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AC conductivity in rare earth ions doped vanadophosphate glasses

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Abstract Room temperature density and AC conductivity in the temperature range 300–525 K and frequency range 50 Hz to 5 MHz have been investigated in a set of La_2O doped vanadophosphate glasses. The density decreased and total conductivity increased with increase of La_2O content. The high temperature electrical conductivity has been analyzed using Mott's small polaron model and polaron activation energies were determined. The polaron activation energy decreased marginally with increase of lanthanum content, at all frequencies of interest. These results have been attributed to the presence of mixed ion–polaron conduction in the present glasses. It is for the first time that La_2O doped vanadophosphate glasses have been investigated for AC conductivity and despite heaviness of lanthanum ions, the mixed ion–polaron conduction has been detected. Frequency dependence of AC conductivity has been considered under the correlated barrier hopping (CBH) model of single electron hopping.

Introduction

Rare earth ions and/or transition metal ions doped phosphate, tellurite, borate, etc., glasses are mainly explored for optical applications [1–3]. Incorporation of rare earth ions such as La, Ce, Nd, Eu, Er, etc., enhances the optical properties such as refractive index, optical band gap, laser amplification and optical amplification [4–7]. The frequency dependent electrical conductivity in many binary and ternary phosphate, borate, and tellurite glasses containing alkali and transition metal ions [8–15] has been reported. The AC conductivity studies in different rare earth ions doped binary tellurite glasses revealed that the conductivity decreases with the doping of RE ions [12–18]. The decrease in conductivity with increase in atomic weight of rare earth ions has been observed in different rare earth ions doped tellurite glasses and is attributed to the slow mobility of rare earth ions due to their heavy masses [13]. However, tellurite glasses in the composition $80TeO_2$–$20ZnO$ doped with Ho^{3+} ions (0.01, 0.05, and 0.1 g of Ho ions for 10 g of blank glass) exhibited decrease in conductivity with increase in Ho ionic content [14]. This has been attributed to the formation of quasi-molecular complex of rare earth ions with the glass network. Lithium doped molybdate–phosphate glasses have shown increased conductivity with increase of Li ions concentration [15]. The impedance studies in lead–iron doped phosphate glasses revealed that the electronic conduction depends on the easy pathways for electron hopping in a non-disrupted pyrophosphate network [16]. AC and DC conductivities, over a wide range of frequency and temperature, in binary $(CoO)_x\ (P_2O_5)_{1-x}$ and ternary $(CoO)_{40-x}\ (P_2O_5)_{0.55}\ (NiO)_x$ glasses have been reported, and the DC conduction mechanism was explained using Mott's small polaron hopping (SPH) model and the frequency dependent conductivity was explained using correlated barrier hopping (CBH) model [17]. There are no reports on the AC conductivity studies in phosphate glasses doped with rare earth ions. It is of academic and research interest to study electrical conductivity in these glasses to understand conduction mechanisms operated in these systems.

In the present article, we report AC electrical conductivity of vanadophosphate glasses doped with La_2O in the

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composition, $(V_2O_5)_{0.3}$ $(P_2O_5)_{0.7-x}$ $(La_2O)_x$; $x = 0.04$, 0.06, 0.08, and 0.1, labeled as RE1, RE2, RE3, and RE4.

Experimental

The vanadophosphate glasses doped with La_2O were prepared by melt-quenching technique using analytical grade vanadium pentoxide (V_2O_5), lanthanum oxide (La_2O_3), and ammonium dihydrogen phosphate ($NH_4H_2PO_4$). The relevant chemicals in appropriate molar ratios were taken in a porcelain crucible and melted in a muffle furnace at 1,100 K. The melt was quickly quenched by pouring on a stainless steel plate and covering with another stainless steel plate. The random pieces of the glass samples thus formed were collected. In order to relieve mechanical stresses, the samples were annealed at 450 K. The glassy nature of samples was confirmed by XRD studies.

Densities, ρ, at room temperature were measured by following Archimedes principle using a sensitive single pan balance (SARTORIUS). The toluene (density = 0.865 g/cc) was used as an immersion liquid.

