Study of Physical Properties of Lithiumborovanadate Glasses

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Abstract:
The glass samples of the Lithium-borovanadate 42.5Li₂O-(57.5-x)B₂O₃-xV₂O₅, x=0-57.5 in the step of 5.75, were prepared by conventional melt-quench technique. The density and molar volume of glasses were determined in order to study their structure. The physical parameters like Oxygen packing density, Refractive index, Molar refractivity, Molar polarizability, Metallization, Electronic polarizability are studied. Averge molecular weight, Molar volume, Inter-ionic distance, Ionic concentration, Dielectric constant, Electronic polarizability are studied. Density can be used for finding out the molar composition of an oxide indicates the volume with the molar composition of an oxide indicates the fraction of the ions forming that structure. The glass structure can be explained in terms of molar volume and Inter ionic distance shows decrease in oxygen packing density; with reverse variation in increasing mol% of V₂O₅. Dielectric constant, Refractive index and Molar refractivity, Molar polarizability varies alike, they also varies linearly, on increase mol% of V₂O₅, Electronic polarizability & Molar polarizability; Molar polarizability & Metallization; Polarizability per unit volume & Metallization lies reverse in order with increase of mol% of V₂O₅, with liner variation. Electronic polarizability and Metallization varies opposite in order with increasing mol % of V₂O₅. The maximum variation of Metallization criterion is within the range of 0.267-0.308.

Key words: Density, Molar volume, Oxygen packing density, Dielectric constant, Refractive index, Molar refractivity, Molar polarizability, Metallization, Electronic polarizability, Polarizability per unit volume, glass composition, mixed glass former effect.

I. INTRODUCTION

Oxide glasses are classically described as a network composed by building entities such as SiO₂, B₂O₃, P₂O₅, Sb₂O₃, Bi₂O₃, Ge₂O₅ and modifiers such as alkaline oxides: Li₂O, Na₂O, K₂O, Ag₂O, or alkaline earth oxides CaO, MgO, SrO [1,2]. In such glasses, the oxygen from the metal oxide becomes part of the covalent glass network, creating new structural units. The cations of the modifier oxide are generally present in the neighborhood of the non-bridging oxygen (NBO) in the glass structure. The extent of the network modification obviously depends on the concentration of the modifier oxide present in the glass. A glass network affects various physical properties such as density, molar volume, glass transition temperature, polarization, etc. The mixed glass former (MGF) and mixed glass former effect (MGFE) is defined as a nonlinear and non-additive change in the ionic conductivity with changing glass former composition at constant modifier composition. Lithium-borovanadate glasses are characterized by an interesting structure on account of the presence of two glass-forming components. Density can be used for finding out the structure of different types of glasses. The density of the glasses is additive and can thus be calculated on the basis of the glass composition [1,4,5,6]. Several formulas have been derived to correlate the glass density to the glass composition [7,9,10,11]. The glass structure can be explained in terms of molar volume rather than density, as the former deals the spatial distribution of the ions forming that structure. The change in the molar volume with the molar composition of an oxide indicates the preceding structural changes through a formation or modification process in the glass network [12,13]. The density, molar volume and packing fraction [14,15,16] could be directly related to the short range structure of alkali oxide modified borate glasses. The densities prove changes in both short range order and co-ordination as the modification, while the molar volume is sensible in terms of size and packing. The packing of the borate based glasses with ions having volume smaller than the oxygen is considered to be covalent, controlled by oxygen covalent network, and heavily dependent on the glass former. The molar refractivity [17,23], is a constitutive-additive property which represents the real volume of the molecules. That is calculated by the Lorenz-Lorentz formula. Electric polarizability [17,23], is the relative tendency of a charge distribution, like the electron cloud of an atom or molecule to be distorted from its normal shape by an external electric field; similarly ionic concentration [17,22,23], inter ionic distance [17]. When an electron in the conduction band of a crystalline insulator or semiconductor polarizes or otherwise deforms the lattice in its vicinity. The polaron comprises the electron plus its surrounding lattice deformation. (Polarons can also be formed from holes in the valence band.) If the deformation extends over many lattice sites, the polaron is “large,” and the lattice can be treated as a continuum. Charge carriers inducing strongly localized lattice distortions form “small” polarons [22]. In present work, these parameters have studied to explain structural features.

