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Electrical properties and infrared spectra of TeO_2–Fe_2O_3 glasses

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The d.c. and a.c. electrical properties on TeO_2–Fe_2O_3 glasses with various compositions of PbO, B_2O_3 and SiO_2 were studied over a frequency range of 10^2–10^5 Hz and in the temperature range 300–500 K. The a.c. conductivity is proportional to w^n, and the conduction mechanism is due to an electronic hopping process. The effects of composition and temperature on the dielectric constant and loss factor ($\tan\delta$) were studied. The infrared absorption spectra of these glasses reveal that the addition of PbO, B_2O_3 and SiO_2 of these glasses does not introduce any new absorption band in the infrared spectrum of TeO_2–Fe_2O_3 glasses. These results prove the distribution of TeO_4 polyhedra which determines the network and basic oscillation of the building units in the tellurite glasses.

1. Introduction

Oxide glasses containing transition metal ions with different valence states are categorized as amorphous semiconductors. The low valency transition metal ions are produced by the loss of oxygen during melting of oxides [1–4]. Electrical conduction in these glasses occurs mostly by the hopping of electrons (or polarons) from an ion of low valency to ions of high valency states of the transition metal [1, 5]. At low temperatures and frequencies, the a.c. conductivity of these glasses shows characteristic frequency-dependent features similar to hopping conduction [6, 7]. The mechanism of hopping conduction at high temperatures has been discussed quantitatively by Austin & Mott [1] who proposed a theoretical relationship between conductivity and temperature, by considering the probability that an electron moves from one site to the adjacent one with the aid of phonons. The theory they suggested has been applied to analyse the electronic conduction of various glasses containing transition metal oxide, and fruitful results have been obtained [8–11].

Glasses containing Fe_2O_3, as well as V_2O_3, are semiconducting glasses whose electrical properties and mechanism of electronic conduction have been investigated extensively. Among the Fe_2O_3-containing glasses, tellurite glasses are known to show electrical conductivity several orders of magnitude higher than silicate, borate and phosphate glasses containing the same amount of Fe_2O_3 [12, 13]. This phenomenon has been speculatively attributed to the existence of a lone pair of electrons in the equatorial position of the TeO_4 trigonal bipyramid which constitutes the tellurite glass network [14, 15]. Glasses containing PbO are widely used as optical glasses: lead silicates and borates have wide glass-forming ranges. The manner by which a lead ion may be present in the glass network has been studied by many investigators [16].

In the present investigation, the electrical conductivity of TeO_2–Fe_2O_3 glasses containing PbO, SiO_2 and B_2O_3 was measured in order to reveal the conduction mechanism.

2. Experimental procedure

Glasses of composition expressed in mol % of TeO_2–Fe_2O_3, having different compositions of PbO, B_2O_3 and SiO_2 were prepared from the appropriate analytical grade component oxide, as shown in Table I. These oxides were mixed together in a platinum crucible. In order to minimize a tendency to volatization, the mixtures were kept for 3 h in a furnace at 200 °C. The crucible was then transferred to the melting furnace at 800 °C for 30 min. The melt was stirred from time to time. The final glass samples were visually inspected for homogeneity. The glass nature was confirmed by X-ray diffraction (XRD), using Cu-filtered CuK_α radiation.

The infrared spectra were measured as usual using KBr discs. A unicam SP 300 double-beam infrared spectrophotometer operating in the frequency range 200–4000 cm^{-1} was used. The spectra are shown in the range of 300–1100 cm^{-1} as there are no measurable bands above this range.

The d.c. and a.c. electrical conductivity measurements were made in the temperature range of 300–500 K. The contacts were highly conductive silver paste. The silvered sample was mounted in an electrode assembly so that it was gripped between flat discs. The a.c. conductivity measurements were taken in the frequency range of 10^2–10^5 Hz by using lock-in amplifier (Princeton Applied Research) model 126.

