The Effect of P_2O_5 and Heat Treatment on the Crystallization of $Li_2O \cdot 2SiO_2$ – $BaO \cdot 2SiO_2$ (LS_2 – BS_2) Glass

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In this paper, the effects of P_2O_5 and heat treatment on the crystalline phases and microstructure of lithium disilicate–barium disilicate glass were examined. A wider and broad peak in the differential thermal analysis curve indicates a presence of surface crystallization instead of volume crystallization despite the use of nucleating agent, P_2O_5 . The heat treatment schedules were planned according to differential thermal analysis data. The controlled crystallization of the compositions studied was carried out using two-stage heat treatment procedure. The glass transition temperature, T_g of the as-cast sample were used to determine the optimum nucleation temperature. The optimum nucleation temperature was determined to be 520 °C. The crystallization was carried out at 720 °C and 880 °C for 15 min. Lithium disilicate and sanbornite was the major phases and moganite or coesite were also present depending on the heat treatment duration. Due to coexistence of lithium disilicate and barium disilicate phases, the change in the melting entropy prevented the formation of spherulitic morphology and recrystallization after further heat treatments. The rise in the crystallization temperature enhanced grain coarsening and formed massive microstructures.

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1. Introduction

Glass-ceramics are polycrystalline materials composed of at least one crystalline phase and a vitreous matrix phase, produced by controlled crystallization heat treatments of appropriate parent glasses. The kinetics of crystallization is critical in determining those glass compositions that can be converted into practical fine grained glass-ceramics. The crystalline phases formed and final size depend not only on the chosen parent glass but also on the imposed thermal treatment. In order to develop desired final microstructure, a two stage heat treatment to enhance crystal nucleation and growth in glasses is employed, which continues to be a fascinating area of investigation [1–3]. The nucleating agents such as TiO_2 , P_2O_5 and ZrO_2 increase the nucleation rates by several orders of magnitude [4]. For the glass-ceramics in BaO – Li_2O – SiO_2 ternary system, P_2O_5 , which alters the type and the amount of the crystal phases present in the system, was proved to be effective in the systems studied [5].

In the present study, the controlled crystallization of a LS_2 – BS_2 glass was carried out. The microstructural examinations were done and phase composition was determined.

2. Experimental procedure

The glass contains 75 mol.% lithium disilicate ($Li_2O \cdot 2SiO_2$) and 25 mol.% barium disilicate ($BaO \cdot 2SiO_2$) phases. 1 mol % of P_2O_5 was used as nucleating agent. In order to prepare glasses, SiO_2 , $BaCO_3$, Li_2CO_3 and P_2O_5 were used as raw materials. A mechanical mixture of the starting materials giving a 70 g batch was melted in a Pt crucible at about 1400 °C and the melts were cast into pre-heated graphite moulds. Glass transition and crystallization

temperatures of the glass compositions were determined by differential thermal analysis (DTA) with a heating rate of 10 °C/min using a simultaneous thermal analyser (Netzsch). Crystallization heat treatments were planned according to the DTA results. Crystallized microstructures were compared with each other using scanning electron microscope (JEOL JSM-330). Crystalline phases were determined by X-ray diffraction (XRD) using a diffractometer (Philips PW1820) employing $Cu K\alpha$, for $2\theta = 10$ – 70° .

3. Results and discussion

The glass transition temperature, T_g , of the as-cast sample were used to determine the optimum nucleation temperature. For each composition, seven nucleation heat treatments were done between 490–550 °C by increasing 10 °C each time. The optimum nucleation temperatures was determined to be 520 °C. After nucleation heat treatments, amorphous as-cast samples became semitransparent with some degree of crystallization, which was confirmed by XRD analysis of nucleated samples. In their XRD pattern, the nucleated samples indicated a hump region around the angles where lithium disilicate has its characteristic triple peaks. This shows the onset of the crystallization of the primary phase. The first phase that was nucleated from the parent glass matrix was lithium disilicate. Scanning electron microscopy (SEM) images of the crystallized samples were given in Fig. 1.

In Fig. 2, XRD diagrams of the samples were given in order to indicate the formation of the silicate phases after heat treatments at two different crystallization temperatures. After the optimum nucleation heat treatment at 520 °C for 3 h, samples were heat treated at 720 °C

Fig. 1. SEM micrographs of crystallized sample: (a) at 5000 $\times$ after 550 $^{\circ}\text{C}$ /1 h and EDS analysis of spherulites, (b) at 5000 $\times$ after 520 $^{\circ}\text{C}$ /2 h, (c) at 3500 $\times$ after 520 $^{\circ}\text{C}$ /3 h + 880 $^{\circ}\text{C}$ /2 h, and (d) at 3500 $\times$ after 520 $^{\circ}\text{C}$ /3 h + 880 $^{\circ}\text{C}$ /4 h.