II. EXPERIMENTAL TECHNIQUES

2.1. PREPARATION OF GLASS SAMPLES

The Lithium-borovanadate glass samples having the general chemical formula 42.5Li₂O-(57.5-x)B₂O₃-xV₂O₅, x=0-57.5 in the step of 5.75, were prepared by conventional melt-quench technique from high-purity reagent grade B₂O₃ mol% of Li₂CO₃, and V₂O₅ reagents were purchased from Aldrich and appropriate amounts of the chemicals were well mixed and then dried in a vacuum oven at 150°C for 15 mins. Dried
mixture samples were melted in Pt crucibles in an electric furnace at the temperature of 1000–1100°C. Melt was kept for 30 mins and rapidly quenched on stainless steel. The prepared samples were then annealed at 300–400 °C temperature for 2 hrs and then kept in vacuum desiccators to avoid possible moisture absorption before testing. The prepared glass samples are polished and the surfaces are made perfectly plane and smoothened by 120 No. emery paper. Thickness of the samples has been measured using digital vernier calipers with an accuracy of 0.0001mm.

2.2. DENSITY MEASUREMENTS
Density of all glass samples are measured at room temperature using toluene as the immersion liquid. Density is generally measured by the fluid displacement method depending on Archimedes principle. According the Archimedes principle, the buoyancy equals the weight of the displaced fluid. Archimedes Principle using toluene as the buoyant medium evaluated the density of the glass samples. The density was obtained by employing the relation:

\[ \rho = \frac{W_a \rho_b}{W_a - W_b} \]

Where \( W_a \) is the weight of glass sample in air, \( W_b \) is the weight of glass sample. The density was obtained by employing the relation:

\[ \rho = \frac{W_a \rho_b}{W_a - W_b} \]

Where \( W_a \) is the weight of glass sample in air, \( W_b \) is the weight of glass sample in buoyant liquid, \( (W_a-W_b) \) is the buoyancy, \( \rho_b \) is density of buoyant. All the measurements were made using a digital balance.

2.3. MOLAR WEIGHT CALCULATIONS
Step I – Calculation of wt/mol
Weight/mole = molar weight of the constituents * mol% / 100
Step II – Calculation of molecular weight of sample (M)
The molecular weight of the sample (M) is nothing but the summations of Wt/mole of its constituents.
Step III – Calculation of Molar volume (\( V_m \))
Using molecular weight and density calculated as from above, the molar volume of the glass samples can be calculated from following expression:

\[ V_m = \frac{M}{\rho} \]

Here, \( V_m \) is molar volume, \( \rho \) is the density of the sample and M is the molecular weight of the sample.

2.4. OXYGEN PACKING DENSITY (O)
The oxygen packing density of the glass samples were calculated using the following relation [24]:

\[ O = n \left( \frac{\rho}{M} \right) \]

where \( \rho \), the density of desired glass samples, M, molecular weight of the sample and n, the number of oxygen atoms in the composition.

2.5 THE IONIC CONCENTRATIONS (N)
The ionic concentrations of the glass samples are determined using the following relation,

\[ N = \left( \frac{6.023 \times 10^{23}}{V_m} \right) \text{mol}^{-1} \text{mol}\% \text{ cation} \times \text{valency of cation} \]

2.6 INTER-IONIC DISTANCE (R)
Inter-ionic distance (R) of the glass samples is given as, Table 2.6.1 indicates, increasing the mol% of \( V_2O_5 \) at the cost of \( B_2O_3 \) by keeping modifier \( Li_2O \) constant. The molar volume, Inter ionic distance, Polaron radius increasing; while Oxygen Packing Density, Ionic concentration decreases, which suggests the increased free space within the glass structure, [25,26] it means that the glass structure becomes loosely packed [27]. The polaron comprises the electron plus its surrounding lattice deformation. (Polarons can also be formed from holes in the valence band.) Due to the increasing values of polaron radius the deformation extends over many lattice sites, and the lattice can be treated as a continuum. Ionic concentration,

\[ R = \left( \frac{1}{N} \right)^{1/2} \]

Were N = ionic concentrations.

Average molecular weight, Density, Molar volume, Oxygen Packing Density Ionic concentrations and Inter-ionic distance, and Polaron radius parameters values of Lithium borovanadate glasses are depicted in Table 2.6.1. Density changes monotonically, which is due to transformation of BO3 triangle units to BO4 tetrahedral units can be expected to increase the network linkage of the glass which is reflected in the monotonically increasing density. There founds inverse variations in Molar volume & Oxygen Packing Density, Inter ionic distance & Ionic concentration, Molar volume & Ionic concentration, Oxygen Packing Density & Inter ionic distance; on increasing the mol% of \( V_2O_5 \) and crosses at 23 mol% of \( V_2O_5 \)(Figure 2.6.1, 2.6.2, 2.6.3 and 2.6.4). Inter-ionic distance and Polaron radius varies linearly with \( R^2 = 0.999 \), indicates structural changes through the modification process in glass network.

