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Short communication

The effect of fluoride ions on the structure and crystallization kinetics of La_2O_3-containing diopside based oxyfluoride glasses

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Abstract

Oxyfluoride glasses in the system CaO–MgO–BaO–SiO_2–Al_2O_3–La_2O_3–CaF_2 were obtained by adding CaF_2 (3–8 wt%) to a parent diopside based glass composition, $Ca_{0.8}Ba_{0.1}MgAl_{0.1}La_{0.1}Si_{1.9}O_6$. The characterization of the glasses has been made by density, dilatometry and FTIR measurements. Non-isothermal crystallization kinetic studies in conjunction with XRD and SEM have been employed in order to investigate the effects of fluoride ion additions on crystallization behaviour and mechanism of glasses.

Keywords: D. Glass; D. Glass-ceramics; D. Silicate; D. Halide; CaF_2

1. Introduction

Oxyfluoride-aluminosilicate glasses and glass-ceramics (GCs) have received a great deal of attention in the recent past due to their wide range of applications in different technological areas [1–4]. Oxyfluoride GCs doped with rare earth (RE) ions have been researched widely in the past few decades, since they possess not only higher chemical and mechanical stability than fluoride glass but also lower phonon energy than oxide glass [5]. The GCs of this kind usually contain such small crystalline phases as the nano-size $Pb_xCd_{1-x}F_2$ or PbF_2 crystals in the glass hosts that they can improve the optical properties with no loss of transparency [5–7]. However, both CdF_2 and PbF_2 are poisonous so that they cannot be used extensively. Some researchers have developed GCs containing LaF_3 or CaF_2 nanocrystals [8–10]. The alkaline-earth fluoride lattice consists of a body-centered (fluorite) cubic structure. The F^- ions form a cubic cage with the alkaline-earth cation residing at the centre of each alternate cage. Trivalent RE ions can be substituted for the divalent alkaline-earth cation [11]. This brings possibilities of preparing transparent GCs containing MF_2:RE^{3+} (M = Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) nanocrystals.

Recently, Sroda and Paluszkiewicz [3] investigated the effect of alkaline-earth ions on the structure of oxyfluoride-aluminosilicate glasses. Previously, Agathopoulos et al. [12] had investigated the structural behaviour of the CaO–MgO–SiO_2–CaF_2 glasses. However, the amount of CaF_2 was almost constant in all the investigated glasses. According to the best of our knowledge, no study pertaining to the influence of fluoride ions on the structure and crystallization kinetics of the RE-doped pyroxene-based glasses has been reported so far. Therefore, the present study is an attempt to fill in this lacuna. Three glass compositions have been prepared by adding different amounts of CaF_2 (3, 5 and 8 wt%, respectively) in the La_2O_3-containing diopside based parent glass composition, $Ca_{0.8}Ba_{0.1}MgAl_{0.1}La_{0.1}Si_{1.9}O_6$ [13]. The glasses have been labelled according to the amount of CaF_2, i.e. parent glass ($Ca_{0.8}Ba_{0.1}MgAl_{0.1}La_{0.1}Si_{1.9}O_6$) will be labelled as 7–0 (0 wt% CaF_2). Similarly, glasses with 3 and 8 wt% CaF_2 will be labelled as 7–3 and 7–5, respectively. The results pertaining to the parent glass composition (7–0) have been already published

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elsewhere [13] but will be presented and discussed along the manuscript for the convenience of the readers.

2. Experimental

Powders of technical grade SiO_2 (purity > 99.5%) and $CaCO_3$ (>99.5%), and of reactive grade $BaCO_3$, Al_2O_3, $MgCO_3$, La_2O_3, NiO and CaF_2 were used. In order to be consistent with our previous investigation [13], 1 wt% of NiO was added to all the three glass batches. Homogeneous mixtures of batches (~100 g), obtained by ball milling, were calcined at 900 °C (1173 K) for 1 h and then melted in Pt-crucibles at 1550 °C (1823 K) for 1 h. Glasses in bulk form were produced by pouring the melts on preheated bronze moulds followed by annealing at 550 °C (823 K) for 1 h.

Dilatometry measurements were done on prismatic samples with a cross section of 4 mm × 5 mm (Bahr Thermo Analyze DIL 801 L, Hüllhorst, Germany; heating rate 5 K min^{-1}). A minimum of 3 samples for each composition was analyzed. Glass transition temperature (T_g) softening point (T_s) and CTE were obtained in the permissible limits of experimental errors.

Infrared spectra for the glasses were obtained using an Infrared Fourier spectrometer (FT-IR, model Mattson Galaxy S-7000, USA). For this purpose samples were crushed to powder form in agate pestle-mortar, mixed with KBr in the proportion of 1/150 (by weight) and pressed into a pellet using a hand press.

