Abstract

Preparation of PbO-PbF$_2$-B$_2$O$_3$ glass system with different concentrations (0.1 to 0.5 mol %) of V$_2$O$_5$ doped into the system by reducing the corresponding mol% in V$_2$O$_3$ by the technique of melting and quenching. XRD (X-Ray Diffraction), SEM (Scanning Electron Microscope) and DTA (Differential Thermal Analysis) show that the prepared samples are amorphous in form. As the concentration of the dopant is increased from 0.1 to 0.3 mol% the glass forming ability of the system is increased from 0.453 to 0.561. Further increase of the dopant to 0.5 mol% the glass forming ability comedown to 0.534. The analysis of the results of these studies has been done with regard to the different oxidation states of Vanadium with the help of the data on IR (Infra Red), Optical absorption and magnetic susceptibility measurements. It is observed that vanadium ions exist mainly in V$^{4+}$ state and occupy tetrahedral position increasing the stability of the system, when the concentration of the dopant is increased up to 0.3 mol% and later on beyond that concentration, V$^{5+}$ ions are increased at the expense of V$^{4+}$. Nevertheless, in the presence of V$_2$O$_5$ at 0.3 mol% in the system, i) BO$_4$ structural units are maximized and vanadium ion chiefly exists in V$^{4+}$ state and occupies tetrahedral sites in the glass matrix, ii) The magnetic moment (evaluated from magnetic susceptibility) has been observed to increase to a value of 1.73 µB. These results prove that vanadium ions chiefly exist in V$^{4+}$ state at 0.3 mol% range of concentration.

Keywords: PbO-PbF$_2$-B$_2$O$_3$ Glass System, V$_2$O$_5$ Doping, Spectroscopic and Magnetic Properties

1. Introduction

Boron trioxide is a white, solid, glassy oxide of Boron. It is generally found in the vitreous form, but it can be crystallized by extensive annealing; hence it is one of the most difficult compounds known to crystallize. It is a glass forming oxide. PbO is conditional glass former. With these two chemicals in the glass network, a low rate of crystallization, moisture resistance, stable and transparent glasses could be obtained due to the dual role played by PbO as a glass former and as a modifier too (Lakshminarayana & Buddhudu, 2006).

PbO-PbF$_2$ glasses are believed to be of special interest because of their effective use in IR fiber optics, laser windows and multi functional optical components. These glasses are highly transparent in the mid-infrared range up to 8 µm and are more stable against atmospheric moisture. They are also believed to be favourable material for electro chemical applications in the field of solid state batteries and as power sources (Damarawi, 2000). A wide range of Lead oxy fluoro borate glasses can be synthesized in various combinations with PbO from 30 to 80% range. These
glasses also have the ability to accept the transitional metal ion like vanadium ions in both network forming and modifying positions (Ardelean et al, 1999); like any other heavy metal oxide based glasses. A lot of literature is available on the recent extensive studies which includes glass transition temperature, EXAFS, XANES etc. on PbO-PbF₂ glasses containing different transition metal ions (Khattak et al, 2003; Montani & Frechero, 2003; Sharma et al, 2003 and Shash et al, 2004). All these recent studies have shown that distorted octahedral structural units like PbO₂F₂ are found these glasses.

The glasses consisting of vanadium ions become very important in solid state chemistry and materials science, because V₂O₅ is known to take part in the glass matrix with V₂O₅ pyramidal structural units. Vanadium ions, when mixed in small qualities into the glass matrices, make them useful in memory and switching devices. Many of the glasses having vanadium behave like semiconductors with an electrical conductivity of 10⁻¹⁻¹⁸(Ω cm)⁻¹. This is possible because of the electron hopping between V⁴⁺ and V³⁺ ions in the glass net work. These glasses are known as n-type semiconductors for low value of V⁴⁺/V³⁺ ratio. The vanadium ions may also exist in the glass net work in V⁴⁺ and V³⁺ states. Moreover, the vanadium oxide structural groups are believed to combine easily into the PbO-PbF₂-B₂O₃ network (Rao et al, 2004; Rao & Veeraiah, 2004; Raghavaiah et al, 2005 a and b). This is possible because some of the infrared vibration bands of the structural groups of these ions are found in the same region as those of PbO₂F₂ and BO₂ structural units. They are also believed to occupy diverse sites with different crystal field strengths because of the site variability. A great number of studies, on some of glasses containing V₂O₅, are available, yet most of them are limited to electrical properties only.

