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Dielectric relaxation and ac conductivity of sodium tungsten phosphate glasses

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Abstract. Studies of dielectric relaxation and ac conductivity have been made on three samples of sodium tungsten phosphate glasses over a temperature range of 77–420 K. Complex relative permittivity data have been analyzed using dielectric modulus approach. Conductivity relaxation frequency increases with the increase of temperature. Activation energy for conductivity relaxation has also been evaluated. Measured ac conductivity $(\sigma_m(\omega))$ has been found to be higher than σ_{dc} at low temperatures whereas at high temperature $\sigma_m(\omega)$ becomes equal to σ_{dc} at all frequencies. The ac conductivity obeys the relation $\sigma_{ac}(\omega) = A\omega^S$ over a considerable range of low temperatures. Values of exponent S are nearly equal to unity at about 78 K and the values decrease non-linearly with the increase of temperature. Values of the number density of states at Fermi level $(N(E_F))$ have been evaluated at 80 K assuming values of electron wave function decay constant α to be 0.5 (Å)$^{-1}$. Values of $N(E_F)$ have the order 10^{20} which are well within the range suggested for localized states. Present values of $N(E_F)$ are smaller than those for tungsten phosphate glasses.

Keywords. Dielectric relaxation; ac conductivity; glasses.

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1. Introduction

Electrical transport properties of transition metal ion oxide glasses have been studied by different research workers [1–8]. The electron–phonon interaction in these glasses is strong enough to form small polarons and the electrical conduction takes place by the hopping of small polarons from reduced to more oxidized ions. The ac conductivity of tungsten phosphate [9] and iron phosphate glasses [10] and also dielectric dispersion of vanadium telluride [11] and molybdenum phosphate glasses [12] has been studied and the results have been interpreted in terms of different models such as quantum mechanical tunneling (QMT) model and hopping over barrier (HOB) model. Mansingh *et al* [11] have analyzed the complex relative permittivity data using dielectric modulus approach and have evaluated the conductivity relaxation as well as the activation energy. Mansingh *et al* [9] have also reported that the ac conductivity $(\sigma_{ac}(\omega))$ at low temperature is

almost independent of temperature but it shows strong frequency dependence according to the relation $\sigma_{ac}(\omega) = A\omega^S$. Values of the exponent S has been reported to be less than unity. At high temperatures the frequency dependence becomes weak at low frequencies but becomes strong at higher frequencies. If σ_{dc} is subtracted from $\sigma_m(\omega)$ (where $\sigma_m(\omega) = \sigma_{dc} + \sigma_{ac}(\omega)$) then the dielectric dispersion exhibits Debye-type dielectric loss peak. Not much work have been reported on the dielectric relaxation and ac conductivity studies of ternary glasses. The present work, therefore, deals with the study of ac conductivity and the related dielectric properties of three glass samples of sodium tungsten phosphate ternary glasses.

2. Experimental details

Three samples of Na_2O–WO_3–P_2O_5 ternary glass systems having different compositions were prepared by melting appropriate mixture of $NaNO_3$, WO_3 and P_2O_5 in a crucible for 1 h at 1200°C. The glass samples were then formed by pouring the melt on a brass plate held at room temperature. Samples were grinded using different grades of emory powders. Samples were polished to give rectangular shape and were given a conducting coating using silver paint. Then the samples were annealed at 150°C for 3 h to make the contacts stabilized and to free the samples from mechanical stresses. The ohmic contacts were verified from the linearity of V–I characteristics. The amorphous nature of the prepared glass samples were confirmed by X-ray diffraction studies. The absence of well-defined peaks ensured the amorphous character of samples. Measurements of $\varepsilon'(\omega)$, $\varepsilon''(\omega)$ and $\varepsilon_m(\omega)$ were made by measuring the capacitance and conductance of the samples using 1620-A capacitance bridge, 1311-A audio oscillator and 1232-A tuned amplifier and null detector.

3. Results and discussion

3.1 *Dielectric properties*

Values of $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ have been measured in the temperature range of 77–420 K and in the frequency range of 0.4–10 kHz. Plots of $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ vs. temperature T are shown (for sample 3 only) in figures 1 and 2 respectively. Similar plots have been observed for samples 1 and 2 which are not shown here. These plots indicate that the values of $\varepsilon'(\omega)$ increase very slowly at low temperatures. As the temperature rises, the values of $\varepsilon'(\omega)$ increase comparatively rapidly towards higher temperatures. Therefore, at high temperatures and low frequencies, observed values of $\varepsilon'(\omega)$ are seen to be effected by contact polarization as well as by Maxwell–Wagner polarization due to inhomogeneity. However, at lower temperatures, the results do show bulk behavior. Therefore, present analysis has been made at lower temperatures. The trend of present curves are found to be similar to those given for different TMI glasses by Sayer and Mansingh [2] and for copper phosphate glasses by Duran *et al* [13].