3. Results

3.1. X-ray diffraction

The amorphous character of the glasses was investigated by XRD (Fig. 1) which shows no crystallinity in

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TABLE I Some physical parameters of (0.9–x) TeO_2–0.1Fe_2O_3

Glass no.	Composition	Parameter n		Activation energy E (eV) at 1 Kz				V_m (eV)	N (cm^{-3}) at $w = 6.28 \times 10^4 s^{-1}$
		at 10^3 Hz	at 10^4 Hz	at 310 K		at 385 K			
				$E_{d.c.}$	$E_{a.c.}$	$E_{d.c.}$	$E_{a.c.}$		
I	0.8TeO_2–0.1PbO–0.1Fe_2O_3	0.875	1.138	0.475	0.302	0.56	0.337	1.243	3.071×10^{18}
II	0.8TeO_2–0.1B_2O_3–0.1Fe_2O_3	0.921	1.152	–	–	–	–	1.971	7.914×100^{17}
III	0.7TeO_2–0.1PbO–0.1B_2O_3–0.1Fe_2O_3	0.898	1.38	0.334	0.289	0.432	0.466	1.526	1.4×10^{18}
IV	0.75TeO_2–0.1PbO–0.05SiO_2–0.1Fe_2O_3	0.76	1.29	0.453	0.345	0.491	0.3884	0.647	–

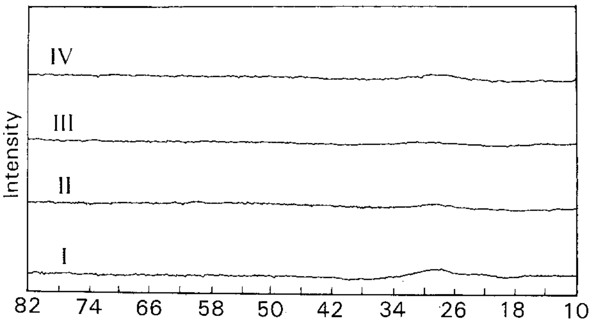

Figure 1 X-ray diffraction patterns of 0.9–$x$$TeO_2$–0.1$Fe_2O_3$ glasses for samples I–IV.

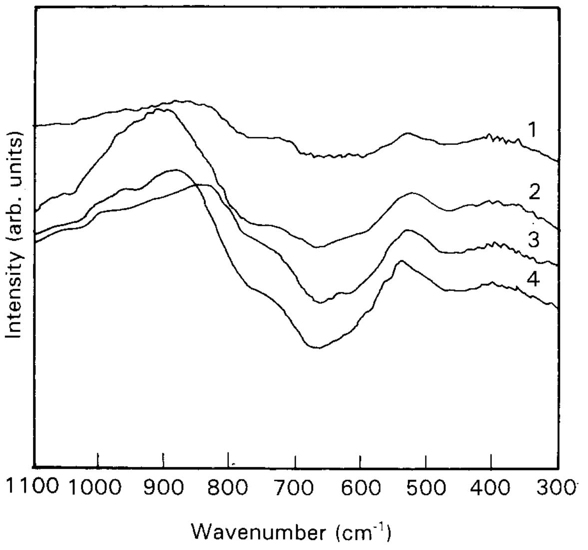

Figure 2 The infrared absorption spectra of 0.9–$x$$TeO_2$–0.1$Fe_2O_3$ glasses. 1, 0.8TeO_2–0.1B_2O_3–0.1Fe_2O_3; 2, 0.7TeO_2–0.1PbO–0.1B_2O_3–0.1Fe_2O_3; 3, 0.8TeO_2–0.1PbO–0.1Fe_2O_3; 4, 0.75TeO_2–0.1PbO–0.05SiO_2–0.1Fe_2O_3.

