Structural and Optical Investigation of Aluminium-Lithium-Borate Glasses

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Abstract - **Glass samples of compositions xAl_2O_3-(30-$_x$) Li_2CO_3–$70B_2O_3$ with x varying from 0 to 8% mole fraction are prepared by melt quench technique. Decrease in the band gap from 3.12 to 2.91 eV for lithium borate glasses with an increase in the Al_2O_3 content has been observed and discussed. The FTIR spectral studies have pointed out the conversion of structural units of BO_3 to BO_4. Due to the formation of BO_4 and AlO_6 units, changes in the atomic structure with Al_2O_3 composition are observed and discussed.**

Keywords: **X-ray diffraction, Optical properties, FTIR**

I. Introduction

The study of oxide glasses has received considerable attention due to their structural peculiarities [1]. These glasses have wide applications in the fields of electronics, nuclear and solar energy technologies and acoustic-optic devices [2]. In addition, they are often used as dielectric and insulating materials and it is known that borate glass constitutes a good shield against IR radiation . It is well known that the main structural units of the borate network which are [BO_3] triangles and [BO_4] tetrahedral, may form different super -structural units; boroxol and meta-borate rings, meta-borate chains, penta-borate,tri-borate, diborate and pyro-borate [3].

The addition of alkali oxides can improve many properties of borate glasses as well as modify, even improve their preparation conditions. Lithium is an important alkali cation and Al_2O_3 is an important modifier. Glasses based on the lithium aluminum system have attracted considerable interest in recent years due to their significant applications in science and industry. Borate glasses containing Lithium have been extensively studied due to their technological applications as solid electrolyte in electro chemical devices such as batteries [4]. Alkali borate glasses are highly useful materials for vacuum ultra violet optics and semiconductors lithography owing to the presence of stable glass forming range and transparency from the near UV to the middle infrared region [5].

Another oxide, Al_2O_3 cannot form a glass by itself. It can form glass once it is added with another suitable oxides and it will take part in the formation of the glass structural unit. Alkali free alumina lead borate glasses are very stable against devitrification possess high mechanical strength, toughness, moisture resistant and excellent electrical properties. Due to this these glasses have application in battery sealing and microelectronic packing [6-8]. The addition of an Al_2O_3 is anticipated to enhance the chemical durability of the glasses while simultaneously increasing the glass transition temperature and reducing the thermal expansion coefficient [9-11].

The present work investigates the dominant role of Al_2O_3 on structural and optical properties in Li_2CO_3-B_2O_3 glass system. The structural properties are studied by using XRD (x-ray diffraction), Fourier transform infrared spectroscopy (FTIR) techniques. The optical properties of glasses are determined by using UV-visible spectroscopy measurements.

II. Experimental Detail

A. Sample Preparation

Glass samples xAl_2O_3-(30-x)Li_2CO_3–$70B_2O_3$ with x varying from 2 to 10 mol % are prepared by the conventional melt quench technique. The raw materials of Lithium Carbonate (Li_2CO_3), Aluminium Oxide (Al_2O_3) and Boric oxide (B_2O_3) of appropriate amounts are mixed together and melted in silica crucible at temperature range of 1100° C for 60 minutes until a bubble free liquid was formed. The melt is then poured in to preheated steel mould and annealed at temperature of 380° C for 1 hour to avoid breaking of the samples by residual internal strains. The obtained samples are grinded with different grade of silica carbide and polished with cerium oxide in order to obtain maximum flatness. The nominal composition of the prepared glasses is given in the Table I.

The amorphous/crystalline nature of the samples is confirmed by X-ray diffraction (XRD) study using (Shimadzu, Japan) X-ray diffractometer at the scanning rate of 2 degree/min and 2θ varied from 10–70°.

The Optical Absorption spectra of polished samples are recorded at room temperature by using UV-Visible Spectrophotometer (Perkin Elmer) in the range from 200-800 nm.

The infrared transmission spectra of the glasses are measured at room temperature in the wave number range 400–4000 cm^{-1} by a Fourier Transform computerized infrared spectrometer type (Thermo Nicolet 380 spectrometer). The prepared glasses are mixed in the form of flne powder with KBr in the ratio 1:100 mg glass powder: KBr, respectively. The weighed mixtures are then subjected to a pressure of 150 kg/ cm^2 to produce homogeneous pellets. The infrared transmission measurements are measured immediately after preparing the pellets.

III. Results And Discussions

A. X-Ray Diffraction

The x-ray diffraction pattern (Fig. 1) does not reveal any crystalline phase in Al_2O_3-Li_2CO_3–B_2O_3 glass samples which indicate the amorphous nature of the samples.

Table I Nominal Composition (mole %), And Band Gap Of Glasses

Glass Code	Al_2O_3	Li_2CO_3	B_2O_3	Band Gap
A1	0	30	70	2.91
A2	2	28	70	2.95
A3	4	26	70	3.00
A4	6	24	70	3.08
A5	8	22	70	3.12

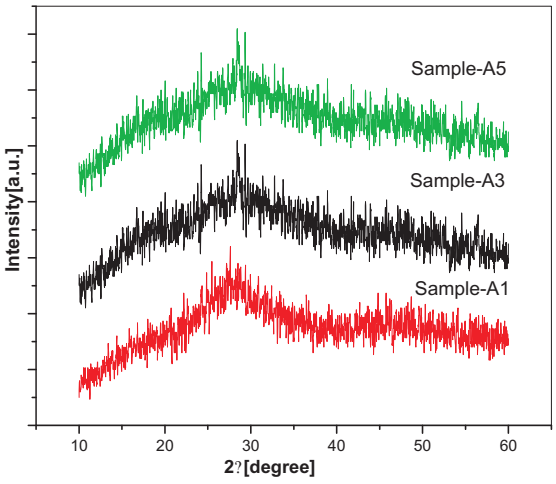

Fig. 1 XRD of glass samples

B. FTIR

The infrared transmittance spectra of glasses in the 400–4000 cm^{-1} region shown (Fig.2) has large, medium, weak and broad peaks.