Values of $\varepsilon'(\omega)$ at 80 K and at a frequency of 10 kHz for three samples are given in table 1. These values may not be very accurate but these values show comparative change of $\varepsilon'(\omega)$ with the change in concentration. For the first two samples the values of $\varepsilon'(\omega)$ are seen to decrease with the decrease of WO_3 concentration. For the last two samples, the values of $\varepsilon'(\omega)$ increase slightly with increase in concentration of Na_2O.

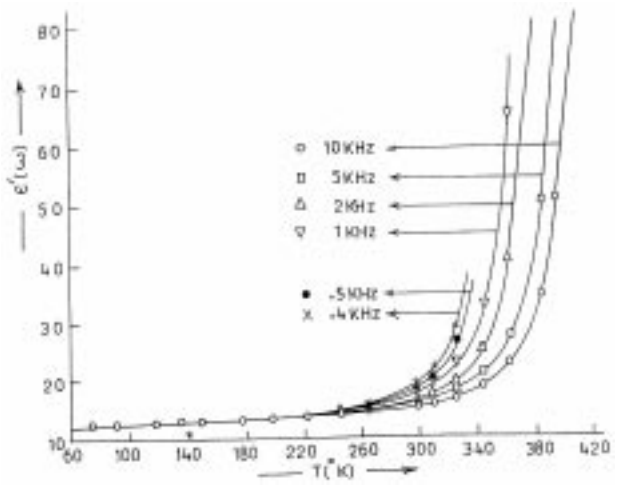

Figure 1. Plot of $\varepsilon'(\omega)$ vs. T (K) for sample 3 at different frequencies.

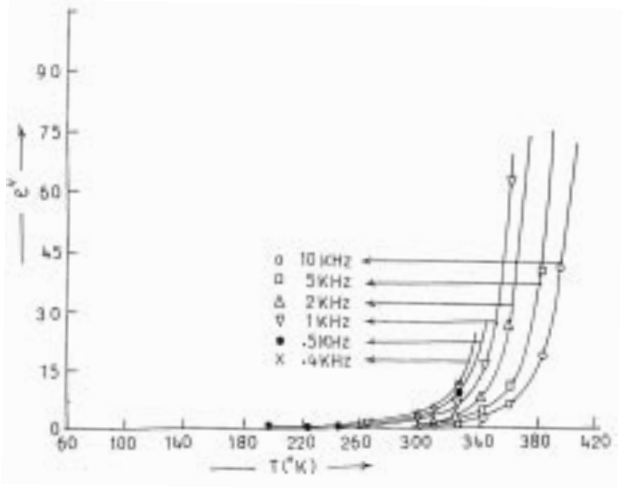

Figure 2. Plot of $\varepsilon''(\omega)$ vs. T (K) for sample 3 at different frequencies.

Table 1. Values of W_c, $\varepsilon'(\omega)$, $\varepsilon''(\omega)$, $\sigma_m(\omega)$ and $N(E_F)$ for different compositions of glasses.

Sample no.	Composition Na_2–WO_3–P_2O_5 (mole %)	W_c (eV)	$\varepsilon'(\omega)$ at 80 K	$\varepsilon''(\omega)$ at 80 K	$\sigma_m(\omega) \times 10^{-11}$ at 80 K for 1 kHz (Ω^{-1} cm^{-1})	$N(E_F) \times 10^{20}$ for $\alpha = 0.5$(Å)$^{-1}$ and at 1 kHz (eV^{-1} cm^{-3})
1	10%–70%–20%	0.51	17.5	0.037	1.78	3.08
2	10%–60%–30%	0.79	10.3	0.023	1.25	2.16
3	20%–50%–30%	0.68	12.5	0.026	1.41	2.44