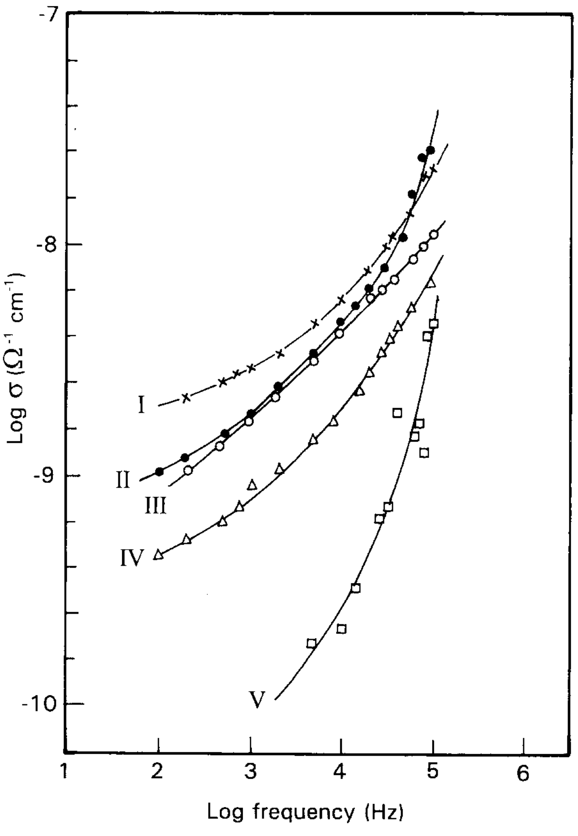

Figure 3 Frequency dependence of $\sigma_{a.c.}$ conductivity for different compositions (samples I–V).

the glass samples and thus confirms the amorphous nature of the sample.

3.2. Infrared absorption

The infrared spectra of glassy materials have been used to explain the structure of glass, and are involved with the type of bonding and arrangement of the atoms in the glass network. The infrared absorption spectra of 0.9–x TeO_2–0.1Fe_2O_3 glasses where X = 0.1PbO; 0.1B_2O_3; and 0.05SiO_2 (Table I) are similar in shape, as shown in Fig. 2. The infrared spectra of the glasses show broad bands at 665 and 460 cm^{-1}, and a shoulder at 780 cm^{-1} which could be attributed to the distribution of the TeO_4 polyhedra [17] determining the form of the network and basic oscillation of the building units in the tellurite glasses. The band at 460 cm^{-1} is due to Te–O–Fe stretching vibrations [17]. The main infrared absorption band at 665 cm^{-1} (which becomes deeper in samples II and III) is attributed to symmetrical vibrations of Te–O bonds.

3.3. Electrical conductivity

The frequency variation of a.c. conductivity can be expressed as

$$\sigma_{a.c.} = Aw^n \qquad (1)$$

where w is the angular frequency, A is a complex and n a parameter ($0.5 \leqslant n \leqslant 1$). This equation is valid for several low mobility amorphous and even crystalline materials [18]. Fig. 3 shows the variation of a.c. conductivity as a function of frequency for different glass compositions, which indicates that conductivity increases as the frequency increases. From this figure it is clear that the binary 0.9TeO_2–0.1B_2O_3 glass has the lower conductivity. The glass composition $0.75TeO_2$–$0.1PbO$–$0.05SiO_2$–$0.1Fe_2O_3$ has a higher conductivity. The value of n changes with the change in frequency and composition. The values of n calculated from Fig. 3 are listed in Table I. An interesting point emerging from these curves is the apparent power-law relationship between a.c. conductivity and frequency.

The frequency dependence of the dielectric constant (ε) for five different compositions at constant temperature (room temperature) are shown in Fig. 4. It is seen that the dielectric constant increases with decreasing frequency. This behaviour is similar to that of V_2O_5–Bi_2O_3 [19] and Fe_2O_3–Bi_2O_3 [4] glasses. The variation of loss factor $\log\tan\delta$ as a function of frequency for different compositions is shown in Fig. 5. As indicated, $\tan\delta$ increases with decreasing frequency and the peaks appear, probably due to relaxation mechanisms.

The logarithms of the conductivity $\sigma(w)$ at 1 KHz for different glass compositions are shown in Fig. 6 as a function of $10^3\ T^{-1}$. The general behaviour of the $\sigma_{\text{a.c.}}(w)$–T curves is very similar to that of the other transition metal oxide glasses [6]. The a.c. conductivity is strong, dependent on the temperature, and is higher than the d.c. conductivity at low temperature. As the temperature increases the conductivity becomes strongly dependent. At high temperatures, the d.c. and a.c. conductivities become almost equal; the temperature at which this phenomenon occurs differs from one composition to another, as shown in Fig. 6. The values of activation energy calculated from the curves are listed in Table I.

