DIELECTRIC PROPERTIES OF MnO SUBSTITUTED FOR PBO IN EUTECTIC LEAD VANADATE SYSTEM

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ABSTRACT

Results of X-ray diffraction, chemical analysis and dielectric constant and dielectric loss in A.C conductivity obtained on the series of XMnO:(50-X)PbO:50 V₂O₅ where (x=5%,10%,15%) lead vanadate glass prepared by melt quenching method and heat treated at 150°C are reported. It is observed that density and concentration of V⁴⁺ decreases as MnO is substituted for PbO. The A.C conductivity (or) dielectric loss gradually increases with increase in MnO concentration. The dielectric constant also increases as MnO concentration increases.

Key words: XRD, A.C conductivity, lead vanadate, dielectric loss, dielectric constant

1. INTRODUCTION

The study of non-crystalline (amorphous) materials has been receiving a lot of attention from physicists, chemists and material scientists not only due to their technological importance but also because of their interesting physical properties when compared to their crystalline analogues. Inspite of a large number of investigations, there is always something new to be understood about the physical properties of these amorphous materials. These materials exhibit short range order similar to their crystalline analogues. Mott [1] and others have proposed several theoretical models which explained electrical, magnetic, optical etc. physical properties. Glass is an amorphous material which can be prepared by different combinations. W.Vogel [2] was first to investigate the constitution of glasses. He described glasses as strongly under cooled liquids. According Lebedev [3] crystallite theory the structure of glass was regarded as an accumulation of microcrystalline entity called crystallite. X-ray, XAFS, EPR, IR, NMR, Mössbauer spectra etc. are very useful probes to investigate the structure of glassy materials. These methods could be employed to have a glimpse of the structure of amorphous materials [4-10].In most of the studies, a comparison of the data of the glasses with those of the corresponding crystal phase is adopted for interpretation of IR spectra. This method of structural study is very suitable for vanadate glasses because of the characteristic
vibration of isolated vanadium-oxygen bonds in the 1020-900 cm\(^{-1}\) [11]. The PbO - 
\(V_2O_5\) glass system has been extensively studied and crystal structures of PbO-\(V_2O_6\) 
or PbO-\(V_2O_7\) etc., phases are known [12]. This is an ideal system to study the effect 
of doping or substitution on the physical properties of glass system. In our laboratory 
a program was initiated to understand the effect of different oxide groups in the place 
of PbO in PbO-\(V_2O_5\) glass system chosen at the eutectic composition i.e., 1:1 molar 
ratio. As a part of this program, Ramesh [13-15] has studied ZnO, CuO and TiO\(_2\) 
substituted glass systems. XRD, DTA, IR, ESR and in D.C conductivity 
investigations were carried on the glass systems. However no A.C conductivity 
studies were carried out at that time. Later many studies were carried out for AC 
conductivity [16-19].

In this paper the results obtained in the X-ray diffraction (XRD), chemical 
analysis and AC conductivity (or) dielectric loss of \(x\)MnO:(50-\(x\))PbO:50\(V_2O_5\) (where 
\(x=\) 0.5%, 10%, 15%) lead vanadate glass system prepared by melt quenching method 
and heat treated at 150\(^{\circ}\)C are presented.

2. PREPARATION OF GLASS SYSTEM

Glass system of composition \(x\)MnO:(50- \(x\))PbO:50\(V_2O_5\) (where \(x=\) 0.5%, 
10%, 15%) are prepared using reagent grade starting materials \(V_2O_5\), PbO&MnO of 
99.9% purity.

The chemicals were measured in required molar ratio for each batch of 
composition using an electrical balance (Dhona Model 200D) of 0.0001 g accuracy. 
Each batch of composition was taken in an agate mortar and was mixed thoroughly 
for several hours for homogeneity. This mixture, whose total weight was around 2 g 
for each batch of composition was taken in a glazed silica crucible with lid and was 
melted in an electrical furnace kept at a temperature of 950 - 1000\(^{\circ}\)C range. The 
completely melted samples were periodically stirred for homogeneity and were kept 
at that state for nearly 15 minutes before quenching. The melts were quenched on a 
large stainless still block maintained at room temperature (30\(^{\circ}\)C) and consisting of 9 
mm cylindrical cavities to get samples of cylindrical shape of 2 to 3 mm width. The 
glass samples were annealed at 150\(^{\circ}\)C for nearly 2 hours. The annealed samples cut 
into discs 2 mm or 3 mm thickness were polished with very fine lapping papers. The 
samples were washed thoroughly with acetone and dried. For the samples used for 
conductivity measurements, a gold coating was deposited on both the polished 
surfaces using a thin film coating unit (Model JFC 1000 of JEOL). All samples were 
stored in a desiccators containing cacl\(_2\) in order to avoid any moisture on the sample 
surfaces prior to the measurements. All measurements were carried out at 
atmospheric pressure. This glass system is used for XRD, chemical analysis and AC 
electrical conductivity characterization.
3. RESULTS AND DISCUSSION

3.1 XRD studies

The X-ray diffractograms showing perfect amorphous nature of the samples are shown Fig.1. The DTA patterns for these glass systems shown in Fig.2 are slightly different when compared to the pristine glass system.

