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Crystallization of lithium borate glasses

A. AYDIN GOKTAS, G. F. NEILSON, M. C. WEINBERG
Arizona Materials Laboratory, University of Arizona, 4715 East Fort Lowell Road, Tucson, Arizona 85712, USA

The glass-forming ability and crystallization behaviour of lithium borate compositions, in the diborate to metaborate range, were studied. In particular, the nature and sequence of formation of crystalline phases and the tendency towards devitrification were investigated as functions of temperature, thermal history and batch composition. It was found that the sequence of crystalline phase formation was sensitive to all of the three latter factors, and it was observed that under certain conditions metastable defect structures of the metaborate can appear.

1. Introduction

Borate-based glass compositions containing large concentrations of R_2O (R = lithium, sodium, silver) are of potential technological importance due to their fast ionic conductivity behaviour [1, 2]. The electrical properties of these glasses have been studied as a function of composition by several investigators [3–5], and it has been observed that, generally, the conductivity is enhanced as the alkali concentration is increased.

Lithium borate (LB) glasses are of particular interest because it has been found that they can form over a very broad range of L/B ratios [6]. Shelby [7] investigated the thermal expansion of these compositions, and Kamitsos *et al.* [8, 9] performed structural studies of lithium borate glasses with large amounts of lithia via detailed vibrational spectroscopic measurements.

In the light of the above features LB glasses could be potential candidate compositions for containerless processing in microgravity experiments. If container-induced heterogeneous crystallization is the primary cause which limits the further expansion of the glass-forming region, then space processing could yield glasses with even larger L/B ratios.

Whether one is concerned with space processing, or improvement of electrical properties, or the understanding of structure versus glass-forming tendencies of LB compositions, it is essential to ascertain the details of the crystallization processes which impede glass formation. It was the objective of this work to provide a qualitative, introductory examination of the crystallization behaviour of LB glasses over a limited composition range. Emphasis was placed upon the study of high-temperature crystallization processes because these are most likely responsible for devitrification during the cooling of the melt. In particular, the following questions were addressed. (1) At which sites (e.g. free surface, crucible-melt, bulk) do crystals form? (2) Is there evidence for metastable phase formation? (3) What is the temperature region of rapid crystallization? (4) What is the temporal sequence of crystal phase formation? (5) How does the crystallization behaviour vary with lithia concentration?

The results given here allow for a qualitative picture of the crystallization behaviour of the LB compositions, and provide a framework for future quantitative studies. Subsequently, crystal growth rates as functions of temperature and composition will be measured in the critical temperature regimes. These future investigations will provide a quantitative means of evaluating glass-forming ability.

2. Glass formation

2.1. Glass preparation

The lithium borate compositions were prepared by conventional glassmaking methods using Li_2CO_3 (Fisher, certified ACS) and B_2O_3 (Alfa Products, 99.99% pure). All batches were between 80 and 100 g. The raw materials were thoroughly mixed by means of rolling for times of 5 to 10 h. The batch was melted for 4 h at 1050 °C in a platinum crucible covered with platinum foil. During heating the melt was stirred twice with a platinum rod. Compositions containing 33.3, 36, 40, 42, 45, and 50 mol % Li_2O were prepared by this procedure.

Several techniques were used to cool the molten materials. These methods were (1) pouring into a brass mould, (2) cooling the melt in the crucible in air (natural cooling), and (3) splat cooling by pressing the molten material between metal plates.

2.2. Glass-forming results

In addition to the glass-forming trials described above, glass formation was studied for small samples utilizing a strip heating apparatus. The results of these experiments are summarized in Table I. One may note that compositions L33.3, L36, L40, and L42 formed clear glasses when the respective melts were cooled in the crucible, but crystallized totally when they were poured into a mould. This result may appear a bit surprising because the cooling rates were undoubtedly

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TABLE I Glass-forming ability

	L33.3	L36	L40	L42	L45	L50
Poured	Crystal	Crystal	Crystal	Crystal	Crystal	Crystal
Cooled in crucible	Glass	Glass	Glass	Glass	Crystal	Crystal
Splat cooled	~ 60% glass	~ 70% glass	~ 80% glass	~ 80% glass	~ 70% glass	Crystal
Strip heater	Glass	Glass	Glass	Glass	Glass	Crystal

