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Structural Investigations of Lithium Vanadoxide Bismo-Borate Glasses

S Khasa[a*], M. S. Dahiya[a], Ashima[a], Shely[a], A. Agarwal[b]

[a]Department of Physics, Deenbandhu Chhoturam University of Science & Technology, Murthal, Sonepat, Haryana, India-131039
[b]Department of Physics,Guru Jambheshwara University of Science & Technology, Hisar, Haryana, India-125001

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ABSTRACT

Lithium vanadoxide bismuth borate glasses with composition (30-x)$Li_2O \cdot xV_2O_5 \cdot 50B_2O_3 \cdot 20Bi_2O_3$ (x=5, 10, 15) has been prepared with the traditional melt-quenching technique. The density measurements were performed using Archimedes Principal and using density data molar volume was calculated. To determine the oxygen covalency theoretical optical basicity was calculated. To get an idea about the structure FTIR spectroscopy was carried out in the mid-IR region. The spectra revealed absence of boroxol ring and presence of absorption bands corresponding to the combined contributions of tri and tetra borate stretching vibrations. The increasing basicity reveals decrease in the covalence nature of oxygen as we replace the Li_2O content with V_2O_5. The decrease in molar volume may be due to the increase in compactness of the network structure.

Keywords: Melt-quenching, FTIR, Molar Volume, Non-Bridging Oxygen

Introduction

Oxide glasses containing multiple components are known for their wide range of applications such as IR transmission, low phonon energy and high refractive index [1]. The glasses containing bismuth and boron as the base glass formers exhibit low softening point making these glasses suitable for applications in thick film microelectronics [2]. Also the glasses doped with transition metals such as V, Cu etc shows good semiconducting properties [3]. Another fact is that the transition metal ions exists in more than one valence state giving rise to different non-linear optical properties [4]. The alkali ions having good ionic conductivity can act as promising materials for increasing the semi-conducting nature of the oxide glasses [5]. The above facts encouraged the authors to study the lithium vanadoxide bismo-borate glasses for their structure.

Address:
Dr. Satish Khasa
Department of Physics, Deenbandhu Chhotu Ram University of Science & Technology, Murthal, Sonepat, Haryana, India
Tel: +91-9812818900
Email: skhasa@rediff.com

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Material & Method

AR/GR grade Li_2CO_3, V_2O_5, H_3BO_3 and Bi_2O_3 were taken as the starting material to prepare samples. The chemicals were weighed into proper proportion with the help of digital electronic balance having least count 0.1 mg. The constituents were than mixed thoroughly to obtain homogeneous mixture which was the put inside a muffle furnace in a high alumina crucible at 1273 K for melting. The melt was shaken frequently so as to obtain good homogeneity. This melt was then quenched by sandwiching the melt between two preheated SS quenching plates to obtain the samples in palletized form.

The room temperature density (D) was determined with the help of digital balance and using Archimedes Principal with Xylene as the buoyant liquid. The formula used for density is

$$\mathbf{D = (W_A/W_L)*D_X} \qquad \textbf{(i)}$$

Where W_A is weight of sample in air, W_L is the loss in weight when sample is placed from air to immersion liquid (here xylene) and D_X is the density of xylene.

The data obtained for density was used for calculation of molar volume (V_m) using formula

$$\mathbf{V_m = M/D} \qquad \textbf{(ii)}$$

Where M is the molar mass.

Sample Code	Chemical Content (percentage)				Density (gm/cc)	Molar Volume (cc/mol)	Optical Basicity	Band Center Positions in FTIR Spectra (cm^{-1})				
	V_2O_5	Li_2O	B_2O_3	Bi_2O_3								
VLBB1	5	25	50	20	3.15	48.23	0.7035	1147	1077	1044	764	572
VLBB2	10	20	50	20	3.49	44.97	0.7305	1149	1079	1045	764	571
VLBB3	15	15	50	20	3.65	42.44	0.7500	1148	1079	1045	764	571

Table 1. Composition, density (D), molar volume (V_m), theoretical optical basicity (Λ_{th}) and FTIR band positions of $(30-x)Li_2O \cdot xV_2O_5 \cdot 50B_2O_3 \cdot 20Bi_2O_3$ (x=5, 10, 15) glasses

The theoretical optical basicity (Λ_{th}) was calculated by using the relation given in literature[6]

$$\Lambda_{th} = X_{V2O5}\Lambda(V_2O_5) + X_{Li2O}\Lambda(Li_2O) + X_{B2O3}\Lambda(B_2O_3) + X_{Bi2O3}\Lambda(Bi_2O_3) \quad \text{(iii)}$$

Where $\Lambda(V_2O_5)$, $\Lambda(Li_2O)$, $\Lambda(B2O3)$ & $\Lambda(Bi2O3)$ are optical basicities assigned to different oxides[7] and X_{V2O5}, X_{Li2O}, X_{B2O3}, and X_{Bi2O3} are corresponding mole fractions of different oxides.

