ROLE OF V$_2$O$_5$ IN STRUCTURAL PROPERTIES OF V$_2$O$_5$-MnO$_2$-PbO-B$_2$O$_3$ GLASSES

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Abstract. Glass samples of compositions $x$V$_2$O$_5$–(20-$x$) MnO$_2$-20PbO-60B$_2$O$_3$ with $x$ varying from 0 to 15% mole fraction are prepared by melt quench technique. The structural analysis of glasses is carried out by XRD, FTIR and density measurement techniques. The FTIR spectral studies have pointed out the conversion of structural units of BO$_3$ to BO$_4$ with the presence of VO$_4$ and VO$_5$ structural units of vanadium in these glasses. Due to the formation of BO$_4$ groups, an increase in density from 3.52 to 4.33 g·cm$^{-3}$ for MnO$_2$-PbO-B$_2$O$_3$ glasses is observed with an increase in V$_2$O$_5$ content.

1. Introduction

Among oxide glasses, structural and optical properties of the borate glasses have been studied by various physical and chemical methods including XRD, FTIR, Raman infrared spectroscopy, NMR and UV-visible spectroscopy [1-3]. FTIR spectroscopy is one of the important techniques which are used to study the local arrangement in inorganic glasses. The main structural units of borate glasses are BO$_3$ triangles. By the addition of modifiers it can convert from BO$_3$ to BO$_4$ units.

Borate glasses are generally insulating in nature and the addition of transition metal such as V$_2$O$_5$, Fe$_2$O$_3$, WO$_3$, 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. The transition metal doped borate glasses have been extensively studied by several 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 [4-6].

Among transition metals, V$_2$O$_5$ is an important semiconductor whose electrical conductivity is due to the electron hopping between V$^{5+}$ and V$^{4+}$ ions [7]. The semiconducting nature of V$_2$O$_5$ is due to two valence states V$^{5+}$ and V$^{4+}$ of vanadium [8]. 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.

Much work has been made on the borate glasses containing MnO$_2$ [5, 9] but the work on glasses containing MnO$_2$ and V$_2$O$_5$ together is found very few. In present work efforts are made to study the effect of the structure properties and physical properties of the glasses in the presence of multiple transition metals with the help of x-ray diffraction (XRD), density measurement and Fourier transform infrared spectroscopy (FTIR).

2. Experimental procedure

Sample preparation. $x$V$_2$O$_5$–(20-$x$) MnO$_2$-20PbO-60B$_2$O$_3$ with $x$ varying from 0 to 15% mole fraction are prepared by melt quench technique. The raw materials of lead oxide (PbO), Vanadium oxide (V$_2$O$_5$), Manganese oxide (MnO$_2$) and boric oxide (B$_2$O$_3$) of
appropriate amounts are mixed together and melted in silica crucible at temperature range of 1000 °C for 60 minutes until a bubble free liquid has formed. The melt is then poured into 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 1.

### Table 1. Glass matrix compositions (mole %) and density of the glass samples respectively.

<table>
<thead>
<tr>
<th>Glass</th>
<th>V$_2$O$_5$ (%)</th>
<th>MnO$_2$ (%)</th>
<th>PbO (%)</th>
<th>B$_2$O$_3$ (%)</th>
<th>Density (D)* (g·cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mv1</td>
<td>0</td>
<td>20</td>
<td>20</td>
<td>60</td>
<td>3.52</td>
</tr>
<tr>
<td>Mv2</td>
<td>3</td>
<td>17</td>
<td>20</td>
<td>60</td>
<td>3.57</td>
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<td>Mv3</td>
<td>6</td>
<td>14</td>
<td>20</td>
<td>60</td>
<td>3.68</td>
</tr>
<tr>
<td>Mv4</td>
<td>9</td>
<td>11</td>
<td>20</td>
<td>60</td>
<td>3.81</td>
</tr>
<tr>
<td>Mv5</td>
<td>12</td>
<td>08</td>
<td>20</td>
<td>60</td>
<td>4.04</td>
</tr>
<tr>
<td>Mv6</td>
<td>15</td>
<td>05</td>
<td>20</td>
<td>60</td>
<td>4.33</td>
</tr>
</tbody>
</table>

*The errors in the measurement of density and band gap are estimated to be 0.008 g·cm$^{-3}$ and 0.0084 respectively.