TABLE II Devitrification products

	L40	L42	L45	L50
Poured	Li_2O–B_2O_3 Li_2O–$2B_2O_3$ (equal amounts)	Li_2O–B_2O_3 Li_2O–$2B_2O_3$ ($LB > LB_2$)	Li_2O–B_2O_3 Li_2O–$2B_2O_3$ ($LB \gg LB_2$)	Li_2O–B_2O_3
Splat cooled	Li_2O–$2B_2O_3$ Li_2O–B_2O_3 ($LB_2 \gg LB$)	Li_2O–$2B_2O_3$ Li_2O–B_2O_3 (equal amounts)	Li_2O–B_2O_3 Li_2O–$2B_2O_3$ ($LB \gg LB_2$)	Li_2O–B_2O_3

larger in the latter case. The explanation of this finding appears to be the following. As will be demonstrated, in all cases, crystallization at high temperatures initiates heterogeneously. Because molten glass is a good solvent, heterogeneities on the platinum crucible in contact with the melt probably dissolve during processing. Hence, when the melt is allowed to cool in the crucible glass formation ensues because there are few (if any) heterogeneous particles in contact with the melt. On the other hand, when the melt is poured it has the opportunity to encounter heterogeneities present on the portion of the crucible which was not previously in contact with the melt, as well as those on the mould. Thus, when the melt is poured, heterogeneous crystallization occurs. Additional evidence for the proclivity of the melt to crystallize when heterogeneous nucleation sites are available is provided by a comparison of the stripheater and splat-cooling results shown in Table I. Both of these methods produce rapid cooling, but the splat-cooling technique provides cooling rates at least one or two orders of magnitude larger than that obtained in the strip heater. Nevertheless, splat-cooled samples of all compositions were found to be partially divitrified, while glassy material could be formed with the strip heater. The splat-cooled material comes into contact with metal plates which contain heterogeneities, but the molten material in the strip heater remains in contact with only that portion of the strip with which it was in contact during melting.

2.3. Characterization

The glasses were characterized with respect to composition, water content, and devitrification products.

The chemical compositions were determined with the aid of atomic absorption spectroscopy and the reported variation of the refractive index with composition [10]. The analysed compositions varied from the theoretical compositions at most by 0.8%.

The devitrification products for compositions L40, L42, L45, and L50, which were determined by X-ray diffraction analysis, are shown in Table II. Several features of these results should be noted. First, there was no evidence for metastable phase formation, even for the rapidly cooled samples. The phases which were produced were those corresponding to the equilibrium phase diagram. Second, the relative amounts of the two phases which formed reflect the thermal histories as well as the differing crystallization rates of the two crystalline species. This feature will be considered in greater detail subsequently. Finally, it should be noted that when rapid cooling was employed, usually less lithium metaborate formed than when the melts were poured.

The water content of the glasses was determined with the aid of infrared spectroscopy. The absorption bands of the glasses in the 2.8 to 2.9 μm region were measured, and the water concentrations were computed using the extinction coefficients reported by Franz [11]. The water content of the glasses was quite similar, varying from 0.25 to 0.28 $mol\,l^{-1}$.

3. Crystallization behaviour

The crystallization behaviour of selected lithium borate compositions was examined. In particular, the crystallization temperatures, crystalline phase formation sequences, and the sites of initiation of crystallization were determined.

3.1. Crystallization temperatures

Crystallization temperatures were determined for compositions L40, L42, and L45 via DTA measurements. Samples were heated from room temperature at $10\,°C\,min^{-1}$ to a given temperature above the liquidus and held at this temperature for a prescribed time period. The samples then were cooled at $10\,°C\,min^{-1}$. The results of these experiments are