The Infrared Transmission spectra of the samples were recorded at room temperature by using Perkin Elmer Frontier FTIR in the mid-IR range i.e. 400-4000 cm^{-1}. KBr pallet technique was used to record the IR spectra. The sample was fine powdered and mixed with 0.3g KBr in the ratio 2:100 and put into a 13 mm dye and pressed with a pressure of 7-8 ton using hydraulic press to obtain transparent pallets of approximate 1 mm thickness. The spectra of these pallets were then recorded by using universal sample holder with the resolution of 4 cm^{-1} and 16 scans per sample. The background removal and baseline correction was done with the help of Spectrum 10 software.

Results and Discussion

The value of the density and molar volume are reported in Table 1. Also Figure 1 shows the variation of density and molar volume with the corresponding increase in V_2O_5 i.e. the Transition Metal Oxide (TMO) content.

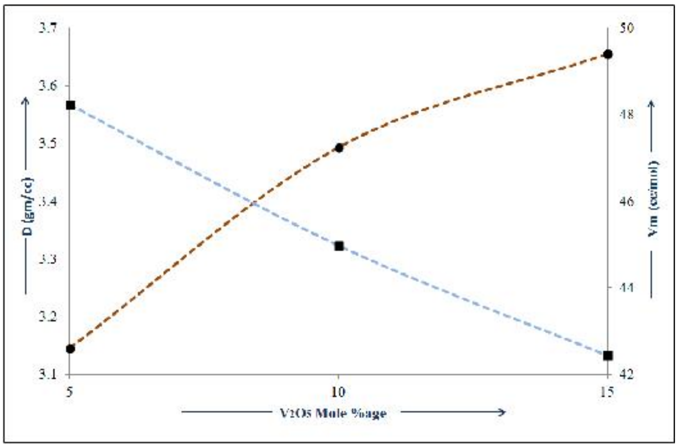

Figure 1. Variation of D and V_m with the V_2O_5 content (dotted line is guide for eyes)

It is found that the density increases and molar volume decreases with increase in V_2O_5 content. The increase in density may be due to the higher molecular mass of V_2O_5 as compared with the Li_2O which is in accordance with our predictions. Again the decrease in molar volume may be due to the dependency of molar volume on both density and molar mass of the glasses. But this change is not as much as it should be due to the replacement of Li_2O with V_2O_5 indicating that addition of V_2O_5 results into the conversion of some triangular borate units into tetrahedral units which shows the network modifying role of V_2O_5.

The Theoretical optical basicity serves as the first approximation towards the determination of oxygen covalency in case of oxide glasses. The decreasing basicity corresponds towards the enhancement in covalent character i.e. decrease in ionic character. Also the optical basicity enables us to know about the electron density associated with oxygen and it is strongly dependent on electronic polarizability.

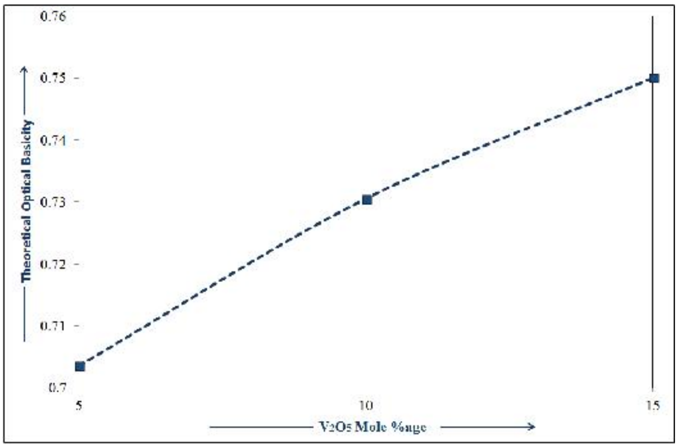

Figure 2. Variation of Theoretical Optical Basicity with V_2O_5 content (dotted line is guide for eyes)

The calculated values of Theoretical optical basicity are reported in Table 1 and the variation of this basicity with the corresponding TMO content is shown in Figure 2. From this figure it is observed that the optical basicity is increased with increase in TMO content which leads to the increase in covalent character resulting into the reduction of tendency of oxygen to donate electron. These results are also well supported by the increase in structure compactness indicated by the decrease in molar volume and increase in density.

