Materials Physics and Mechanics 15 (2012) 66-73 Received: August 16, 2012

STRUCTURAL INVESTIGATION OF B_2O_3- Li_2CO_3- Al_2O_3 GLASSES BY MOLAR VOLUME MEASUREMENTS AND FTIR SPECTROSCOPY

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Abstract. A lithium aluminoborate glass system is prepared by the conventional melt quenching technique. The powder XR diffraction analysis of the prepared samples confirms the amorphous nature of the samples. The density and molar volume studies report the change of structure with the increase of aluminium content. The FTIR analysis of the samples revealed that the network structure of the prepared samples is mainly based on the BO_3 and BO_4 units.

1. Introduction

Borate is one of the most important glass former and has been incorporated in many kinds of glass systems to attain desired chemical and physical properties. In borate glasses, B_2O_3 is the fundamental glass former because of its higher bond strength, lower cation size, small heat of fusion and trivalent nature of B, in which, B^{3+} ions are triangularly coordinated by oxygen and corner bonded in a random configuration [1]. Borate glasses containing Li^+ ions are considered to be the potential candidates for electrolytes of thin film batteries as they exhibit isotropic ion conductivity and stability at high voltage [2]. High valence cations such as Al^{3+} are commonly used as intermediate species [3]. The structure of glasses with composition x B_2O_3 – (1-x) M_2O, (M= Li, Na, K, Rb, Cs) consists of B – O network, built up from planner three- coordinated and tetrahedral four coordinated B atoms [4]. Pure vitreous B_2O_3 contains only three coordinated boron atoms $[BO_3]^{3-}$ and if an alkali oxide (M_2O) is added some of these units transform into four coordinated tetrahedral [5]. If an alkali impurity creates non-bridging oxygen, the resulting network gets loose and the connectivity of B_2O_3 network decreases. Therefore, some of the glass parameters such as thermal coefficient expansion and electrical conductivity increase with increase in modifier content. If an alkali impurity causes boron atom to be tetrahedral, the connectivity increases followed by decrease in strength of these glass properties.

In this work, an attempt has been made for the preparation and characterization of aluminoborate glasses with the addition of lithium oxide as modifier. The structural investigation of the glasses has been studied with the help of molar volume measurements and FTIR spectroscopy.

2. Experimental procedure

The $80\%B_2O_3-(20-y)\%Li_2CO_3-y\%Al_2O_3$ glasses ($0\leq y\leq 7.5$) were prepared using stoichiometric powders by mixing Li_2CO_3, B_2O_3 and Al_2O_3. The chemical composition (by weight) of the glass samples prepared by using conventional melt quenching technique is given in Table 1. The finely mixed batches were melted in silica crucibles at 1150 °C for two hours in air with the melts being stirred from time to time to maintain homogeneity and then they were poured on a pre- heated graphite block. Further the glasses were annealed at 400 °C for 12 hours.

Table 1. Composition of prepared samples.

Sample No	Al_2O_3*, %	Li_2CO_3, %	B_2O_3, %
1	1.5	18.5	80
2	3.0	17.0	80
3	4.5	15.5	80
4	6.0	14.0	80
5	7.5	12.5	80

*Percentage by weight used.

To confirm the amorphous state of the prepared samples, the powder X- ray diffraction (XRD) analysis was made.

For measuring density of glass samples, Archimedes principle was used with benzene as the immersion fluid using the following formula

$$d=\left(\frac{w_a}{w_a-w_b}\right)d_b,$$

where w_a is weight of sample in air, w_b is weight of sample in benzene, d_b is density of benzene.

Then the molar volume values of the prepared samples were calculated using the obtained densities and weight of one mole of the sample, with the help of the following equation:

$$V_m=\frac{1}{d}w_m.$$

Finally, the Infrared absorbance measurements over the range of 400- 4000 cm^{-1} were made at room temperature using Perkin-Elmer infrared spectrometer.

3. Results and discussion

3.1. X R Diffraction analysis. The powder XR diffraction analysis of the samples in consideration is shown in Figs. 1-5.

These figures exhibit no detectable peaks which confirmed the proper preparation of glass samples.

