

Structural Characterization of Lithium Aluminum Borate Glasses

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Abstract

Glasses in the $x\text{Li}_2\text{O} (40-x)\text{Al}_2\text{O}_3.60\text{B}_2\text{O}_3$ system ($0 \leq x \leq 40$) have been prepared by melt quenching technique. ^{27}Al NMR measurements are applied to determine the structure role of Al_2O_3 in a wide range of composition. A great difference in the structure of the studied glasses is revealed by changing Li_2O to Al_2O_3 molar ratios. The AlO_6 , AlO_5 and AlO_4 structured groups are the major units of pure Al_2O_3 . On the other side, AlO_4 and AlO_5 are the main units in the binary $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glass ($\text{Li}_2\text{O}=0$ and 40 mol% Al_2O_3). Increasing $\text{Li}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio results in the decreasing AlO_5 concentration. In addition, AlO_4 is considered the dominant species. Further increase in Li_2O concentration results in formation of non-bridging oxygen atoms (NBOs) in AlO_4 groups. Glasses of the high $\text{Li}_2\text{O}/\text{Al}_2\text{O}_3$ ratio have an amorphous structure. More ordered crystalline phases are considered in glasses of a high Al_2O_3 concentration. The difference in the cation field strength (CFS) between Al^{3+} , B^{3+} and Li^+ cations was observed to affect the generation of AlO_5 , AlO_6 and BO_4 units.

Keywords

Borate Glasses, NMR Investigation, Coordination Number, Crystallized Phases

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1. Introduction

A great deal of attention in recent decades [1-3] have been concentrated on Al_2O_3 modified glasses and their derivative. The addition of Al_2O_3 to borate, silicate, borosilicate and phosphate glasses enhances the network stability [3, 4] through reinforcing of the mechanical properties. ^{27}Al spectroscopy of glasses containing high Al_2O_3 concentration has confirmed that AlO_4 , AlO_5 and AlO_6 are all the well formed species in the glass network [3, 5, 6]. It has been reported that the physical properties of Al_2O_3 containing glasses such as micro-hardness, conductivity and chemical durability are closely associated with their Al coordination [7-10]. Accordingly, it is important to follow the change of the Al coordination in the investigated glasses to get the desirable glass network of enhanced structure and properties.

The tetrahedral AlO_4 type is the most dominant species found as the main groups in many of investigated glasses [1-6]. However, relatively higher coordinated units such as AlO_5 and AlO_6 [10, 11] were suppressed with increasing modifier at expense of Al_2O_3 .

Most of the previous studies have been concentrated on properties of the amorphous glasses in the low Al_2O_3 concentration. Our aim in this work is to extend the glass formation region to contain crystalline structural units which have a great uses in the field of applications. For instance, Al_2O_3 reinforced crystallized borate phases [12-15] are increasingly used to enhance the hardness and other mechanical properties of materials [16, 17].

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2. Experimental

2.1. Preparation of Glasses

Glasses in the $x\text{Al}_2\text{O}_3 \cdot (40-x)\text{Li}_2\text{O} \cdot 60\text{B}_2\text{O}_3$ ($x = 0-40$ mol%) system were prepared by fast quenching technique. Stoichiometric fine powders (Aldrich, 99.9 purity) of Li_2CO_3 , H_3BO_3 and Al_2O_3 were well mixed together in a porcelain mortar and melted for 40 minutes in a platinum crucible at temperature between 1320°C and 1550°C . Subsequently, the melts were quenched on a metal plate that was pre-heated to 300°C to avoid solid samples from cracking. The amorphous or ordered nature for the prepared samples was checked by X-ray diffraction. The resulting glasses had stored after preparation in evacuated dissector until used.

2.2. ^{27}Al NMR Measurements

NMR measurements were carried out at ambient temperature on a JEOL RESONANCE GSX-500 spectrometer operating at a high external magnetic field (11.747 T). ^{27}Al NMR spectra were measured at the resonance frequency of 130.2 MHz, using a 3.2 mm MAS NMR probe operated at a rotor frequency of 15 kHz. Typical pulse lengths were 2.5 μs and 60 seconds delay time was sufficient to enable relaxation.