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

**Density measurements.** The density of glass samples at room temperature is measured by the standard principle of Archimedes using a sensitive microbalance with pure benzene as the immersion fluid.

The density is calculated using the formula:

$$D = \frac{W_A}{W_A - W_B} \cdot d,$$

where $W_A$ is a weight of sample in air, $W_B$ is a weight of the sample in benzene and $d$ is a density of the benzene.

**FTIR measurements.** 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 infra-red spectrometer type (Thermo Nicolet 380 spectrometer). The prepared glasses are mixed in the form of fine 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.

### 3. Results and discussion

**X-ray diffraction.** X-ray diffraction pattern of V$_2$O$_5$-MnO$_2$–PbO–B$_2$O$_3$ glass samples (Fig.1) shows no continuous or discrete sharp peaks but exhibit broad halo which reflects the characteristics of amorphous glass structure. The absence of long range atomic arrangement is
a clear indication of the glassy nature of the samples [10-13].

Fig. 1. X-Ray diffraction pattern of V$_2$O$_5$–MnO$_2$–PbO–B$_2$O$_3$ glasses.

**Density.** Density measurement is a very sensitive tool that can easily detect any structural change in the glass network. The modification in atomic geometrical configuration, co-ordination number and the dimensions of the interstitial space in the glass network decides the density and for that reason the density is a mechanism which reveals the degree of change in the structure with the glass composition. In borate glasses, density is controlled by the fraction of four-coordinated borons. It is a fact that boron has a coordination number of three or four [8, 14-15]. Consequently, boron can have its structure in triangular or tetrahedral form. The BO$_4$ tetrahedral are considerably denser than the symmetric BO$_3$ triangle [10]. Therefore tetrahedral groups are more rigid as compared to triangular groups.

The density of prepared V$_2$O$_5$-MnO$_2$–PbO–B$_2$O$_3$ glasses is given in Table 1. Proceeding with results, density of the glass system increases (from 3.52 to 4.33 g·cm$^{-3}$) has been observed with the substitution of V$_2$O$_5$ contents. It has been pointed out that the presence of V$_2$O$_5$ increases the density of glass due to the availability of more oxygen from V$_2$O$_5$ which shifts the coordination of BO$_3$ to BO$_4$. In sample Mv1 to Mv3 increase in density is due to the formation of BO$_4$ structural units. As the tetrahedral BO$_4$ groups are strongly bonded than the triangular BO$_3$ groups, therefore a compact structure is expected leading to a higher density [16]. Further increase in density with incorporation of V$_2$O$_5$ from sample Mv3 to Mv6 is due to the formation of VO$_4$ and VO$_5$ groups. These groups [VO$_4$, VO$_5$] have higher value of field intensity. Hence the addition of V$_2$O$_5$ has modified the borate glass structure by creating more BO$_4$, VO$_4$ and VO$_5$ groups.

The variation in density with V$_2$O$_5$ contents is shown in Fig. 2. The increase in density reveals the change in the structure of glasses with the increase of oxide contents.

**FTIR.** The infrared spectra for V$_2$O$_5$–MnO$_2$–PbO–B$_2$O$_3$ glasses shows large, medium, weak and broad peaks as shown in Fig. 3.

According to the literature survey, the vibrations of borate groups are mainly present in the following spectral regions:

A. The region at 700 cm$^{-1}$ is due to the bending of the B–O–B linkage.
B. The region 800-1200 cm$^{-1}$ is due to B–O bond stretching of various tetrahedral BO$_4$ units.
C. The region 1200-1600 cm$^{-1}$ is due to the stretching of various trigonal BO$_3$ units [17-20].
Fig. 2. Dependence of density of MnO2-PbO-B2O3 glasses on V2O5 content.

In the studied glasses V2O5-MnO2–PbO–B2O3, IR bands assignments has been summarized as followings.

1. Absence of band at 806 cm\(^{-1}\) shows the non existence of boroxol rings in glasses and hence consists of only BO\(_3\) and BO\(_4\) groups [21-22].

2. The band at 680 cm\(^{-1}\) which is present in sample Mv4, Mv5 and Mv6 is due to B-O-B bending vibrations of BO\(_3\) groups which are not seen in other samples with lower concentration of V\(_2\)O\(_5\) and higher concentration of MnO\(_2\) in the glass network [11, 23].

