work, the results obtained by dilatometry were compared with the ones obtained by density measurements. In Fig. 6, the CTE and the density of glass samples, heat treated for 1 h at different temperatures, are plotted.

The density decreases for temperatures higher than 700 °C due to the decreasing of crystallisation fraction. The CTE curve trend obtained in this work shows the same behaviour but with a higher slope. The explanation might rely in the fact that the

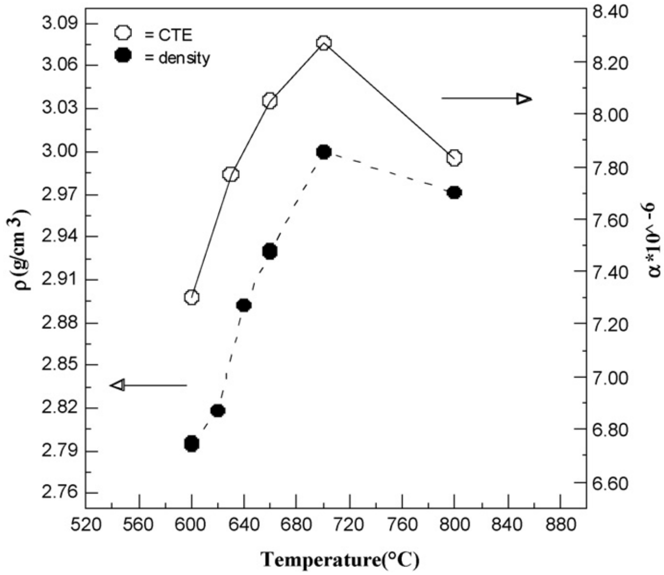

Fig. 6. Experimental density and CTE of 1 h heat treated glass-ceramic as a function of temperature (black points: density, white points: CTE).

density decreases with the percentage of crystal phase variation while the CTE is affected by the variation of composition of the residual glass and the percentage of crystal phase; both, as shown in Fig. 5, have a CTE higher than the parent glass.

Fig. 7 compares the percent of crystal phase evaluated by the density method[7] and by the dilatometric method developed in this work using Eq. (3). The two methods yields almost identical results in the limit of the associated error, $\pm 0.001\ \mathrm{g\,cm^{-3}}$ and $\pm 0.1 \times 10^{-6}\ \mathrm{K^{-1}}$, respectively.

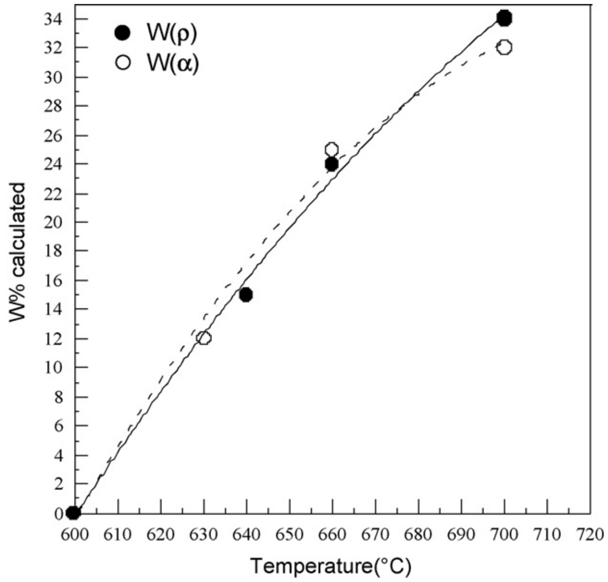

Fig. 7. Calculated percent crystal phase as a function of temperature by means of density and CTE method (black points: density, white points: CTE).

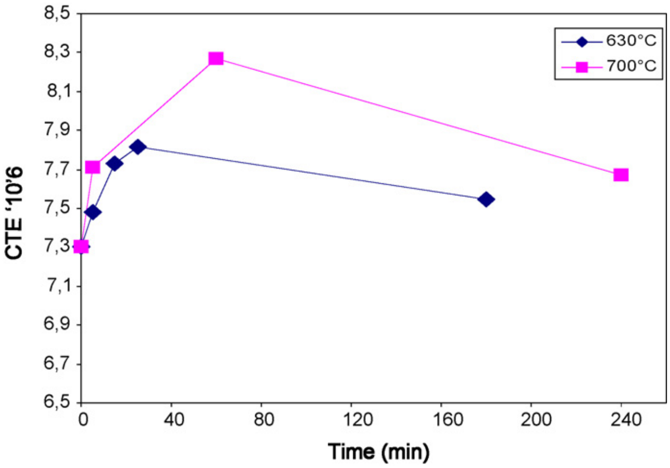

Fig. 8. Experimental CTE of glass-ceramic as a function of heat treatment time at 630 and 700 °C.

The crystallisation kinetic of the glass was investigated by means of dilatometry at 630 and 700 °C. In Fig. 8, the CTE values in the 20–300 °C range have been reported as a function of time. The curve at 630 shows a maximum at about 30 min heat treatment while the curve at 700 °C has the maximum at 60 min, both having the same trend. As expected, the CTE of the glass-ceramic increases with the time of thermal treatment, i.e. the fraction of crystal phase, because the thermal expansion of the crystal phase and residual glass are higher than the parent glass. The decreasing of the thermal expansion, after the maximum in the curves, i.e. 30 and 60 min at 630 and 700 °C, respectively, can be ascribed to the increasing of the apparent viscosity[11] of the residual glass. The shrinkage due to crystallisation is not compensated by the viscous flow of the residual glass yielding internal voids at the interface between crystals and glass. Therefore, the linear dilatation decreases due to the internal spaces available for the expansion. A similar behaviour was found in the devitrification of other glass systems such as $CaO–SiO_2–Al_2O_3–Y_2O_3$ and $MgO–BaO–Al_2O_3–SiO_2$.[13,14] Moreover, in our previous investigation[9] on the same glass composition, a bent in curve of dilatometric glass transition temperature, T_g, and of the dilatometric softening point, T_s, was observed when the crystal phase exceeded about 30%.

5. Conclusions

A liquid immiscibility with the formation of two liquid phases, one richer in iron, has been highlighted during the thermal treatment of iron rich glass composition, by combining FTIR and XRD techniques and by TEM observation.

A theoretical approach has been developed for the evaluation of the fraction of crystal phase by means of dilatometric measurements and it has been successfully applied to the crystallisation of the iron rich glass composition.

The evaluation of the percentage of the crystal phase formed resulted to be comparable with the data obtained by density measurements; a sensible difference occurred at high degree of crystallisation. The reason was attributed to the variation of viscosity connected with the crystallisation.

The dilatometric method could be applied to any phase transformation process, generating a dimensional change, i.e. crystallisation, crystal phase transformation, etc. However, it can be utilised if the variation of connected to the above-mentioned transformation is sufficiently large for the sensitivity of the technique employed. In the investigated iron rich glass, the formed crystal phases and the residual glass have a CTE larger than the parent glass.

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