![Figure: 2.6.1. Variation of oxygen packing density, Molar volume with mol% of \( V_2O_5 \)](image-url)
Table 2.6.1 Average molecular weight, Density, Molar volume, Oxygen packing density, Ionic concentrations, Inter-ionic distance and polaron radius for Na2O•B2O3-P2O5 glass system.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average molecular weight (g/mole)</th>
<th>Density (g/cm3)</th>
<th>Molar volume (cm3/mole)</th>
<th>Oxygen packing density (1024 cm3/mole)</th>
<th>Ionic concentration (%)</th>
<th>Inter-ionic distance (Å)</th>
<th>Polaron radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LBV.1</td>
<td>52.731</td>
<td>2.27</td>
<td>22.594</td>
<td>11.02</td>
<td>0.068</td>
<td>0.181</td>
<td></td>
</tr>
<tr>
<td>LBV.2</td>
<td>50.106</td>
<td>2.26</td>
<td>20.180</td>
<td>9.484</td>
<td>0.074</td>
<td>0.183</td>
<td></td>
</tr>
<tr>
<td>LBV.3</td>
<td>65.641</td>
<td>2.26</td>
<td>28.981</td>
<td>12.14</td>
<td>0.033</td>
<td>0.192</td>
<td></td>
</tr>
<tr>
<td>LBV.4</td>
<td>72.090</td>
<td>2.25</td>
<td>32.045</td>
<td>7.780</td>
<td>0.075</td>
<td>0.175</td>
<td></td>
</tr>
<tr>
<td>LBV.5</td>
<td>78.551</td>
<td>2.25</td>
<td>35.907</td>
<td>7.235</td>
<td>0.090</td>
<td>0.132</td>
<td></td>
</tr>
<tr>
<td>LBV.6</td>
<td>85.000</td>
<td>2.25</td>
<td>37.112</td>
<td>7.425</td>
<td>0.111</td>
<td>0.105</td>
<td></td>
</tr>
<tr>
<td>LBV.7</td>
<td>87.516</td>
<td>2.25</td>
<td>33.918</td>
<td>7.085</td>
<td>0.132</td>
<td>0.128</td>
<td></td>
</tr>
<tr>
<td>LBV.8</td>
<td>90.176</td>
<td>2.26</td>
<td>34.112</td>
<td>8.090</td>
<td>0.141</td>
<td>0.128</td>
<td></td>
</tr>
<tr>
<td>LBV.9</td>
<td>110.833</td>
<td>2.25</td>
<td>40.988</td>
<td>6.162</td>
<td>0.172</td>
<td>0.162</td>
<td></td>
</tr>
<tr>
<td>LBV.11</td>
<td>117.282</td>
<td>2.25</td>
<td>52.125</td>
<td>4.911</td>
<td>0.157</td>
<td>0.137</td>
<td></td>
</tr>
</tbody>
</table>

Figure: 2.6.2. Variation of Ionic concentration, Inter-ionic distance with mol% of V2O5

Figure: 2.6.3. Variation of Ionic concentration and Molar volume with mol% of V2O5

Figure: 2.6.4. Variation of Inter-ionic distance and oxygen packing density with mol% of V2O5

2.7 PHYSICAL PROPERTIES: RESULTS AND DISCUSSION

The mean atomic volume (V_M) of each glass was obtained from the values of densities (ρ) and mean atomic weights. The calculated values are given in Table 2.6.1.

Other physical parameters such as, Refractive index (n) of samples was calculated by using the following relation [28].

\[ n^2 - 1/n^2 + 2 = 1 - \sqrt{E_g/20} \]

Where, \( E_g \) is the energy gap.

The dielectric constant (\( \varepsilon \)) was calculated from the refractive index of the glass using [29].

\[ \varepsilon = n^2 \]

The Lorentz-Lorenz equation [30, 31, 32, 33] relates molar refraction \( R_m \) to refractive index n and molar volume \( V_m \) of the substance by,

\[ R_m = \left[ \frac{(n^2 - 1)}{(n^2 + 2)} \right] V_m \]

where \( V_m \) is equal to the molar volume.

This equation gives the average molar refraction of isotropic substances, i.e., for liquids, glasses and cubic crystals. The Lorentz-Lorenz equation presents the polarizability, i.e., the magnitude of the response of the electrons to an electromagnetic field.

On the other hand, Duffy [34] has obtained an empirical formula that relates energy gap \( E_g \) to molar refraction \( R_m \).

\[ R_m = V_m(1 - \sqrt{E_g/20}) \]

The ratio of \( R_m/V_m \) is called polarizability per unit volume. According to the Herzfeld theory of metallization [35]. If \( R_m/V_m > 1 \) and \( R_m/V_m < 1 \) samples predicting metallic or insulating. From Table 1.2 it is clear that present glass samples behave as non-metal. The difference \( M = 1 - R_m/V_m \) is so-called metallization criterion [36].

