

STRUCTURAL INVESTIGATION OF B₂O₃- Li₂CO₃- Al₂O₃ GLASSES BY MOLAR VOLUME MEASUREMENTS AND FTIR SPECTROSCOPY

M. Kaur¹, S.P. Singh^{2*}, D.S. Mudahar³, G.S. Mudahar²

¹Department of Physics, Government Mohindra College, Patiala,
Punjab, 147001, India

²Department of Physics, Punjabi University Patiala, Punjab-147002, India

³Department of Physics, Shri Guru Granth Sahib World University, Fatehgarh Sahib (Punjab),
140406, India,

*e-mail: supreet_phy@pbi.ac.in

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 BO₃ and BO₄ 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, B₂O₃ 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, B³⁺ 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 Al³⁺ are commonly used as intermediate species [3]. The structure of glasses with composition $x \text{ B}_2\text{O}_3 - (1-x) \text{ M}_2\text{O}$, (M= Li, Na, K, Rb, Cs) consists of B – O network, built up from planar three- coordinated and tetrahedral four coordinated B atoms [4]. Pure vitreous B₂O₃ contains only three coordinated boron atoms [BO₃]³⁻ and if an alkali oxide (M₂O) 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 B₂O₃ 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.

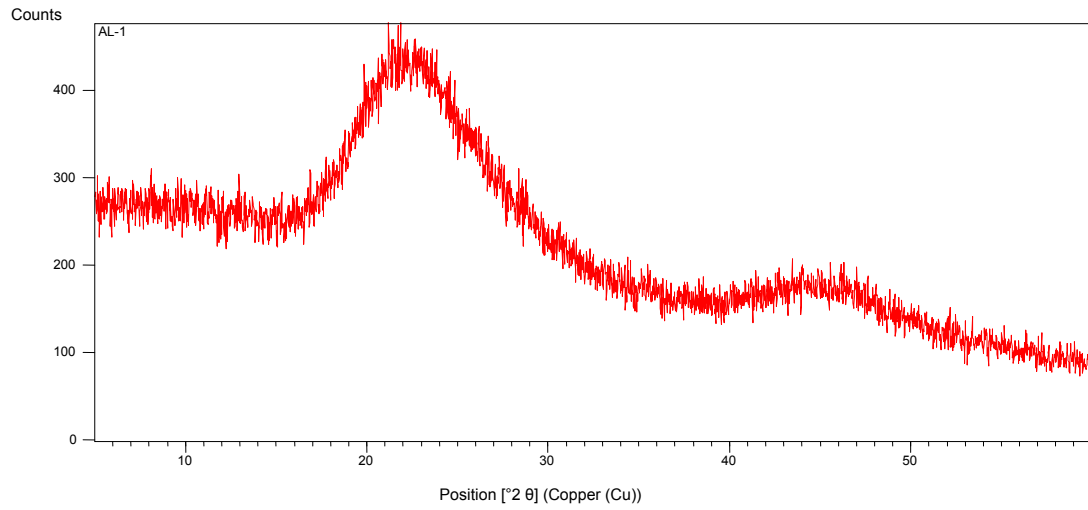


Fig. 1. XRD of the sample with 1.5 % Al_2O_3 composition.

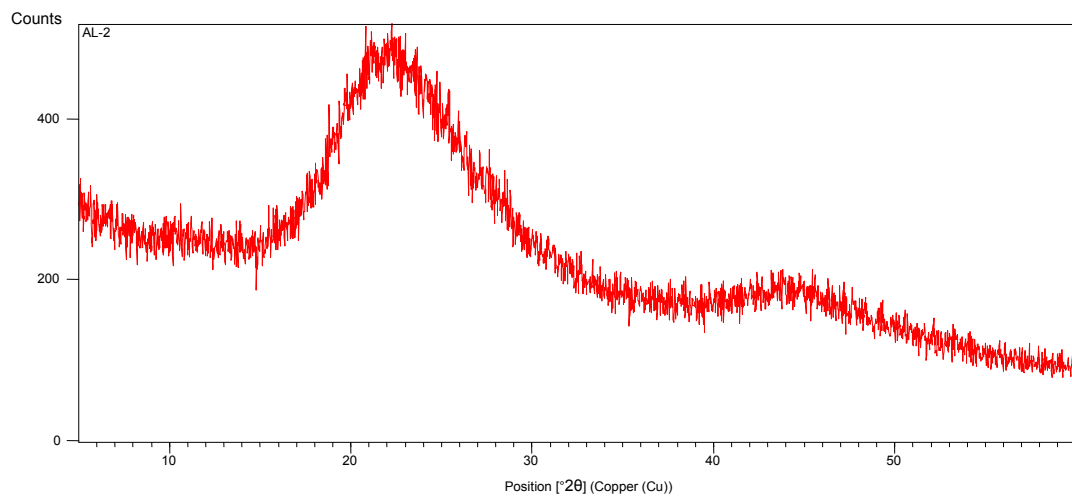


Fig. 2. XRD of the sample with 3.0 % Al_2O_3 composition.