Archimedes' method (i.e. immersion in diethyl phthalate) was employed to measure the apparent density of the bulk-annealed glasses and resultant GCs. The mean values and the SD presented for density have been obtained from (at least) 10 different samples.

In order to investigate the crystallization kinetics bulk-annealed glasses were crushed into powder form by hand using agate pestle-mortar. The mean particle size of the glass powders as determined by light scattering technique (Beckman Coulter LS 230, CA USA; Fraunhofer optical model) was in the range 180–250 μm. Crystallization kinetics of the glasses was studied by using differential thermal analysis (DTA, Netzsch 402 EP, Germany). The glass powder weighing 50 mg was contained in an alumina crucible and the reference material was α-alumina powder. The samples were heated in air from ambient temperature to 1000 °C (1273 K) at different heating rates (β) in the range of 5–20 K min^{-1}.

The crystallization behaviour of the glasses was investigated by heat treating the small pieces of bulk glasses in an electric furnace, in air, in accordance with the following thermal cycles: (1) room temperature (RT) → 700 °C (973 K) for a dwell time of 1 h at 700 °C; (2) room temperature (RT) → 800 °C (1073 K) for a dwell time of 1 h at 800 °C; (3) RT → 900 °C °C (1173 K) for a dwell time of 1 h at 900 °C; (4) RT → 1000 °C (1273 K) for a dwell time of 1 h at 1000 °C; (5) RT → 600 °C (873 K) for a dwell time of 2 h at nucleating temperature (T_n), i.e. 600 °C, and then 600 → 900 °C for a dwell time of 1 h at 900 °C; (6) RT → 700 °C (973 K) for a dwell time of 2 h at nucleating temperature, i.e. 700 °C, and then 700 → 900 °C for a dwell time of 1 h at 900 °C. The heating rate in all the thermal cycles was 5 K min^{-1}. The crystalline phases were determined on the powdered (crushed by hand using agate pestle-mortar) GCs by X-ray diffraction analysis (XRD, Cu $K\alpha_1$ radiation, Bruker AXS, D8 Advance, Germany; 2θ angle range 10–80°; step 0.02 $degs^{-1}$). Microstructure observations were done at polished (mirror finishing) and then etched (by immersion in 2 vol.% HF solution for 2 min) surfaces of GCs by field emission scanning electron microscopy (FE-SEM, Hitachi S-4100, Japan; 25 kV acceleration voltage, beam current 10 μA) under secondary electron mode.

3. Results and discussion

All the glasses obtained after melting were XRD amorphous, which was also confirmed by SEM analysis, afterwards. The density of the glasses varied between 3.08 and 3.12 g cm^{-3} and was found to increase with an increase in CaF_2 content in the glasses (Table 1). The density values of all the investigated glasses are higher than those of BaO- and ZnO-containing diopside-Ca-Tschermak glasses [14,15]. The molar volume (V_m) and excess molar volume (V_e) were calculated using the apparent density data for the bulk glasses using the relations that have already been reported in our previous work [13–15]. The values of V_m and V_e decreased with an increase in CaF_2 content in the glasses (Table 1). This decrease in V_m and V_e may be attributed to the high ionic character of CaF_2. Since, the ionic bonds are non-directional in nature, increasing CaF_2 will lead to the collapse of the structural skeleton into a closer packing, thus, decreasing the excess volume (V_e) [16] and, therefore, increasing the CTE of the glasses (Table 1). The values of V_m,

Table 1
Properties of the glasses.

Glass	7-0	7-3	7-5	7-8
Density (g cm^{-3})	3.08 ± 0.001	3.10 ± 0.003	3.11 ± 0.002	3.12 ± 0.005
V_m (cm^3 mol^{-1})	19.71 ± 0.012	19.70 ± 0.014	19.72 ± 0.010	19.60 ± 0.020
V_e (cm^3 mol^{-1})	0.24 ± 0.012	0.11 ± 0.02	0.063 ± 0.012	−0.18 ± 0.036
T_g (±2) (K)	958	930	890	865
T_s (±5) (K)	989	968	959	950
CTE × 10^6 (K^{-1}) (200–500 °C)	8.69 ± 0.01	8.69 ± 0.05	8.87 ± 0.04	9.31 ± 0.06
T_p (± 2) (K)	1185	1181	1168	1148
n	–	2.08 ± 0.01	1.98 ± 0.005	1.94 ± 0.002
E_c (kJ mol^{-1})	300	328	339	342

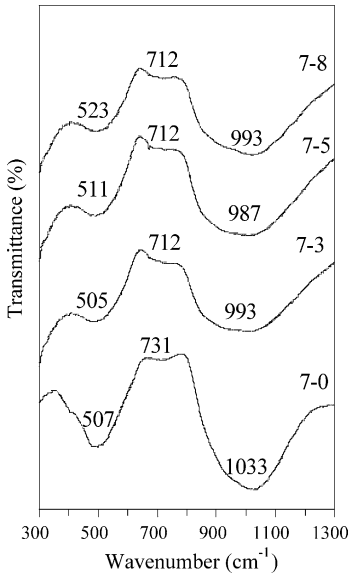

Fig. 1. FTIR spectra of the investigated glass powders.

