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Abstract. The AC electrical properties of the glasses of compositions $(PbO)_{100-x}(Fe_2O_3)_x$, where $x = 5$–30 mol% are reported in the temperature range 90–300 K and in the frequency range 0.4–100 kHz. The experimental data have been analysed in the light of theoretical models proposed for AC conduction in semiconducting glasses. Analysis shows that classical hopping of electrons over a barrier can adequately explain the temperature and frequency dependence of the AC conductivity and its frequency exponent. Reasonable values of the relaxation time and barrier height have been obtained from the fits of the experimental results to the model.

1. Introduction

Extensive studies on the electrical properties of semiconducting glasses (both chalcogenides and transition-metal ion glasses) have been reported [1–4]. Transition-metal oxide glasses show semiconducting properties due to the presence of more than one valence state of transition-metal ions [5]. These glasses are important because of their possible application in the field of threshold and memory switching, cathode materials, etc [6–8]. Although there are papers on the electrical properties of the glasses based on conventional network formers such as P_2O_5 and SiO_2 [5, 9–11], reports are scarce for the transition-metal oxide glasses, in which PbO plays the role of network former [12–14]. Recently, the glass-forming ability, structural and other physical properties [15, 16] of lead iron glass have been reported.

In this report the frequency-dependent conductivity of the lead iron glasses is studied in the temperature range 90–300 K and in the frequency range 0.4–100 kHz. The experimental results are analysed in the light of various theoretical models based on quantum tunnelling and classical hopping of charge carriers.

2. Experimental procedure

The details of glass preparation have been reported elsewhere [15]. Glass samples of composition $(PbO)_{100-x}(Fe_2O_3)_x$ with $x = 5$–30 mol% were prepared from reagent-grade PbO and Fe_2O_3. The mixtures of PbO and Fe_2O_3 were melted in pure alumina crucibles. The melts were kept for 1 h at temperatures in the range 1000–1200 °C depending on composition. Glass samples were obtained by pouring the melts in a copper twin roller. The amorphous nature of the samples was confirmed by x-ray diffraction studies. The final composition of the glass samples were determined by redox titration of the solution of the glass samples in hydrochloric acid [16]. It was observed that the batch composition of the glasses changed slightly due to evaporation loss of the melts during preparation. The

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estimated glass compositions are shown in table 1. The glass samples were annealed at 150 °C to remove mechanical strain if any was present in the samples. Gold electrodes were deposited on both surfaces of the samples by vacuum deposition for electrical measurements. The gold-coated samples were kept at 150 °C (which is below the glass transition temperature) for 2 h to stabilize the gold coating. The AC measurements were carried out in a GenRad (model 1615-A) capacitance bridge in the frequency range 0.4–100 kHz. Measurements were made in the temperature range 90–300 K using a cryostat.

Table 1. Parameters obtained from fits of the AC and total conductivity to the classical hopping model for the lead iron glass compositions.

Glass composition (mol%)		W_M	τ_0	N
PbO	Fe_2O_3	(eV)	(10^{-13} s)	(10^{21} cm^{-3})
72	28	0.81	6.00	1.03
81	19	1.26	3.55	4.70
91	9	1.30	2.00	1.83
95	5	1.64	1.65	3.70

3. Results and discussion

Figure 1 shows, for the 28 mol% Fe_2O_3–72 mol% PbO glass composition, the measured total conductivity $\sigma_{tot}(\omega)$ together with the DC conductivity, σ_{DC} as a function of reciprocal temperature. It is seen from the figure that the DC contribution is significant at low frequencies and high temperatures, while the frequency-dependent term dominates at high frequencies and low temperatures. Similar behaviour was observed for the other glass compositions reported in table 1.