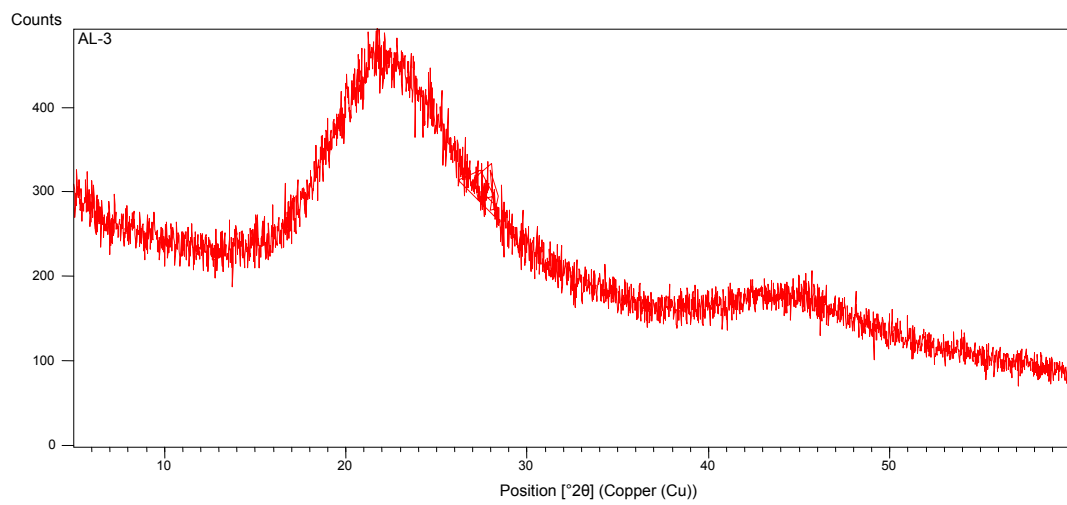


Fig. 3. XRD of the sample with 4.5% Al_2O_3 composition.

The density of our samples appears to increase gradually from 2.10 to 2.21 gm cm⁻³ with the increase of Al₂O₃ 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 Al₂O₃ 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].

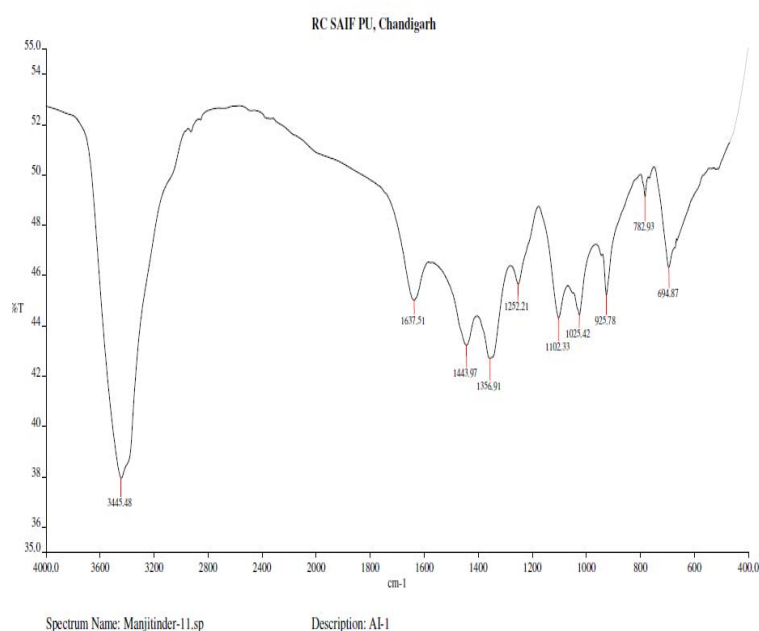


Fig. 6. FTIR spectra of the prepared glass sample No 1.

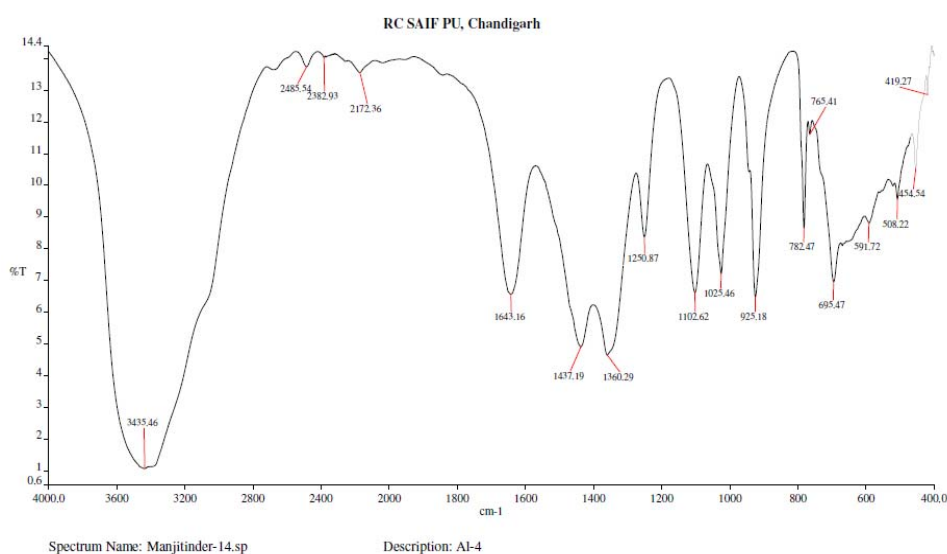


Fig. 9. FTIR spectra of the prepared glass sample No 4.