3. Results and Discussion

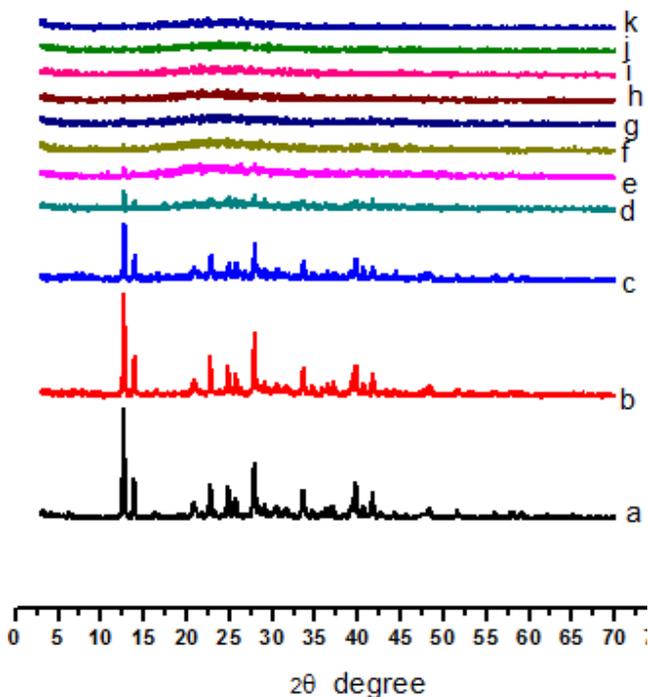


Figure 1. Change of XRD spectra with Li_2O concentration (a-d) high Li_2O content, (e-k) lower Li_2O concentration.

The as obtained glasses of extremely high $\text{Li}_2\text{O}/\text{Al}_2\text{O}_3$ ratios (>1) are characterized with their amorphous structure, figure

1. At lower molar ratio, the fine grained alumina-borate crystals in some investigating glasses are formed. The well-formed crystalline $\text{Li}_2\text{Al}_2\text{B}_2\text{O}$ phase [18] provides the glasses additional and useful advantages. The ordered crystal plays a role in improvement of hardness and compactness of the material network and consequently enhances its resistance to corrosion. This may be due to the precipitation of two types of mixed aluminium coordination (Al_4 and Al_5) in the borate matrix. Presence of even low concentration from Al_5 in the network can simply improve micro-hardness and resistivity of the material.

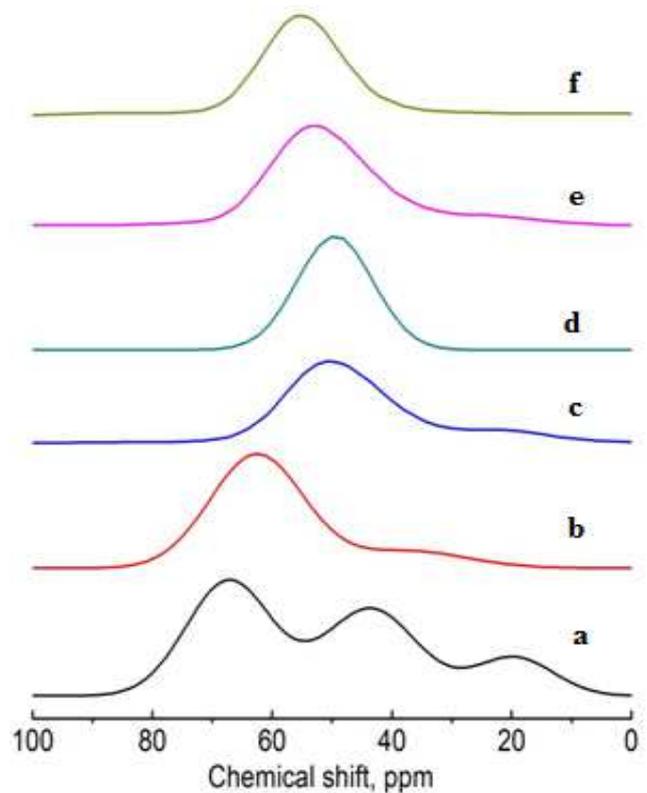


Figure 2. ^{27}Al NMR spectra as a function of $\text{Li}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio.