The samples of 4 mm in thickness and cross-sectional areas ranging from 30 to 60 mm^2 were cut for frequency dependent conductivity measurement, and the silver electrodes were painted on two major surfaces of the samples. The frequency dependent measurements of capacitance, C, and dissipation factor, $\tan\delta$, were obtained using a computer controlled LCR HiTester (HIOKI, 3532-50) for different frequencies in the range 50 Hz to 5 MHz and temperature from 300 to 525 K. The dielectric constant (ε'), dielectric loss factor (ε''), and AC conductivity (σ_{AC}) were determined as per the following expressions [16]:

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A} \tag{1}$$

$$\varepsilon'' = \varepsilon' \tan\delta \tag{2}$$

$$\sigma_{AC} = \omega\varepsilon_0\varepsilon'' \tag{3}$$

where ε_0 is the permitivity of free space, d is thickness, and A is cross-sectional area of the sample.

Results and discussion

Density

The densities of the present glasses were found to be in the range 3.44–2.94 g/cm^3 (Table 1) and were found to decrease with increase in La_2O content. The decrease in density of present glasses indicates that the glass network will become increasingly loose packed with increase in La_2O concentration. Vanadium doped glasses have been reported to form close packed structure with the increase in VO_4 polyhedra unit concentration [18] and loose packed structure with increase of VO_5 polyhedra unit concentration [18, 19]. The decrease in density of present glasses with increasing La_2O concentration indicates an increase in VO_5 polyhedra unit concentration.

Conductivity

The AC conductivity of all the samples at different frequencies was estimated using Eq. 3. The following results have been noted from the conductivity data.

(i) Conductivity of all the samples in the frequency range studied increases with increase in temperature, which reveals that the present samples are electronically semiconducting in nature.
(ii) Within the studied temperature range, the conductivity varied in the range of 10^{-4}–10^{-7} ohm^{-1} m^{-1}.
(iii) The measured AC conductivity of all the samples in the temperature range studied is found to be greater than that of their DC conductivity.
(iv) In the frequency range studied, the conductivity increased with increase in frequency indicating dispersive behavior of conductivity.
(v) The conductivity at all studied frequencies increased with increase in the rare earth ion concentration giving an indication that there is also ionic contribution to the conductivity in addition to electronic. Variation of Conductivity with La_2O content at 10 kHZ and temperature 450 k are tabulated in Table 2.

The temperature dependence of conductivity has been analyzed in the light of Mott's SPH model. According to this model [20, 21], the electrical conductivity in non-adiabatic regime is expressed as

$$\sigma = (\sigma_0/T)\exp(-W/k_BT) \tag{4}$$

where W is the activation energy, and σ_0, the pre-exponential factor, is given as

$$\sigma = v_0Ne^2R^2C(1-C)\exp(-2\alpha R)/k_B \tag{5}$$

where $v_0 = (\theta_D k_B/h)$ is optical phonon frequency [22], $\theta_D = 2T_D$ is Debye's temperature, N is the concentration of transition metal ions, R is mean spacing between the TMI given as $R = N^{-1/3}$, α is the tunneling factor, and C is fraction of reduced TMI concentration to that of total TMI concentration. The estimated values of N and R for the present glasses are presented in Table 1. From the table it can be seen that the value of R slowly increases with increase in rare earth ion concentration. This means that

Table 1 Measured room temperature density, ρ, and estimated values N and R for the RE glasses

Sample	Composition in mole fractions			ρ (±0.090) (gm/cm^3)	$N \times 10^{21}$ (10^{21} cm^{-3})	R (nm)
	V_2O_5	P_2O_5	La_2O			
RE1	0.30	0.66	0.04	3.442	6.84	0.527
RE2	0.30	0.64	0.06	3.277	6.51	0.536
RE3	0.30	0.62	0.08	3.110	6.18	0.545
RE4	0.30	0.60	0.10	2.946	5.85	0.555

Table 2 Conductivity of the studied glasses at 10 kHz and temperature 450 K

Glass	RE1 $\times 10^{-5}$	RE2 $\times 10^{-5}$	RE3 $\times 10^{-5}$	RE4 $\times 10^{-4}$
σ (ohm^{-1} m^{-1})	(2.01 ± 0.04)	(3.40 ± 0.08)	(8.20 ± 0.25)	(1.70 ± 0.03)

polaron conduction has to decrease with increase in La_2O concentration. However, the measured total conductivity has been observed to be slowly increasing with increase in La_2O content implying that there is an additional contribution to the total conductivity coming from lanthanum ions.

