Dielectric relaxation studies in some rare earth ions doped vanado-tellurite glasses

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ABSTRACT

Vanado-tellurite glasses containing La and Ce rare earth ions were investigated for dielectric properties in the frequency range 50Hz to 5MHz and temperature range 300K to 500K. The dielectric constant and dielectric loss were found to decrease with increase in frequency in both the series of glasses. Activation energies for dielectric losses derived by employing Hunt's model indicated that the relaxation process has a local character and can be described by hops between each pair of sites. Activation energies for dielectric loss process were found to be in close agreement with dc activation energies. BNN's linear relation between ac and dc conductivities has been verified in both the glass systems. It is for the first time that Hunts and BNN's theories have been verified in rare earth ions doped tellurite glasses.   © 2008 Trade Science Inc. - INDIA

INTRODUCTION

Rare earth ion doped tellurite, phosphate and borate glasses have been mainly investigated for optical applications[1-3]. The optical properties such as refractive index, optical band gap, laser amplification and optical amplification can be enhanced by incorporating rare earth ions such as La, Ce, Nd, Eu, Er, etc., into the glass matrix[4-5]. However, it is interesting to study the electrical conductivity in these glasses to understand conduction mechanisms operated in these systems. The dc and ac conductivity studies in various different types of glasses doped with transition metal ions (TMI) revealed the conduction mechanism in them was due to small polaron hopping[6-10]. One of the most important

properties of TMI doped oxide glasses is that the activation energies associated with the conductivities are identical to that for the relaxation and dielectric processes[11,12]. These studies also confirmed that the same charge carriers are involved in the dielectric losses and the dc conductivity[13].

A correlation between dc conductivity and the dielectric relaxation peak has been established by Barton[14], Nakijama[15] and Namikawa[16] (BNN). Also, Hunt's model correlates the peak frequency in dielectric spectra to the electron transfer between multivalent TMI sites present in the glass network[17]. The applicability of Hunt's theory in the pair approximation regime postulates a linear relation between ac for a given frequency and dc conductivity[18,19]. This relation suggests

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the existence of a single mechanism for all the processes operated in the glass system, probably connected with electron transfer between multivalent TMI sites[17-19].

Dielectric properties of iron and vanadium phosphate glasses containing different glass modifiers have been studied and the data has been interpreted in the framework of Hunt's model[19-20]. Chomka et al[21] reported the conductivity, dielectric properties and internal frictions of Mg, Ca, Ba doped iron-metaphosphate glasses and observed a similar value of activation energy for conductivity, dielectric relaxation and internal friction and concluded that a single mechanism was responsible for all the processes. The ac conductivity behavior in V_2O_5-B_2O_3 glasses was successfully explained using Hunt's and BNN models and showed that the relaxation process has a local character[13]. Using the coupling model, the microscopic activation energy for conductivity relaxation processes were determined in a set of Na_2O-TeO_2-GeO_2 glasses[22]. Though ac conductivity studies on rare earth ions doped tellurite glasses have been reported[23-26], there are no reports on TMI-rare earth ions doped tellurite glasses.

Here we report the studies of dielectric properties of La_2O and CeO_2 doped vanado-tellurite glasses in the following mentioned compositions,

1. $(V_2O_5)_{0.4}$-$(La_2O)_x$-$(TeO_2)_{0.6-x}$, x=0.10, 0.15 and 0.20; labeled as VLT1, VLT2 and VLT3 glasses.
2. $(V_2O_5)_{0.4}$-$(CeO_2)_x$-$(TeO_2)_{0.6-x}$, x=0.10, 0.20 and 0.30; labeled as VCT1, VCT2 and VCT3 glasses.

The present work is aimed at understanding the dielectric relaxation processes and activation energies associated with it and to check whether frequency dependent and independent conductivities can be correlated as per Hunt's and BNN models.

EXPERIMENTAL

Using the analytical grade V_2O_5, La_2O_3, CeO_2 and TeO_2 (Sigma-Aldrich), the glasses were synthesized by melt-quenching technique. The glassy nature was confirmed by XRD studies.