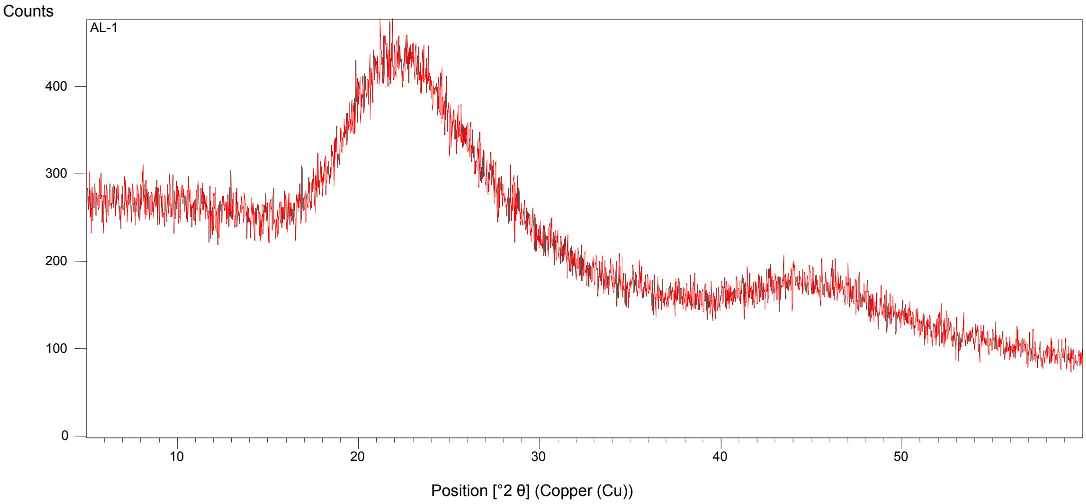

Fig. 1. XRD of the sample with 1.5 % Al_2O_3 composition.

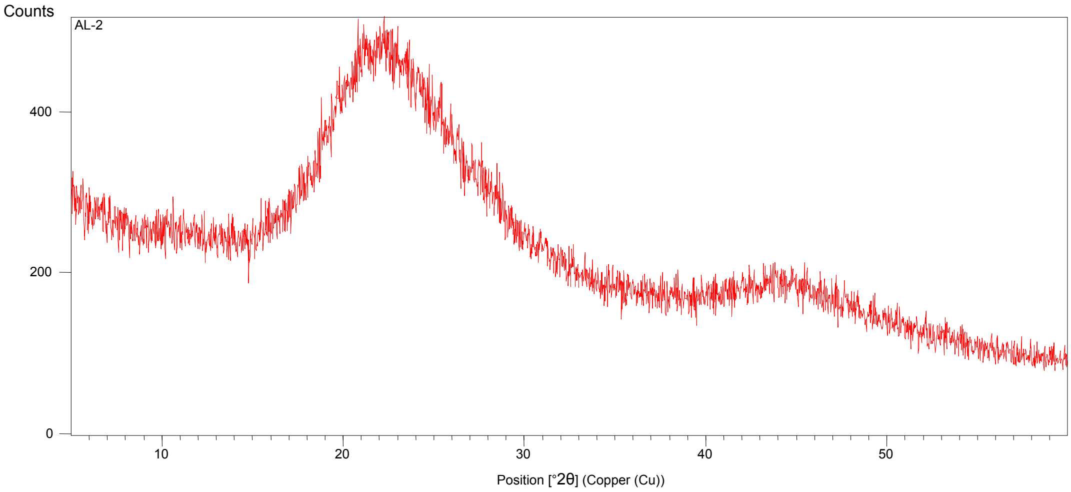

Fig. 2. XRD of the sample with 3.0 % Al_2O_3 composition.