The measured total conductivity $\sigma_{tot}(\omega)$ at a particular frequency ω and temperature can be written as [17]

$$\sigma_{tot}(\omega) = \sigma_1(\omega) + \sigma_{DC} \tag{1}$$

where $\sigma_1(\omega)$ is the real part of the frequency-dependent conductivity and σ_{DC} is the DC conductivity. It is to be noted that equation (1) is valid when the AC and DC contributions arise from completely separate mechanisms; otherwise the DC conductivity represents the AC conductivity in the limit $\omega \to 0$ [18].

A feature common to all amorphous semiconductors and insulators [1] is that the frequency-dependent conductivity obeys the power law

$$\sigma_1(\omega) = A\omega^s \tag{2}$$

where A is a constant dependent on temperature and s is an exponent, generally less than or equal to unity. According to equation (1), the AC conductivity $\sigma_1(\omega)$ of the present glasses was obtained by subtracting the DC contribution σ_{DC} from $\sigma_{tot}(\omega)$. The variation of $\sigma_1(\omega)$ with frequency at several temperatures is shown in figure 2 for the same glass composition as in figure 1. It is seen that the variation in the logarithmic AC conductivity is almost linear with the variation in logarithmic frequency. Other glass compositions also showed similar behaviour. The frequency exponent s was obtained by the least-squares straight-line fit of the experimental data. The temperature variation of s is shown in figure 3 for the 5 mol% Fe_2O_3–95 mol% PbO glass composition. It is clear that s decreases slowly

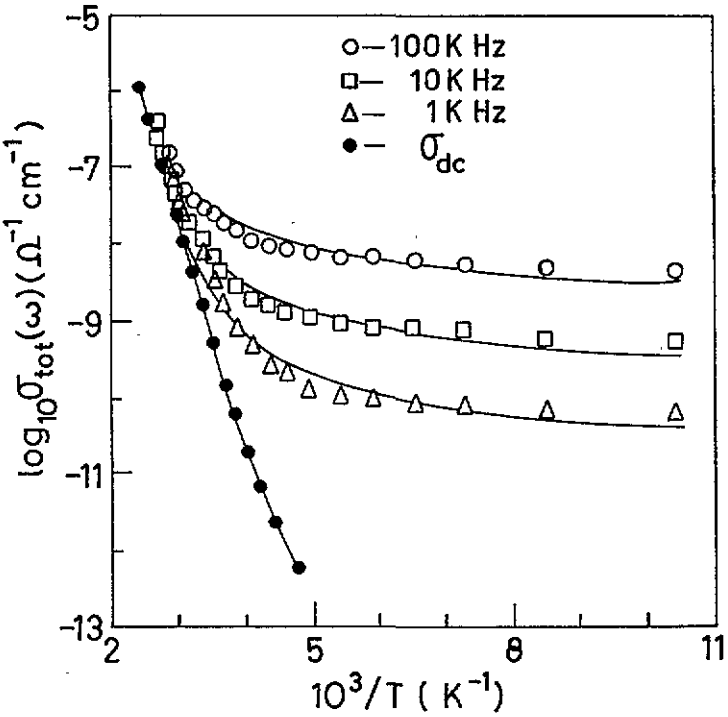

Figure 1. Measured total conductivity $\sigma_{tot}(\omega)$ shown as a function of inverse temperature at three frequencies for the 28 mol% Fe_2O_3–72 mol% PbO glass composition. The measured DC conductivity is also shown. The solid curves are the theoretical fits to the AC conductivity (equation (7)) predicted by the classical hopping model plus the DC conductivity.

with increase in temperature. It is also seen from figure 2 that there exists no appreciable frequency dependence of s in the investigated frequency domain.