The frequency dependent measurements of capacitance, C, and dissipation factor, tanδ, were obtained using a computer controlled LCR HiTester (HIOKI, 3532-50) for different frequencies in the range 50Hz to 5MHz and temperature from 300K to 500K[23]. The

dielectric constant (ε') and dielectric loss factor (ε") were determined as per the following expressions,

$$\varepsilon'=Cd/\varepsilon_0 A \qquad (1)$$
$$\varepsilon''=\varepsilon' \tan \delta \qquad (2)$$

Where, ε_o is the permittivity of free space, d is thickness of the glass sample and A is cross sectional area of the sample.

RESULTS AND DISCUSSION

Dielectric constant and loss

The dielectric constant, ε', and dielectric loss, ε", were observed to be in the range 5 to 5×10^5 for VLT glasses and 20 to 6×10^5 for VCT glasses. The typical plots of dielectric constant, ε', versus frequency, F, for glasses VLT1 and VCT1 at various temperatures is shown in figures 1 and 2 respectively. It can be noticed that in both the glasses, ε' decreases with frequency and increases with increase in temperature. Similar results were observed in the case of other TMI doped glasses[22-26].
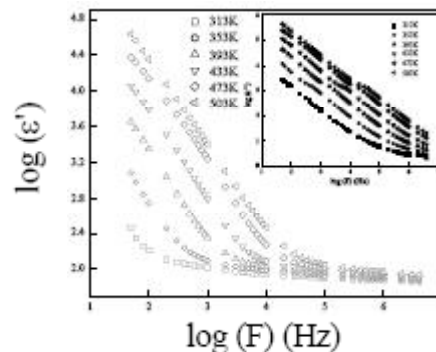

Figure 1 : Plot of log (ε') versus log (F) for the glass VLT1 at different temperatures. Inset shows the frequency dependency of ε" for the same sample

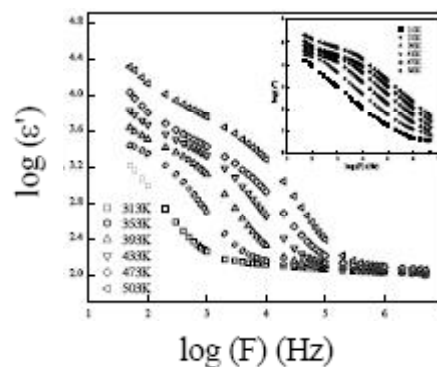**Figure 2 : Plot of log (ε') versus log (F) for the glass VCT1 at different temperatures. Inset shows the frequency dependency of ε" for the same sample**

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The increase of ε'' with increase in temperature is usually associated with the decrease in bond energies, that is, as the temperature increases two effects on the dipolar polarization may occur; (i) it weakens the inter-molecular forces and hence enhances the orientational vibration, (ii) it increases the thermal agitation and hence strongly disturbs the orientational vibrations. The dielectric constant becomes larger at lower frequencies and at higher temperatures, which is normally observed in oxide glasses[27]. This may be due to the fact that as the frequency increases the contribution to the total polarization from ionic and orientation sources decreases and finally disappears due to the inertia of the ions.

Dielectric relaxation process

For present glass systems the Hunt's model is used to study the dielectric relaxation processes, which has been used to the oxide glasses[17-21]. Hunt's model considers two distinct charge migration processes depending on the frequency domains i.e., $\omega < \omega_m$ and $\omega > \omega_m$, where ω_m is the frequency corresponding to the peak in dielectric loss. In these two domains, the total conductivity is expressed as,

$$\sigma_t(\omega) = \sigma_{dc}\left(1 + A\left(\frac{\omega}{\omega_m}\right)^5\right) \text{ for } \omega > \omega_m \tag{3}$$

$$\sigma_t(\omega) = \sigma_{dc}\left(1 + K(d)\left(\frac{\omega}{\omega_m}\right)_r\right) \text{ for } \omega < \omega_m \tag{4}$$

where, $r = 1 + d - d_f$, d being the dimensionality and $d_f = 2.66$[12], A and K(d) are the constants[13].

