

Crystallization Studies of Lithium Borosilicate Glasses

Pervez Iqbal Qazi *, Wajid Ali Shah and Fadia Shaheen

Glass and Ceramics Research Centre, PCSIR Laboratories Complex, Lahore-54600, Pakistan

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Abstract. Lithium borosilicate ternary system is analogous to the most commercially exploited $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ system. The tendency towards liquid-liquid immiscibility is enhanced when sodium is replaced by lithium, which facilitates the crystallization process. In the present work, three compositions of lithium borosilicate glasses were formulated and melted by varying the mol percent ratio of SiO_2 and Li_2O . The glasses were subsequently subjected to crystallization by isothermal heat-treatments at identical temperatures for various specific time durations. The crystal growth was found to be linear and the rate of crystallization was dependent on $\text{SiO}_2/\text{Li}_2\text{O}$ ratio. The phases that developed during heat-treatments were identified using XRD.

Keywords: glass ceramic, nucleation, crystallization, lithium borosilicate

Introduction

Crystallization of lithium, di- and meta-solid solutions from $\text{Li}_2\text{O}-\text{SiO}_2$ glasses has been studied extensively (Hasdemir *et al.*, 1998; Rindone, 1962). It has been established that low temperature crystallization leads to the formation of a transient lithium monosilicate phase, which later on converts to proper lithium monosilicate (Vogel, 1971). It has been reported that on heating at 300°C for 5 h, the XRD pattern resembled that of lithium metasilicate, though it was not identical with it. Heating below 300°C for 5 h resulted in diffused, unidentified scattering, and identification was not possible. However, when heated at 342°C for 1 h, characteristic line of the metasilicate appeared. Longer heat-treatments at the same temperature, nevertheless, resulted in the formation of a transition structure. This transition structure has been reported to persist up to about 500°C , at which temperature lithium disilicate with cristabolite appeared. The glass when heated above 500°C , developed only lithium disilicate phase.

Crystal nucleation kinetics of lithium disilicate glasses have been studied (Barker *et al.*, 1988; Rowlands and James, 1979). Phase separation was reported to have significant effect on the nucleation rate (James, 1974). In glasses containing 17.7, 31 and 33.2 mol % Li_2O , it was found that crystal nucleation rate of the glasses with 31 mol % Li_2O , which had undergone phase separation, increased with time at 461°C , whereas the glasses with 33.2 mol % Li_2O , that lay outside the immiscibility region, had a lower nucleation rate.

Lithium borosilicate glasses have attracted great attention during the recent years, particularly in the area of crystalli-

zation (Salaman *et al.*, 2000; Rouse *et al.*, 1981). In the present investigation, crystallization of lithium borosilicate ternary glasses was studied. The effect of $\text{SiO}_2/\text{Li}_2\text{O}$ ratio on the development of various crystalline phases in the presence of the same mol fraction of B_2O_3 is discussed.

Materials and Methods

Three glass batches (M-1, M-2, M-3) having different mol % composition of SiO_2 and Li_2O were formulated (Table 1). The glass formulation constituents comprised lithium carbonate and boric acid (Merk, Germany), and quartz (Swabi, NWFP, Pakistan) of 99% purity as the respective sources of Li_2O , B_2O_3 and SiO_2 . The glass batches were melted by heating up to 618°C at the rate of 10°C per min for 30 min. Melting was followed by refining at 1350°C for 1 h in an electric furnace. Melts were cast into preheated die and then annealed at different temperatures depending upon the glass transition temperature (T_g) of the glasses. The annealed glass samples were nucleated in platinum crucibles at 550°C for 6 h and allowed to cool down to room temperature. The glass samples were subsequently subjected to the higher temperature of 700°C for their crystal-

Table 1. Compositions of three batches of glass containing different mol percent of SiO_2 and Li_2O in the presence of fixed mol percent of B_2O_3

Glass batch	Glass batch composition (mol %)		
	SiO_2	Li_2O	B_2O_3
M-1	50	27	23
M-2	46	31	23
M-3	42	35	23

*Author for correspondence; E-mail: pcsir@brain.net.pk

lization. After heat-treatment, the samples were observed under an optical microscope and, if found clear, were subjected to further higher temperatures. The heat-treatment for each glass was done over a wide range of identical temperatures and time. The heat-treatment was carried out in a high temperature, rapid heating electric resistance furnace (RHF/3 Carbolite, UK). For both nucleation and crystallization, the furnace was preheated at the desired temperature. Powder X-ray diffraction (Siemen's diffractometer D5000) database was used to study the crystalline phases that appeared during heat-treatment. The samples were crushed and ground to pass through BSS 200 mesh. The experiments were run from 10-60 °C 2θ values. The crystalline phases were identified by matching the spectra with the probable phases available on the database.