The present study mainly intends to have a general understanding about the influence of vanadium ions on the structure of PbO-PbF₂-B₂O₃ glasses by doing a systematic study with the help of IR (Infra Red), OA (Optical Absorption) and magnetic susceptibility studies. By doing so the role of the vanadium ions and their structural modifying capacity is revealed, with the help of data on magnetic and spectroscopic properties.

2. Experimental Methods

Six samples of glasses are prepared for the present study, with the combination of chemicals in mol% as shown here under. All the samples of glasses (from the visual examination) are prepared with an increasing concentration of V₂O₅:

V₁: 40 PbO-10 PbF₂-50 B₂O₃
V₂: 40 PbO-10 PbF₂-49.7 B₂O₃: 0.3 V₂O₅
V₃: 40 PbO-10 PbF₂-49.6 B₂O₃: 0.4 V₂O₅
V₄: 40 PbO-10 PbF₂-49.5 B₂O₃: 0.5 V₂O₅

Measured quantities of PbF₂, PbO, H₃BO₃ and V₂O₅ powders were mixed thoroughly in an agate mortar. Then the mixture is melted in a platinum crucible in the temperature of 950-1000 °C in a PID temperature controlled furnace for one hour until a bubble free transparent liquid appeared. The so formed liquid was poured into a brass mould and then annealed at 300 °C using an annealing chamber. X-Ray Diffraction (XRD) and SEM (Scanning Electron Microscope) analyses were used to determine the amorphous state of the glasses.

The differential thermal analysis on the samples under study was done using STA 490C, Model DTA-TG with a programmed heating rate of 10 °C /min at 30-1000 °C temperature range.

Then the samples were ground and optically polished. By using the standard principle of Archimedes, with the 99.99% pure O-xylene on the buoyant liquid, the density (d) of these glasses was estimated to 0.001 accuracy. KBr pellet method was used to record the IR spectra of the glass. 2 mg of glass powders were mixed with anhydrous KBr powder of 150 mg and were pressed into pellets at 2000 kg /cm². The spectra were recorded using an FT-IR digital Excalibur 3000 spectrometer with a resolution of 0.1 nm. Fine powders of these glasses were used to measure their magnetic susceptibility at room temperature by Guoy’s method.

3. Results

The samples thus prepared were amorphous in nature. This is indicated crystalline temperature Tc in the DTA (Differential Thermal Analysis) traces (Figure 1).

![Figure 1. Differential Thermal Analysis Patterns of PbO-PbF₂-B₂O₃ V₂O₅ Glasses](image)

Physical parameters such as vanadium ion concentration N, mean vanadium ion separation R, Polaron radius rp and the field strength around the dopant ion F of these glasses...
Further at higher temperatures an exothermic peak, $T_c$ (Chen, 1969) were calculated from the measured value of density $d$ and calculated average molecular weight, $M$. They are shown in Table 1.

The thermal analysis of all the glasses under study was shown in Figure 1. The curves show an endothermic effect due to the glass transition temperature, $T_g$, in all samples. Further at higher temperatures an exothermic peak, $T_m$, minus (-) sign is for the crystal growth and an endothermic effect, $T_m$, were also detected. Table 2 shows the values of $T_g$, $T_c$, and $T_m$ obtained for all glasses. The good homogeneity of all the glass samples prepared is proved by the appearance of single peak due to the glass transition temperature in DTA pattern of all the glasses.

Table 1. Summary of Data on Various Physical Parameters of PbO- PbF$_2$- B$_2$O$_3$; V$_2$O$_5$ Glasses

<table>
<thead>
<tr>
<th>Property</th>
<th>Glass Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density $d$ (g/cm$^3$)</td>
<td>$V_0$</td>
</tr>
<tr>
<td>Avg. mol. Wt. $M$</td>
<td>148.59</td>
</tr>
<tr>
<td>Vanadium ion conc. N$_i$ (10$^{21}$ ions/cm$^3$)</td>
<td>----</td>
</tr>
<tr>
<td>Inter ion distance of vanadium ions R$_i$ (Å)</td>
<td>----</td>
</tr>
<tr>
<td>Field Strength F$_i$ (10$^{13}$ cm$^{-2}$)</td>
<td>----</td>
</tr>
<tr>
<td>Polaron Radius $r_p$ (Å)</td>
<td>----</td>
</tr>
</tbody>
</table>

The values of different thermal stability parameters of PbO-PbF$_2$-B$_2$O$_3$; V$_2$O$_5$ glasses are shown in Table 2. From the measured values of $T_g$, $T_c$, and $T_m$, the parameters $T_c - T_g$, $T_m - T_g$, and Hruby’s parameter (The glass forming parameter) $K_{gl} = (T_c - T_g)/(T_m - T_g)$ were calculated and shown in Table 2. In glasses doped by V$_2$O$_5$, the parameter $T_c - T_g$ which is proportional to glass forming ability is found to increase. The quantity $T_m - T_c$, which is inversely proportional to glass forming ability, is decreased as the content of V$_2$O$_5$ was increased from 0.1 mol% to 3.0 mol% and beyond this concentration these parameters were reversed in nature and it is clear from the data of Table 2. The variation in the parameter $K_{gl}$ with the variation of concentration of V$^{4+}$ ion, shows the maximum value for glass $V_5$ (Table 2) showing its highest glass forming ability among all the glasses under study.