Plot of $\varepsilon''(\omega)$ vs. temperature T is shown in figure 2 for sample 3. Absence of well-defined peaks in these plots make it difficult to use conventional methods of estimating the relaxation frequency and the nature of dispersion. Therefore, another approach has been adopted using dielectric modulus (M^*) which has been defined by Macedo *et al* [14] as

$$M^* = M' + \iota M'' = 1/\varepsilon^*(\omega) = 1/(\varepsilon' - \iota\varepsilon'')$$
$$= \varepsilon'/[(\varepsilon')^2 + (\varepsilon'')^2] + \iota\varepsilon''/[(\varepsilon')^2 + (\varepsilon'')^2], \quad (1)$$

where M^* and $\varepsilon^*(\omega)$ are complex quantities and $\iota = \sqrt{-1}$. Values of M' and M'' for sample 3 have been plotted vs. temperature which are shown in figures 3 and 4 respectively. Peaks in the plot of M'' vs. T give the temperature at which the measuring frequency is equal to the conductivity relaxation frequency f_c. With the increase of measuring frequency the peaks shift towards higher temperatures. This reveals that when the frequency is high, the temperature at which measuring frequency is equal to f_c is also high. The conductivity relaxation frequency f_c is given by the relation

$$f_c = \nu_0 \exp(-W_c/kT), \quad (2)$$

where ν_0 is the characteristic phonon frequency and W_c the activation energy for conductivity relaxation. Values of W_c have been evaluated from the plots of log f_c vs. 1000/T and are given in table 1 for three samples. These values are somewhat higher than the values evaluated from dc conductivity studies for tungsten phosphate and lead tungsten phosphate glasses [1].

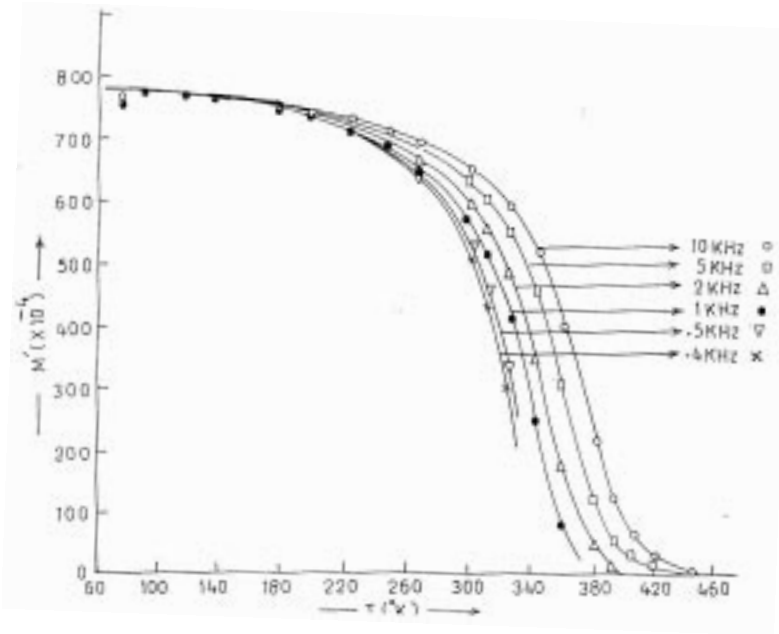

Figure 3. Plot of M' vs. T (K) for sample 3 at different frequencies.

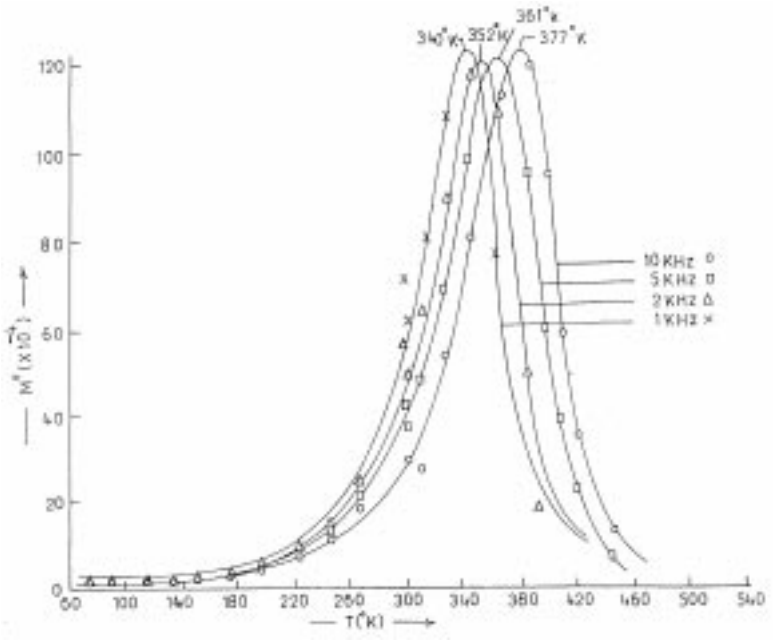

Figure 4. Plot of M'' vs. T (K) for sample 3 at different frequencies.