The plots of $\ln(\sigma T)$ versus $(1/T)$ were made for the present glasses at 10 kHz, as per Eq. 4 and shown in Fig. 1. To compare AC and DC conductivities, DC conductivity as a function of temperature has been extracted by extrapolating AC conductivity data to zero frequency and shown in Fig. 3. In the figure, it can be noticed that DC conductivity lies below AC conductivity curves. It can also be observed that the curves are linear at high temperature and non-linear at low temperature region. The least square linear lines were fit to the data corresponding to the temperature above 425 K, using Origin graphics version 6.1. The correlation coefficient for these linear fits was between 0.98 and 0.99. From the slopes of the linear lines, the activation energies, W, were determined. For example, the activation energies at 10 kHz were obtained to be in the range of 0.57 eV to 0.52 eV and found to decrease marginally with increase in the rare earth ion concentration (Fig. 2). Similar result has been obtained when the data corresponding to different frequencies were analyzed. As per the variation of R (see Table 1), the conductivity has to decrease and activation energy of polarons has to increase with La_2O. However, the measured conductivity increased by an order of magnitude and activation energy remained constant or decreased negligibly with increase of La_2O. Therefore, it can be argued that there is an ionic contribution to the total conductivity in addition to electronic.

The plots of $\ln(\sigma T)$ versus $(1/T)$ for all the samples at different frequencies were plotted, and linear lines were fit to high temperature data as shown in Fig. 3 for sample, RE3. In the figure, the solid lines shown are the least square linear fits to the high temperature data. The activation

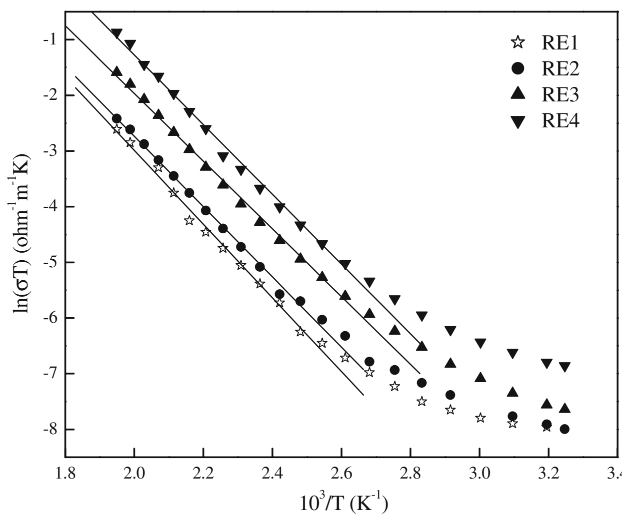

Fig. 1 Plots of $\ln(\sigma)$ versus $(1/T)$ at 10 kHz for the glasses RE1, RE2, RE3, and RE4

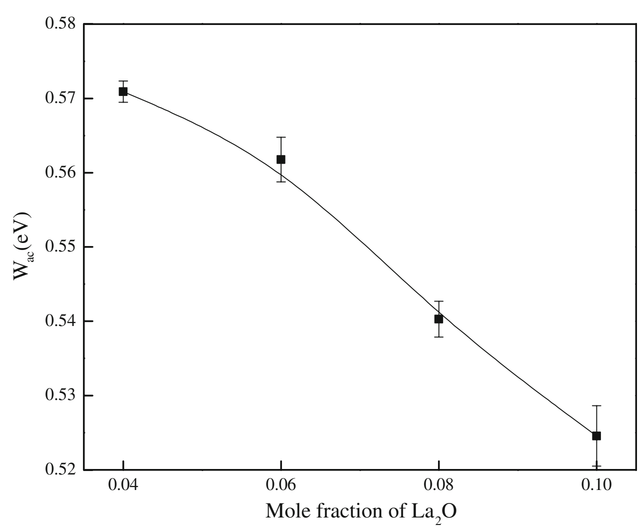

Fig. 2 AC activation energy, W_{AC}, versus mole fraction of La_2O at 10 kHz. Line drawn is a guide to the eye

