ISSN: 2249-6661
Vol-43, No.-04 (IV) July-September (2020)

Study of Physical Properties of Silver Doped Lithium Borate Glasses

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Abstract

present paper explains the preparation and characterization methods of lithium borate glasses doped with Ag ions with the chemical composition $40Li_2O$-$(60-x)B_2O_3$-xAg_2O (with x = 0, 0.5, and 1 mol%). Three glasses have been prepared by doping of Ag_2O. The experimental techniques like XRD discussed in detail. This paper also explains determination of different physical properties like density, refractive index, molar volume, oxygen packing density, silver ion concentration, inter ionic distance and polaran radius.

Keywords: Physical Properties, Lithium Borate Glasses, Refractive index

Introduction

A study of the physical properties of the glasses is of considerable importance because of the insight it gives into the fundamental process taking place in them. Such a study paved the way for the application of some of these glasses in technology. In fact, the physical properties of the glasses are to a large extent controlled by the structure, composition, and the nature of the bonds of the glasses. The investigation of the changes in the physical properties of glasses with controlled variation of chemical composition, doping etc., is of considerable interest from the application point of view [1-4].

Borate glasses are an important class of oxide glasses, whose anionic structure consists of diverse structural and superstructural units represented by different boro-oxygen groupings and complicated anionic complexes [5, 6]. It has been determined that when the framework of alkali borate glasses undergoes polymerization bridge bonds of the type – B – O – B – as well as non-bridge bonds M – O – B – coordinated by alkali metal ions (M = Cs, Rb, K, Na, Li) can form. The fraction of the nonbridge bonds is related with the ratio of boron in ternary and quaternary coordination, depends on the alkali-metal fraction, and has a large effect on the physical properties of glass [7, 8].

The covalent radii of the elements decrease from left to right across a row in the transition series (Sc, Ti, V, Cr, Mn, Fe, Ag, Co, Ni, Cu, Zn) until near the end when the size increases slightly. On passing from left to right, extra protons are placed in the nucleus and extra orbital electrons are added. The orbital electrons shield the nuclear charge incompletely (d electrons shield less efficiently than p electrons, which in turn shield less effectively than s electrons). Because of this poor screening by d electrons, the nuclear charge attracts all of the electrons more strongly: hence a contraction in size occurs [9-12].

Due to their potential applications in various domains of modern technology, glasses containing transition-metal oxides have been the subject of intensive investigations. For example, the glasses containing transition metal ion such as Ag_2O is used in electrochemical, electronic and electro-optic devices. The addition of silver oxide to borate glass makes it electrically ionic. Borate glasses are also of academic interest because of the boron anomaly and also B_2O_3 is one of the best glass formers [11].

In view of the importance of the alkali borate glasses and the role played by Ag metal ion, present glass system is chosen as: Li_2O-B_2O_3-xAg_2O

The glasses used for the present studies are $40Li_2O$ –$(60-x)B2O_3$:-xAg_2O (with x = 0, 0.5 and 1.0 mol.%) From the approximate glass forming regions, $40Li_2O$-$(60-x)B_2O_3$-xAg_2O glass systems was prepared. The details of the glasses used for the present studies are:

SERIES 1: $40Li_2O$-$(60-x)B_2O_3$-xAg_2O
(with x = 0, 0.5, 0.1 mol%)

For x=0 mol%, LB 1: 40 Li_2O –60 B_2O_3
x = 0.5 mol%, LB 2: 40 Li_2O –59.5 B_2O_3-0.5 Ag_2O
x = 0.1 mol%, LB 3: 40 Li_2O –59 B_2O_3-1.0 Ag_2O

Preparation of Glasses

The glasses used for the present study are prepared by the melting and quenching techniques [46-48]. The starting materials used for the preparation of the present glasses were Analytical grade reagents Li_2O, B_2O_3, Ag_2O: the appropriate amounts of these compounds were thoroughly mixed in an agate mortar and melted in a porcelain crucible. PID temperature controlled furnace was used in present study. The glasses were melted in the temperature range 900-950 ^oC for an ½ hour till a bubble free liquid was formed. The glass samples were obtained by pouring the melt into a preheated brass mould shown in figure 1. The samples were subsequently annealed at lower temperatures and then sliced and polished. The approximate final dimensions of the glasses used for studying the of XRD and Evaluation of Physical parameters are 1 cm x 1 cm x 0.2 cm.