3.2 *ac Conductivity*

The values of $\sigma_{\mathrm{m}}(\omega)$ at 80 K for 1 kHz frequency for all the three samples are given in table 1. These values vary only slightly with the change in composition and have the same order. Plots of $\sigma_{\mathrm{m}}(\omega)$ vs. $1000/T$ are shown for different fixed frequencies for only sample 3 in figure 5. The overall behavior of the plots is similar to that for other TMI oxide glasses [9–12]. At low temperatures, $\sigma_{\mathrm{m}}(\omega)$ is higher than σ_{dc}. As the temperature increases, the temperature dependence of $\sigma_{\mathrm{m}}(\omega)$ becomes strong. At still higher temperatures $\sigma_{\mathrm{m}}(\omega)$ become equal to σ_{dc} for all frequencies. Similar type of temperature dependence has been observed in other samples with the only difference of temperature at which $\sigma_{\mathrm{m}}(\omega)$ become equal to σ_{dc}. Therefore, these plots for other samples have not been given.

Plots of $\log_{10}\ \sigma_{\mathrm{ac}}(\omega)$ vs. $\log_{10}\ f_{\mathrm{c}}$ at different temperatures for sample 3 are shown in figure 6. At low temperatures, $\sigma_{\mathrm{ac}}(\omega)$ obeys the relation $\sigma_{\mathrm{ac}}(\omega) = A\omega^S$. The values of exponent S determined from the slopes of these plots (called experimental values) at different temperatures for all the samples are given in table 2. These values are roughly equal to or slightly greater than unity at temperatures of 78 ± 1 K. The values of S decrease with the rise of temperature. Pike [15], Elliott [16] and Springett [17] have suggested that such a frequency dependence of conductivity is an outcome of the HOB of charge carriers. HOB model explains the temperature dependence of conductivity and the exponent S is determined from the relation

$$1 - S = 6kT/W, \tag{3}$$

where k is the Boltzmann's constant and W the activation energy. Values of S determined from this relation are denoted as the theoretical values and are given in table 2 for all the samples. The theoretical values of S agree within $\pm$ 10% with the experimental values at $\approx$ 78 K.

Plots of experimental as well as theoretical values of S vs. T are shown in figure 7 for all the three samples. Plots indicate that the theoretical values of S decrease slightly as expected due to the variation of the activation energy. The experimental values of S decrease non-linearly and at a faster rate with the rise of temperature. However, assuming the variation of S with T to be linear, values of $\mathrm{d}s/\mathrm{d}t$ have been evaluated and using these values of slope, values of W have been evaluated as 0.20, 0.29 and 0.46 eV for samples 1, 2 and 3 respectively. These values are lower than the values of W_c given in table 1. These values are seen to increase with the decrease in concentration of tungsten ions.

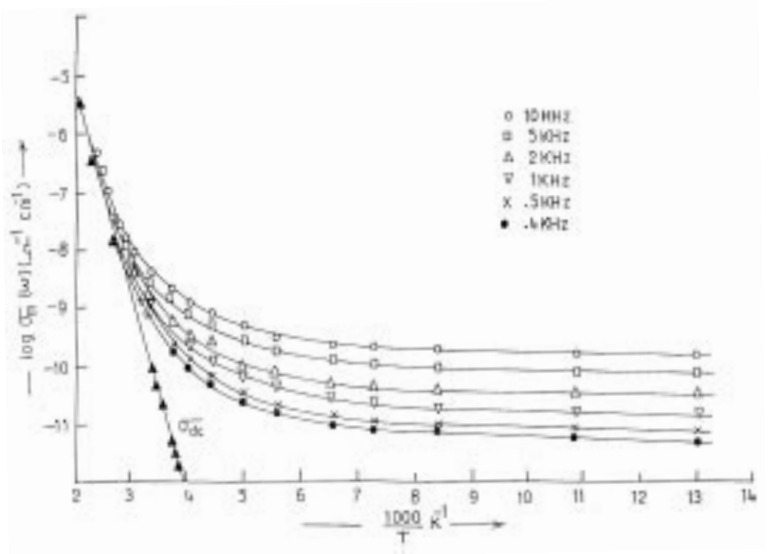

Figure 5. Plot of $\sigma_m(\omega)$ vs. $1000/T$ for sample 3 at different frequencies.

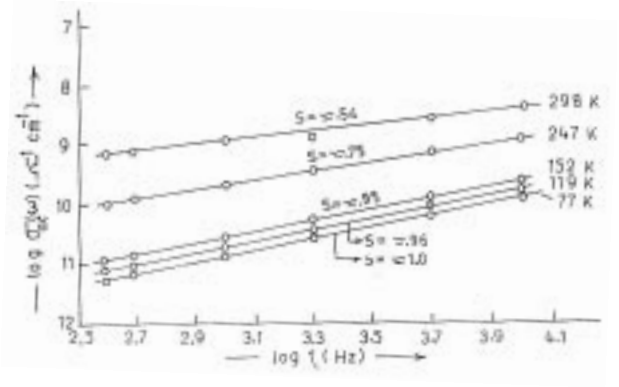

Figure 6. Plot of $\sigma_m(\omega)$ vs. log f_c at different temperatures for sample 3.