The frequency dependence of dielectric loss, ε'' for the systems VLT1 and VCT1 at different temperatures are shown as insets to figures 1 and 2 respectively. From these figures it can be inferred that if there was a maximum in dielectric loss in both the glass systems, it would have appeared below the starting frequency i.e., 50HZ. This kind of behavior has been observed in V_2O_5-TeO_2, V_2O_5-P_2O_5 and V_2O_5-B_2O_3 glasses[6-7,13]. Hence, the determination of characteristic frequency ω_m of the dielectric loss for present glasses is not possible. However, it has been demonstrated that the Arrhenius law holds not only for the peak frequency ω_m but also for frequencies lower or higher than ω_m[13,17-21]. The relation between characteristic frequency, f_m, and temperature, T, is expressed as,

$$f_m = f_{mo}\left(\frac{-W_f}{K_B T}\right) \tag{5}$$

From insets of figures 1 and 2 the characteristic frequency values corresponding to some ε'' values at different temperatures have been determined. As per Eq.(5), the reciprocal temperature dependence of characteristic frequency, f_m, for the glasses VLT1 and VCT1 are plotted and shown in figure 3. The data appeared to be perfectly linear in these glasses. The activation energies, W_f, associated with dielectric loss process were calculated from the slopes of the least square linear lines that were fit to the data. The W_f values are presented in TABLE 1 and are of the same size as that of dc activation energies (the dc conductivities were obtained by extrapolating ac conductivity data to zero
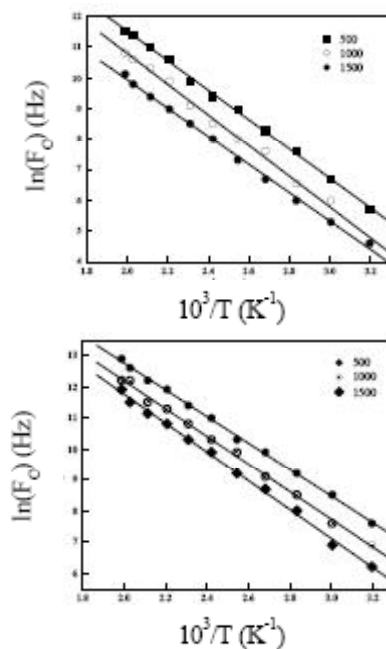
Figure 3 : Variation of characteristic frequency, F_c vs(1/T) for the glass samples (a) VLT1 and (b) VCT1 at different dielectric loss values. Solid lines are the least square linear fits to the data

TABLE 1 : Variation of dc activation energy, W and activation energies W_f associated with dielectric loss processes for VLT and VCT glasses

Code	Glass composition	W (eV)	W_f (eV)
VLT1	$(V_2O_5)_{0.40}$-$(La_2O)_{0.10}$-$(TeO_2)_{0.50}$	0.492	0.495
VLT2	$(V_2O_5)_{0.40}$-$(La_2O)_{0.15}$-$(TeO_2)_{0.45}$	0.533	0.529
VLT3	$(V_2O_5)_{0.40}$-$(La_2O)_{0.20}$-$(TeO_2)_{0.30}$	0.561	0.576
VCT1	$(V_2O_5)_{0.40}$-$(CeO_2)_{0.10}$-$(TeO_2)_{0.50}$	0.387	0.372
VCT2	$(V_2O_5)_{0.40}$-$(CeO_2)_{0.20}$-$(TeO_2)_{0.40}$	0.449	0.441
VCT3	$(V_2O_5)_{0.40}$-$(CeO_2)_{0.30}$-$(TeO_2)_{0.30}$	0.508	0.516
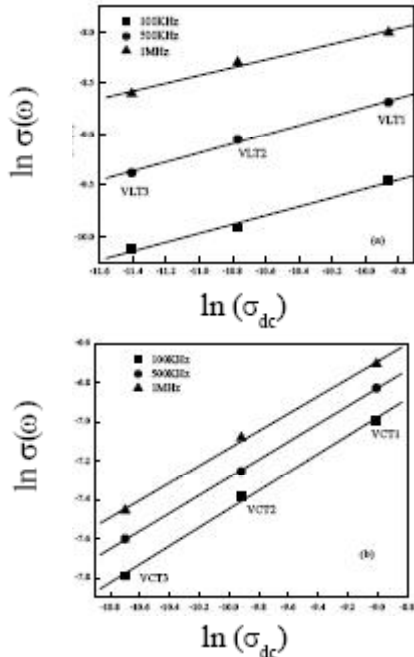
Figure 4 : The plots of ln (σ_{ac}) vs ln (σ_{dc}) for frequency of 1MHz and temperature of 400K for (a) VLT and (b) VCT glasses. Solid lines are the least square linear fits

