a c-Conductivity and dielectric study of ferro electric (lead titanate) doped zinc-vanadate-borate glass

S K Ubale

(Department of Physics, Dharampeth M P Deo Memorial Science College, Nagpur 440 010)

and

C S Adgaonkar

Department of Electronics, Institute of Science, Nagpur 440 001

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The dielectric study of glass composition (1-x)[45 ZnO - 5V₂O₅ - 50 B₂O₃] + x [PbTiO₃] where x = 0, 0.02, 0.05, 0.1, 0.15, 0.2 has been carried out at various temperatures. The value of permittivity constant $\varepsilon'$ increases with increasing percentage of the ferroelectric dopant and also increases with temperature. This rise in $(\varepsilon')$ may be attributed to other sources of polarization possibly from enhanced electrode polarization as the temperature rises. It is observed that the ac-conductivity $[\sigma(\omega)]$ is temperature dependent. The results of ac conductivity are discussed on the basis of quantum mechanical tunnelling (QMT) model. Values of the density of states at the Fermi level $N(E_F)$ for all glass samples are finite and of the order of $10^{20}$ eV$^{-1}$ cm$^{-3}$.

1 Introduction

Glasses are amorphous solids which can be prepared with various compositions and properties. They are used in the field of electronics in a variety of applications. Vanadate glasses are used as surface junction detectors by Bausch and Lomb Inc. Iron-vanadium–borate glasses are used by General Electric Co. in making of television camera tubes.

Dhote et al.1 studied transport properties of zinc-bismuth glasses, Chakraborty et al.2 found that BaTiO₃, (ferroelectric material) doped vanadate–bismuth glasses have high permittivity than the undoped glasses. Electrical conduction in these glasses was experimentally studied by Sadhukhan et al.3 and was shown to be due to variable range hopping. Recently, Yawale et al.4 investigated infrared vibration spectra of some borate glasses. The authors have also studied dc conductivity and dielectric properties of another zinc-vanadate-borate glass composition with ferroelectric dopant and found the properties to be influenced by ferroelectric dopant5. The hopping conduction in localized states gives rise to frequency dependent ac-conductivity of semi-conducting oxide glasses. Therefore ac-conductivity measurements are important to characterize the nature of the conduction processes. Temperature dependent ac-conductivity has been reported by many workers6,7 and they used different models to explain this dependence such as quantum mechanical tunnelling, overlapping polaron tunnelling, correlated barrier hopping and hopping over the barrier model etc.

In the present paper, the authors report the dielectric constant and ac-conductivity of zinc-vanadate-borate glasses at temperatures varying between 303-573 K at 1 kHz frequency.

2 Theory

In general the ac-conductivity of the amorphous material, where charge carriers experience an approximately random potential energy on diffusing is found to obey the equation8:

$$\sigma(\omega) = A\omega^s$$  \hspace{1cm} (1)

With $s < 1$ up to frequency of 1 MHz.

According to QMT model, only those pairs of carriers separated by hopping distance $R_i$ given by:

$$RI = 1/2 \alpha \ln (\nu ph / \omega)$$  \hspace{1cm} (2)

contribute significantly to conduction. With this, the equation for ac-conductivity due to QMT is given by9:

$$\sigma(\omega) = n^2 kT |N(E_F)|^{1/2} \alpha^{5/2} \omega \ln (\nu ph / \omega)$$  \hspace{1cm} (3)
where \( N(E_f) \) is density of energy states near the Fermi level, \( \alpha \) is electronic wave function decay constant, \( \nu_{ph} \) is phonon frequency. \( \eta \) is a constant and its values are given by, \( \eta = \pi/3 \) (Ref. 9); \( \eta = 3.66 \pi/6 \) (Ref. 10) and \( \eta = \pi/96 \) (Ref. 11). Though the values of numerical factors are different but while plotting \( \sigma (\omega) \) versus \( T \) the nature of plot remains the same only the value of energy density of states changes. The value of \( \alpha \) is determined by plotting \( \log \sigma_\omega \) against the hopping distance \( R \).

3 Experimental Details

The glasses of composition \((1-x) \) \([45 \text{ ZnO-} 
S\text{V}_2 \text{O}_5-50 \text{ B}_2 \text{O}_3 \] \(+ x[\text{PbTiO}_3] \) where \( x = 0, 0.02, 0.05, 0.1, 0.15, 0.2 \) were prepared by using appropriate amounts of AR grade \( \text{ZnO, H}_3 \text{BO}_3 \) and \( \text{V}_2 \text{O}_5 \) and \( \text{PbTiO}_3 \). The chemicals were mixed thoroughly by repeated grinding. It was subjected to melting in a fire clay crucible at a temperature of \( 950 ^\circ\text{C} \) in a muffle furnace for about 2 hr until a bubble free liquid was formed, the melt was quenched on a steel disc of 1.5 cm diameter. The glasses were immediately annealed at \( 300 ^\circ\text{C} \) for half an hr. The samples were polished using fine lapping paper (100 No.) and a quick drying silver paint was applied to act as electrodes. The samples were again baked at \( 150 ^\circ\text{C} \) for half an hour in order to remove the mechanical stresses due to polishing and for stabilizing the contacts. The amorphous nature of glass was earlier confirmed by XRD. There were no peaks in the XRD which confirmed the amorphous nature of glass. The samples thus obtained were of diameter 1.5 cm and 0.2 to 0.5 cm thickness. The glasses were named as A, B, C, D, E, F for \( x = 0, 0.02, 0.05, 0.1, 0.15, 0.2 \) respectively. The dielectric measurements at constant frequency of \( 1 \) kHz were made on an LCR meter (Aplab 4910D with least count of 0.1 pf) and between temperature range 303-573 K by placing the sample holder in a furnace. The ac-conductivity of the samples at different temperatures was determined by using the relation \( \sigma_\omega = \omega \varepsilon, \varepsilon' \) where \( \varepsilon \) is permittivity of free space. The density of all samples was determined by Archemedes' principle with an accuracy of 0.0001 gm/cc. Benzene was used as buoyant liquid.