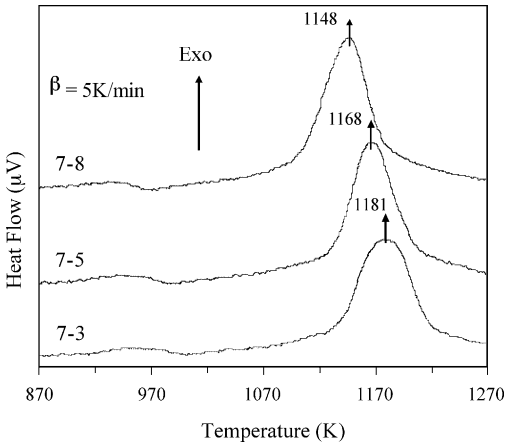

Fig. 2. Differential thermal analysis thermograph of the glasses at $\beta = 5$ K min^{-1}.

as obtained for all the glasses under investigation, are lower than their B_2O_3-containing analogues investigated in our recent study [17]. This is due to the fact that unlike CaF_2, B_2O_3 is covalent in nature and thus, promotes directional bonding in the glass structural network.

The room temperature FTIR transmittance spectra of all the investigated glasses are shown in Fig. 1. All spectra exhibit three broad transmittance bands in the region of 300–1300 cm^{-1}. This lack of sharp features is indicative of the general disorder in the silicate network mainly due to a wide distribution of Q_n (polymerization in the glass structure, where n denotes the number of bridging oxygens) units occurring in these glasses. The most intense bands in the 800–1300 cm^{-1} region correspond to the stretching vibrations of the SiO_4 tetrahedron with a different number of bridging oxygen atoms while bands in the 300–600 cm^{-1} region are due to bending vibrations of Si–O–Si and Si–O–Al linkages [18,19]. The least intensive bands in the region 650–800 cm^{-1} are related to the stretching vibrations of the Al–O bonds with Al^{3+} ions in fourfold coordination [18]. The transmittance bands in 800–1300 cm^{-1} region for CaF_2-containing glasses are registered at considerably lower wave numbers than those observed for CaF_2-free parent glass (7-0). Thus, it is evident that the introduction of fluoride ions breaks up Q_3 units and favours the formation of Q_2 units. This depolymerization of glass network and formation of NBOs leads to decrease in the T_g of glasses (Table 1). The band in the region 650–800 cm^{-1} shifted towards lower wave number with the addition of CaF_2. This may be due to the overlapping of band corresponding to the stretching vibrations of Al–O binds with that of F^- as the characteristic band for F^- lies around ~740 cm^{-1} [20].

The DTA plots of all the CaF_2-containing glasses exhibit single exothermic effects at all the heating rates which shifted towards higher temperatures with increase in heating rate. The existence of a single crystallization exotherm signifies that either the GC formed as a result of crystallization is mono-mineral or different crystalline phases appear from the glass matrix almost simultaneously and the crystallization curve is the resultant of all the crystallization curves formed due to the appearance of different crystalline phases. The peak temperature of crystallization, T_p decreased with an increase in CaF_2 content in the glasses as shown in Fig. 2. XRD results of the heat treated glasses reveal that addition of CaF_2 in the parent glass, $Ca_{0.8}Ba_{0.1}MgAl_{0.1}La_{0.1}Si_{1.9}O_6$ disturbed the formation of pyroxene solid solution and led to the crystallization of diopside (ICDD card: 01-078-1390; $CaMgSi_2O_6$) and La_2O_3-containing crystalline phase named, britholite (01-076-0340; $La_{9.31}(Si_{1.04}O_4)_6O_2$) in all the thermal cycles except that of heat treatment at 800 °C. All the investigated glasses were amorphous after heat treatment at 800 °C. No fluorine containing phase could be detected after any thermal treatment evidencing that the F^- ions were accumulated in the glassy phase. Fig. 3a shows the microstructural image of glass 7–8 after heat treatment at 700 °C (step 1) and presents a clear evidence of phase separation in the glasses in the form of network like structures with the introduction of fluoride ions in the glasses. The tendency to form such structures increased with an increase in the concentration of fluoride ions. Further, after heat treatment at 800 °C (step 2) (Fig. 3b), though the glasses were XRD amorphous, nucleation occurred on the edge of the glasses through rosette morphology, evidencing the initiation of surface nucleation. Fig. 3c shows the initiation of crystallization from the surface of sample signifying the presence of surface crystallization while Fig. 3d shows the existence of crystalline phases with different microstructure in the GCs confirming the XRD results. Also, it is noteworthy that all the obtained GCs had either an amorphous glass or a hollow cavity in the core of the GC, thus pointing towards the existence of surface crystallization mechanism. The heating of glasses at different nucleating temperatures (step 4 and step 5) followed by heating them at final crystallization temperature was also ineffective in achieving three-dimensional bulk crystallization in any of the investigated glass compositions. The crystallization kinetics of the CaF_2-containing glasses was studied using the formal theory of transformation kinetics as developed by Johnson and Mehl [21] and Avrami [22], for non-isothermal

