Letter to the Editor

XRD investigation of metastable phase formation in Li₂O–2SiO₂ glass

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Abstract

Metastable crystal phase formation in lithium disilicate glass has been a subject of controversy for many years. However, recent evidence mainly obtained via the use of electron microscopy has provided strong evidence for formation of metastable phases during the early stages of crystallization in this composition. Very recently, however, a study has appeared which suggests that these metastable phases are long-lived and can be detected with the aid of XRD. Here, we present XRD results obtained for lithium disilicate glasses which were heated for various time periods at several temperatures in the nucleation regime. In no case do we find any evidence for metastable phase formation. Possible causes for the discrepancy between the present and previous experimental results are discussed. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Metastable phase formation in systems that presumably crystallize homogeneously is an important and controversial area of inquiry. The issue of metastable phase formation is of considerable scientific importance because it offers a possible explanation for the observed discrepancies between theoretically predicated and experimentally determined nucleation rates in glasses. Of the few glass-forming compositions which appear to exhibit homogeneous nucleation, lithium disilicate (LS₂) has been the most extensively studied system. Among

other reasons, crystal nucleation in the LS₂ composition has received particular attention because it is a pseudo one component system. As observed in other systems, classical nucleation theory fails to quantitatively predict the experimentally observed nucleation rates in LS₂ glasses [1–3]. Furthermore, most reports of metastable phase formation have been for compositions in the neighborhood of LS₂. Although there is convincing evidence that metastable phase formation does indeed occur during the early stages of crystallization in LS₂ glasses, the role metastable phases play with respect to the crystallization mechanism remains unclear. There is considerable controversy over whether metastable phases form and serve as precursors for subsequent precipitation of the stable phase, or if precipitation of the stable phase occurs

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independently of the formation of metastable phases [4–7].

Based on X-ray diffraction (XRD) results, Kalinina et al. [8] suggested the formation of metastable phases in both sub- and super-stoichiometric LS_2 glasses. The results of small angle X-ray scattering (SAXS) and electrical conductivity experiments conducted by Hench et al. [9,10] on sub- and stoichiometric LS_2 glasses that had been heated-treated at 500°C, suggested that a metastable phase formed prior to equilibrium crystallization of LS_2. Joseph and Pye [11] performed Raman spectroscopy on stoichiometric LS_2 glasses which had been heat-treated at 450°C and 500°C. Their Raman results support the conclusions of Hench [10] that a metastable phase forms during the initial stages of the nucleation process. More recently, Deubener and Brückner [12] performed TEM on glasses with 33.5 mol% Li_2O that had been heat-treated at 454°C. Deubener provided provocative electron diffraction patterns of the metastable phases present in the heated glass. Zanotto [6] recently repeated the SAXS experiments of Hench and TEM experiments of Deubener and Brückner. Zanotto also observed the formation of metastable phase(s), thus confirming the previous reports. In Refs. [6,12], metastable phases were detected in the very early stages of crystallization, when the crystallized volume fractions were smaller that ∼2%, i.e., for short treatments at 454°C ($t < 20$ h). For higher volume fractions (longer treatments) the stable LS_2 phase appeared.

The most recent results of James et al. [7] concerning metastable phase formation in lithium disilicate glasses are quite striking in that they find that the metastable phases persist to very long times. In their investigation, James et al. utilized XRD to follow the early stages of crystallization in LS_2 glasses. Lithium disilicate glasses with 33.9 mol% Li_2O were given single stage heat-treatments at 454°C for extensive time periods. Employing scanning speeds of 0.25 and 0.125°/min, they obtained XRD traces of glasses heated for 50, 120, 312, 331, 480, and 551 h. Following the progression of the crystallization process via XRD traces, James et al. observed the formation of metastable phase(s), and subsequent transformation of these phases to stable LS_2.

The remarkable findings of James et al. provided the motivation for the present work. The authors of this study thought it would be interesting to not only repeat the experiments performed by James, but also to extend the experiments to other temperatures within the nucleation range of the lithium disilicate system.