Results and Discussion

Assuming that crystallization rate was dependent on the available nuclei, the glass M-2 was nucleated at 550 °C for 2, 4, 6 and 9 h, and crystallized at 700 °C for 2 h. The crystallized samples were analyzed by X-ray diffraction techniques under identical conditions. The XRD spectra (Fig.1) indicate that the peak intensity of the principal peak (relative intensity 100) was 1140 (arbitrary units) for the glass nucleated for 2 h. This increased to 1290 on nucleation for 4 h, which further increased to 1350 on nucleation for 6 h, and finally to 1385 on nucleation for 9 h. It is obvious from these values that the nuclei formation for first 2 h was very high. It further shows that the induction period at 550 °C was very small. Although for longer nucleation time the peak intensity had shown higher value, the growth rate had gradually fallen down with time (Fig. 1e). Hence, all the three glasses studied during the present study were nucleated at 550 °C for 6 h.

The glass M-2 nucleated at 550 °C for 6 h, was then crystallized at 700 °C for 1, 2 and 3 h. The crystallization behaviour is shown in Fig. 2. The phase crystallized in the sample heat-treated for 1 h was identified as lithium monosilicate ($\text{Li}_2\text{O} \cdot \text{SiO}_2$). Fig. 2a also indicates the presence of a significant proportion of glassy phase. As the duration of heat-treatment was raised to 2 h, the glassy phase turned into crystalline material, as halos gradually diminished and relative peak intensity increased (Fig. 2b). However, the crystalline phase remained the same. The time duration of 3 h finally completed the crystallization. Fig. 2c depicts that the peak intensity of the major lithium monosilicate phase was considerably increased along with the appearance of a second phase, namely, lithium disilicate ($\text{Li}_2\text{O} \cdot 2\text{SiO}_2$).

The glass M-1 was nucleated at 550 °C for 6 h and crystallized at 700 °C for 1, 2, 3 and 4 h. The results obtained are

