Effect of ferroelectric (lead titanate) doping on dielectric properties of zinc-borate glasses

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Semi-conducting glasses of the composition (1-x) [50 ZnO -10 V_2O_5 -40 B_2O_3] + x PbTiO_3, where x = 0, 0.1, and 0.2 were prepared in the laboratory by usual quenching method. The dielectric measurements were carried out within frequency range 10-100 kHz and Cole-Cole plots were drawn from which relaxation time for all the three samples was determined.

The dielectric properties are found to be influenced by ferroelectric dopant.

1 Introduction

Glasses are basically amorphous solids. It has been a subject of great interest to produce the ferroelectric doped glasses\(^1\). But this process leads to glasses with micro-crystallization or a glass ceramic. Ferroelectric (barium titanate) doped vanadate-bismuth glasses were prepared by Chakraborty et al.\(^2\). They found that these glasses have higher permittivity than the undoped glasses. Electrical properties of these glasses were studied by Sadhukhan et al.\(^3\). A comparative study of the dielectric properties of undoped and ferroelectric doped vanadate-borate glasses of the following composition (1-x) [50 ZnO -10 V_2O_5 -40 B_2O_3] + x PbTiO_3, where x = 0, 0.1 and 0.2 is reported here.

2 Theoretical Considerations

Dielectric absorption is a measure of energy dissipation in the medium. The expression for dielectric permittivity and loss are given as follows:\(^4\):

\[
e' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2 \tau^2}
\]

\[
e'' = \frac{\omega \varepsilon_0 \varepsilon_\infty}{1 + \omega^2 \tau^2}
\]

where \(\omega\) is the angular frequency (2\(\pi f\)), \(\tau\), a constant with time dimension or relaxation time.

Much of the interest in the dielectric properties of materials is concerned with the frequency region, where dielectric dispersion occurs. The region where the permittivity falls off with rising frequency, because the dipolar polarization can no longer change fast enough, to reach the equilibrium with the polarizing field and the dielectric loss reaches its maximum. The dielectric dispersion covers a wide range of frequency.

3 Experimental Details

Appropriate amount of AR Grade H_3BO_3, ZnO and NH_4VO_4 were weighed on monopan K-Roy balance with an accuracy of 0.0001 g PbTiO_3 used for doping was prepared in the laboratory and its ferroelectric properties were confirmed. They were mixed in an agate mortar, using acetone, for 30 min ensuring complete homogenization and was fired in a muffle furnace at 900 °C for two hours. Glasses were prepared by quenching method in the form of circular discs of diameter 2.5 cm and 0.2-0.4 cm thickness. The glasses were named as A, B and C for \(x\) = 0, 0.1 and 0.2, respectively. The amorphous nature of glass was confirmed by X-ray diffraction. The glasses were annealed for half an hour at 150 °C. Then they were polished using fine emery paper (100 No). A conducting silver paint was applied on both the surfaces and again the glasses were baked for two hours at 150 °C for drying the paint and to remove the mechanical stresses due to polishing. The sample capacitance and dissipation factor were measured at room temperature (303 K) on HIOKI 3520 LCR Hi tester (Japan) with an accuracy of 0.01 pF, for frequency range 10-100 kHz. The dielectric constant \(\varepsilon''\) was determined from the thickness and area of silver electrode.
The dielectric constant and dielectric loss for glasses A, B and C are plotted against frequency (Figs 1 and 2). Dielectric constant increased with doping concentration though the change is not linear with doping and it decreased with frequency (Fig. 1). The overall rise in dielectric constant may be ascribed to defects produced in the lattice. Similar trend was observed by Sadhukhan et al. for vanadate-bismuth glasses doped with barium titanate and Venkateshwar Rao et al. and Rao et al. for fluoroborate glasses doped with PbO and transition metal oxide, respectively. A peak is observed in the frequency dependent curve of dielectric loss (Fig. 2). It is observed that the peak value of loss has increased with doping. Resonance and relaxation types of losses appear in glass under alternating electric fields. The size of each effect depends on the temperature, the frequency of applied field, the composition of glass and its structural arrangement. There is gradual rise in the value of $\varepsilon''$ in the mid-frequency range (Fig. 2).

Whenever the applied electric field alternates at a frequency closer to that one of the constituent atoms, they are excited to high resonant amplitudes accompanied by high dielectric loss. Further in the present case the peak value of loss has increased with doping percentage and PbTiO$_3$ is the dopant used here. Pb$^{++}$ ions are responsible for glasses of high loss. This is Debye type relaxation and a
method of displaying this type of relaxation is by drawing Cole-Cole plots. Cole-Cole plot for A is plotted (Fig. 3) (Cole-Cole plots for B and C are not shown). The plot cuts $\varepsilon'$ axis at high frequency side at an angle of $\left(\frac{\pi}{2}\right)\beta$, where $\beta$ is the spreading factor for relaxation times. The losses observed in glasses do not usually show very sharp maxima. That is why the Cole-Cole plot is not a very well defined semicircle. However, from this plot the value of spreading factor $\beta$ is determined (Table 1). As the value lies between 0 and 1, which confirms the distribution of relaxation time.

Table 1 — Spread factor and relaxation time for glasses

<table>
<thead>
<tr>
<th>Sr No.</th>
<th>$\beta$</th>
<th>$T$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.5</td>
<td>8.147</td>
</tr>
<tr>
<td>B</td>
<td>0.37</td>
<td>8.132</td>
</tr>
<tr>
<td>C</td>
<td>0.24</td>
<td>2.75</td>
</tr>
</tbody>
</table>

Relaxation time for all the three samples is determined and is presented in Table 1. The knowledge of dielectric relaxation time gives better understanding about the intermolecular and intramolecular motion and structure details of a molecule. From Table 1 it can be seen that the magnitude of relaxation time changes very slightly with the doping percentage. The relaxation time depends on the viscosity of the surrounding medium and the shape of molecule. Density of the medium also affects the relaxation phenomenon and the relaxation time. However, here this effect is not seen very prominently. This might be due to very small percentage of dopant used.

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References