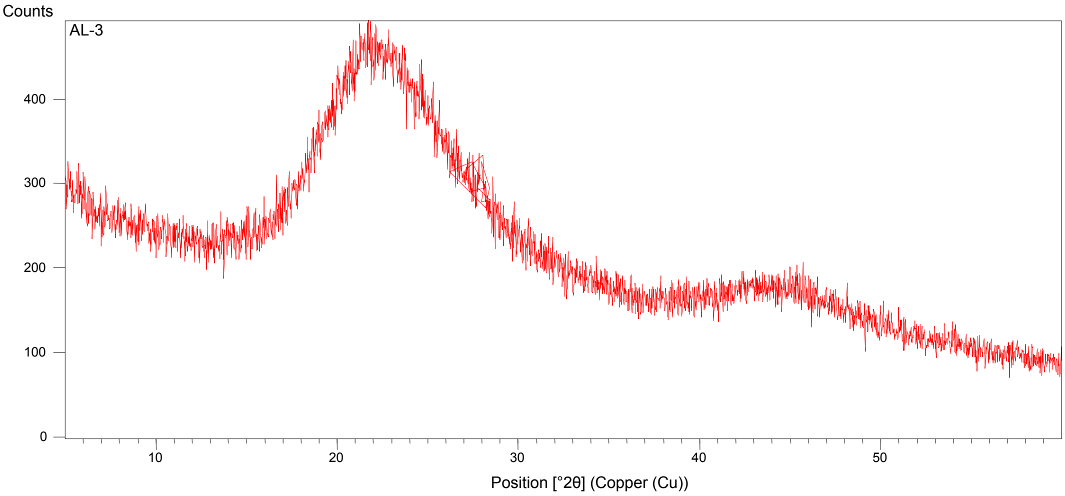

Fig. 3. XRD of the sample with 4.5% Al_2O_3 composition.

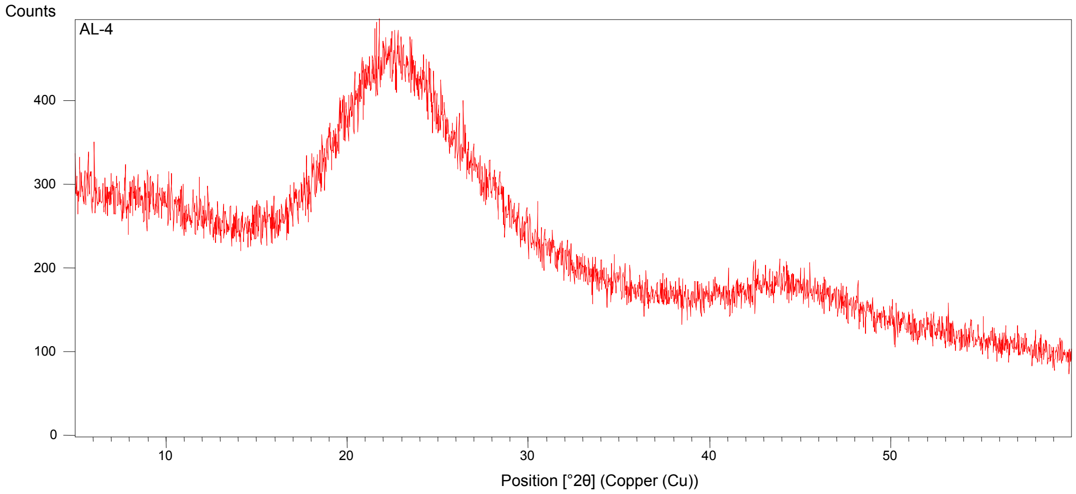

Fig. 4. XRD of the sample with 6.0 % Al_2O_3 composition.

