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AC Conductivity of Lead-Tungsten Phosphate Glasses

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AC conductivity of six samples of lead-tungsten phosphate glasses having compositions x mol% PbO-(60-x) mol% WO_3-40 mol% P_2O_5 has been studied at low frequencies in the temperature range 77 K to 300 K. Measured ac conductivity, $\sigma_t(\omega)$ at 1 kHz or at 10 kHz has been observed to decrease with the increase of tungsten ion concentration whereas for 60 mol% WO_3-40mol% P_2O_5 glass values of $\sigma_t(\omega)$ are larger than those for lead-tungsten phosphate glasses. The ac conductivity obeys $\sigma_{ac}(\omega) = A\,\omega^s$ relation over a considerable range of low temperatures. At higher temperatures the ac conductivity starts deviating from linearity and the temperature at which the deviation from linearity starts, increases with increasing frequency. Values of s are slightly greater than unity for glass samples having lead ions concentration larger or equal to the tungsten ion concentration whereas for other samples the values of s are less than unity and the values decrease with the increase of tungsten ion concentration. Theoretical values of 's' are evaluated by applying the hopping over barrier model (HOB). Values of density of states at the Fermi level for different compositions of glasses have the order 10^{19} (assuming α to 0.5 A^{-1}), which suggest that the states are localized near the Fermi level.

Key Words: AC conductivity, Lead, Tungsten, Semiconducting glasses.

INTRODUCTION

The electrical properties of semi conducting glasses have been of considerable interest because of their potential applications as memory switching devices[1,2] cathode materials in batteries[3] and magnetic materials[4]. Transition metal oxide glasses having two different valence states of transition metal ions behave as electronic conductors. The loss of oxygen from the melt produces lower valence transition metal ions. Conduction in these glasses is due electron hopping between high and low valence transition metal ions. An ac conductivity, having a frequency dependence $\sigma_{ac} \propto \omega^s$, with $s \leq 1$, has been observed in many glasses and amorphous semiconductors. The index s has temperature dependence and generally s increases as temperature decreases.

Sakata[5] studied the hopping conduction mechanism in vanadium and iron telluride glasses. Both glass systems exhibit small polaron

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hopping conduction. Singh *et al.*[6] have analysed the dielectric relaxation and ac conductivity of sodium tungsten phosphate glasses using dielectric modulus approach. The present work deals with the effect of doping with lead ions of tungsten phosphate glasses on the ac conductivity and other related parameters.

EXPERIMENTAL

Six samples of lead-tungsten phosphate glasses having different compositions were prepared by melting $Pb(NO_3)_2$, WO_3 and P_2O_5 in a platinum crucible for 1 h at 1200°C in an atmosphere of air. The glass samples were then formed by quenching the melt on a brass plate held at room temperature. The absence of well-defined Laue's spots in the X-ray photograph confirmed the amorphous nature of glass samples. Samples were then grinded and polished into a rectangular shape having the thickness of 1 mm. Samples were given a conducting coating using conducting silver paint. Samples were annealed at 150^0C for about three hours to stabilize the contacts and also to remove mechanical stresses. Relative permittivity and dielectric loss factor were measured using Gen-Rad 1615-A capacitance measuring assembly.

RESULTS AND DISCUSSIONS

Values of $\sigma_t(\omega)$ at 77 K at the frequency of 1 kHz as well as 10 kHz are tabulated in Table 1. These values indicate that the increase of lead ions (or decrease of tungsten ions) leads to the increase of ac conductivity at 77 K for both of the frequencies. However, for 60% WO_3-40% P_2O_5 glass the value of $\sigma_t(\omega)$ is larger than those for all the lead-tungsten-phosphate glasses.

Plots of log of measured ac conductivity ($\log_{10} \sigma_t(\omega)$ *vs.* $10^3/T$) at different fixed frequencies for sample 4 is shown in Fig.1. The values of $\sigma_t(\omega)$ is also higher for higher frequency. At higher temperatures the temperature dependence becomes strong and variation of $\sigma_t(\omega)$ with frequency is small. At still higher temperatures, ultimately the measured conductivities at all frequencies become equal and also equal to dc conductivity.