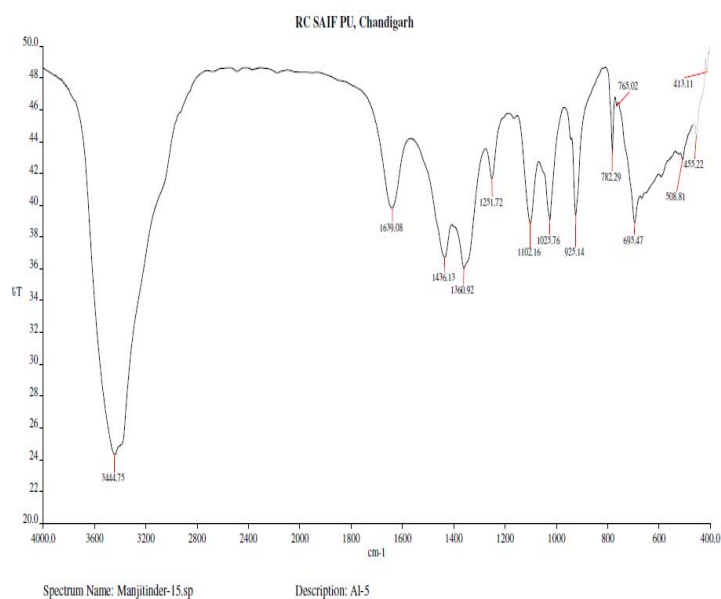


Fig. 10. FTIR spectra of the prepared glass sample No 5.

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 BO₃ group to BO₄ group. The BO₃ and BO₄ groups act as network structural groups while lithium and aluminium appear in interstitial positions.

References.

- [1] S.G. Motke, S. P. Yawale // *Bull. Mater. Sci.* **25** (1) (2002) 75.
- [2] Young-II Lee, Jong-Heun Lee, Seong-Hyeon Hong, Youngsin Park // *Solid State Ionics* **175** (2004) 687.
- [3] J. Mauro, Report from: Glass Laboratory, College of Ceramics, Alfred University (Private communication through the Internet), (2000).
- [4] J. Wong, C. A. Angell, *Glass Structure by Spectroscopy* (Dekker, New York, 1976).
- [5] D. L. Griscon, In: *Borate Glasses, Structure, Application*”, ed. by I.D. Pye, V.D. Frechette and N.J. Kreidl (Plenum, New York, 1978).
- [6] A. Chahine, M. Et-tabirou, J.L. Pascal // *Mater. Lett.* **58** (2004) 2776.
- [7] T. Abe // *J. Am. Ceram. Soc.* **35** (1952) 11.
- [8] L. Stoch, M. Sroda // *J. Mol. Struc.* **511** (1999) 77.
- [9] E.I. Kamitsos // *Phys. Chem. Glasses* **44** (2003) 79.
- [10] A.J. Karki, S. Feller, H.P. Lim, J. Stark, C. Sanchez, M.J. Shibata // *J. Non-Cryst. Solids* **92** (1987) 11.
- [11] O. Cozar, I. Ardelean, I. Bratu, S. Simon, C. Craciun, L. David, C. Cefan // *J. Mol. Struc.* **563**, (2001), 421.
- [12] E.I. Kamitsos, M.A. Karakassides, G.D. Chyrssikos // *J. Phys. Glasses* **91** (1987) 1073.
- [13] E.I. Kamitsos, A.P. Patsis, M.A. Karakassides, G.D. Chyrssikos // *J. Non-Cryst. Solids* **126** (1990) 52.
- [14] M. Toderas, S. Filip, I. Ardelean // *J. Opt.elec. and Adv. Mater.* **8** (2006), 1121.
- [15] Gamal El- Deen, Abd El-Raheem Yahya // *Turk. J. Phys.* **27** (2003) 255.
- [16] H.A. Silim, *Egypt. J. Solids*, **29**, **2**, (2006), 293.
- [17] Vandana, S.P. Singh, Devinder Singh, Gopi Sharma, Gurmel S. Mudahar // *Intl. J. App.Phys.* **2** (2012) 1.
- [18] T.W. Bril // *Philips Res. Rep. Suppl.* **1** (1976) 117.
- [19] W.L. Konijnendijk, J.M. Stevels // *J. Non-Cryst. Solids* **18** (1975) 307.
- [20] B. Sumalatha, I. Omkaram, Rao T. Rajavardhana, Ch. Linga Raju // *J. Non Cryst. Solids* **367** (2011) 3143.
- [21] H. Scholze // *Glass Ind.* **47** (11) (1966) 622.
- [22] F.M. Ernsbjer // *Glastech. Ber.* **32** (3) (1959) 81.