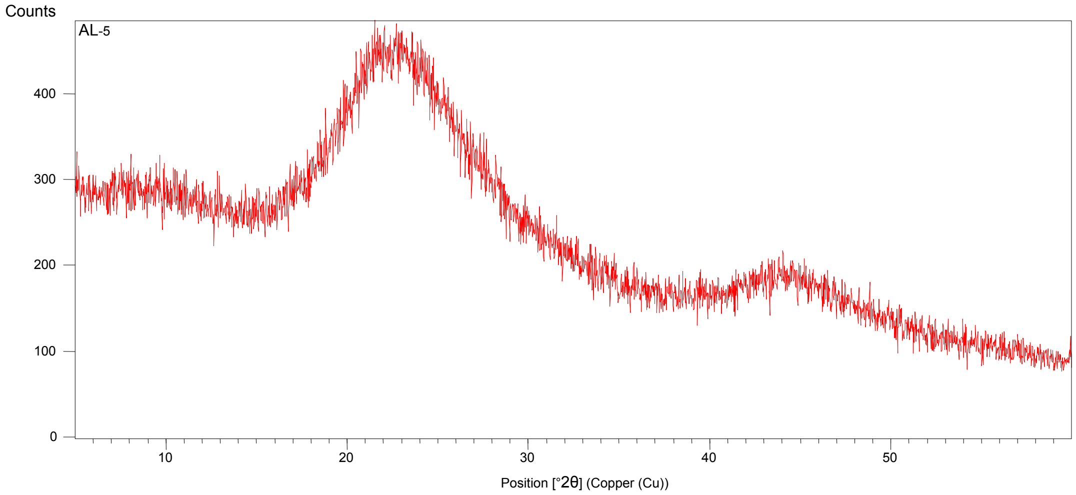

Fig. 5. XRD of the sample with 7.5 % Al_2O_3 composition.

3.2. Density and molar volume. The density measurement is considered to be a very important tool to detect the structural changes in the glass network. The density is supposed to change abruptly when the structure of the glass is slightly changed and Table 2 shows the calculated molar volume values.

Table 2. The density and molar volume versus Al_2O_3 content.

Sample No	1	2	3	4	5
Al_2O_3*, %	1.50	3.00	4.50	6.00	7.50
Density	2.10	2.16	2.18	2.19	2.21
Molar volume	33.7	33.0	32.9	32.9	32.8

*Percentage by weight used.

The density of our samples appears to increase gradually from 2.10 to 2.21 gm cm^{-3} with the increase of Al_2O_3 content which further increases at the expense of lithium oxide. This increase in the density can be due to replacement of low density lithium element (0.53 gm. cm^{-3}) by high density aluminium element (2.70 gm. cm^{-3}) [6]. Also non-bridging oxygen decreases in the glass network on increasing the Al_2O_3 content, which tend to consolidate their structure, maintaining homogeneity of the glasses and thus increasing density [7]. Molar volume indicates the spatial distribution of the oxygen in the glass network. The gradual decrease in the molar volume can be attributed to closing up of glass structure.

3.3. FTIR analysis. For structural analysis of oxide glasses the following information is required [8]:

(i) Type of the bridging bonds of oxygen which link the coordination polyhedra of framework and the composition of chemical inhomogeneities in the structure of glass.

(ii) The coordination number of the compound with respect to oxygen, especially of network formers.

(iii) The change in oxygen bonds of the framework, induced by the cation modifiers which combine with the oxygen bonds.

Borate glasses provide an ideal case in comparison to other glass forming systems which demonstrate the effectiveness of infrared spectroscopy in glass science [9]. Boron has the smallest mass as compared to the other network forming elements, and thus the main vibrational modes associated with the glass network appear well above 500 cm^{-1} (in the mid–infrared region) [10].

Figures 6-10 show some IR absorption spectra of the prepared samples. A weak band appears around 415 cm^{-1} showing the presence of lithium oxide in the glass samples [11]. Another band appears around 450 cm^{-1} which can be due to vibration of lithium cations [12]. The band observed around 500 cm^{-1} can be attributed to B-O-B bonds bending vibrations. The band around 700 cm^{-1} can be due to some deformation modes of the network structure [13-14].

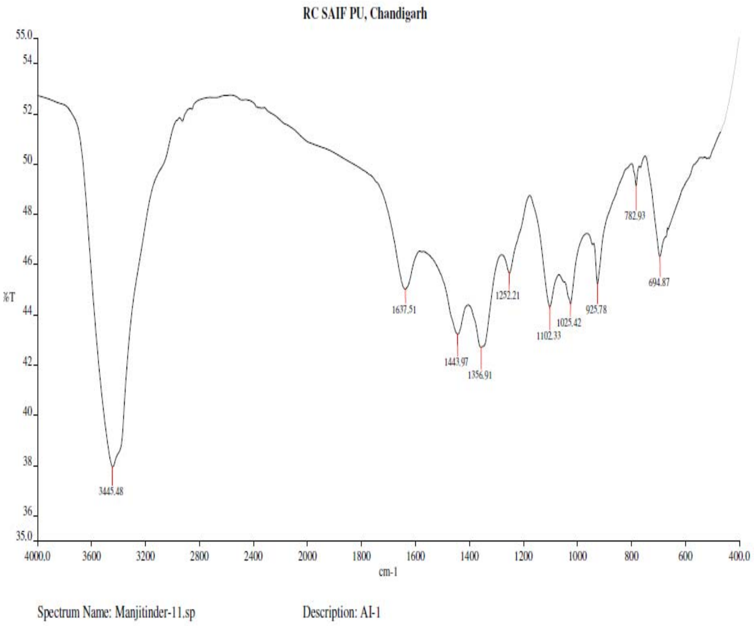

Fig. 6. FTIR spectra of the prepared glass sample No 1.