Plots of $\log_{10} \sigma_{ac}(\omega)$ *vs.* $\log_{10}$ f are shown in Fig. 2 at different temperatures for sample 5 only. At low temperature the ac conductivity obeys the relation $\sigma_{ac}(\omega) = A\omega^s$. The values of exponent 's' determined from the slopes of these plots (called experimental values) at 77 K for all the samples are shown in Table 1. For the samples having dominant ionic conduction (samples having > lead ions concentration ≥ tungsten ions concentration) the values of s are, in general greater than unity. For samples having dominant electronic conduction (tungsten ions

Concentration > lead ions) values of s are less than unity. The values of s decrease with the increase of temperature

TABLE-1
VALUES OF $\sigma_T(\omega)$ AT 77 K AT 1 KHZ AND 10KHZ; $N(E_F)$, EXPONENT S_{EXPT}, S_{THEOR} FOR VARIOUS COMPOSITIONS OF GLASSES

Sample No.	Composition $PbO-WO_3-P_2O_5$	Frequency (kHz)	of $\sigma_t(\omega)$ 77 K (Ω^{-1} cm^{-1})	$N(E_F) \times 10^{19}$ (eV^{-1} cm^{-3})	S_{expt} (77 K)	S_{theor} (77 K)
1.	50%-10%-40%	1	2.07×10^{-11}	5.65	1.02	0.99
		10	2.20×10^{-10}	7.35		
2.	40%-20%-40%	1	1.39×10^{-11}	4.63	1.16	0.96
		10	1.82×10^{-10}	6.68		
3.	30%-30%-40%	1	1.18×10^{-11}	4.27	1.16	0.96
		10	1.70×10^{-10}	6.46		
4.	20%-40%-40%	1	9.12×10^{-12}	3.75	1.02	0.93
		10	9.90×10^{-11}	4.93		
5.	10%-50%-40%	1	7.28×10^{-12}	3.35	0.94	0.91
		10	6.56×10^{-11}	4.01		
6.	0%-60%-40%	1	4.71×10^{-11}	8.52	0.86	0.90
		10	3.45×10^{-10}	9.20		

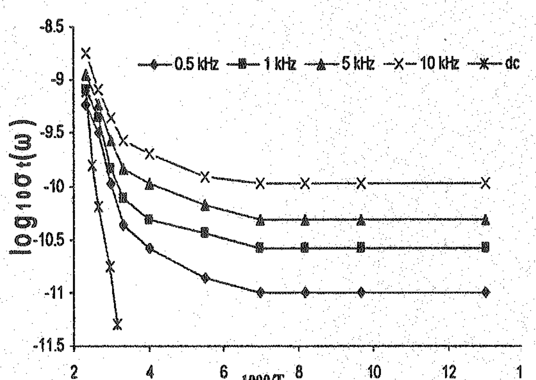

Fig.1. Plots of $\log_{10}\sigma_t(\omega)$ vs. $10^3/T$ for sample 4 at different frequencies

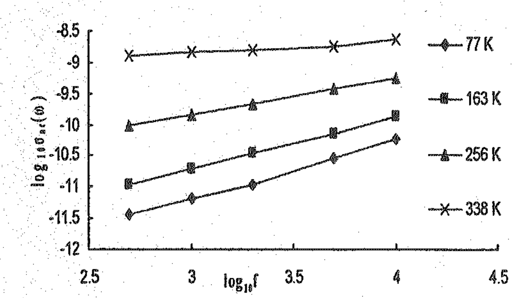

Fig.2. Plots of $\log_{10}\sigma_{ac}(\omega)$ vs. $\log_{10}f$ for sample 5 at different temperatures

Elliot[7] have suggested that such a frequency dependence of conductivity is an outcome of the hopping of charge carriers over the barrier (HOB). HOB model explain the temperature dependence of conductivity and the exponents s is determined from the relation

$$1 - s = 6kT/W \qquad (1)$$

Where k is the Boltzmann's constant and W is the activation energy. These values are denoted as the theoretical values and are inserted in Table1. It is seen that the calculated values of 's' agree within ± 10%

with the experimental values at 77 K. The plot of theoretical and experimental values of s *vs.* temperature for samples 5 and 6 is shown in Fig. 3. Plot show that the theoretical values of s show a decrease with increasing WO_3 concentration as is expected due to the decrease of activation energy with increasing WO_3 concentration. The experimental values of 's' are found to decrease more rapidly than the theoretical values.. It is also noted that the temperature at which the faster decrease in s begins, decrease with increasing content of WO_3 in the glasses.