The IR spectra of the prepared samples contains various band as shown below in the region of i) 1300-1400 cm$^{-1}$ due to the stretching relaxation of B-O bond of the trigonal B$_2$O$_3$ units, ii)1100-1200 cm$^{-1}$ due to the vibration of BO$_4$ structural units, iii) 710 cm$^{-1}$ due to the bending vibrations of B-O-B linkages (Khalifa et al, 1998; Nageswara Rao et al, 2006 and Veerabhadra Rao et al, 2006). PbO$_4$ structural units in all the glasses prepared showed a band at about 520 cm$^{-1}$ (Laudiso Catauro et al, 1997 and Wu et al, 1997). The IR spectra shown in Figure 2.

From the application point of view, the glass should be thermally stable. This thermal stability of glasses can be estimated on the basis of calorimetric measurements using the DTA. Generally, unstable glasses show crystallization peak close to the glass transition temperature. Therefore, the temperature difference $T_c - T_g$ is a good indication of thermal stability because the higher the value of this difference, more the delay in nucleation (Mehta et al, 2006). Thus, the Hruby parameter i.e. Hruby number $K_{gl}$ (Hruby, 1972) is calculated to determine sample stability. This parameter shows that thermal stability of the sample increases with increase in the concentration of vanadium from 0.1 to 0.3 mol %.

When V$_2$O$_5$ of 0.1 mol% was introduced into the glass matrix, three new bands i.e. i) at 1020 cm$^{-1}$ due to V=0, ii) at 815 cm$^{-1}$ due to V-O-V symmetric stretching vibrations and iii) at 605 cm$^{-1}$ (Garbaczynk et al, 2001 and Krishna Mohan et al, 2006) due to bending vibrations of V-O-V structural units have appeared.

As the study moves from glass sample $V_0$ to $V_5$ the brightness of the second group of bands (due to BO$_4$ units) is observed to increase with the meta-centre slightly shifting.
towards lower wave number, while the intensity of the first group of bands (due to BO₃ structural units) decreased. On further increase of V₂O₅ (for the samples V₄ & V₅), the intensity of the first group of bands increased at the expense of second group of bands. Table 3 shows the details of IR bands.

Table 3. Summary of the Data on Band Positions (cm⁻¹) of Various Absorption Bands in the IR Spectra of PbO- PbF₂-B₂O₃: V₂O₅ Glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>Borate Groups</th>
<th>Band due to PbO₂F₄(cm⁻¹)</th>
<th>Band due to V=O(cm⁻¹)</th>
<th>Band due to V-O-V(cm⁻¹)</th>
<th>Band due to V-O-V Bending(cm⁻¹)</th>
<th>Band due to PbO₃ units(cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V₀</td>
<td>BO₃ (cm⁻¹)</td>
<td>1362</td>
<td>1175</td>
<td>710</td>
<td>1050</td>
<td>1020</td>
</tr>
<tr>
<td>V₁</td>
<td>BO₄ (cm⁻¹)</td>
<td>1370</td>
<td>1159</td>
<td>710</td>
<td>1050</td>
<td>1020</td>
</tr>
<tr>
<td>V₂</td>
<td>BO₄ (cm⁻¹)</td>
<td>1378</td>
<td>1150</td>
<td>710</td>
<td>1050</td>
<td>1020</td>
</tr>
<tr>
<td>V₃</td>
<td>BO₃ (cm⁻¹)</td>
<td>1383</td>
<td>1146</td>
<td>710</td>
<td>1050</td>
<td>1020</td>
</tr>
<tr>
<td>V₄</td>
<td>BO₃ (cm⁻¹)</td>
<td>1374</td>
<td>1150</td>
<td>710</td>
<td>1050</td>
<td>1020</td>
</tr>
<tr>
<td>V₅</td>
<td>BO₃ (cm⁻¹)</td>
<td>1370</td>
<td>1165</td>
<td>710</td>
<td>1050</td>
<td>1020</td>
</tr>
</tbody>
</table>