ISSN: 2249-6661
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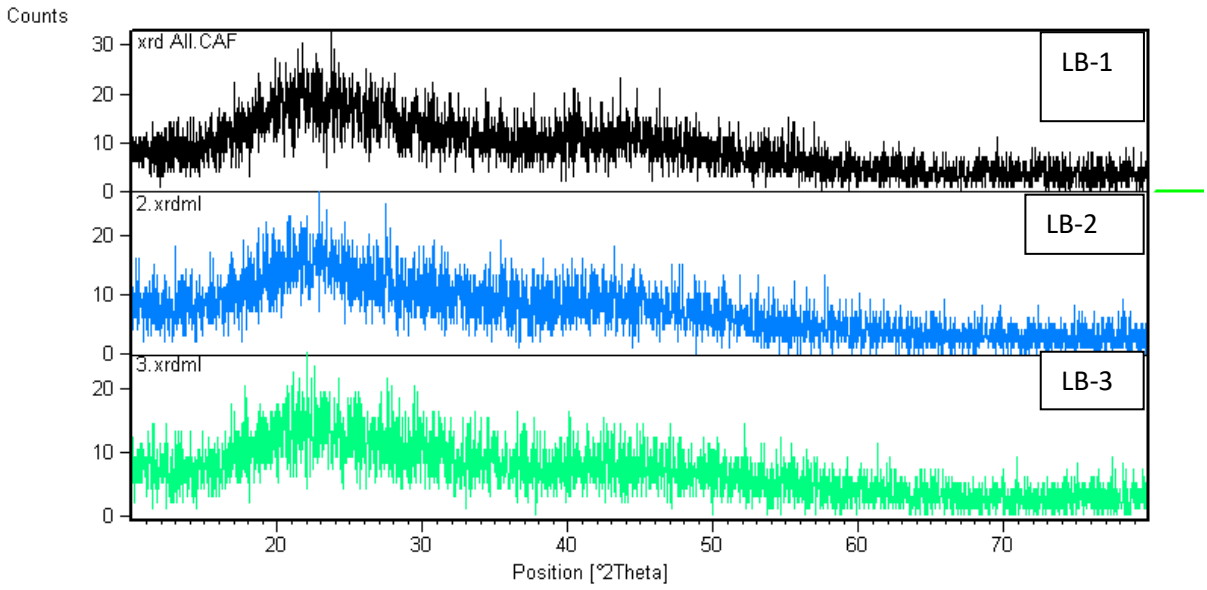
Fig. 1: glass preparation method

Results and discussions

X-ray Diffraction

The amorphous state of the prepared glasses was checked by X-ray diffraction spectra recorded on Panalytical X-ray Diffractometer having copper target with nickel filter operated at 40 kV, 30 mA. The curves confirm the amorphous state of the glasses used in the present investigation.

As glassy or amorphous materials do not have long-range order, a diffraction pattern containing sharp peaks is not expected as observed in crystalline materials. The X-ray diffraction patterns of $40Li_2O_3$-$(60-x)B_2O_3$-xAg_2O glasses are shown in Fig. 2; the absence of sharp peaks indicate the amorphous nature of these samples.



ISSN: 2249-6661
Vol-43, No.-04 (IV) July-September (2020)

Fig. 2 XRD spectra of $40Li_2O_3$-(60-x)B_2O_3-xAg_2O glass system

Physical Parameters

Some physical parameters useful for characterization of $40Li_2O$-(60-x)B_2O_3-xAg_2O glasses are estimated from the measured value of density (d) and the average molecular weight $\overline{M}$, using the following equations [12,13]:

Density **(**ρ):

The density of the glasses was determined by the standard principle of Archimedis' using o-xylene (99.99% pure) as the buoyant liquid. A direct reading balance (capacity 100 gm, readability 0.1 mg) was used for weighing. The bulk glass was suspended on a very thin copper strand that was set in the immersion liquid container; the density of the samples was determined by weighing in the liquid and air using the below equation

ρ = (weight of the sample in air /weight loss of the sample in O-Xylene) * density of O-Xylene

$$\rho = \frac{W_a}{W_a - W_x}\rho' \qquad (1)$$

Molar volume

The molar volume values are calculated by using the average molecular weight ($\overline{M}$) and density (ρ) of the glass sample, with the help of the following well known equation:

$$V_m(\text{cc/mole}) = \overline{M}/\rho \qquad (2)$$

$\overline{M}$ denotes the average molecular weight of the glass and $\overline{M}$ =Σ C_iA_i. Here A_i and C_i are the molecular weight and molar concentrations of the i^{th} component, respectively and ρ is measured density

Dopant ion concentration (Ni)

The dopant ion concentration (N_i) could be obtained from:

$$N_i \ (\text{ions/cm}^3) = \frac{N_A M(mol\%) d}{\overline{M}} \qquad (3)$$

Where N_A is the Avagadro number; from the obtained N_i values, inter – ionic distance (r_i) and the polaron radius (r_p) of dopant ions can be evaluated:

$$\text{Inter–ionic distance } r_i \text{ (Å)} = \left[\frac{1}{N_i}\right]^{1/3} \qquad (4)$$

$$\text{Polaron radius } r_p \text{ (Å)} = \frac{1}{2}\left[\frac{\pi}{6N_i}\right]^{1/3} \qquad (5)$$

The field strength (F_i) of dopant ion in the glass network is described through the oxidation number (Z) and the polaron radius (r_p) of the transition metal ions by:

$$\text{Field strength } F_i \ (\text{cm}^{-2}) = \frac{Z}{r_p^2} \qquad (6)$$

The molar volume (V_m) of glass samples was calculated using the average molecular weight($\overline{M}$) and density (ρ) with the following relation

$$\text{Molar volume } V_m(\text{cc/mole}) = M/\rho \qquad (7)$$

Oxygen packing density (O), is calculated using the following relation and presented in Table1

$$\text{Oxygen packing density } O = (\rho/M) \times n \qquad (8)$$

Where 'n' is the no. of Oxygen atoms per unit volume.