4 Result and Discussion

The properties of glass depend not only upon its composition but also to a considerable degree upon its structure. The \( \text{ZnO-V}_2 \text{O}_5-\text{B}_2 \text{O}_3 \) glass with \( \text{PbTiO}_3 \) as dopant has a complex composition. It is an admixture of network former \([\text{ZnO, B}_2 \text{O}_3 \) and \( \text{V}_2 \text{O}_5 \) and a network modifier \([\text{PbTiO}_3 \). Variation in dielectric constant with temperature for all six samples [Fig. 1] shows an overall rise in value of \( \varepsilon' \) with an increase in temperature and also doping percentage. The permittivity constant \( \varepsilon' \) of a material is due to electronic, ionic, dipolar and space charge polarization. Space charge polarization depends upon purity and perfection of glasses. The increased value of dielectric constant may be ascribed to the defects produced in the glass lattice due to introduction of dopant material and also rise in temperature. The value of \( \varepsilon' \) for doped samples is higher than that for undoped sample but the change is not directly proportional to \( x \) value i.e. doping concentration. Fig. 2 shows variation of ac-conductivity with temperature for all samples. There is an overall rise in ac conductivity for all doped samples as compared to undoped sample A (except

![Fig. 1 — Plot of dielectric constant (\( \varepsilon' \)) versus temperature (\( T \)) for zinc-vanadate-borate glasses (A-E)](image-url)
for sample F). The ac-conductivity is temperature dependent at higher temperature for all the samples. Electronic wave function decay constant $\alpha$ was determined from the plot of $-\log \sigma_{dc}$ (at 573 K) versus $R$ (Fig. not shown). It is equal to 1.125 Å$^{-1}$. The dc conductivity plots are not shown here, only its value at 573 K is used. The value of $v_m$ is equal to $10^3$ Hz. Using Eq. (3) value of $N(E_F)$ for all six samples is determined at frequency 1 kHz (Table 1). The values are found to be of the order of $10^{20}$ eV$^{-1}$ cm$^{-3}$ These values are found to be influenced by the ferroelectric dopant. They are found to agree well with the literature values for borate glasses$^{15}$. Same range of values of $N(E_F)$ appear in literature for lead-bismuth glasses$^{16}$ suggesting the localization of states.

![Log vs 1/T](image)

Fig. 2 — Plot of log $\sigma$ versus (1/T) for zinc-vanadate-borate glasses (A-E)

Table 1 — Values of $N(E_F)$ at frequency 1 kHz and temperature 573 K

<table>
<thead>
<tr>
<th>Glass</th>
<th>Austin &amp; Mott</th>
<th>Butcher &amp; Hyden</th>
<th>Pollak +value of $x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.3974</td>
<td>1.4169</td>
<td>6.1273</td>
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<tr>
<td>B</td>
<td>4.5359</td>
<td>1.8918</td>
<td>8.1806</td>
</tr>
<tr>
<td>C</td>
<td>4.6388</td>
<td>1.9347</td>
<td>8.3662</td>
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<tr>
<td>D</td>
<td>4.4184</td>
<td>1.7439</td>
<td>7.5413</td>
</tr>
<tr>
<td>E</td>
<td>4.0864</td>
<td>1.7043</td>
<td>7.3699</td>
</tr>
<tr>
<td>F</td>
<td>3.9026</td>
<td>1.6276</td>
<td>7.0385</td>
</tr>
</tbody>
</table>

+value of $x$ as in glass composition $(1-x)[45 \text{ ZnO} - 5\text{V}_2\text{O}_5 - 50 \text{B}_2\text{O}_3] + x [\text{PbTiO}_3$

5 Conclusion

The dielectric constant $\varepsilon'$ increases with addition of PbTiO$_3$ as a network modifier. The ac-conduction is also influenced by this doping. At higher temperature ac conductivity is strongly temperature dependent for all the glass samples. The range of $N(E_F)$ is found to be of the order of $10^{20}$ eV$^{-1}$ cm$^{-3}$ suggesting conduction in localized states near Fermi level for all six samples. Thus the quantum mechanical tunnelling model satisfactorily explains the results of high temperature ac conductivity of this ferroelectric doped and undoped zinc-vanadate-borate glasses.

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