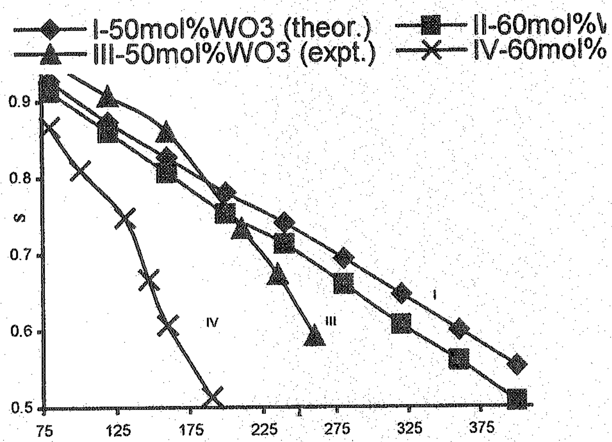

Fig.3. Plots of values of $s_{expt.}$ and $s_{theor.}$ vs. temperature for sample 5 and 6.

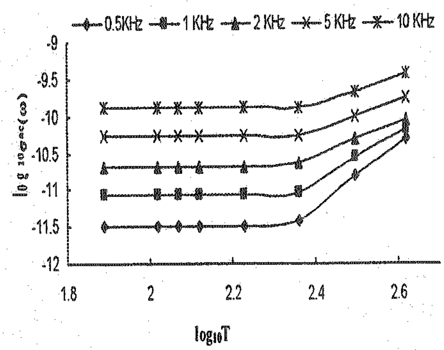

Fig.4. Plots of $\log_{10}\sigma_{ac}(\omega)$ vs. $\log_{10}T$ for sample 5 at different frequencies

Quantum mechanical tunneling model QMT) have suggested by Austin and Mott[8] and Pollak[9] and for single electron motion undergoing QMTthe ac conductivity has been expressed by the relation:

$$\sigma_{ac}(\omega) = (\pi^3/96)\, e^2 kT[N(E_F)]^2\, \alpha^{-5}\omega\, [(in(\nu_0/\omega)/\,]^4 \qquad (2)$$

where $N(E_F)$ is the energy density of states at the Fermi level, the electronic charge (e), the Boltzmann's constant (k)and characteristic phonon frequency (ν_0). This relation can be used to estimate the value of $N(E_F)$ which depends strongly on the values of ν_0 and is comparatively insensitive to the value ν_0 which has been taken as 10^{13} Hz. The value of $N(E_F)$ calculated at 1 kHz as well as at 10 kHz at the temperature of 77 K (assuming α to be $0.5^o\ A^{-1}$) have been inserted in Table 1. The range of $N(E_F)$ is $10^{19}\ (eV)^{-1}\ cm^{-3}$. Such a value of $N(E_F)$ near the Fermi level suggests localized states. Hence the value of α as $0.5^o\ A^{-1}$seems to be the appropriate value which gives the order of $N(E_F)$ as $10^{19}(eV)^{-1}\ cm^{-3}$.

Eq.2 shows temperature dependence of the ac conductivity in the form $\sigma_{ac}(\omega) \propto T^n$ with n = 1. From the plot of $\log_{10}\sigma_{ac}(\omega)$ *vs.* $\log_{10} T$ (Fig. 4) for sample 5, it is observed that the ac conductivity increases linearly with temperature over a considerable range of low temperatures. But at higher temperatures, the value of $\sigma_{ac}(\omega)$ starts deviating from the linearity and the temperature at which deviation from the linearity starts, increases with increasing frequency. This behaviour is similar to that reported for iron-bismuth oxide glasses by Chaudhuri *et al.*[10]

Conclusions

The ac conductivity of six samples of lead-tungsten-phosphate glasses has been studied from 77 to 300 K. The results indicate that the total or measured ac conductivity $\sigma_t(\omega)$ at 1 or 10kHz has been observed to decrease with the increase of tungsten ion concentration whereas for 60 mol% WO_3-40 mol% P_2O_5 glass values of $\sigma_t(\omega)$ are larger than those for lead-tungsten glasses. Values of exponents (from the relation $\sigma_{ac}(\omega) = A\omega^s$) at 77 K are slightly greater than unity for glass samples having lead ions concentration larger or equal to that of tungsten ion concentration whereas for other samples the values of 's' are less than unity and decreases with the increase of tungsten ion concentration. Values of the density of states at the Fermi level for different compositions of glasses have the order 10^{19} eV^{-1} cm^{-3} (assuming α to be 0.5° A^{-1}) which suggest that the states are localized near the Fermi level.

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