Fig. 2. XRD pattern of the crystallized samples heat treated at (a) 520 $^{\circ}\text{C}$ /3 h + 720 $^{\circ}\text{C}$ /15 min and (b) 520 $^{\circ}\text{C}$ /3 h + 880 $^{\circ}\text{C}$ /15 min (x lithium disilicate, • barium disilicate and o coesite phases).

and 880 $^{\circ}\text{C}$ for 15 min. Both of the XRD patterns exhibit characteristic triple lithium disilicate diffractions at 23.965, 24.515 and 25.010 $^{\circ}$ having relative intensities of 34.9, 61.5 and 100.0, respectively. The d spacings of the highest three peaks of lithium disilicate phase were 3.7102, 3.6282, and 3.5575 in the same order. JCPDS card no. of lithium disilicate phase was 40-0376 and the lattice parameters were $a = 5.80$ Å, $b = 14.66$ Å and $c = 4.806$ Å with an orthorhombic crystal structure.

In Fig. 2a, lithium disilicate is present as the major and moganite as the minor phase. JCPDS card no. of moganite is 38-0360 with a crystal structure of monoclinic. Despite XRD pattern of the sample heat treated at 720 $^{\circ}\text{C}$ indicates lithium disilicate as the only phase, heat treatment at 880 $^{\circ}\text{C}$ resulted in dual phase of lithium disilicate and barium disilicate along with a minor phase of coesite. Barium disilicate (sanbornite) has orthorhombic crystal structure with the lattice parameters of $a = 4.68$ Å, $b = 7.64$ Å and $c = 13.58$ Å according to JCPDS card no. 26-0176.

The highest intensity peak of barium disilicate was initially observed after heat treatment at 720 $^{\circ}\text{C}$, the rest of

the peaks could only be observed after heat treatment at 880 $^{\circ}\text{C}$. Heat treatment at 880 $^{\circ}\text{C}$ enhanced the formation of barium disilicate phase more than lithium disilicate since the highest triple peaks of lithium disilicate were present in XRD patterns of the samples heat treated at both of the crystallization temperatures. Free SiO_2 phase that was formed after 880 $^{\circ}\text{C}$ for 15 min was determined to be coesite with JCPDS card no. 14-0654.

The particular characteristic of the composition, which contains lithium disilicate ($\text{Li}_2\text{O}\cdot 2\text{SiO}_2$) as the major and barium disilicate ($\text{BaO}\cdot 2\text{SiO}_2$) as the minor phases, is that the formation of the spherulites began even after nucleation heat treatments at 520 $^{\circ}\text{C}$ and 550 $^{\circ}\text{C}$ as shown in Fig. 1a. The reason for this is the higher content of lithium disilicate in the particular composition, which is known for readily evolution of spherulites and fibrillar morphology. This fibrillar morphology which forms after nucleation heat treatment can also be composed of barium disilicate ($\text{BaO}\cdot 2\text{SiO}_2$) secondary phase as it is evident from energy dispersive spectroscopy (EDS) analysis in Fig. 1a. The close view of the fibrillar structures can be seen in Fig. 1b. Since at around 722 $^{\circ}\text{C}$, only lithium disilicate is present in the microstructure, the spherulitic morphology can be observed. However, after heat treatment at 880 $^{\circ}\text{C}$ where both phases are present together, massive microstructures were observed as in Fig. 1c and d. The grain coarsening due to further heat treatment was observed to be slight.

4. Conclusion

The crystallization process of $0.75\text{Li}_2\text{O}\cdot 2\text{SiO}_2 - 0.25\text{BaO}\cdot 2\text{SiO}_2$ glasses was investigated. The nucleating agent, P_2O_5 did not result in volume crystallization, a surface crystallization was dominant. DTA curves of all the compositions studied exhibited a small endothermic peak (glass transition) and a broad exothermic peak (crystallization of the dual phase). The optimum nucleation temperature was determined to be 520 $^{\circ}\text{C}$. DTA curve of nucleated sample indicated two exothermic peaks corresponding to lithium disilicate (at 722 $^{\circ}\text{C}$) and barium disilicate (880 $^{\circ}\text{C}$), respectively. Because of the beginning of the coexistence of lithium disilicate and barium disilicate phases, there was no sign of spherulitic morphology in the microstructure after heat treatment at 880 $^{\circ}\text{C}$.

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