As the concentration of V₂O₅ was increased up to 0.3 mol%, the shifting of the meta-centres of these two bands, towards lower wavelength with a gradual raise in the intensity was noticed. Three bands on the basis of energy level scheme for molecular orbitals of VO⁺⁺ ion can be expected, for the vanadyl ions, in a ligand field of C₄ᵥ symmetry provided by Ballhausess & Gray (1962), conforming to the transitions ^3B₂ → ^5B₁, ^3B₁ → ^5E and ^3B₃→^1A₁. But in the present study only the first two bands are studied. The greatest intensity and half width of these bands for V₃ glass indicate the largest concentration of VO²⁺ ions. The highest concentration of vanadyl ions is the obvious cause for the greatest intensity of these bands in the spectrum of V₃ glasses.
but beyond this concentration the Tg decreased. This shows that glass V3 is more prone to glass formation which is
due to very high Tc and Tc-Tg. Hence it is proved that vanadium ions in this glass network take up network forming positions with VO2+ units. The DTA results also show that the vanadium ions occupying network forming position in the glass networks of V1 to V3 may increase the rigidity of those glass networks.

On reviewing the IR spectra data, it was observed that the bands due to BO3 structural units have been decreased and at the same time the intensity of the band due to BO3 units is increased, when the concentration of V2O3 is increased up to 0.3 mol%. With the help of these observations it is suggested that in this concentration range of V2O3 vanadium ions act as builders and create more order in the glass net work. This arrangement is supported by the decrease in the intensity of the band due to BO3 units. Because of the distorted octahedral PbO2F2 structural units with the increase in the concentration of V2O3, the IR spectra of glasses V4 and V5 shows that the intensity of the bands due to more ordered BO3 structural units decreased and the intensity of bands due to BO3 structural units increased (Cozar et al, 2001).

Optical absorption spectra of the glasses under study showed two prominent absorption bands at 630-1000 nm wave length region. The spectrum was analyzed using tanabe-sugano diagrams for d8 ions and the bands are consigned to 3B2 → 1B1, 3B2 → 1E transitions respectively. In addition to this observation, it was clearly noticed that widths of 3E and 3T1 bands increased when the concentration of vanadium ions was increased from 0.1-0.3 mol%. This kind of increase in the band width shows an increase of orderliness in the glass network. This may be due to decreasing concentra tion of incited heterogeneous nucleation centers in the glass network, which leads to the increase in the long range order of vanadium and Borate groups (Ballhausen, 1962).

IR spectra data show that the intensity of the bands due to BO3 structural units was decreased at expense of the bands due to BO3 units with increase in the concentration of V2O3 up to 0.3 mol%. This fact suggests a gradual increase in the concentration of V4+ ions in the glass network act as formers and creates more orderly arrangement in the glass network.

The highest concentration of V4+ ions in the glass is confirmed by the effective magnetic moment value 1.73 µB – got from glass V3. A gradual growing concentration of diamagnetic V4+ ions indicated by the decrease in the value of ⟨µeff⟩ from 1.73 µB to 1.37 µB in the glasses V4 and V5. The increase of V5+ ions and simultaneous decrease in the concentration of V4+ ions may raise the degree of disorder in the glass network.

5. Conclusions
The following conclusions are derived about PbO-PbF2 -B2O3: V2O5 glass system:

The magnetic susceptibility measurements show that V4+ ion concentration is growing from 0.1 to 0.3 mol% and became maxima for 0.3 mol%. When the concentration of V2O3 is increased beyond 0.3 mol%, V4+ ions are convert ed into V3+ (if any) or V5+ state ions. Hence, it can be concluded from the magnetic susceptibility measurements that the sample V3 glass is very stable, compared to the other samples.

From the IR spectral investigations it is proved that the increase in the concentration of V2O3 from 0.1 to 0.3 mol% in the glass matrix gradually increases the concentration of V4+ ions, which occupy tetrahedral positions and improve the orderliness and increase the stability of concentration of V2O5 beyond 0.3 mol%. V3+ or V5+ ions are increased at the expense of V4+ ions. Thus sample V3 represents a good glass.

The optical absorption spectral studies show that a part of V ions exist in V4+ state and occupy tetrahedral position when V2O3 of 0.1 to 0.3 mol% concentration is added, but these ions seem to exist in V3+ or V5+ state, when the concentration of V2O3 is higher (>0.3 mol%).

The Analysis of the results of the studies on the various physical properties (viz optical and magnetic) and DTA finally prove that the structure of PbO-PbF2 -B2O3 glass, is more stable when the concentration of V2O3 is about 0.3 mol %.

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