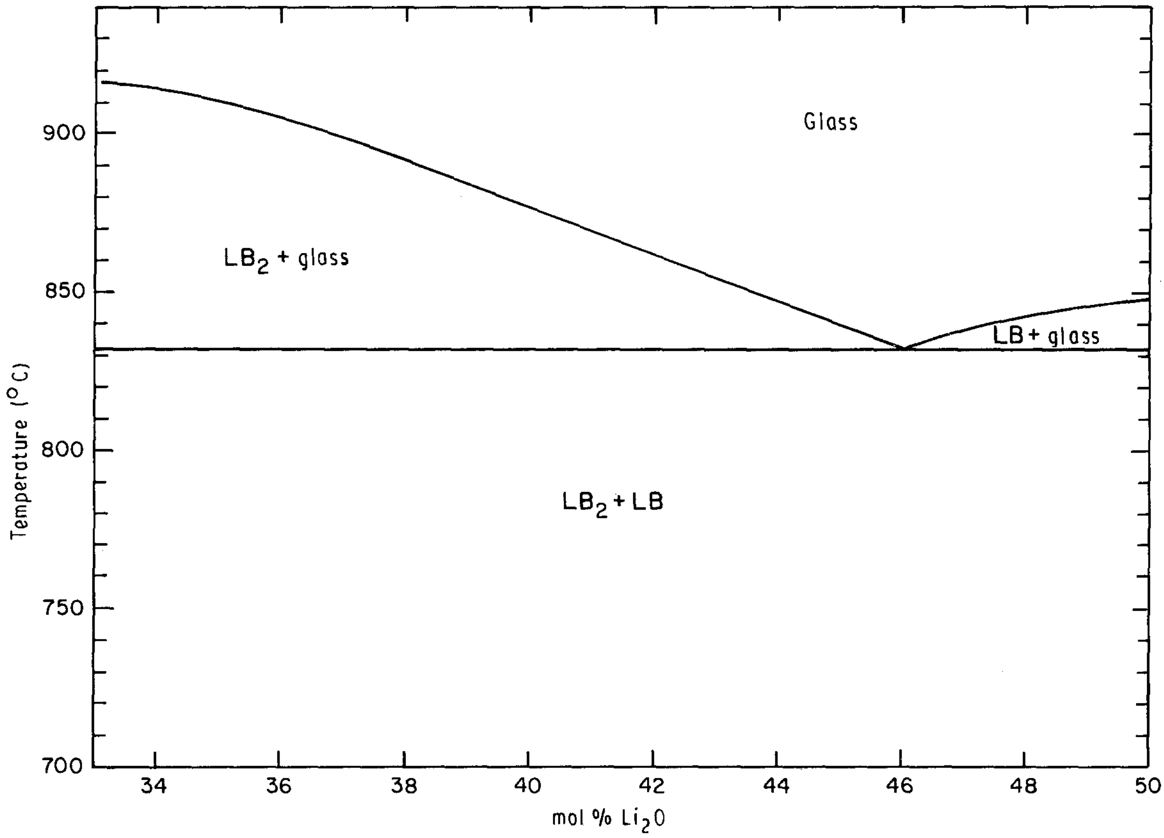

Figure 1 Phase diagram for Li_2O–B_2O_3 in region between LB_2 and LB (after Sastry and Hummel [10]).

summarized in Table III. It is observed that the crystallization temperatures are dependent upon the isothermal hold time and temperature. This result probably indicates that remnant crystallites persist in the melt, and (relatively) long heating times or elevated temperatures are required for their removal. It is interesting to note that for composition L40, melting conditions alone determine the glass-forming results. For compositions L42 and L45 the results seem to indicate that there are two regions of rapid crystallization for each glass (730 to 750 °C and 585 °C for L42 and 765 and 650 °C for L45). Also, it is seen that appropriate melting conditions can ensure that the high-temperature crystallization peak is by-passed when cooling each composition at 10 °C min^{-1}.

3.2. Crystalline phases

It is of interest to determine the crystalline phases which form in the regions of rapid crystallization. From inspection of the phase diagram for this system (see Fig. 1) one anticipates that lithium diborate (DB) and lithium metaborate (MB) will form at all temperatures. However, the time evolution of these phases, the sequence of phase formation, and the possible formation of metastable phases are important features of the crystallization process which cannot be ascertained solely from an inspection of the phase diagram. To obtain information concerning these features, a series of isothermal heat treatments were performed for various time periods using solid samples of L40, L42, and L45 at those temperatures where DTA showed significant crystallization to be occurring. Two types of thermal histories were employed; cooling the liquid directly to the crystallization temperature (henceforth termed from above), and heating the solid glass to the crystallization temperature (termed from below). After a given heat treatment, each sample was polished and examined microscopically, and portions of the surface and interior were separately ground and subjected to XRD. In this manner the size, number density, shape, and other characteristics of the crystallites were determined.