The NMR resonance spectra of a pure Al_2O_3 (figure 2 a) exhibit three groups of resonance bands. The well resolved resonance band in the region 60-80 ppm is assigned to the well formed four-fold coordinated aluminium (AlO_4) units. The second group of band in the region 30-50 ppm is attributed to presence of five-fold coordinated aluminium (AlO_5) units. Whereas, the band between 0 and 25 ppm is due to six-fold coordinated aluminium (AlO_6) units [11-14, 19]. The latter coordinated units are consumed in the glass network as a modifier. The other two types (AlO_4 and AlO_5) are both represent glass forming species. Upon introduction of Li_2O into the glass network at expense of Al_2O_3 , the relative area representing AlO_6 and AlO_5 is obviously decreased. At extremely high Li_2O concentrations, only a resonance peak characterizing AlO_4 unit is appeared and no additional resonance bands are observed (figure 1, d, e and f).

In addition, there is a clear shift in the peak position toward lower values of chemical shift with increasing Li_2O (decreasing Al_2O_3). This change is attributed to disintegration of AlO_5 units to form AlO_4 groups. More addition of Li_2O leads to more formation of AlO_4 units containing non bridging bond.

However, the intensity of the resonance band of AlO_6 and AlO_5 is hardly decreased upon increasing $\text{Li}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio. The relatively decrease of the resonance bands of both six and five-fold coordinated Al strongly leads that Al_2O_3 enters the network as a glass former. As a result, comparatively more AlO_4 units of NBO would be constructed which in turns form the skeleton of the glass network. As a result of decreasing of AlO_6 and AlO_5 with increasing $\text{Li}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio, B-O-Al₄ and Al₄-O-Al₄ bonds are also decreased. This observation directly supports the view point that a major part of Al_2O_3 ions can exist as a glass former. The shortage in AlO_5 and AlO_6 concentration will result in the decreasing of molar volume and associated free volume with increasing $\text{Li}_2\text{O}/\text{Al}_2\text{O}_3$ ratios. As a result asymmetric BO_4 groups are increased at expense of BO_3 units upon increasing Li_2O .

Figures 3, 4 and 5 present the deconvolution of NMR spectra of some analyzed compositions presented as examples. By deconvoluting the spectra into their separated component bands, the content of four-fold AlO_4 and five-fold AlO_5 units can be quantitatively determined. The obtained results are summarized in figure 6. It can be noted that the concentration of four coordinated groups AlO_4 is higher in all cases than that of AlO_5 concentrations. The clear higher AlO_4 concentrations may reveal that Al_2O_3 can play an intermediate role in the borate glass network. Part enters as a glass former and a small portion enters as a modifier to compensate for the continuous decrease in lithium oxide concentration.

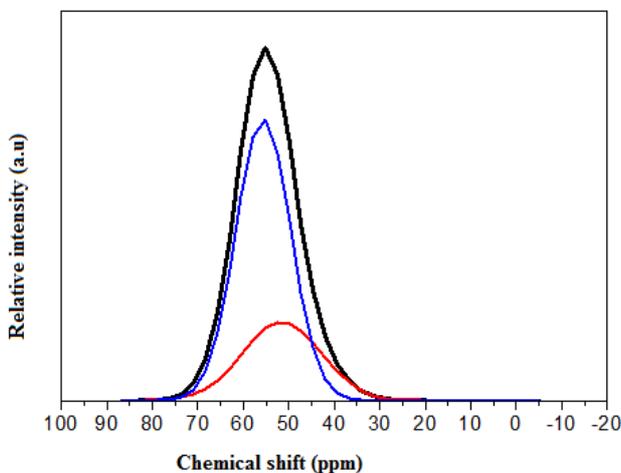


Figure 3. Deconvolution of NMR spectra of glass containing 6 mol% Al_2O_3 .