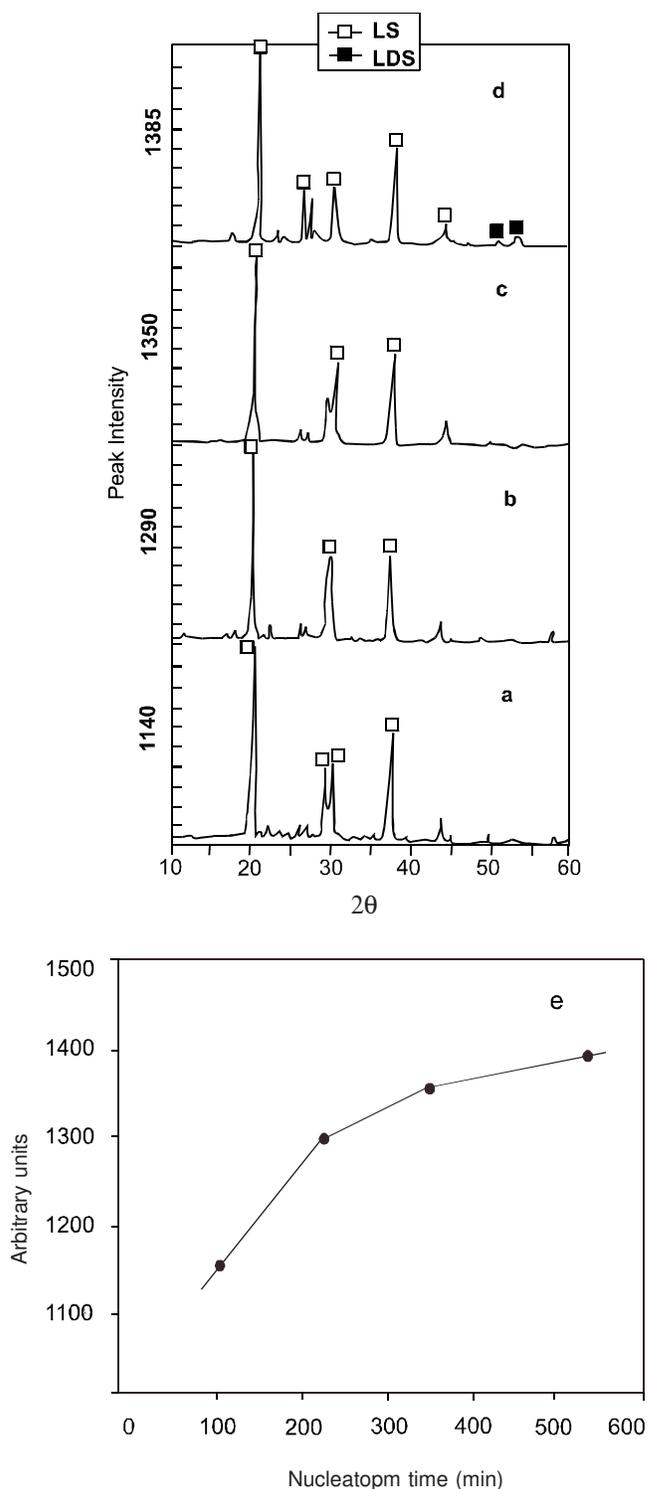


Fig. 1. X-ray diffraction patterns of glass M-2 nucleated at: (a) 550 °C for 2 h; (b) 550 °C for 4 h; (c) 550 °C for 6 h; (d) 550 °C for 9 h; all (a-d) crystallized at 700 °C for 120 min; (e) nucleation time of glass M-2; LS = lithium silicate, LDS = lithium disilicate.

presented in Fig. 3. During 1 h heat-treatment, the glass showed very little crystallization. Only a few peaks appeared at the halos (Fig. 3a), which means that the sample was predominantly glassy. The crystalline phase identified was lithium disilicate. As the time duration of heat-treatment increased to 2 h, the intensity of the peaks almost doubled (Fig. 3b). The sample, however, mainly remained non-crystalline. The crystalline phase was still the same, that is, lithium disilicate. A few additional peaks with small intensity emerged, which on further heat-treatment for 3 h were identified as the lithium monosilicate phase (Fig. 3c). The sample appeared to be much better crystallized. When the time was raised to 4 h, considerably high crystallization was observed (Fig. 3d). Lithium disilicate phase was the major, while lithium monosilicate appeared as the minor phase. The effect of heat-treatment for 4 h is shown in Fig. 3d.

The glass melt M-3 was nucleated at 550 °C for 6 h. Its crystallization was carried out at 700 °C for 1, 2, 3 and 4 h. The XRD spectra of these samples are given in Fig. 4. The sample

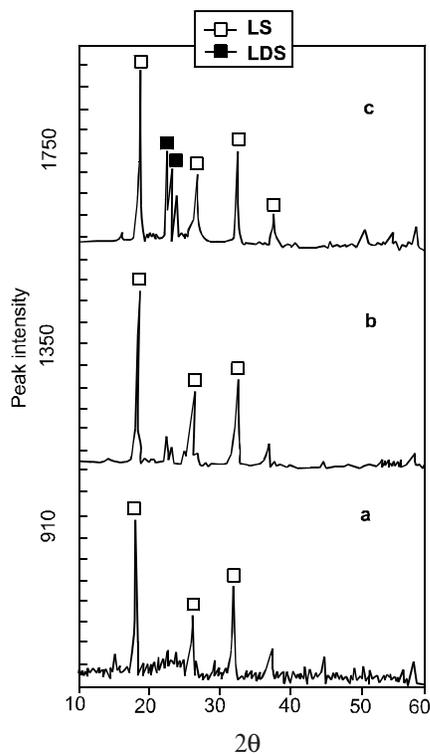


Fig. 2. X-ray diffraction patterns of glass M-2 nucleated at 550 °C for 6 h, and crystallized at: (a) 700 °C for 60 min; (b) 700 °C for 120 min; and (c) 700 °C for 180 min; LS = lithium silicate; LDS = lithium disilicate.

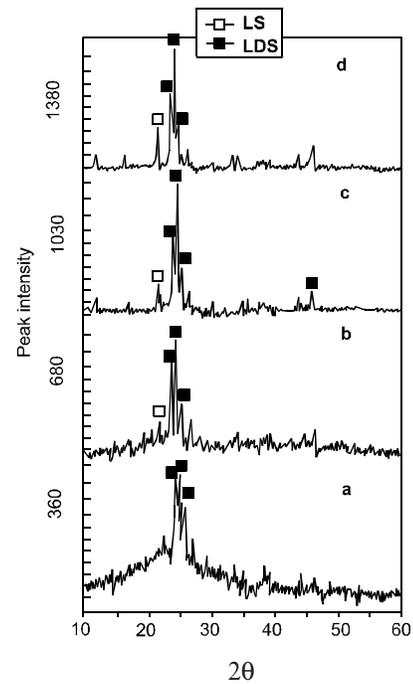


Fig. 3. X-ray diffraction patterns of glass M-1 nucleated at 550 °C for 6 h, and crystallized at: (a) 700 °C for 60 min; (b) 700 °C for 120 min; (c) 700 °C for 180 min; (d) 700 °C for 240 min; LS = lithium silicate; LDS = lithium disilicate.