To account for such an AC response of amorphous materials it is generally assumed that the system obeys a Debye-type dielectric response with a distribution of relaxation times [17, 18]. The relaxation occurs by a process involving an activation energy which is related to the disordered structure of the material. The overall conductivity is given by a summation over all contributions of the individual microscopic process acting in parallel. If the distribution of relaxation times τ is $n(\tau) \propto 1/\tau$, then the real part of the AC conductivity obeys a linear frequency dependence. Any deviation from linearity discloses information on the particular type of loss mechanism involved. Different models [17, 18] were developed for different microscopic relaxation processes. In each of the models it is assumed that the relaxation is due to transfer of charge carriers in pairs, i.e. the pair approximation is valid. In essence, two distinct processes have been proposed for the relaxation mechanism: quantum-mechanical tunnelling through a barrier and classical hopping over a barrier of a charge carrier.

The quantum-mechanical tunnelling model [5, 19–21] was developed for that type of material whose DC conductivity exhibited an $\exp(-T^{-1/4})$ temperature dependence believed to result from variable-range phonon-assisted tunnelling between defect states. The expression for the real AC conductivity in this model for tunnelling of electrons is

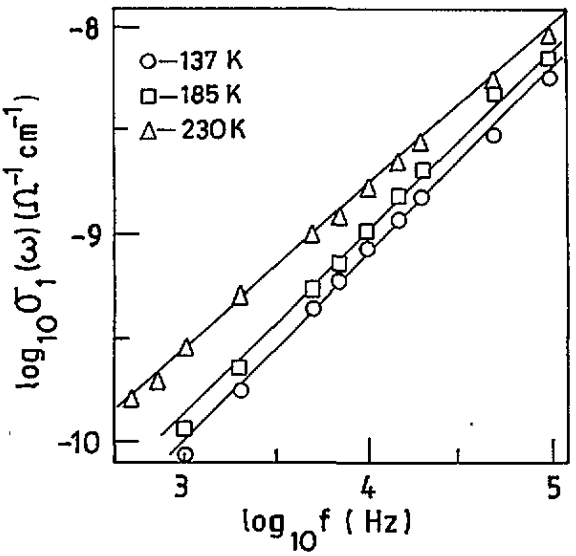

Figure 2. Frequency dependence of the AC conductivity $\sigma_1(\omega)$ for several temperatures shown for the 28 mol% Fe_2O_3–72 mol% PbO glass composition. The solid curves in the figures are the best fits to the classical hopping model (equation (7)).

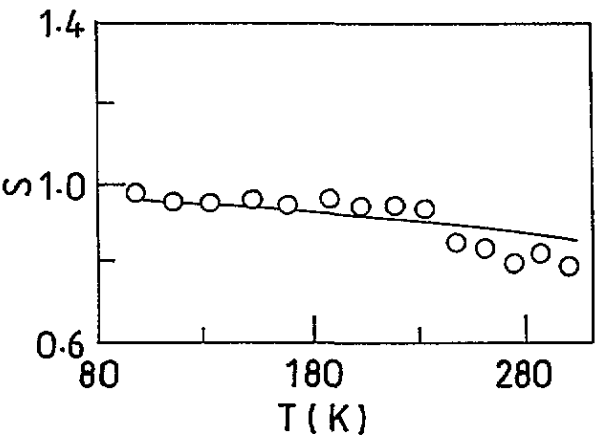

Figure 3. The temperature dependence of the frequency exponent s for the 5 mol% Fe_2O_3–95 mol% PbO glass composition. The solid curve is the fit to the classical hopping model (equation (9)).

expressed as

$$\sigma_1(\omega) = \frac{Ce^2kT}{\alpha}N^2(E_F)\omega R_\omega^4 \tag{3}$$

where $C = \pi^4/24$, $1/\alpha$ is the localization length, $N(E_F)$ is the density of states at the Fermi level and R_ω is the tunnelling distance. The frequency exponent is given by

$$s = 1 - \frac{4}{\ln(1/\omega\tau_0)} \tag{4}$$

where the relaxation time τ_0 is proportional to the inverse phonon frequency. For electron tunnelling, it is seen from equation (3) that the AC conductivity is proportional to T as the