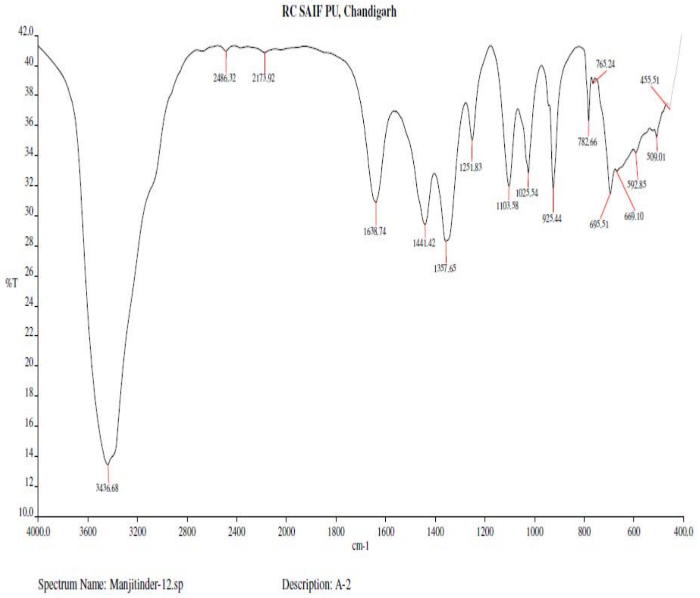

Fig. 7. FTIR spectra of the prepared glass sample No 2.

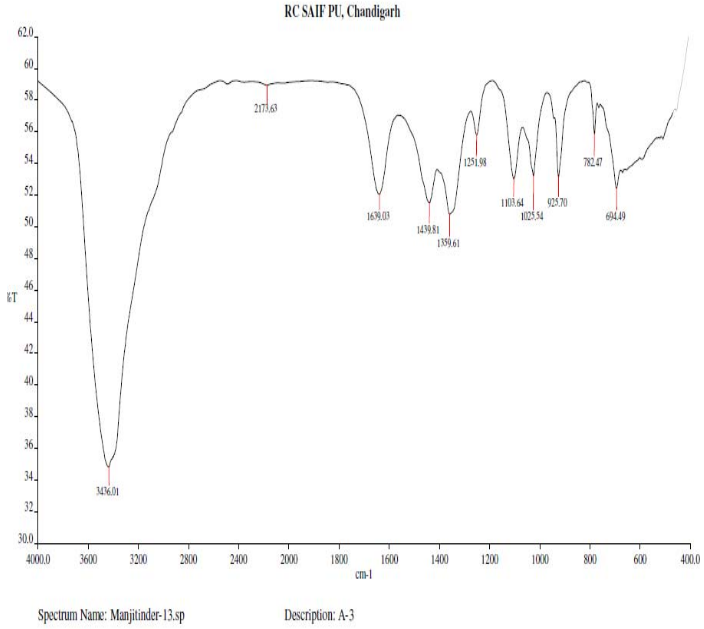

Fig. 8. FTIR spectra of the prepared glass sample No 3.

Another band near 770 cm^{-1} can be an indication to the B-O-B bending vibrations of bridges containing one trigonal and one tetrahedral boron [15].

Absorption band at 925 cm^{-1} points to diborate network [16-17]. The band appearing at 1025 cm^{-1} may characterize vibrations of diborate bridging to pentaborate groups, and to the asymmetric and stretching vibrations of BO_4 groups [15]. The band that arises around 1100 cm^{-1} can be due to stretching of the BO_4 structural units [15-18].