TABLE III Crystallization temperature on cooling (DTA cooling at 10 °C min^{-1})

	Crystallization temperature (°C)		
	5 min at 950 °C	15 min at 950 °C	15 min at 1150 °C
L40	690	No crystallization	No crystallization
L42	752	730	585
L45	765	763	648

Henceforth, attention is focused upon the high-temperature crystallization peaks in the glass compositions. In the high-temperature regime only the DB and MB phases formed for all isothermal heating times investigated. However, the details of the nucleation and crystallization processes were found to be strongly dependent upon composition, heat-treatment temperature, and thermal history. For example, the relative amounts of the DB and MB phases which formed at a given temperature, when heated for a fixed time period, were observed to depend upon thermal history.

For the DB phase, the measured intensity (I) ratios and d values were always in acceptable agreement with both the lithium diborate calculated pattern

TABLE IV Experimental XRD intensity data for MB phases

d	(hkl)	1 L50	2 L50	3 L40 above	4 L40 below	5 L42 below
5.27	100	13	5	6	54	45
3.356	110	18	5	4	100	79
3.195	102	62	70	65	33	100
2.923	002	100	100	100	35	100
2.422	211	17	5	8	33	38
2.174	020	21	5	4	94	69
1.593	104	10	20	8	4	9

(from structure factor data) reported in JCPDS file 22-1140 and the experimental diffractometer data given by Sastry and Hummel [10]. However, this was not the case for the XRD patterns which we obtained for the MB phase. Although the measured d values for the MB phase were always reasonably close ($0.2° 2\theta$) to the reported values [10], the I ratios of the reflections which were measured varied widely as a function of glass composition and thermal treatment. Attention was focused on the most intense MB phase reflections which did not overlap the DB reflections. Two trends were noted for the appearance of the abnormal intensity ratios. First, glasses which were heated from below were more prone to exhibit the abnormal I ratios. Second, the tendency for abnormal intensity ratios decreased as the lithia content of the glass composition was increased (in the DB to MB composition region). These tendencies are illustrated in Table IV, and are discussed in further detail below.

The pertinent reflections of the MB phase obtained from L40 and L42 composition glasses, which were heated (from below) at 630 °C for 1 h, are shown in the last two columns of Table IV. For purposes of comparison, the corresponding reflections for pure lithium metaborate (JCPDS 11-407) are given in column 2 of this table. The relative intensities for these powder diffractometer reflections calculated from the theoretical structure factors for this crystal employing the lattice parameters determined by Zachariasen [12], and using an isotropic temperature factor are shown in column 1. Column 3 gives the relative intensities of the MB phase which formed in composition L40 when heated at 630 °C from above. It may be seen that these intensities are in quite good agreement with the JCPDS values given in column 2, and in acceptable agreement with the calculated values. By contrast, for the glasses heated from below, the strong (0 0 2) reflection is often found to be greatly reduced in intensity, and the weak (1 1 0) and (0 2 0) reflections are greatly enhanced. Although the details of the relative intensities were found to be dependent upon the glass composition and crystallization temperatures, the diffraction patterns shown are typical. Also, for a given glass composition and thermal history, the XRD patterns were quite reproducible. For samples which exhibited the largest intensity abnormalities, the possibility that this behaviour was due to experimental artefacts such as surface orientation or crystal size effects was considered. However, for any given crystallized glass, the XRD pattern was always found to be the same, regardless of sample preparation procedure.