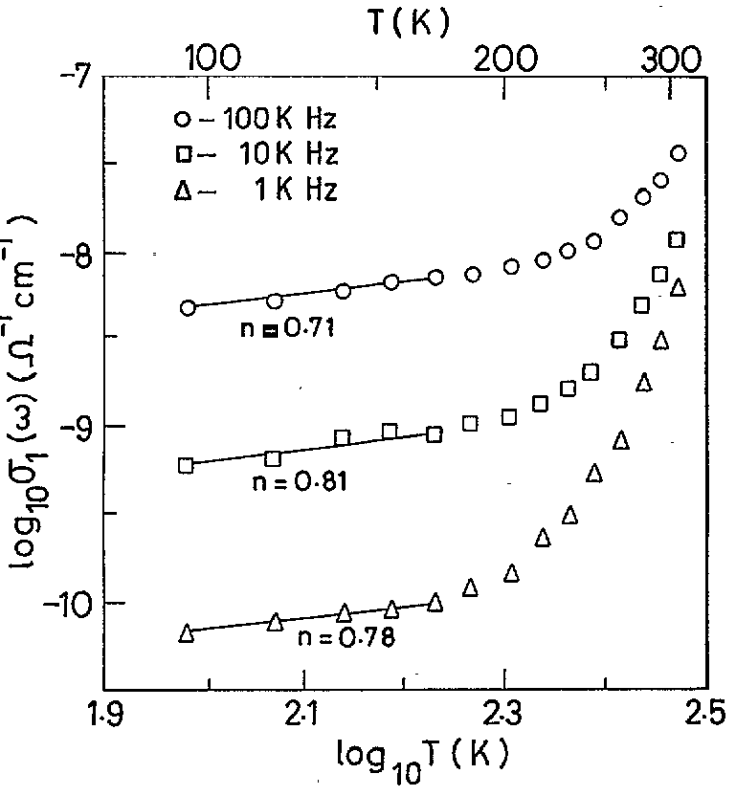

Figure 4. Temperature dependence of the frequency-dependent conductivity for the 28 mol% Fe_2O_3–72 mol% PbO glass composition plotted double-logarithmically for three frequencies.

other parameters are independent of temperature. In figure 4 the variation in logarithmic AC conductivity with the logarithmic temperature for three frequencies is shown for the 28 mol% Fe_2O_3–72 mol% PbO glass composition. It is observed that the conductivity data vary with temperature as $\sigma_1(\omega) \propto T^n$ where n is well below unity in the lowest-temperature range, while n is greater than unity in the higher-temperature range. At intermediate temperatures, $\sigma_1(\omega)$ is linearly dependent on temperature in a short temperature region. Thus the possibility of electron tunnelling as a suitable model to explain the AC conduction in the lead iron glass system is ruled out. This conclusion is further strengthened from the s versus T plot in figure 3. It is observed that s decreases slowly from nearly unity with increase in temperature in contrast with the electron tunnelling model (equation (4)) which predicts a temperature-independent s (equal to about 0.08) [18]. The temperature dependence of s can be met in the tunnelling models if the carrier forms a small or large polaron. The small-polaron tunnelling model [1, 117] is also not a suitable relaxation mechanism because this model predicts an increase in s with increase in temperature in sharp contrast with the experimental observation. Also the large variation in s with frequency as predicted in the small-polaron tunnelling model is absent in this glass system (figure 2). Large-polaron tunnelling is also not applicable for the present glass system, since this model predicts a minimum in the temperature dependence of s which is not observed in figure 3.