2. Experimental

Lithium silicate glass of molar batch composition Li_2O–$2SiO_2$ was prepared using standard reagent grade Li_2CO_3 and SiO_2. The batched precursor powders (100 g) were rolled on a ball mill in a glass jar for 3 h, then transferred to a Pt–Rh crucible and melted at 1350°C for 4 h in an electric furnace. To ensure homogeneity, the melt was periodically stirred with a platinum rod. The melt was quenched (in air) by pressing between steel plates. Subsequent chemical analysis revealed the composition of the prepared glass to be 33.1 ± 0.5 Li_2O–66.9 ± 0.5 SiO_2.

Heat treatments were carried out in a horizontal tube furnace uniform to within ±1°C. Samples were given single stage isothermal heat treatments at 440°C, 454°C, 477°C, and 500°C for periods between 24 and 543 h.

Surface crystallized layers of heat-treated samples were removed and remaining materials subsequently ground into fine powders for XRD analysis. Three different XRD instruments were used in this study. All instruments used Cu K_α radiation, and all scans were performed on scattering angle, 2θ, values from 10° to 60°. However, the scan rates differed among the three instruments. One XRD utilized a step-scan of 0.02°/2 min, another employed a step-scan of 0.008°/3 min, and the third employed a step scan of 0.015°/5 sec counting time.

Differential thermal analysis (DTA) was performed using a system with a platinum crucible at a heating rate of 10°C/min DTA runs were carried out on both bulk and powder forms of the prepared glass.

The prepared glass' water content was measured using a Fourier transform infrared spectrometer (FTIR). Water concentrations were

determined according to the method of Davis et al. [13].

3. Results

The glass transition temperature, T_g, of the prepared glass was determined by DTA. From DTA traces of bulk and powder form samples, T_g was found to be $452 \pm 1°C$ and $453 \pm 1°C$, respectively.

The water concentration of the prepared glass was determined from the FTIR spectrum. Following the work of Davis [13], which only utilizes the peak height of the ~ 3500 cm^{-1} band, and using the form of the Beer–Lambert equation given by Davis, water concentration was found to be about 70 ppm $\pm 10\%$, which is relatively low.

Table 1 summarizes the heat-treatment schedules employed in this study. The results from the different XRD instruments were essentially the same, and are described in the last column of Table 1. Glasses heated at 440°C for 350 h were amorphous. After 543 h at 440°C, the only crystal phase detected was stable LS_2. Samples heated at 454°C remained X-ray amorphous for at least up to 192 h. After 360 h at 454°C, the dominant diffraction peaks of the stable LS_2 crystal phase emerged. These same peaks emerged for samples heated at 477°C for 120 h. After 168 h at 477°C, the dominant LS_2 peaks grew in intensity and several other LS_2 peaks emerged. The amorphous background had almost completely disappeared
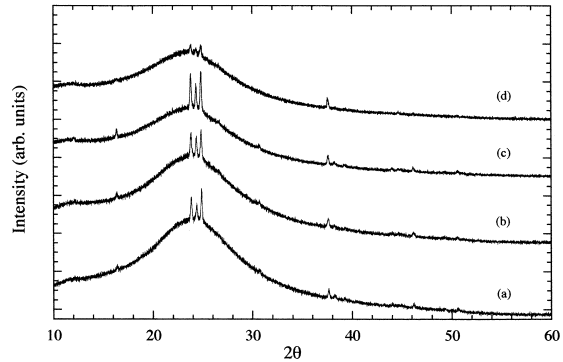

Fig. 1. XRD traces of heat-treated LS_2 glass (a) 454°C for 360 h, (b) 477°C for 120 h, (c) 477°C for 168 h, and (d) 500°C for 24 h.

for samples heated at 477°C for 288 h, and the only crystal phase detected was stable LS_2. For samples heated at 500°C for 24 h, the dominant LS_2 diffraction peaks emerged.