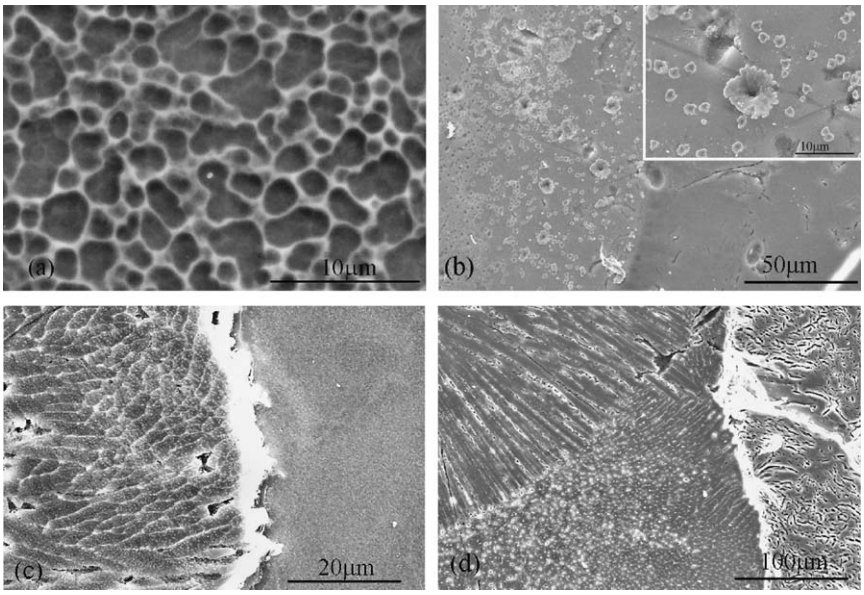

Fig. 3. Microstructure of the glass-ceramics (a) 7-8 (step 1) (a) 7-5 (step 2), (b) 7-3 (step 5) (c) 7-5 (step 6).

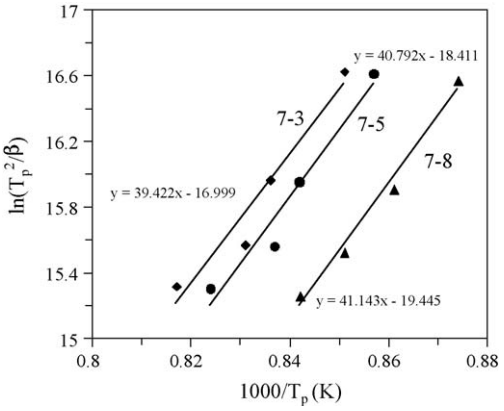

Fig. 4. Plot of E_c for all the investigated glasses.

processes that have already been obtained in our previous work [23,24]. The Avrami parameters for all the three CaF_2-containig glasses were calculated to be in the range 1.93–2.0 (Table 1), signifying towards the two-dimensional crystal growth and intermediate (i.e. simultaneous surface and bulk crystallization) mechanism of crystallization. The activation energy of crystallization (E_c) increased with addition of CaF_2 in the parent glass (7-0) and varied between 300–342 kJ mol^{-1} (Table 1, Fig. 4).

4. Conclusion

In conclusion, effect of CaF_2 addition has been investigated on the structure and crystallization behaviour of La_2O_3-containing diopside based glasses. The V_m, V_e and T_g decreases while density and CTE increases with an increase in fluoride ion content. The addition of fluoride ion causes the silicate glass network to break and thus led to the formation of Q_2 units. The addition of CaF_2 disturbed the solid solution formation and led to the formation of diopside and britholite. Three-dimensional bulk crystallization could not be achieved in any of the CaF_2-containing glasses. The E_c increased with addition of CaF_2.

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