The variation of the dielectric constant with temperature for different composition is shown in Fig. 7. It can be seen from these curves that the dielectric constant remains nearly constant over the temperature range 300–400 K, above which it becomes strongly temperature dependent. This is due to polarization as observed from these peaks in the dielectric constant. This behaviour indicates a Debye-type dielectric dispersion [19, 20] characterized by a relaxation frequency. It was observed that the glasses

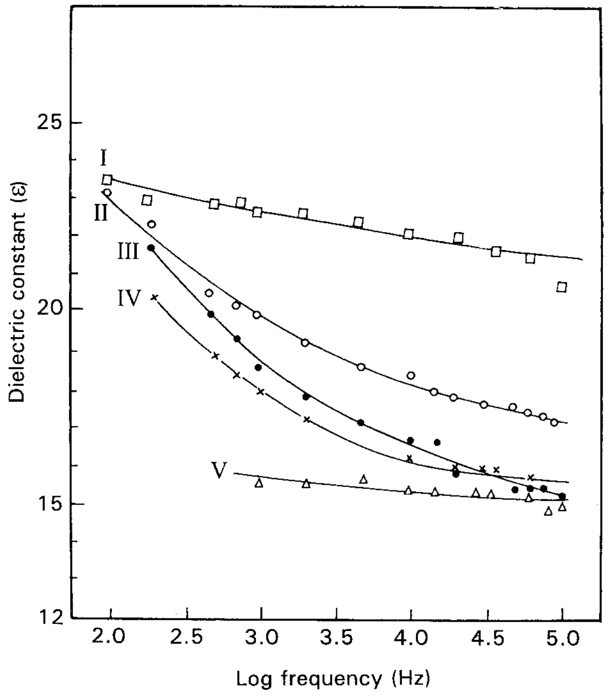

Figure 4 Frequency dependence of the dielectric constant for glass compositions as in Table I (samples I–V).

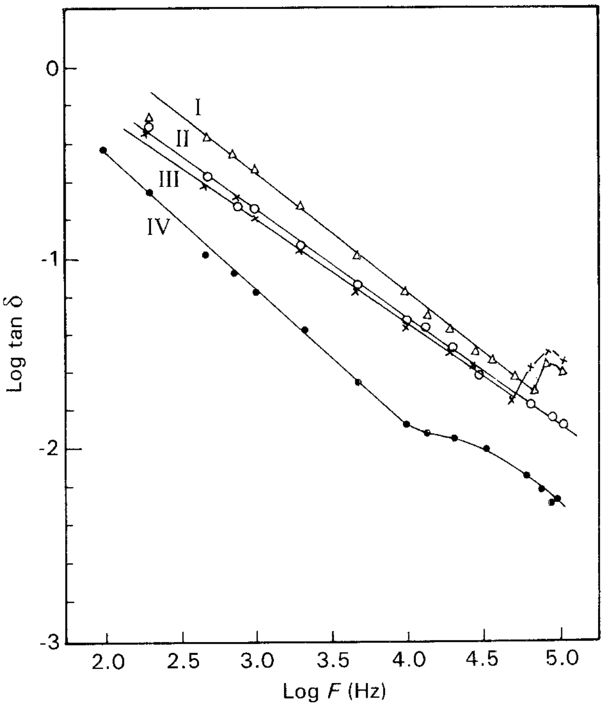

Figure 5 Variation of loss factor $\tan\delta$ with frequency for different compositions (samples I–IV).