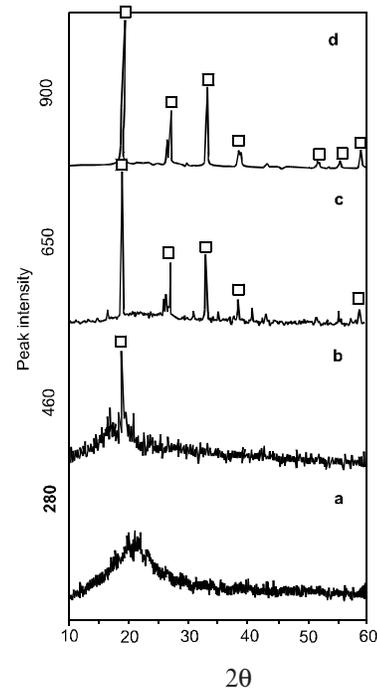


Fig. 4. X-ray diffraction patterns of glass M-3 nucleated at 550 °C for 6 h, and crystallized at: (a) 700 °C for 60 min; (b) 700 °C for 120 min; (c) 700 °C for 180 min, and 700 °C for 240 min.

when heat-treated for 1 h did not show crystallization (Fig. 4a). Only few peaks appeared at halos, which means that the sample was predominantly glassy. After 2 h heat-treatment, crystallization seemed to be initiated, and only few peaks appeared (Fig. 4b). The crystalline phase identified was that of lithium monosilicate. There emerged some peaks with small relative intensity, which however could not be identified and required more time to crystallize in significant amounts. On increasing the heat-treatment time to 3 h, the halos disappeared and the intensity of crystallization was doubled, which may be seen in Fig. 4c. The crystallized phase, however, remained the same. As the time of heat treatment was increased to 4 h, the sample was appreciably crystallized. Although intensity of the principal peak increased from 650 to 900, the crystallized phase, that is, lithium silicate, remained the same.

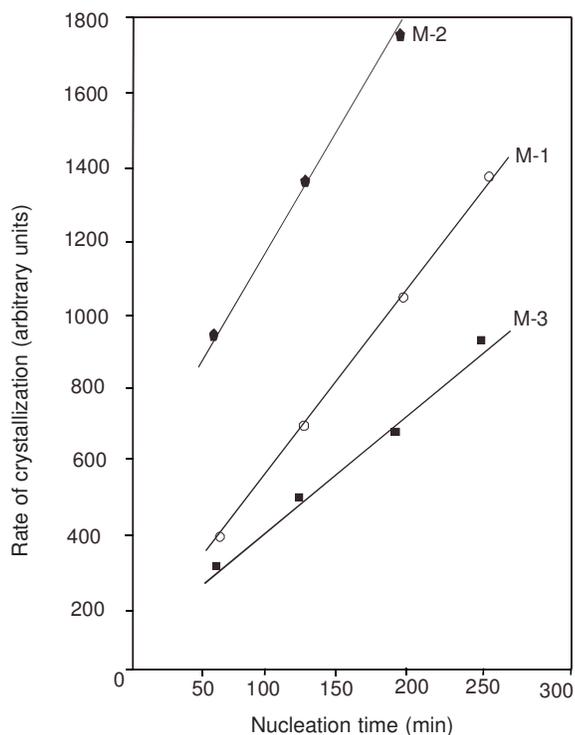


Fig. 5. Rate of crystallization versus the nucleation time for glass batches M-1, M-2 and M-3 (see Table 1 for composition of the batches).

Conclusion

It was observed that in all the three cases, crystallization had a linear relationship with time as illustrated in Fig. 5. The rate of crystal growth was found to be fastest in the case of M-2, comparatively slow in M-1, and slowest in the case of M-3. The $\text{SiO}_2/\text{Li}_2\text{O}$ ratio in these glasses varied from 1.2 to 1.85 mol %. It was observed that in the ternary system $\text{SiO}_2\text{-Li}_2\text{O-B}_2\text{O}_3$, the rate of crystallization was the fastest when $\text{SiO}_2/\text{Li}_2\text{O}$ ratio was 1: 4, which decreased on lowering or raising the ratio.

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