frequency[23]). Similar result has been reported for V_2O_5-B_2O_3 glasses[13].

According to BNN theory, the dc conductivity is related to the frequency ω_m of the dielectric relaxation peak as[13-16],

$$\sigma_{dc} = 2\pi\omega_m\varepsilon_0(\Delta\varepsilon)p \qquad (6)$$

where p is a constant which is generally taken as unity for the glasses containing TMI and $\Delta\varepsilon=\varepsilon_s$-$\varepsilon_\infty\omega$. From Eq.(5) and Eq.(6) we have,

$$\sigma(\omega) = A(\varepsilon_0\Delta\varepsilon\omega)^s \sigma_{dc}^{1-s} \text{ or } \text{ln}(\omega)= \text{ln}\,k+(1-s)\text{ln}(\sigma_{dc}) \qquad (7)$$

where, $k=(A(\varepsilon_0\Delta\varepsilon\omega)^s$

This expression shows that at a given frequency, the $\sigma(\omega)$ and σ_{dc} are linearly related to each other with a slope (1-s). figures (4a) and (4b) illustrates the linear relation between ln(σ_{ac}) and ln(σ_{dc}) in both the glass systems. Similar behavior was observed between ln(σ_{ac}) and ln(σ_{dc}) for the remaining VLT and VCT glasses. The parameter *s* evaluated from the slopes of the least square linear fits is of the order of 0.60 and 0.46 for VLT and VCT systems respectively. The frequency exponent, s values at 400K, determined using the relation $\sigma=A\omega^s$ have been reported to be in the range 0.52 to 0.60 and 0.45 to 0.53 for VLT and VCT glasses respectively[23]. The fact that frequency exponent de-

termined from different methods are almost same indicates that the Hunt's model is good enough to explain the frequency dependence of conductivity in the present glasses. The study is limited to frequency domain $\omega>\omega_m$ and in this frequency range the relaxation process occurs with a local character and can be described by electronic hops between multivalent vanadium ion sites. Similar conclusions were drawn in[13-19].

CONCLUSION

Two sets of vanado-tellurite glasses containing La and Ce rare earth ions were synthesized following melt quench method and their dielectric properties have been investigated as a function of frequency and temperature. The dielectric constant and dielectric loss decreased with increase in frequency which is ascribed to the decrease in electronic contribution and increase in dipolar contribution to the total polarizability with increase of frequency.

Hunt's model has been invoked to determine the activation energies for dielectric relaxation process and they were found to be in close agreement with dc activation energies and therefore it is concluded that in both VLT and VCT glasses, the relaxation process has a local character implying hops of polarons between multivalent TMI sites.

The BNN's linear relation between frequency dependent and independent conductivity has been verified in respect of both VLT and VCT systems, despite the absence of dielectric loss peaks. It is for the first time that the dielectric properties of rare earth ions doped vanado-tellurite glasses has been analyzed and understood in terms of Hunt's and BNN models and verified.

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