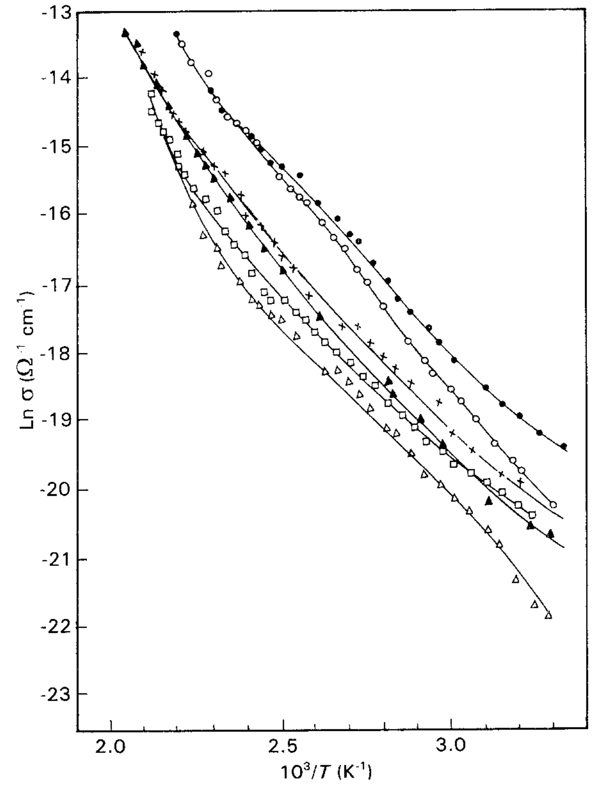

Figure 6 Log σ (d.c. and a.c.) plotted as a function of $10^3\ T^{-1}$ for various glass compositions. $0.7TeO_2$–$0.1PbO$–$0.05SiO_2$–$0.1Fe_2O_3$,$\sigma_{\text{a.c.}}$ (●) and $\sigma_{\text{d.c.}}$ (○); $0.7TeO_2$–$0.1PbO$–$0.1B_2O_3$–$0.1Fe_2O_3$,$\sigma_{\text{a.c.}}$ (×) and $\sigma_{\text{d.c.}}$ (▲); $0.8TeO_2$–$0.1PbO$–$0.1Fe_2O_3$, $\sigma_{\text{a.c.}}$ (□) and $\sigma_{\text{d.c.}}$ (△).

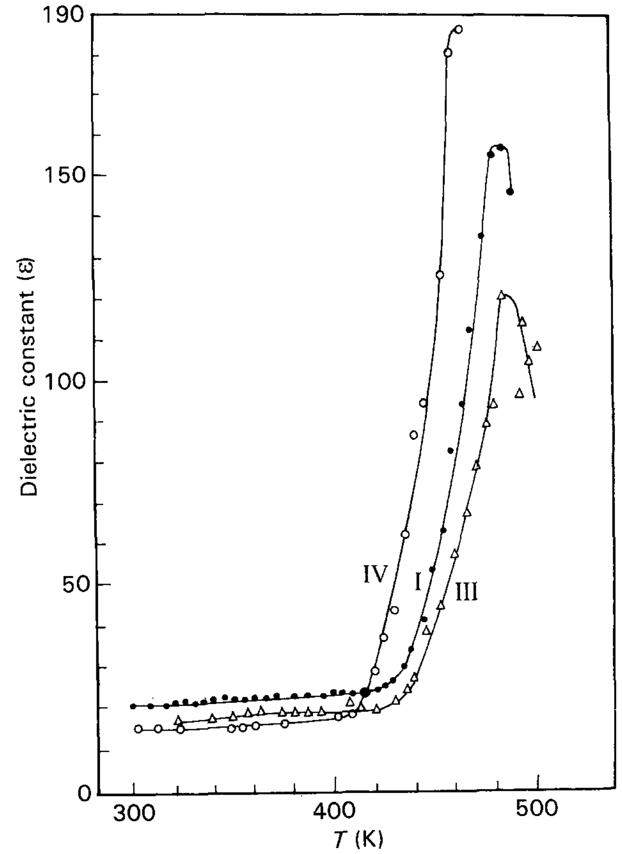

Figure 7 Variation of dielectric constant with temperature for different glass compositions for samples I, III and IV.