![Fig.1: X-ray diffractogram of 50PbO: 50V2O5](image)

There is a slight change in the $T_g$ along with an increase in the number of crystallization peaks. However up to $x = 15$ mole%, there is only one endothermic peak corresponding to the melting point.

![Fig.2: XRD patterns of xMnO:(50-x)PbO:50V2O5 glass system](image)

This indicates that the substituted samples behave like the eutectic composition up to $x = 15$ mole%, and the endothermic peak corresponding to melting exhibits a small shoulder. When the amount of MnO substitution exceeded 15 mole%, DTA patterns exhibited a splitting of the melting point peak (not included in the present studies) which indicates the probability of new stable phases being present at the time of melting.

3.2 Chemical Analysis

The composition, density and concentration of $V^{4+}$, total vanadium ions and their ratio and average vanadium site separation of MnO substituted lead vanadate
glasses are presented in Table 3.2.1. It can be seen that average vanadium site separation does not change appreciably where as V$^{4+}$ concentration decreases as MnO is substituted for PbO.

Table 3.2.1: Variation of density and concentration of V$^{4+}$ of glass system with MnO substitution.

<table>
<thead>
<tr>
<th>Glass composition (mole %)</th>
<th>Density (gm/c.c)</th>
<th>[V$^{4+}$] $10^{20}$/c.c</th>
</tr>
</thead>
<tbody>
<tr>
<td>V$_2$O$_5$</td>
<td>PbO</td>
<td>MnO</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>50</td>
<td>45</td>
<td>5</td>
</tr>
<tr>
<td>50</td>
<td>40</td>
<td>10</td>
</tr>
</tbody>
</table>

3.3 A.C. Conductivity or Dielectric Measurements

The conductivity studies are useful to understand the transport mechanism of cations in glass system. In the present work, the dielectric constant and loss tangent $\tan \delta$ are measured using HP LF4192A impedance analyzer at 150$^\circ$C and the corresponding graphs are presented in fig.3.

3.3.1 Dielectric constant

It can be elucidated from Fig. 3 that the dielectric constant of the sample increases as MnO substitution increases from 0% to 15% at 150$^\circ$C and as the frequency increases dielectric constant value decreases.

Table 3.3.1 variation of dielectric constant of x MnO: (50-x): PbO: 50V$_2$O$_5$ with MnO at 150$^\circ$C.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\varepsilon(0)$</th>
<th>$\varepsilon(\infty)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5MnO:45 PbO:50V$_2$O$_5$</td>
<td>58</td>
<td>38</td>
</tr>
<tr>
<td>10MnO:40PbO:50V$_2$O$_5$</td>
<td>62</td>
<td>40</td>
</tr>
<tr>
<td>15MnO:35PbO:50V$_2$O$_5$</td>
<td>97</td>
<td>54</td>
</tr>
</tbody>
</table>

(i) 0% MnO (ii) 5%MnO (iii) 10%MnO (iv) 15%MnO
Fig. 3: Variation of dielectric constant as a function of frequency for x \( \text{MnO: (50-x) PbO: 50V_2O_5} \) at 150°C

### 3.3.2 Dielectric loss

It can be seen from Fig. 4 that loss tangent (\( \text{Tan} \delta \)) increases as MnO substitution increases from 0% to 15% at 150°C in the given sample and as the frequency increases loss tangent (\( \text{Tan} \delta \)) decreases.

![Graph showing variation of dielectric constant with frequency](image)

**Fig. 4:** Variation of loss tangent (\( \text{Tan} \delta \)) as a Function of frequency for \( \text{xMnO: (50-x) PbO: 50V_2O_5} \) at 150°C

i) 0% MnO ii) 5% MnO iii) 10% MnO iv) 15% MnO

The dielectric constant \( \varepsilon = \varepsilon' - j \varepsilon'' \) is a complex quantity. The \( \varepsilon' \) is obtained from the observed capacitance from the impedance analyser. \( \text{Tan} \delta \) is the loss factor or loss parameter indicated as D in the impedance analyser. According to Debye's theory we have

\[
\varepsilon' = \varepsilon(\infty) \left[ \frac{\varepsilon(0) - \varepsilon(\infty)}{1 + j\omega \tau_0} \right]^\beta
\]

Where \( \varepsilon (0) \) is static dielectric constant and \( \varepsilon (\infty) \) dielectric constant at very large frequencies. \( \tau_0 \) is the most probable relaxation time of the dipoles in the solid and \( \beta \) is a parameter \((< 1)\) indicative of the spread in the relaxation times around \( \tau_0 \).

### CONCLUSIONS

From X-ray diffractograms, it is observed that the samples are perfect amorphous in nature and from chemical analysis, it can be discerned that as MnO concentration increases in lead vanadate glass system the density and \( V^{4+} \) concentration decreases. In the present \( \text{XMnO: (50-X) PbO: 50V_2O_5} \) (where \( X = 0.5%, 10%, 15% \)) glass system, it is observed that both the dielectric constant and dielectric loss increase as MnO concentration increases.
REFERENCES


15. K.V.Ramesh and D.L.Sastry;