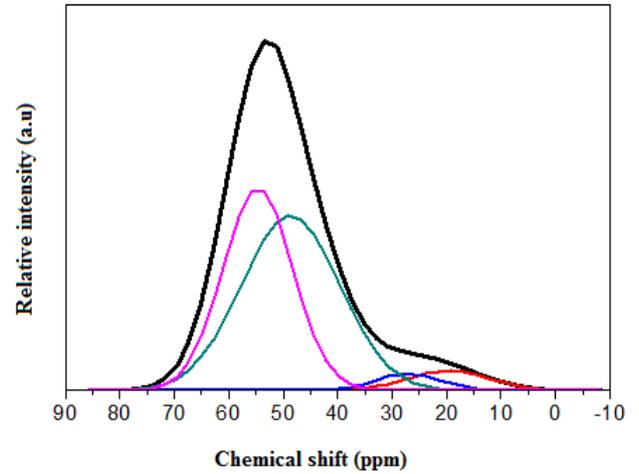


Figure 4. Deconvolution NMR spectrum of the glass containing 15 mol% Al_2O_3 .

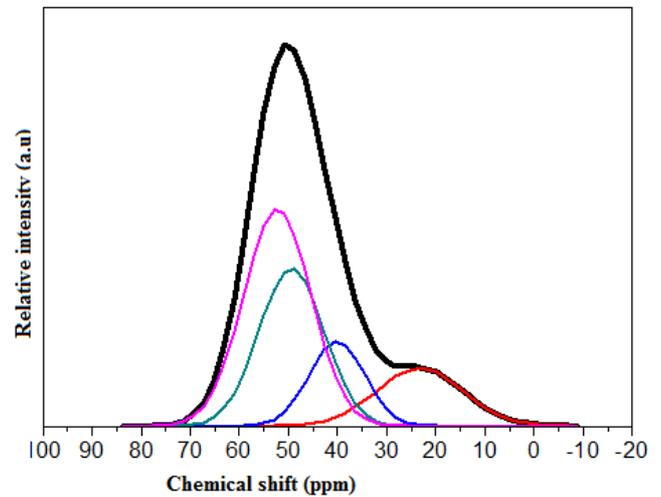


Figure 5. Deconvolution NMR spectrum of the glass containing 24 mol% Al_2O_3 .

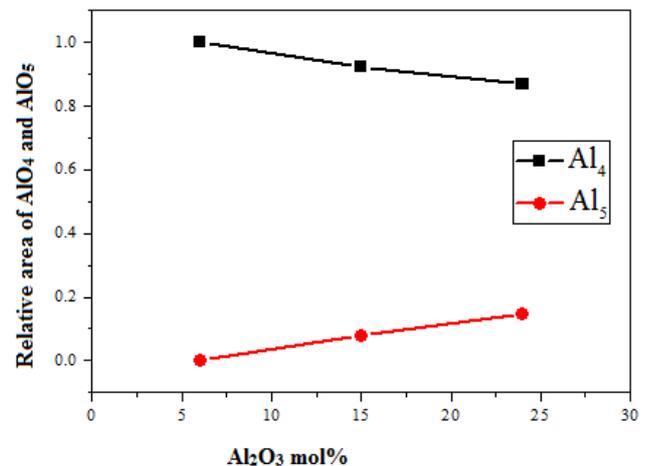


Figure 6. Changes of both AlO_4 and AlO_5 with increasing Al_2O_3 concentration.

4. Conclusion

The phase change and micro-structure determination of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$ glasses have been investigated using nuclear magnetic resonance (NMR) and X-ray diffraction (XRD) spectroscopy. The amorphous structure is the dominant in glasses of a relatively high Li_2O content (≥ 22 mol%). The crystallinity is increased at lower Li_2O concentrations. This finding was due to the development of the material structure through presence of different coordination of Al_2O_3 . ^{27}Al NMR measurements are applied to determine the structure role of Al_2O_3 in a wide range of composition. A great difference in the structure of the studied glasses is revealed by changing Li_2O to Al_2O_3 molar ratios. The AlO_6 , AlO_5 and AlO_4 structured groups are the major units of pure Al_2O_3 . On the other side, AlO_4 and AlO_5 are the main units in the binary $\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$ glass ($\text{Li}_2\text{O}=0$ and 40 mol% Al_2O_3). Increasing $\text{Li}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio results in the decreasing AlO_5 . In addition, AlO_4 is considered the dominant species. The difference in the cation field strength (CFS) between Al^{3+} , B^{3+} and Li^+ was observed to affect the generation of AlO_5 , AlO_6 and BO_4 units.

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