The X-ray diffraction patterns illustrated in Fig. 1 are representative of the results obtained from the different XRD instruments. As shown in Fig. 1, the extent of crystallization is relatively small, and stable LS_2 is clearly the only crystal phase present.

4. Discussion

The results of the present study are in sharp contrast to the results obtained by James et al. [7],

Table 1
Heat treatment schedule and XRD results

Heat treatment temperature (±1°C)	Heat treatment time (h)	XRD results
440	350	Amorphous
440	543	Only stable LS_2 crystal phase
454	120	Amorphous
454	192	Amorphous
454	360	Dominant peaks of LS_2 crystal phase emerged against amorphous background
477	120	Dominant peaks of LS_2 crystal phase emerged against amorphous background
477	168	Dominant peaks of LS_2 intensified and additional LS_2 peaks emerged
477	288	Only stable LS_2 crystal phase
500	24	Dominant peaks of LS_2 crystal phase emerged against amorphous background

who performed XRD on lithium disilicate glasses that had been given single stage heat-treatments at 454°C for various times. They found that the XRD pattern of a glass that was heated for 120 h showed the presence of a crystal phase which could not be identified with any previously known phase in the binary Li_2O–SiO_2 system. The authors referred to this phase as metastable α'-LS_2. After heating for 312 h, they found that most of the α'-LS_2 peaks remained, but a number of additional peaks also emerged which could indicate the appearance of stable LS_2. However, based on subsequent TEM results, it was suggested that these additional peaks were associated with another metastable phase, intermediate between the α'-and stable LS_2 phases. This intermediate metastable phase was denoted as β'-LS_2. The XRD results for the glass heated for 480 h showed the presence of stable LS_2, and a decrease in the intensities of the peaks due to phase(s) other than stable LS_2. Some time between 480 and 551 h, the metastable phase(s) peaks disappeared entirely. After 551 h, apart from stable LS_2, they also observed the presence of several major lithium metasilicate (LS) peaks, but the LS peak intensities were much lower than those of the stable LS_2 phase.

Our XRD results for lithium disilicate glasses heated for prolonged periods at 454°C are quite different from those described above. First, in no instance was crystalline material detected in our glasses after heating for 120 h. Further, no crystalline material was detected in our glasses even after heating for 192 h. When diffraction peaks did emerge against the amorphous background, which occurred after heating for 360 h, they were positively identified with the stable LS_2 phase. Also, upon comparison of our 360 h XRD trace (Fig. 1(a)) with the 312 h XRD trace in Ref. [7], it is apparent that the extent of crystallization is markedly lower in our glass than in the glass studied by James et al., even though it had been heated for a longer time.

There are several potential reasons for the apparent discrepancies. The disparate results could be due to the differences in glass composition. The glass in the present work was sub-stoichiometric (33.1 mol% Li_2O), while the glass studied in Ref. [7] was hyper-stoichiometric (33.9 mol% Li_2O).

However, this difference is an unlikely cause of the discrepancies since metastable phases have been detected in sub-stoichiometric as well as hyper-stoichiometric compositions. Another possibility resides in the glass preparation procedures. Although we followed the procedure reported by James et al. closely, they employed one step which we did not, namely, sintering precursor powders at 1000°C for 10 h prior to melting. It is conceivable that some type of solid state reaction occurred during the sintering process which produced a species that would not have been present in our melt. The types and amounts of impurities inherent to the raw materials used by the respective parties is another possible source for the disparate results. Differences in water content could also be responsible for the observed differences. However, this possibility is unlikely when one considers the work of Davis [13]. Davis showed that nucleation rates in the LS_2 system exhibited self-similar behavior as a function of water content, which suggests that mechanisms involved in nucleation are accelerated by water, and that no new reaction pathways arise with the addition of water. Lastly, we speculate that particles which were not nucleated during heating, but that were quenched-in during glass preparation, may affect the appearance of metastable phases. Each of the above possibilities is currently being investigated by the authors.

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