Effect of $V_2O_5$ on the Properties of Lithium Bismuth Borate Glasses

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Abstract. The series of the glasses with general formula \((40-x)Li_2O:30B_2O_3:30Bi_2O_3:xV_2O_5\), with \(x = 0, 0.5, 1.0, 1.5\) and \(2.0\) mol\% was prepared using conventional quenching technique. The glass transition temperature \(T_g\) for these samples were determined from Differential Thermal Analysis. The glass transition temperature increases beyond 0.5 mol\%. It was found that the glasses under study consist of randomly connected \(BO_3\) & \(BO_4\) structural units. The density and molar volume of glasses were found to depend on \(V_2O_5\) content. Initially the density increases, molar volume and glass transition temperature decrease with the addition of \(V_2O_5\). This suggests that when \(V_2O_5\) is added to the glass initially up to 0.5 mol\% it may be entering as a modifier. Beyond 0.5 mol\% density decreases and molar volume increases as \(V_2O_5\) goes as former. This reveals the role of \(V_2O_5\) as a glass network former beyond 0.5 mol\%. Optical band gap energy decreases and cut off wavelength increases with increase in \(V_2O_5\) content.

Keywords: Molar volume, Glass transition temperature, Oxygen packing density, Cut-off wavelength, Optical band gap.

1. Introduction
Glasses have many technological applications due to their electrical and optical properties. Borate glasses generally exhibit insulating nature and the addition of transition metal such as \(V_2O_5\), \(Fe_2O_3\), \(ZnO\) etc. makes these glasses semiconducting in nature. These glasses have been studied due to their potential application as optical and electrical memory switching, cathode material for making solid state devices and optical fiber. Borate glasses doped with transition metal have been extensively studied by a number of authors. Many authors have been studied the effect of multiple transition metals on structural and optical properties of borate glasses with the help of IR, UV and dc conductivity etc. [1-3]. Among transition metals, \(V_2O_5\) is an important semiconductor whose electrical conductivity is due to the electron hopping between \(V^5+\) and \(V^4+\) ions [4]. The semiconducting nature of \(V_2O_5\) is due to two valence states \(V^5+\) and \(V^4+\) of vanadium [5]. This oxide is classified as a conditional glass-former and can enter the same network either as a network former or as a network-modifier, depending on its concentration.

In the last decades, attention has been focused on vandate- based glasses in view of their low crystallization tendency, low melting point, good semiconducting properties, high chemical durability, thermal resistivity, etc. which make them an excellent material for memory switching devices [6-7]. The transitional metal ions are used because they have an incomplete 3d orbital with a broad radial distribution function and they are very sensitive to the surrounding of the cations. The non-
conventional glass former B\textsubscript{2}O\textsubscript{3}, participates in the glass structure with two possible coordinations [BiO\textsubscript{3}] pyramidal and [BiO\textsubscript{6}] octahedral units [8-10].

In order to study the effect of V\textsubscript{2}O\textsubscript{5} addition on different properties of the lithium bismuth borate glasses, the present work is aimed at “Effect of V\textsubscript{2}O\textsubscript{5} on the properties of Lithium Bismuth Borate Glasses”

2. Experimental
The series of the glasses with general formula (40-x)\text{Li}_2O:30\text{B}_2O_3:30\text{Bi}_2O_3:x\text{V}_2O_5 with x = 0, 0.5, 1.0, 1.5 and 2.0 mol\% was prepared using conventional quenching technique. For the glass preparation, appropriate amount of AR grade \text{Li}_2\text{CO}_3 (E Merk), \text{B}_2\text{O}_3 (E Merk), \text{Bi}_2\text{O}_3 (E Merk) and \text{V}_2\text{O}_5 were used. About 15 gram of raw material was weighed using a Denver-610 electronic balance and was mixed thoroughly under acetone. The dried mixture was melted in platinum crucible at around 780 °C and kept for 2 hours with frequent stirring to ensure homogeneity; the melt was quenched in preheated aluminum mould at room temperature to get rectangular as well as cylindrical samples. The quenched samples were annealed for 2 hours at 200°C. The glass transition temperature (T\textsubscript{g}) for these samples was determined from Differential Thermal Analysis with a heating rate of 10°C/min. The density values of these glasses were measured using Archimedes principle with toluene as an immersion liquid. IR transmission spectra of the glasses were recorded at room temperature using KBr pellet technique in the range 400–4000 cm\textsuperscript{-1}.