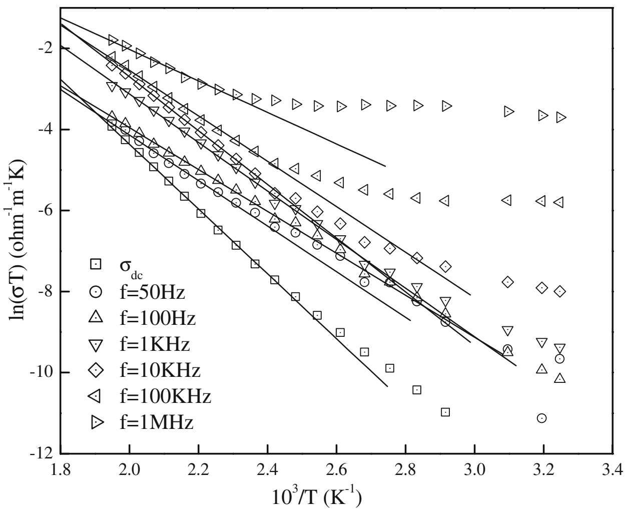

Fig. 3 Plots of ln(σ) versus (1/*T*) at different frequencies for the glass RE3. The solid lines are the least square linear fits to the data

energies thus determined for different frequencies were in the range of 0.31–0.63 eV and observed to be decreasing with increase in frequency. This is in agreement with the reported results on many glasses [15–17].

The frequency dependency of the electrical conductivity analyzed using the general relation [23],

$$\sigma_{AC}(\omega) = A\omega^s \quad \text{or} \quad \ln\sigma_{AC}(\omega) = A + s\ln(\omega) \qquad (6)$$

where *A* is a temperature dependent constant and *s* is the frequency exponent.

Equation 6 has been found to be applicable for all low mobility amorphous and crystalline materials [23]. The frequency dependence of AC conductivity at different temperatures is shown in Fig. 4 for the sample RE4. Similar nature of variation of ln(σ) with ln(*f*) has been observed for remaining samples. In Fig. 4, curves appear to be linear over wide range of frequency at lower temperatures and short range of frequency at high temperatures. This observation is in agreement with [15–17]. On each curve, in Fig. 4, least square linear lines were fit to the data over the range of frequency in which the linear behavior is observed. The slopes of the least square fit lines gave directly the frequency exponent, *s* values.

The values of frequency exponent *s* for all four samples determined to be in the range 0.94 and 0.33. These ranges of *s* values indicate that the carrier transport is predominantly due to hopping of electrons [14].

Owen [24] reported that the electrical properties of glasses in an alternating field depend not only on the mobile ions but also on the relatively immobile ions, which also take part in network forming. Several authors [22, 25, 26] have evaluated the AC conductivity for single electron motion undergoing quantum mechanical tunneling (QMT). In this model [22], prediction was made to the effect that the conductivity is linearly dependent on temperature and the frequency exponent; *s* is independent of temperature but frequency dependent. However, it can be clearly seen from the Fig. 5 that the frequency exponent *s* decreases with increase in temperature, thereby conflicting with the prediction of QMT model.

Elliott's CBH model relates potential barrier to the inter site separation. At a site separation *R*, the column well overlaps between the neighboring hopping sites, resulting in lowering of the effective barrier from W_M to *W*, which for two-electrons case is given by [27, 28],

$$W = W_M - \frac{4ne^2}{\varepsilon R} \qquad (7)$$

where W_M is the maximum height of the energy band, ε is the effective dielectric constant, *n* is the number of