Refractive indices **(n_d)**:

The refractive indices of the optically polished glasses were measured using following method. Schematic diagrams of this method are shown in Fig.1(a), 1(b), 1(c).

This is the ratio of the velocity of light in free space to that in the material. Refractive Index measured using a short focus travelling microscope, focus on a mark on a white surface, microscope set to focus on mark on surface and distance recorded as Z_1.

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Vol-43, No.-04 (IV) July-September (2020)

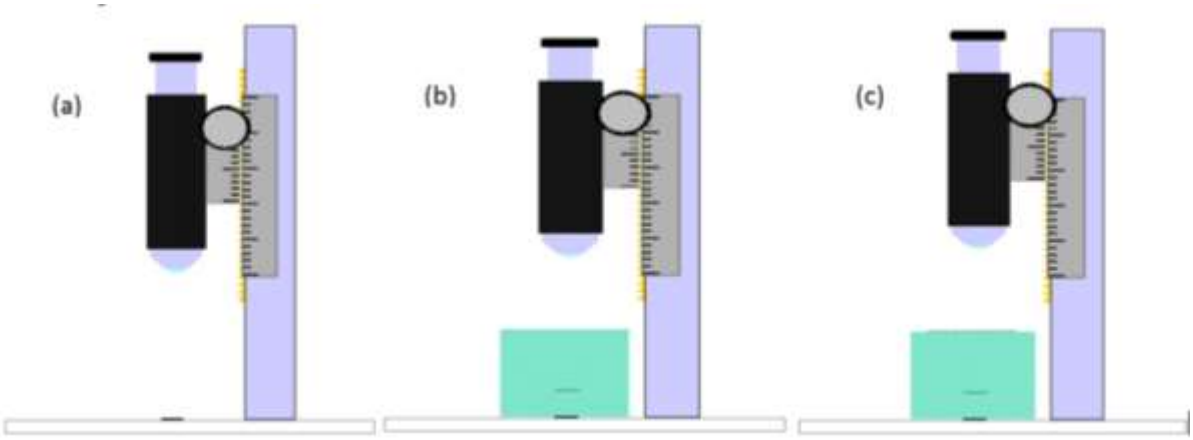

Fig.1(a):
Microscope set to focus on mark on surface, distance recorded as Z_1.
Fig. 2(b): Microscope set to focus on image of the mark on surface, distance recorded as Z_2.
Fig. 1(c): Microscope set to focus on top surface of the material, distance recorded as Z_3.

Place the material to be measured over the mark and re-focus on the image of the mark, microscope set to focus on image of the mark on surface and distance recorded as Z_2.

Then place a mark on the top surface of the material (eg use lycopodium powder) and focus on this, Microscope set to focus on top surface of the material. Distance recorded as Z_3. The refractive index, n is then calculated using these recorded distances:

$$n = \frac{Z_3 - Z_1}{Z_3 - Z_2}$$

From the measured values of the density d and calculated average molecular weight $\overline{M}$, various physical parameters such as ferrous ion concentration N_i, mean ferrous ion separation R_i, Polaron radius R_p, refractive index, molar volume, Oxygen packing density and Field strength that are useful for understanding physical properties of the glasses are evaluated and presented in Table 1.

Table 1 : Various Physical properties of $40Li_2O_3$-$(60x)B_2O_3$-xAg_2O glasses

Parameter (± error limits)	LB 1	LB 2	LB 3
Density, d (g/cm^3)	2.0093	2.1296	2.1309
Refractive index	1.420	1.642	1.695
Average molecular weight,(g)	71.328	71.778	72.228
Molar Volume(V_m)	26.7376	25.4225	25.6494
Oxygen packing Density, O (g atm/l)	82.28	86.537	85.771
Polaron radius, R_p(Å)	-	0.0309	0.0614
Field strength Fi (cm^{-2})	-	3129.03	794.74
Silver ion concentration, N_i (10^{21}/cc)	-	0.355	0.704
Inter-ionic distance of siver ions, R_i (Å)	-	1.4121	1.1238

Conclusions

There different glass samples have been prepared using melt quenching technic. The glass samples were checked by X-ray diffraction, where the obtained patterns indicated that all the samples are in pure non-crystalline phase. All determined physical parameters are increased with increasing composition except Oxygen packing Density and Inter-ionic distance of siver ions and these values decreases at higher composition.

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ISSN: 2249-6661
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