3. Results and discussion
3.1 Density and Molar volume
Figure 1 shows the variation of density and molar volume of glasses with mol % V\textsubscript{2}O\textsubscript{5}. The density is affected by the structural softening or compactness, change in coordination number, cross-link density and dimension of interstitial spaces in the glass [11].

![Figure 1](image1.png)

**Figure 1.** Variation of density and molar volume with mol% V\textsubscript{2}O\textsubscript{5} for the glasses.

![Figure 2](image2.png)

**Figure 2.** Variation of glass transition temperature T\textsubscript{g} and oxygen packing density with mol% V\textsubscript{2}O\textsubscript{5} for the glasses.

Density initially increases up to 0.5 mol% and then decreases. As V\textsubscript{2}O\textsubscript{5} is replacing \text{Li}_2O, initial increase in density is due to heavier mass of V\textsubscript{2}O\textsubscript{5}. Although the relative molecular mass of V\textsubscript{2}O\textsubscript{5} is higher than that for \text{Li}_2O and \text{B}_2O_3, V\textsubscript{2}O\textsubscript{5} contributes to decrease in the density beyond 0.5 mol%. Addition of V\textsubscript{2}O\textsubscript{5} may randomize the structure, which causes the density to decrease [12]. Table 1.0 presents the Boron-Boron distance d\textsubscript{B-B} for the glasses. From the table it is observed that boron-boron distance, d\textsubscript{B-B} decreases and then increases with addition of V\textsubscript{2}O\textsubscript{5}. This further supports the variation in density.

Molar volume initially decreases with addition of V\textsubscript{2}O\textsubscript{5} as it goes in the interstices. Beyond 0.5 mol% its role changes to former thus molar volume increases with increase in V\textsubscript{2}O\textsubscript{5} content. The results obtained for the present glass system are consistent with the already reported results for vanadium borate glasses [13, 14].
Table 1 Boron-Boron distance $d_{<B-B>}$ for the glasses.

| mol% $V_2O_5$ | Boron-Boron distance $d_{<B-B>}$ (nm) |
|---------------|-------------------------------------|
| 0             | 34.59                               |
| 0.5           | 34.46                               |
| 1.0           | 34.62                               |
| 1.5           | 34.72                               |
| 2.0           | 34.89                               |

All the studied properties of glasses like glass transition temperature, density, molar volume, oxygen packing density and boron-boron distance exhibit changeover beyond 0.5 mol% of $V_2O_5$. This suggests that Vanadium is serving one role in the structure up to 0.5 mol% $V_2O_5$ and different role beyond 0.5 mol% $V_2O_5$. Similar results have been reported by Wing et al. [15] in which the density, molar volume and $T_g$, all exhibit an inflection around 0.1 to 0.2 mol% $V_2O_5$ addition in 15 Na$_2$O:11 CaO: 74 SiO$_2$ glass.

3.2 Glass transition temperature $T_g$ and Oxygen packing density
Variation of glass transition temperature $T_g$ and oxygen packing density with mol% $V_2O_5$ for the glasses is shown in Figure 2. From the figure it can be observed that glass transition temperature initially decreases with the addition of $V_2O_5$ and then increases. This suggests that when $V_2O_5$ is added to the glass initially up to 0.5 mol% it may be entering as a modifier and it is being added at the cost of Li$_2$O. Hence modifier content remains constant, but $T_g$ decreases which may be due to predominant role of $V_2O_5$ in modifying the structure compared to Li$_2$O. Increase in $T_g$ beyond 0.5 mol% can be attributed to decrease in total modifier content, since $V_2O_5$ may be entering the network as former. The increase in $T_g$ is also associated with the formation of BO$_4$ tetrahedra which serves to cross-link the network by covalent B–O bonds.

It is observed from the figure that oxygen packing density initially increases with the addition of $V_2O_5$ and then slightly decreases. Initially being a modifier, $V_2O_5$ provides oxygens and it goes in interstices. Beyond 0.5 mol% it enters as former and there is slight decrease in oxygen packing density.