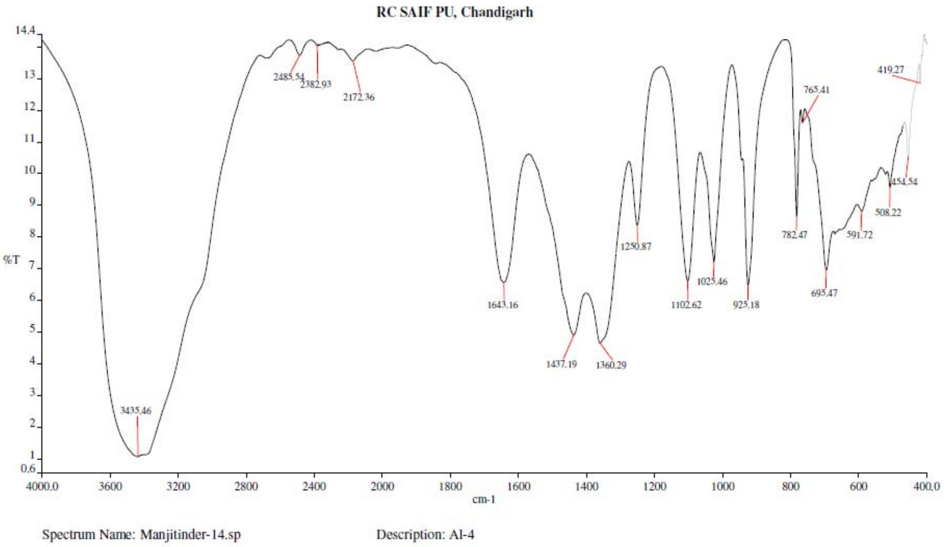

Fig. 9. FTIR spectra of the prepared glass sample No 4.

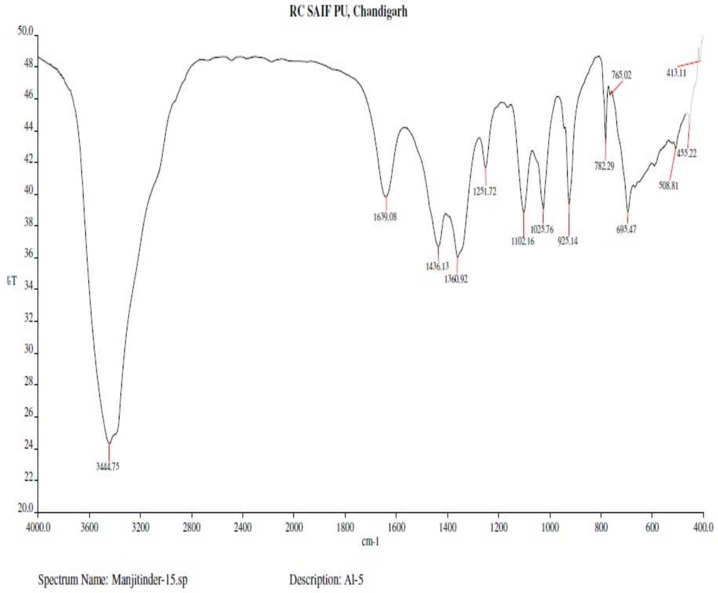

Fig. 10. FTIR spectra of the prepared glass sample No 5.

Another band which appeared at 1252 cm^{-1} can be assigned to B-O stretching vibrations mainly the linkages between oxygen and different groups as well as B-O bridging between boroxol rings and trigonal BO_3 [15-16]. At 1356 cm^{-1}, a band emerges and it is due to asymmetric stretching relaxation of the B-O bond of trigonal BO_3 units and various borate groups [19-20]. Another band is observed around 1430 cm^{-1} can be due to stretching vibrations of borate triangles with NBO. B-O bond stretching vibrations of borate units in which boron atoms are coordinated with three oxygen atoms leads to formation of a band around 1600 cm^{-1}. The bands that appeared after that are attributed to presence of water groups and O-H bond vibrations [21-22].

4. Conclusions

XRD analysis confirms the amorphous nature of the prepared samples. The increase in density is attributed to closing up of glass structure and results also suggest the change from BO_3 group to BO_4 group. The BO_3 and BO_4 groups act as network structural groups while lithium and aluminium appear in interstitial positions.

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