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Effect of cobalt oxide on the a.c. conduction mechanism of copper tellurite glasses

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Electrical measurements on binary and ternary glasses of compositions $65TeO_2$–35CuO and $65TeO_2$–34CuO–1CoO (mol %) are reported at temperatures between 293–458 K in the frequency range up to 10^{-6} Hz. The measured conductivity shows a frequency dependence obeying the equation $\sigma(\omega) = A\omega^s$ with $s < 1$ but taking different values at different temperatures. The capacitance of the glasses shows an increase in value with increase in temperature at low frequencies. The tangent of the loss angle (tan δ) and dielectric loss factor ε_r'' were found to increase with the increase in temperature and decrease in frequency but the usual Debye loss peaks were absent even at high temperatures. The relative dielectric constant ε_r was unexpectedly high, approximately 10^3, and was found to decrease very slightly with increasing frequency. Overall the effect of a small amount of CoO ($\sim$ 1 mol %) is found to have a dominant effect on the dielectric properties of copper tellurite glasses.

1. Introduction

Recently a considerable interest has been shown in the study of the dielectric properties of disordered semiconductors and insulators because they can provide information about the structure of the materials. The localized electronic states within the material are created due to the presence of disorder in the atomic configuration and/or the compositions.

A number of papers have been published concerning the dielectric properties of phosphate [1–4] and tellurite [5] glasses in which studies have been reported of the variation with frequency of conductance, capacitance and dielectric loss over a wide range of frequencies and temperatures. Some aspects of high permittivity polar glasses (ferroelectric glasses) have also been discussed by Lines [6].

Elliott [7] has proposed a model for the mechanism responsible for a.c. conduction in chalcogenide glasses and suggested that the frequency dependent conductivity is a consequence of hopping of charge carriers over a barrier between two wells rather than tunnelling as suggested by Pollak and Geballe [8], Austin and Mott [9] and Pollak [10]. The model is a combined variable-energy and variable-range hopping model because the height of the potential barrier is correlated with the intersite separation and appears to account for some aspects of our results.

In oxide glasses or ionic crystals, the polarization also involves the movements of ions over distances of one or two ionic diameters from one equilibrium position to another. Continuous localized charge carrier movements, both backwards and forwards, under the influence of an alternating field, result in a continuous absorption of energy by the material and this is dissipated as heat. The losses vary with frequency of the applied field and the temperature of the dielectric and in the oxide glassses these are mainly attributed (1) to small displacements of the oxygen atoms (i.e. deformation of the network) (2) to the movements of lattice vacancies and (3) to the vibrations of ions in their neighbouring interstices. This loss mechanism plays a vital role in studying the dielectric properties of the glassy matrix.

In this paper we present our experimental results for the a.c. conductivity of copper tellurite glasses and also the effect of CoO on its dielectric properties.

2. Experimental technique

2.1. Glass preparation

Binary and ternary glasses with compositions $65TeO_2$–35CuO and $65TeO_2$–(35-x)CuO–xCoO (mol %) with x = 1, 2, 3, 4 were prepared by the melt quenching technique. The mixture of oxides was heated at 950–960° C in an alumina crucible for about 2 h in air. The melt was then quenched by pouring on to a steel plate maintained above room temperature which helped to avoid cracks due to thermal stress and at the same time allowed a sufficiently high rate of cooling that crystallization did not take place. The disc-shaped samples so formed were then annealed for 1 h at 250° C. The two faces of the glass samples were ground smooth and parallel and were then polished with diamond paste. For electrical measurements, gold electrodes together with a guard-ring assembly for reducing edge and surface leakage effects, were deposited by vacuum evaporation.

2.2. Measurements

The electrical measurements were made by standard techniques with the samples under a vacuum of 10^{-5} torr. A Hewlett Packard impedance analyser (5–13 MHz) type 4192A LF, was used to take direct

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measurements of the conductance and the capacitance of the sample by setting the analyser in the parallel mode. An a.c. signal of 500 mV$_{\text{r.m.s.}}$ was applied across each sample and zero offset adjustments were made for the different frequency-ranges to ensure that the curves were continuous over the frequency range covered. The necessary formulae used in measuring the parameters of the dielectric properties of the present glassy samples are given below.