Variation of glass transition temperature $T_g$ and oxygen packing density with mol% $V_2O_5$ for the glasses is shown in Figure 2. From the figure it can be observed that glass transition temperature initially decreases with the addition of $V_2O_5$ and then increases. This suggests that when $V_2O_5$ is added to the glass initially up to 0.5 mol% it may be entering as a modifier and it is being added at the cost of Li$_2$O. Hence modifier content remains constant, but $T_g$ decreases which may be due to predominant role of $V_2O_5$ in modifying the structure compared to Li$_2$O. Increase in $T_g$ beyond 0.5 mol% can be attributed to decrease in total modifier content, since $V_2O_5$ may be entering the network as former. The increase in $T_g$ is also associated with the formation of BO$_4$ tetrahedra which serves to cross-link the network by covalent B–O bonds.

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3.3 IR Transmission Spectra
It has been reported that vanadium ions in phosphate glasses [16-18] occur mostly in the lower valence states V$^{3+}$ and V$^{4+}$, while in alkali borate and borosilicate glasses [19-22] the pentavalent V$^{5+}$ ions are predominant.

Figure 3 shows the FTIR Spectra for the glasses which indicate bands at 543, 729, 875, 978, 1306, 1421 and 1558 cm$^{-1}$. The observed IR bands are mentioned in Table 2.0. $V_2O_5$ spectrum exhibits a
band at 978 cm\(^{-1}\) related to vibrations of isolated V=O vanadyl groups in VO\(_5\) trigonal bipyramids which shifts to high wave number side. The band at 875 cm\(^{-1}\) is related to vibrations of V-O-V chains. Bi\(_2\)O\(_3\) participates in glass network by showing the presence of strong band at 543 cm\(^{-1}\). The band at 543 cm\(^{-1}\) corresponds to vibrations of strongly distorted BiO\(_6\) octahedra. Therefore, the bismuthate network of the glasses is built up of (BiO\(_6\)) octahedral units. In the present study IR band observed at 543 cm\(^{-1}\) shifts to lower wave numbers with increasing V\(_2\)O\(_5\) content, which is due to the change of local symmetry in (BiO\(_6\)) polyhedra [23].

Figure 3. FTIR spectra for the glasses

Table 2. FTIR bands for the glasses.

| mol % V\(_2\)O\(_5\) | Li ion and Stretching vibrations of B-O in distorted BiO\(_6\) units | Bending vibrations of B-O-B in BO\(_3\) and symmetrical modes of V-O-V bonds | Stretching vibrations of B-O bonds in BO\(_4\) units and Vibrations of V-O-V chains | Stretching vibrations of B-O-Bi linkages and V=O stretching vibrations in VO\(_5\) trigonal bipyramids | B-O asymmetric stretching vibrations in BO\(_3\) from varied types of borate groups | Stretching vibrations of NBOs of BO\(_4\) units | Anti-symmetrical stretching vibrations with NBOs of BO-B groups | Asymmetric stretching vibrations of B-O and B-O bond in trigonal BO\(_3\) units |
|------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| 0                | 543                                            | 729                                            | 875                                            | 978                                            | 1149                                            | 1306                                            | 1421                                            | 1558                                            |
| 0.5              | 525                                            | 729                                            | 867                                            | 991                                            | 1152                                            | 1314                                            | 1425                                            | 1536                                            |
| 1                | 529                                            | 729                                            | 867                                            | 991                                            | 1149                                            | 1319                                            | 1425                                            | 1541                                            |
| 1.5              | 538                                            | 725                                            | 867                                            | 1000                                           | 1149                                            | 1319                                            | 1430                                            | 1545                                            |
| 2                | 538                                            | 725                                            | 867                                            | 1004                                           | 1162                                            | 1319                                            | 1421                                            | 1545                                            |
The band observed at 729 cm\(^{-1}\) is assigned to B-O-B bending vibrations in BO\(_3\) triangles. This band shifts to lower frequency side with increase in V\(_2\)O\(_5\) content. Its intensity increases progressively with an increase in the content of V\(_2\)O\(_5\). The band at 878 cm\(^{-1}\) is assigned to symmetric stretching vibrations of Bi-O bonds in BiO\(_3\) units and stretching vibrations of B–O bonds in BO\(_4\) units from diborate groups [23].