According to literature survey, the borate spectra are divided into following three regions [12-14].The regions are;

(a) 600-800 cm^{-1} for the B-O-B vibrations

(b) 800-1200 cm^{-1} for BO_4 groups

(c) 1200-1600 cm^{-1} for BO_3 groups

There is another band from 2300-4000 cm^{-1}, which is due to hydrogen bonding in OH group [15].

1. The band centered at 699 cm^{-1} has been assigned to B-O-B bending vibration of BO_3 and $[BO_4]$ groups [16]. Its Intensity increases with the increase in contents of aluminum contents, which is due to presence of $[AlO_6]$ group of aluminium in glass network [16].
2. In sample A1, the band observed at 1024 cm^{-1} is due to B-O bond stretching of $[BO_4]$ groups [15].
3. This band is shifting towards the lower wave number (from 1024 to 981 cm^{-1}) side in sample A5 with the increase in the percentage of Al_2O_3. Also, its intensity increases with the increase in contents of Al_2O_3, which is due to increase in tetrahedral $[BO_4]$ groups in the borate network [15].

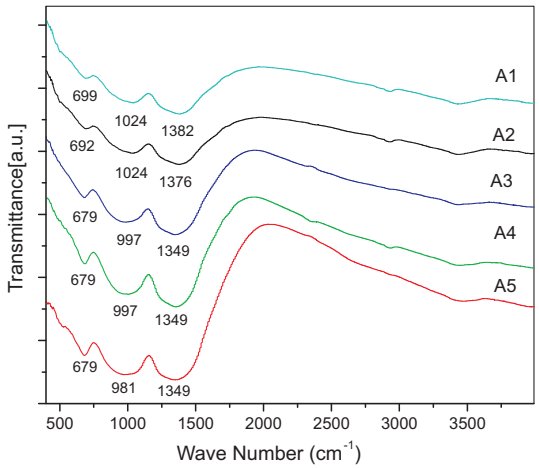

Fig. 2 FTIR spectra of Al_2O_3-Li_2CO_3–B_2O_3 glass with varying concentration of Al_2O_3

4. As the concentration of Al_2O_3 increases shifting of band arises (from 1024 to 981 cm^{-1}) which is due to presence of [AlO_6] units of aluminium. This is attributed to combined presence of aluminium [AlO_6] group and tetrahedral [BO_4] groups of borate [16].
5. The band in the region 1200-1500 cm^{-1}, centered at 1382 cm^{-1} is due to B-O stretching of [BO_3] groups in ortho and meta-borate units [17].

C. Optical Band Gap

1. The plots between $(\alpha h\nu)^{1/2}$ and energy ($h\nu$) of glasses are used to determine the optical band gap as shown in fig.3.
2. The optical band gap energy value E_{opt}, decreases with an increase of tungsten oxide and lithium oxide contents.
3. It indicates that a compact structure is formed.
4. With the addition of aluminium at the expense of lithium content, a large number of oxygen ions become available in the glass network and changes it from trigonal [BO_3] to tetrahedral [BO_4] which results in compact the network [17].
5. The gradual increase in the concentration of aluminium ions cause to increase in tetrahedral group [AlO_6] units [17].
6. Formation of [AlO_6] has shifted the absorption edge to the lower energy that leads to a significant shrinkage in the band gap. This change in band gap shows that the aluminum enters the glass structure as network modifier [18].

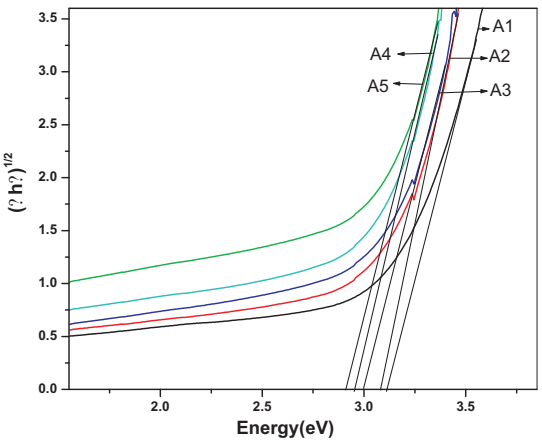

Fig. 3 Optical band gap of Al_2O_3-Li_2CO_3–B_2O_3 glasses with varying concentration of Al_2O_3

IV. Conclusion

In conclusion, with the increasing contents of Al_2O_3 against the decreasing Li_2CO_3 and fixing the B_2O_3 leads to the compaction of glass network due to the formation of tetrahedral [BO_4] units of borate and [AlO_6] unit of aluminium. In this way it has been observed that it decreases the optical band gap energy. The FTIR study shows the incorporation of [BO_3], [BO_4] and [AlO_6] units as network modifiers with B-O-B vibration in glasses network. It has also been observed that Al_2O_3 content helps in converting [BO_3] group to [BO_4] units. This reveals that aluminium ions also enter the glass structure as a network modifier.

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