The Infrared Transmission spectrum is a handy tool to get an idea about the different structural units present in oxide glasses. Hence we have recorded the FTIR spectra in the mid-IR range. The different band positions obtained in the spectra of all samples are listed in Table 1. The IR transmission spectra of borate glasses cans be broadly consists of three absorption band groups 600-750, 750-1100 and 1100-1600 cm^{-1} [8]. Although some bands around 2700-3600 cm^{-1} can be observed but these are mainly due to the hydroxal groups and hydrogen bonding present due to the moisture absorption by oxide glasses, but these bands are not considered much as these have nothing to do with the different structural units present in oxide glasses. The first band around 600-750 cm^{-1} is due to different band bending vibrations of B-O-B linkage in boron-oxygen network [9]. The absorption region around 750-1100 cm^{-1} is an attribute of asymmetric B-O stretching of tetrahedral BO_4 units. **T**he absorption region around 1100-1600 cm^{-1} is a result of B-O band stretching vibrations of triangular BO_3 units.

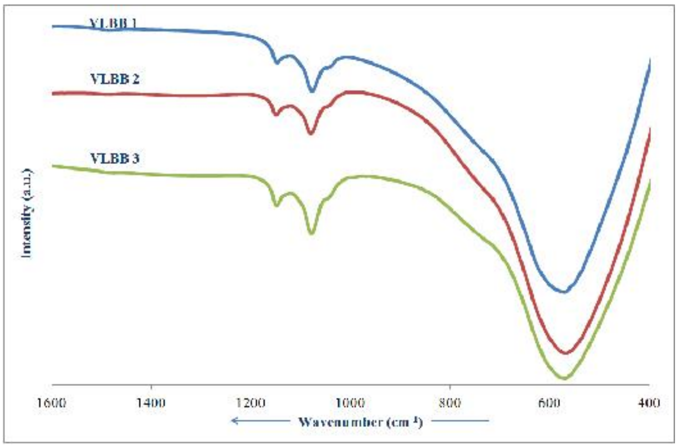

Figure 3. FTIR spectra of $(30\text{-}x)Li_2O \cdot xV_2O_5 \cdot 50B_2O_3 \cdot 20Bi_2O_3$ (x=5, 10, 15) glasses.

In present study the bands in all these three regions are being observed. Figure 3 shows the bands observed in the frequency range of 400-1600 cm^{-1} which is IR active region for oxide borate glasses. The observation of a weak band around 1150 cm^{-1} may be attributed to asymmetric stretching vibrations of B-O bonds in triangular BO_3 units. This can also give us information that the Li_2O and V_2O_5 both are acting as network modifiers as the BO_3 units have very weak band associated with them as compared with the BO_4 absorption bands. The band around 1050 - 1100 cm^{-1} and a faint shoulder around 1030 - 1050 cm^{-1} may be assigned to BO_4 vibrations in triborate groups [8]. Also the very weak shoulder around 760 cm^{-1} is attributed to the B-O-B bending vibrations of bridges having one trigonal and one tetrahedral boron[10]. The infrared absorption below 610 cm^{-1} is attributed to various modes of Bi-O vibrations in BiO_6 [11-13]. Also the stretching vibrations of BiO_3 results into a peak around 840 cm^{-1} [8,14], but this can be observed in case of very high concentration of Bi_2O_3[15]. The absence of band around 840 cm^{-1} hence suggests that the Bi_2O_3 will influence the borate network and which is quite visible due to the absence of boroxol ring [16] i. e. band around 806 cm^{-1} which is a characteristic of pure borate groups. The very strong and deep band visible in the range from 400 – 700 cm^{-1} may be due to the overlapping of individual bands of different vibrations of V-O bonds and Bi-O bonds. This region also includes the absorption band of bond vibrations of Bi-O bonds in BiO_6 octahedra [17] which is being observed around 470 cm^{-1}.

Conclusions

1. The density is increasing and molar volume is decreasing indicating the increase in compactness of structure with increase in TMO content.
2. The theoretical optical basicity is decreasing indicating the decrease in ability of oxygen to donate electron.
3. The boroxol ring and BiO_3 tetrahedra is absent and the boron is present in both triangular and tetrahedral form.
4. The Bi_2O_3 is present in form of BiO_6 octahedra and modifies the borate structures.

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Dr. Satish Khasa is an Associate Professor in Physics at Deenbandhu Chhotu Ram University of Science & Technology. Dr. Khasa has done his Ph. D. in 1999 and is active in research since then. He have more than 50 publications in international journals of high repute. Dr. Khasa has presented more than 50 papers in national/international conferences. He has almost 20 years experience in teaching Physics.