3.3. Sequences of crystalline phase formation

In order to provide a reasonable explanation for the observed abnormal intensity ratios, it is first necessary to discuss, briefly, the sequence of phase formation. When each composition was brought to the highest temperature from above, the MB phase was the first to form (see Table V), and it always formed at the glass surface. The MB phase was observed to nucleate at the air–glass-container interface and grow along the air–glass interface away from the container. It was this region of the sample which was removed and ground for XRD analysis, and which showed the formation of MB with a standard ratio of intensities. However, when the glasses were heated at this temperature from below, crystallites of both MB and DB were observed, and the time to detect the appearance of crystallites was shorter than in the former case. Also, the MB phase which formed invariably exhibited abnormal intensity ratios. Although when heated from below at high temperature both phases appeared to form nearly concurrently, glasses heated for short times at lower temperatures crystallized to form only the DB phase. Hence, it is plausible to expect that at least a small amount of DB phase formed first (during elevation of the temperature) when the glass was heated from below at high temperature.

4. Discussion

Here an explanation will be offered for the observed anomalous intensity ratios. Because the d values of the reflections did not vary by more than about 1% for even large intensity deviations, and because no new reflections were observed, it was concluded that the basic MB unit cell (as reported by Zachariasen [12]) is not dependent upon glass composition or crystallization history. Thus, we postulate that the unusual MB structures which form are, in fact, metastable defect structures deficient in Li_2O. This hypothesis is consistent with the observation that the structure becomes more abnormal in glasses of lower lithia content. The L45 composition crystallizes to form

TABLE V Sequence of crystal phase formation (from above and below)

	15 min	30 min	60 min	90 min
L40 at 690 °C				
Above	Glass	LB	LB, LB_2	LB, LB_2
Below	$LB_2 \gg LB$[a]	$LB_2 \gg LB$[a]	$LB_2 \gg LB$[a]	$LB_2 \gg LB$
L42 at 752 °C				
Above	Glass	LB	LB	LB
Below	LB, LB_2	LB, LB_2	LB, LB_2	LB, LB_2
L45 at 765 °C				
Above	LB	LB	LB	LB
Below	$LB \gg LB_2$	$LB \gg LB_2$	$LB \gg LB_2$	$LB \gg LB_2$

[a] Metaborate with abnormal intensity ratios.

normal MB, whether heated from above or below. The L36 composition, on the other hand, always exhibits a highly abnormal MB phase when heated from above or below. The intermediate compositions studied (L40 and L42) crystallize to either normal or abnormal MB, depending on thermal history.

The specific model which we propose for the formation of these metastable structures is as follows. First, we assert that to form the defect structures the DB phase must form prior to the MB phase and that the MB phase nucleates on or near the DB crystals. These assertions are supported by our experimental observations. Near the glass–DB interface the glass is enriched in lithium with respect to the average glass composition, and a diffusion zone exists in the immediate vicinity of this interface. This feature has two consequences. First, it enhances the probability of MB phase formation in this region because the glass composition is closer to that of the MB than in the rest of the glass. Second, however, it makes growth of MB phase with the correct stoichiometry difficult because lithium ions must diffuse "uphill" against the concentration gradient formed in the region near the DB crystal. Therefore, for some time period the MB phase grows to form a lithia-deficient metastable species. However, one would expect that after the growing MB species passes through the enrichment zone it would begin to grow normally. Hence, after long-term heat treatments one would anticipate to see mainly normal MB intensity ratios. We have, indeed, observed this transition. Samples of L40 heated at 690 °C for 1 h show anomalous I ratios, but samples of the same composition which were heated for 5 h at this temperature exhibited nearly normal intensity ratios.

Thus, although we do not claim that our model is unique, it is consistent with our experimental observations in several respects. It accounts for the composition dependence of the abnormal intensities as well as the thermal history effects. It also provides an explanation as to why long-term heat treatments produces normal intensities.

5. Conclusions

The crystallization behaviour of LB glasses in the composition range between the DB and MB were studied, and it was seen that although the phases which form are those indicated by the equilibrium phase diagram, the time dependence of the formation of the phases is a strong function of composition, temperature, and thermal history. As discussed, under certain conditions of the latter parameters, metastable phases can appear and grow, at least at sufficiently short times. The phases which form initially depend not only upon glass composition, but also are sensitive to thermal history. In all cases crystallization initiated on the surface. However, a small degree of internal crystallization was in evidence when composition L40 was heated at low temperatures.

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