Table 2. Values of S (expt. and theor.) for three samples at different temperatures.

Sample no.	Temperature (K)	S	
		Expt.	Theor.
1	78	1.13	0.92
	114	1.00	0.88
	231	0.88	0.76
	261	0.63	0.73
	295	0.38	0.69
2	79	1.04	0.93
	141	0.96	0.88
	194	0.88	0.83
	256	0.75	0.78
	300	0.68	0.74
3	77	1.00	0.94
	119	0.96	0.91
	152	0.95	0.88
	247	0.75	0.81
	298	0.75	0.76

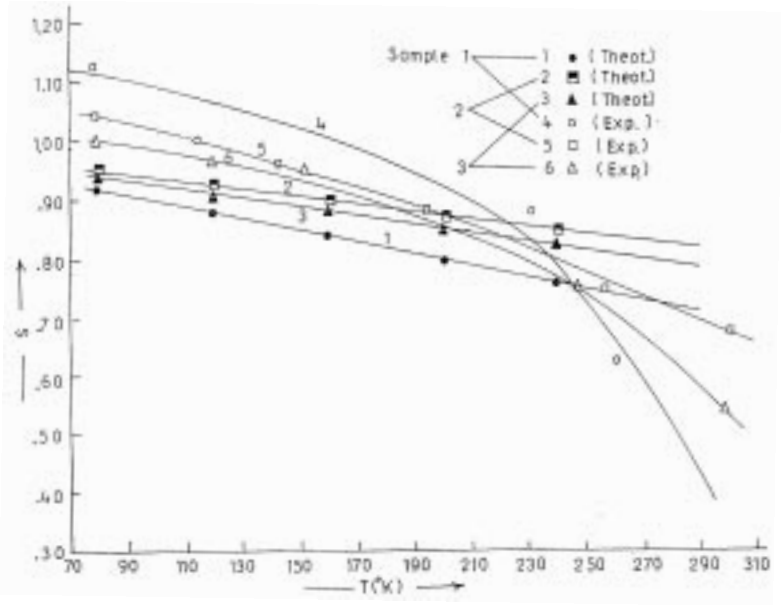

Figure 7. Plot of exponent S vs. T (K) for all samples.

Austin and Mott [18] and Pollak [19] have suggested QMT model for ac conductivity at low temperatures. For single electron motion undergoing QMT the ac conductivity has been expressed by the relation

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

where $N(E_F)$ is the energy density of states at the Fermi level, e the electronic charge, k the Boltzmann's constant and ν_0 the characteristic frequency. This relation may be used to estimate the value of $N(E_F)$ which depends strongly on the value of α and is comparatively insensitive to the value of ν_0 which has been taken as 10^{13} Hz. The value of $N(E_F)$ calculated by using the values of $\sigma_{ac}(\omega)$ at 80 K and $\alpha = 0.5\,(\text{Å})^{-1}$ are given in table 1. These values of $N(E_F)$ are well within the range suggested for localized states. Present values of $N(E_F)$ are smaller than that for tungsten phosphate glasses [9].

4. Conclusions

Complex relative permittivity as well as ac conductivity has been studied for three samples of sodium tungsten phosphate ternary glasses. Values of $\varepsilon'(\omega)$ increase with the increase of tungsten ions whereas its value increases slightly by increasing the concentration of sodium ions and decreasing the concentration of tungsten ions by the same amount. Similar trends have been observed for values of $\varepsilon''(\omega)$. Complex relative permittivity data have been analyzed using dielectric modulus approach. Conductivity relaxation frequency increases with the rise of temperature. Values of W_c have been observed to be higher than the values of activation energy evaluated from dc conductivity studies for tungsten phosphate and lead tungsten phosphate glasses.

Values of $\sigma_m(\omega)$ have the same order for three compositions at 80 K. Experimental values of the exponent S are slightly greater than unity at about 78 K and these values decrease non-linearly towards higher temperatures.

Values of $N(E_F)$ have been evaluated at 80 K assuming the value of α to be 0.5 $(\text{Å})^{-1}$ and these values have the order 10^{20} which are well within the range suggested for localized states. These values of $N(E_F)$ are smaller than that for tungsten phosphate glasses.

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