3. The band observed at 772 cm\(^{-1}\) is due to B-O-B vibration between BO\(_3\) and BO\(_4\) group. Its intensity increases progressively with an increase in the contents of V\(_2\)O\(_5\) which is due to the vibration of V-O-B bond connecting borate groups [5, 13].

4. The bands at 854 and 871 cm\(^{-1}\)are clear indicator of B-O bond stretching of BO\(_4\) unit in tri, tetra and penta borates groups [10-11]. The band at 854 cm\(^{-1}\) starts appearing in sample Mv4 and shifts from 854 to 871 cm\(^{-1}\) with increasing contents of V\(_2\)O\(_5\) due to V-O stretching of VO\(_4\) group [24].

5. The weak band present at 1011 cm\(^{-1}\) is due to B-O vibration of BO\(_4\) unit in tri, tetra and penta-borate groups. This band is increase in intensity and shifting from Mv2 to Mv6 sample due to V=O vibration of vanadium group in VO\(_5\) bipyramidal [25]. The band at 1079 cm\(^{-1}\) is due to B-O vibration of BO\(_4\) unit [10, 12-13]

6. The formation of band at 1179 cm\(^{-1}\) which is absent in Mv1, Mv2 and Mv3 samples has been assigned to BO\(_4\) stretching vibration [26-27].

7. The regions between 1200-1600 cm\(^{-1}\) are due to B-O asymmetric stretching vibration of BO\(_3\) units in meta-borate, pyro-borate and ortho-borate groups [26-27].

8. The regions 2400-3000 cm\(^{-1}\) are due to water groups [28-29].

Above discussion clearly indicates that, the formation of new band at 1011 cm\(^{-1}\) in sample Mv3 which is due to tetrahedral BO\(_4\) group. This band is shifting towards the higher wave number (1011 to 1020 cm\(^{-1}\)) and also its intensity increases with the increase of V\(_2\)O\(_5\) contents from Mv3 to Mv6 samples. At the same time, it is also observed that the intensity of band (at 1596 cm\(^{-1}\)) is decreased with the increase of V\(_2\)O\(_5\) concentration in samples Mv1-Mv6. This shows an increase in BO\(_4\) units. It is also observed that, shifting of the bands from 854 to 871 cm\(^{-1}\) with an increasing concentration of V\(_2\)O\(_5\) reveals that it affects the local structure of borate network glasses, which has not been observed in the presence of MnO\(_2\) in...
sample Mv1. It shows that V$_2$O$_5$ has dominant effect on the structure of glass in the presence of MnO$_2$. This indicates that V$_2$O$_5$ enters the glass network as network modifiers up to some mole percent, resulting the conversion of BO$_3$ into BO$_4$ group. At higher concentration, presence of VO$_4$ and VO$_5$ groups shows, (samples Mv5, Mv6) it acts as network modifier.

![Fig. 3. FTIR spectra of V$_2$O$_5$ doped MnO$_2$-PbO-B$_2$O$_3$ glasses.](image)

4. Conclusion
In conclusion it has been found that V$_2$O$_5$ has more dominant effect than MnO$_2$ in the glass network. By fixing the lead and borate contents, increase in V$_2$O$_5$ concentration with the decrease in MnO$_2$ leads to compaction of glass network by breaking the bonds between the trigonal elements, allowing the formation of BO$_4$ units and in this way increases the density of the glasses. By infrared spectroscopic study it has been concluded that for V$_2$O$_5$-MnO$_2$–PbO–B$_2$O$_3$ glasses, the main structural unit comes out to be BO$_3$ (in pyro, meta, ortho groups) and BO$_4$ (in tri, tetra, and penta groups) with V-O stretching of VO$_4$ and V=O vibration of VO$_5$ group. As the V$_2$O$_5$ content increases, BO$_3$ group starts converting in to BO$_4$ groups. This reveals that V$_2$O$_5$ enters the glass structure as network former as well as modifier. The presence of VO$_4$ and VO$_5$ states detected by infrared study reveals the network former behavior of vanadium at higher concentration in these glasses. Hence this work may be used for further solid state applications.

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