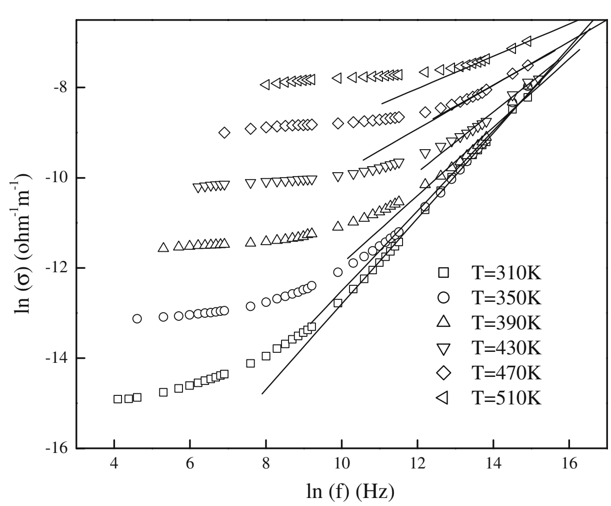

Fig. 4 Plots of ln(σ) versus ln(*f*) for the glass RE4 at different temperatures

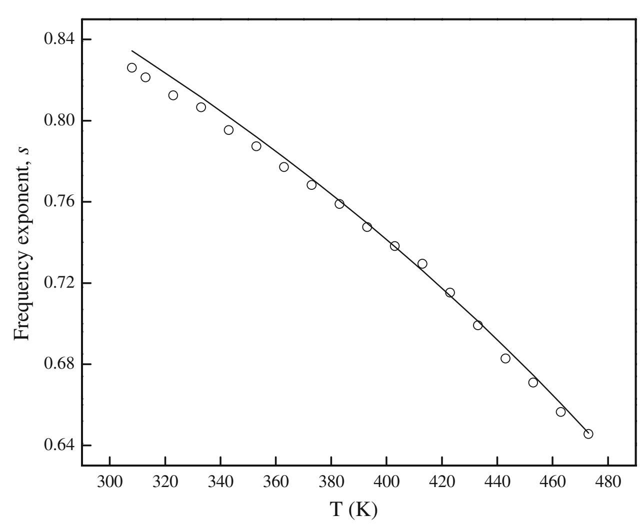

Fig. 5 Temperature dependence of frequency exponent *s* for the sample RE4. Solid line is fit to the correlated barrier hopping model

electrons that hop (in case of glasses, $n = 2$), R is the distance between the hopping sites.

According to the CBH model, the frequency dependence of conductivity is expressed as

$$\sigma_{AC} = \left[\frac{\pi^2 N^2}{24}\varepsilon\left(\frac{8e^2}{\varepsilon W_M}\right)\frac{s}{\tau_0^{\beta}}\right] \quad (8)$$

where N is the concentration of localized states, and β is the stretching parameter given as

$$\beta = 6k_BT/W_M \quad \text{and} \quad s = 1 - \beta$$

The frequency exponent, s, for CBH model is evaluated as per [29],

$$s = 1 - \frac{6k_BT}{W_M + k_BT\ln(\omega\tau_0)} \quad (9)$$

where τ_0 is the characteristic relaxation time.

As per Eq. 9, frequency exponent s is temperature dependent, which is one of the predictions of CBH model. Equation 9 was fit to the experimental values of frequency exponent, s as a function of temperature for all the samples. The W_M and τ_0 were used as variable parameters in the fit. This nonlinear analysis gave W_M values in the range of 1.22–1.63 eV and τ_0 values in the range of 10^{-12}–10^{-13} s, for all the samples. These results are reasonable and agree with that reported in [29]. A representative plot of CBH model fit to measured frequency exponent for sample RE4 is shown in Fig. 5. It can be observed from the figure that the measured frequency exponent values are in agreement with the CBH model of single electron hopping. This confirms the fact that CBH model is adequate to explain the frequency dependence of conductivity of the present glasses.

Conclusion

Lanthanum doped vanadophosphate glasses were investigated for density and frequency dependent electrical conductivity as a function temperature. Density decreased with increase of lanthanum concentration. The estimation of mean distance, R, between vanadium ions as a function of La_2O content hinted at decrease of polaron conduction with increase of La_2O concentration. However, the measured total conductivity increased with increase of La_2O content.

Polaron activation energies at high temperatures derived by fitting data to Mott (SPH) model were found to decrease slowly with increase of La_2O concentration. Based on these results it is concluded that the mixed conductivity due to polarons and lanthanum ions is present in these glasses.

The frequency dependent conductivity has been explained by CBH model as the frequency exponent, s values due to CBH model, agreed with the experimental values of s. The CBH model fit gave reasonable values for barrier height and relaxation time.

It is for the first time that La_2O doped vanadophosphate glasses have been investigated for AC conductivity over a wide range of frequency and temperature, and despite heaviness of lanthanum ions, the mixed ion–polaron conduction has been detected in these glasses.

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