The observation that the frequency exponent s of $\sigma_1(\omega)$ is temperature dependent demonstrates that the hopping or tunnelling length R_ω at a particular frequency is a function

of temperature, or in other words it can be said that the effective dipole moment is temperature dependent. In the atomic hopping model [22] the conductivity is calculated as

$$\sigma_1(\omega) = \frac{\pi p_0^2 N k_B T}{6\omega_0 \Delta_0} \omega \tan\left(\frac{\Delta_0}{2k_B T}\right) \tag{5}$$

where N is the concentration of pair sites, p_0 is the dipole moment and Δ_0 is the energy difference between two hopping sites. It is seen that conductivity is strictly linearly dependent on ω. This arises because there is no dependence of hopping distance R_ω on frequency. The value of frequency exponent $s = 1$ in this model rules out the applicability of this model to our glass system. The same argument is true for the atomic tunnelling model [17] also.

In the atomic hopping model it was assumed that the relaxation variable W, the barrier height, is independent of site separation. Pike [23] has lifted this restriction and proposed a model for electron transfer by thermal activation over the barrier between two adjacent sites. These adjacent sites separated by a distance R have Coulomb wells associated with them which overlap, resulting in a lowering of effective barrier height from W_M to W which for the single-electron transition is

$$W = W_M - \frac{e^2}{\pi \epsilon \epsilon_0 R} \tag{6}$$

where W_M is the value for infinite site separation, and ϵ and ϵ_0 are the dielectric constants of the materials and free space, respectively. The AC conductivity [24] in this correlated barrier hopping model for the case of single-electron transfer was calculated as

$$\sigma_1(\omega) = \tfrac{1}{24}\pi^3 N^2 \epsilon \epsilon_0 \omega R_\omega^6 \tag{7}$$

assuming that the centres are distributed randomly in space. The hopping distance R_ω is given by

$$R_\omega = \frac{e^2}{\pi \epsilon \epsilon_0 (W_M - k_B T \ln(1/\omega\tau_0))}. \tag{8}$$

The frequency dependence of $\sigma_1(\omega)$ in this model arises from the factor ωR_ω^6. The temperature dependence of the frequency exponent s arises due to the temperature dependence of R_ω and is given by

$$s = 1 - \frac{6k_B T}{W_M - k_B T \ln(1/\omega\tau_0)}. \tag{9}$$

The temperature variation in s, shown in figure 3, suggests that classical hopping of electron might be a suitable model for the loss mechanism for the lead iron glass system. This is demonstrated in figures 1–3. In figure 2, the real part of the AC conductivity (equation (7)) is fitted by the best-fit method. The solid line is the best fit predicted by this model (equation (7)) to the experimental data. It is seen that the fitting is reasonably good. Other glass compositions also showed similar fits. The parameters obtained from the best fits are listed in table 1. It may be noted that the values of τ_0 obtained from the fits are higher by one order of magnitude than the values of inverse phonon frequency obtained from DC electrical data [16]. This discrepancy is expected due to the important role of the lattice relaxation effects [18]. Table 1 shows that the values of site concentrations obtained from the fits are nearly equal to the iron ion concentrations for lower-iron-content glasses. However, these values are higher than the iron ion concentrations for the higher-iron-content glass compositions. This suggests that, for higher-iron-content glasses, all sites do not take part

in the conductivity mechanism. The values of the parameters obtained from the best fit in figure 2 are used to fit the variation in frequency exponent with temperature in figure 3. The fit is good, further strengthening the classical hopping model as operative in this glass system. In figure 1, the measured total conductivity of the 28 mol% Fe_2O_3–72 mol% PbO glass composition is fitted to the theoretical values of the AC conductivity calculated from equation (7), using the same values of the parameters (table 1) plus the DC conductivity. The same parameters give here good agreement between experimental data and theory. Similar good fits were also obtained for the other compositions listed in table 1 of the lead iron glasses.

4. Conclusion

The frequency and temperature dependences of the AC electrical transport properties of the lead iron glass system have been presented and analysed in the frequency range 0.4–100 kHz and in the temperature range 90–300 K. Analysis of the data shows that classical barrier hopping of electrons between the adjacent sites makes the dominant contribution to the AC loss mechanism in this system. Fits of the model to the experimental data give reasonable values of the parameters.

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