Materials with large \( M \) close to 1 are typical insulators. The small value of \( M \) close to zero means that the width of both valence and conduction bands become large, resulting in a narrow band gap and increased the metallicity of the solid. The molar refraction \( R_m \) can be expressed as a function of molar polarizability \( \alpha_m \) as

\[ R_m = \frac{4\pi \alpha_m A_v}{3} \]

Where \( A_v \) is Avogadro’s number introduced, with \( \alpha_m \) in (Å³) this equation can be transformed to,

\[ R_m = 2.52\alpha_m \]

Hence molar polarizability \( \alpha_m \) can be calculated.

The electronic polarizability \( (\alpha_e) \) was calculated using the formula [37].

\[ \alpha_e = \frac{3(n^2 - 1)}{4\pi A_v (n^2 + 2)} \]

Where, \( A_v \) is the Avogadro number.
The measured and calculated values of densities, molar volumes and polarizability of oxide ions of V$_2$O$_5$ doped Lithium-borate glasses are listed in the Table 2.7.1.

The trend of dielectric constant and refractive index, Molar refractivity and Molar polarizability with increasing mol% of V$_2$O$_5$ in LBV glasses are alike (Figure 2.7.1, Figure 2.7.2). Linearly variation between them gives $R^2 = 0.999$ and $R^2 = 0.998$ respectively.

Figure: 2.7.1 Variation of Dielectric constant Refractive index with mol % of V$_2$O$_5$

Figure: 2.7.2 Variation of Molar refractivity and Molar polarizability with mol % of V$_2$O$_5$.

Molar polarizability and Metallization varies reverse in nature with increasing mol % of V$_2$O$_5$. (Figure 7.3); similarly Polarizability per unit volumes and Metallization also varies reverse in nature with increasing mol % of V$_2$O$_5$. (Figure 2.7.4); having minimum value 0.692 and maximum value 0.308 at 34.5 mol% of V$_2$O$_5$. Polarizability per unit volumes and Metallization also varies linearly with $R^2=0.999$.

While Electronic polarizability and molar polarizability are lies reverse in order up to 17.25 mol% of V$_2$O$_5$ and later on they varies alike (Figure 2.7.2).

Figure: 2.7.3 Variation of Molar polarizability and Metallization with mol % of V$_2$O$_5$

Molar polarizability and Metallization varies reverse in nature with increasing mol % of V$_2$O$_5$. (Figure 2.7.3); similarly Polarizability per unit volumes and Metallization also varies reverse in nature with increasing mol % of V$_2$O$_5$. (Figure: 2.7.4); having minimum value 0.692 and maximum value 0.308 at 34.5 mol% of V$_2$O$_5$. Polarizability per unit volumes and Metallization also varies linearly with $R^2=0.999$.

While Electronic polarizability and molar polarizability are lies reverse in order up to 17.25 mol% of V$_2$O$_5$ and later on they varies alike (Figure 2.7.2).

Figure: 2.7.4 Variation of Polarizability/unit volumes and Metallization with mol % of V$_2$O$_5$

Figure: 2.7.5 Variation of Electronic polarizability and Molar polarizability with mol % of V$_2$O$_5$

Electronic polarizability, Ionic concentration and Inter ionic distance is due to relative tendency of a charge distribution like electron cloud of an atom or molecule, indicates that higher values are due modification the glass structure by BO$_3$ units with non-bridging oxygen atoms in the network.

III. CONCLUSIONS

Increasing the mol% of V$_2$O$_5$ with respective to the B$_2$O$_3$ by keeping modifier Li$_2$O constant, the molar volume, inter ionic distance, polaron radius increasing, suggests the increased free space within the glass structure, it means that the glass structure becomes loosely packed. Oxygen packing density, ionic concentration monotonically decreases, because the polaron comprises the electron plus its surrounding lattice deformation. Hence, the deformation extends over many lattice sites and the lattice can be treated as a continuum. Transformation of BO$_3$ triangle units to BO$_4$ tetrahedral units can be expected to increase the network linkage of the glass which is reflected in the monotonically increasing density.

Dielectric constant and refractive index varies linearly. Molar refractivity behavior is alike as that of Molar polarizability, they also varies linearly. Electronic polarizability and metallization shows reverse behavior, is also due to the break down of borate & phosphate bonds to create non- bridging oxygen atoms. The study of density and that of oxygen packing density gives a very excellent co-ordination in them, for each value of oxygen packing density there is maximum value of density.

A nonlinear and non-additive change with changing glass former composition at constant modifier composition is due to the mixed glass former effect (MGFE). Polarizability per unit volume predicts present glass samples are non-metals. The formation of BO$_4$ and BO$_3$ which will modify the glass structure by creating NBOs in the network gives parallel variation in Dielectric constant, Refractive index, Molar refractivity and Molar polarizability. Liner trends are found in Molar refractivity.
& the Molar polarizability, Metallization & Polarizability per unit volume, and Mol % of $V_2O_5$ & Molar volume ($V_m$).

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