All the glasses show band around 978-1004 cm\(^{-1}\) which is assigned to the vibrations of some boron atoms attached to non-bridging oxygen atoms in the form of BO\(_4\) vibrations and this band is assigned to the stretching vibrations of B-O-M (B-O-Bi) linkages where M represents the metal cation [24]. Dimitriev et al. [25] have reported that in the region of vibrations of BO\(_4\) units, band due to vibrations of isolated V=O groups in VO\(_5\) trigonal bipyramids are present. Intensity of this band observed at 978 cm\(^{-1}\) increase slightly with increase in V\(_2\)O\(_5\) content and shifts towards high frequency side indicating rise in NBOs.

The band at 1306 cm\(^{-1}\) is assigned to the stretching vibrations of the B-O bond of BO\(_4\) units in metaborates, pyroborates and orthoborate groups which shifts to higher wave number side. The band at around 1421 cm\(^{-1}\) arises due to antisymmetrical stretching vibrations of B–O–B groups with NBOs [26, 27, 24, 28]. This band shifts to higher wave number side. The band at 1558 cm\(^{-1}\) corresponds to asymmetric stretching vibrations of B-O and B-O\(^{+}\) bonds in trigonal BO\(_3\) units [29].

### 3.4 UV–VIS transmission measurements

![Figure 4. Optical transmission spectra for the glasses](image)

![Figure 5. Tauc’s plots for the glasses](image)

| mol% V\(_2\)O\(_5\) | Cut off Wavelength \(\lambda_{\text{cut-off}}\) (nm) | Optical band gap \(E_{\text{opt}}\) (eV) | Electronic Polarizability \(\alpha_{2-\text{opt}}\) (Å\(^3\)) | Theoretical optical basicity \(\Lambda_{\text{th}}\) |
|---------------------|------------------------------------------|---------------------------------|---------------------------------|-----------------|
| 0                   | 472                                      | 2.02                            | 3.655                           | 0.840           |
| 0.5                 | 482                                      | 1.98                            | 3.595                           | 0.842           |
| 1.0                 | 492                                      | 1.90                            | 3.656                           | 0.844           |
| 1.5                 | 496                                      | 1.78                            | 3.715                           | 0.846           |
| 2.0                 | 498                                      | 1.64                            | 3.813                           | 0.848           |
Figure 4 depicts the optical transmission spectra of the glasses. From the figure it is observed that the fundamental absorption edge and cut off wavelength shifts towards red with the increase in V$_2$O$_5$ content. Cut off wavelength, optical band gap, electronic polarizability and optical basicity for the glasses are given in Table 3.0. From figure 4.0 it is evident that the optical absorption edge is not sharply defined, which indicates the amorphous nature of the samples. Due to addition of V$_2$O$_5$ there is a formation of NBOs which shifts the absorption edge.

It is also observed that the cutoff wavelength shifts towards longer wavelength as the content of V$_2$O$_5$ increases. This shift may be attributed to the increase in number of the non-bridging oxygen ions which is also supported by IR.

Figure 5 represents the Tauc’s plots for different glasses. From the table 3, it is observed that the optical band gap values decrease with increasing V$_2$O$_5$. The decrease in E$_{opt}$ with the addition of V$_2$O$_5$ can be attributed to the increase in NBOs with increasing concentration of V$_2$O$_5$ which is supported by IR. The decrease in E$_{opt}$ with increase in V$_2$O$_5$ content corresponds with the red shift in cut off wavelength. The electronic polarizability initially decreases upto 0.5 mol% and then increases it may be due decrease in molar volume up to 0.5 mol% and V$_2$O$_5$ may be entering as a modifier. Optical basicity increases with increasing V$_2$O$_5$ content which is due to increase in NBOs.

4 Conclusions
From the study of properties of the glasses, it is observed that initially the density increases, molar volume and glass transition temperature decrease with the addition of V$_2$O$_5$. This suggests that when V$_2$O$_5$ is added to the glass initially up to 0.5 mol% it may be entering as a modifier. Beyond 0.5 mol% density decreases and molar volume increases as V$_2$O$_5$ goes as former. The glass transition temperature increases beyond 0.5 mol%. This reveals the role of V$_2$O$_5$ as a glass network former beyond 0.5 mol%. Optical band gap energy decreases and cut off wavelength increases with increase in V$_2$O$_5$ content. Optical basicity increase due to increase in NBOs which is supported by IR.

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