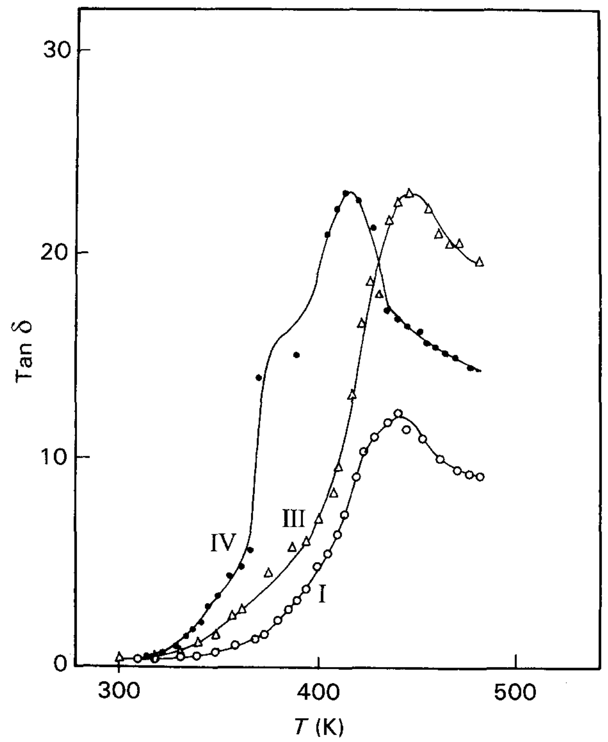

Figure 8 Variation in the value of tan δ with temperature for samples I, III and IV.

containing SiO_2 become more effective at temperatures where the dielectric constant increases rapidly.

The variation of tan δ with temperature is shown in Fig. 8. The peak in dissipation is shifted to higher temperature for $0.7TeO_2$–$0.1PbO$–$0.1B_2O_3$–$0.1Fe_2O_3$ glasses. The sample glass of composition $0.75TeO_2$–$0.1PbO$–$0.05SiO_2$–$0.1Fe_2O_3$ seems to have two peaks due to different relaxation mechanisms. Hansen & Splann [21] measured the dielectric constant and dielectric loss factor at different frequencies and different temperatures for the Fe_2O_3–P_2O_5 glasses.

4. Discussion

The variation of a.c. conductivity with frequency was found to obey the relation given by Equation 1 for a frequency range below 10^4 Hz. The strong frequency dependence of conductivity at high frequency is represented in Fig. 3. The absence of dispersion of permittivity at high frequencies (Fig. 4) suggests that the conduction mechanism is based on electronic hopping. Different theories have been put forward to explain the conduction mechanism under a.c. conditions.

Hopping conduction in amorphous semiconductors has been reviewed by Pollack [22]. A model for the hopping of the carrier over the barrier has been proposed by Pike [23]; this model considers the hopping of the carriers between sites over a barrier separating them, rather than quantum mechanical tunnelling through the barrier. Elliot [24] has proposed a model to explain some a.c. conductivity in chalcogenide materials. This model appears to explain some aspects of our results. The theory put forward [24] considers hopping of carriers between two sites over a barrier separating them. In such materials the two electrons in a D^- site are assumed to transfer to a D^+ site by hopping, converting to a D^- site. The required broad spectrum of hopping times arises from a quasi-continuous distribution of barrier heights derived from the overlapping coulomb potential on nearest pairs.

The a.c. conductivity according to this model is given by

$$\sigma(w) = \frac{TT^2N^2\varepsilon}{24}\left(\frac{8e^2}{\varepsilon w_m}\right)^6 \frac{w^n}{\tau_0^B} \qquad (2)$$

where ε is the dielectric constant; w_m is the barrier height separating distant pairs; $\sigma(w)$ is the a.c. conductivity; w is the angular frequency; τ is the relaxation time ($\sim 10^{-13}$ s); n is an index ($n = 1 - B$); and N is the value of the density of localized states.

The exponent n is related to w_m by the following relation

$$1 - n = 6KT/w_m \qquad (3)$$

where K is the Boltzmann constant and T the absolute temperature. The parameter w_m is approximately equal to the band gap of the materials measured optically. The values of w_m calculated from Equation 3 are listed in Table I.

By substituting the measured value of the optical band gap (2.97 eV) of $0.9TeO_2$–$0.1B_2O_2$ [25] in Equation 3, n is found to be 0.947 at room temperature which is consistent with the calculated [25] values of some chalcogenide materials. The value of the density of localized states (N) for the glasses under investigation, calculated from Equation 2 and angular frequency $w = 6.28 \times 10^4\ \mathrm{s}^{-1}$, is a reasonable value and is comparable to values of N which have been calculated by Elliott [24] by substituting the necessary data obtained from the published work of many investigators [26] for some glassy chalcogenide materials, in Equation 2.

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