The solid glass pressed between two electrodes and using the guard-ring method is equivalent to a capacity C with resistance R in parallel and then the relative permittivity (ε_r) or dielectric constant of the glassy medium is

$$\varepsilon_r = C/C_0 \qquad (1)$$

where C, C_0 are the capacitances of the same capacitor with or without dielectric material. Since the dielectric constant is generally of complex form [11] being dependent on the frequency of the applied field, then $\varepsilon_r = \varepsilon_r' - i\,\varepsilon_r''$ where ε_r' is the real part of the relative dielectric constant and ε_r'' is known as the dielectric loss factor which has been calculated earlier [2, 11]

$$\varepsilon_0 \varepsilon_r'' \omega = \sigma_{\text{a.c.}} = \sigma_{\text{total}} - \sigma_{\text{d.c.}} \qquad (2)$$

$$\varepsilon_r'' = \sigma_{\text{a.c.}}/\varepsilon_0 \omega \qquad (3)$$

On the basis of circuit theory, the tangent of the loss angle δ has been measured by the expression [12]

$$\tan \delta = G/\omega C \qquad (4)$$

where G is the conductance measured directly from the analyser. The value of ε_r' was measured using the well known relation [13]

$$\tan \delta = \varepsilon_r''/\varepsilon_r' \qquad (5)$$

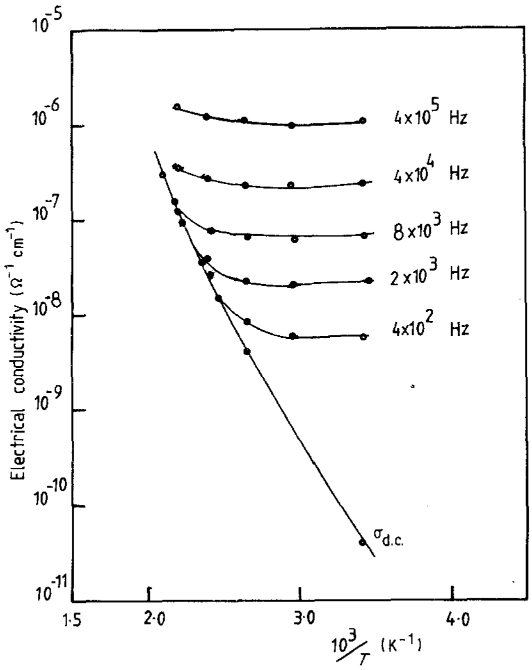

Figure 1 Variation of d.c. and a.c. conductivities of a 65TeO$_2$–35CuO (mol %) glass sample with inverse temperature at five different frequencies.

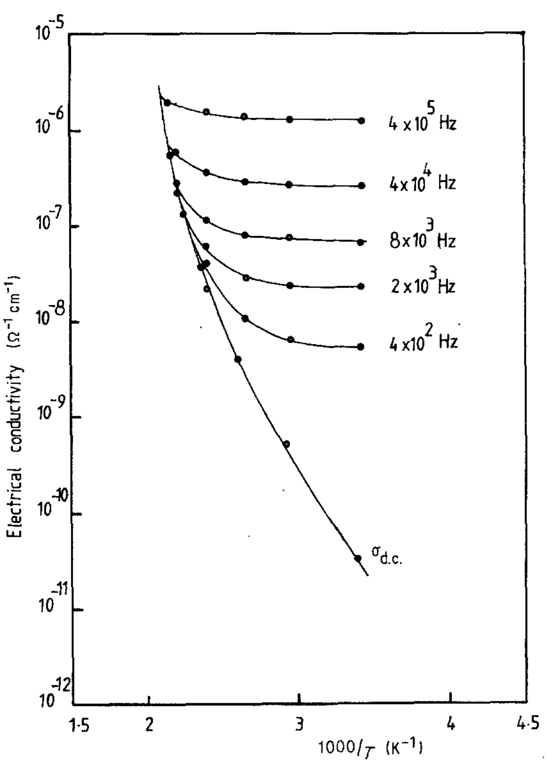

Figure 2 Variation of d.c. and a.c. conductivities of a 65TeO$_2$–34CuO–1CoO (mol %) glass sample with inverse temperature at five different frequencies.

3. Results and discussion

The d.c. and a.c. conductivities as functions of inverse temperature at fixed frequencies 4×10^2, 2×10^3, 8×10^3, 4×10^4, and 4×10^5 Hz and in the temperature range 293–458 K for 65TeO$_2$–35CuO and 65TeO$_2$–34CuO–1CoO (all in mol %) glasses are reported in Figs 1 and 2, respectively. The overall behaviour of these curves is somewhat similar to that reported for other transition metal oxide phosphate [1–4] and tellurite [5] glasses.

It may be noted from Figs 1 and 2 that at low temperatures the a.c. conductivity is very much higher than the d.c. conductivity and in the normal temperature ranges used the a.c. conductivity shows a weaker temperature dependence for the binary than for the ternary glassy systems as expected for the larger ionic hopping distances in the binary system.

However, at higher temperatures, the a.c. conductivity becomes more strongly temperature dependent and the variation with frequency is small and ultimately the a.c. conductivity becomes equal to the d.c. conductivity. The temperature at which the a.c. conductivity becomes equal to the d.c. conductivity increases with increasing frequency and is found to have relatively higher values in the cobalt-coped glasses. Apart from the differences in the numerical values, the overall behaviour of samples with different compositions is similar. Hence the values of the characteristic parameters are reported in Tables I and II for only one representative composition. The frequency dependence of conductivity at different temperatures for the present glassy systems is also shown in Figs 3 and 4. It is observed that in the binary glassy system, from the low to the high temperature range, the a.c. conductivity is broadly proportional to the frequency (see

TABLE I Some derived parameters of a binary and a representative ternary copper tellurite glasses at 378 K

Frequency (Hz)	a.c. Conductivity (Ω^{-1} cm^{-1})	Tan δ	ε_r'	ε_r''	ε_r
Data for binary glass: TeO_2–CuO					
4×10^2	5.8×10^{-9}	2.17×10^{-2}	1.20×10^3	26	1.20×10^3
2×10^3	2.1×10^{-8}	1.55×10^{-2}	1.18×10^3	18	1.18×10^3
8×10^3	6.5×10^{-8}	1.26×10^{-2}	1.16×10^3	14	1.16×10^3
4×10^4	2.3×10^{-7}	9.00×10^{-3}	1.15×10^3	10	1.15×10^3
4×10^5	1.1×10^{-6}	4.65×10^{-3}	1.14×10^3	5	1.14×10^3
Data for ternary glass: TeO_2–CuO–CoO					
4×10^2	1.12×10^{-8}	3.55×10^{-2}	1.39×10^3	49	1.39×10^3
2×10^3	2.9×10^{-8}	1.82×10^{-2}	1.36×10^3	25	1.36×10^3
8×10^3	8.0×10^{-8}	1.33×10^{-2}	1.33×10^3	18	1.34×10^3
4×10^4	3.1×10^{-7}	1.05×10^{-2}	1.32×10^3	18	1.32×10^3
4×10^5	1.4×10^{-6}	5.30×10^{-3}	1.30×10^3	7	1.30×10^3

Fig. 3) but shows a much more pronounced dielectric behaviour with the addition of CoO, and its effect is clearly shown in Fig. 4. It is also noted that at high frequencies (about 5×10^5 Hz), the conductivity shows a square law dependence on frequency but with a relatively small dependence on temperature. This is attributed to the fact that as the frequency increases, the hops will become shorter, and the limit of interatomic distance will no longer be randomly distributed and will settle to a frequency dependence which tends to ω^2 [14]. In the present study the effect is more pronounced in cobalt-doped copper tellurite glasses because Co^{2+} ions make the jumping distances shorter than in the binary copper tellurite glassy system where the distances are comparatively larger. This type of behaviour (Fig. 4) is well known in amorphous or disordered systems and has been attributed to the distribution of relaxation times arising from the disorder [1] introduced with the addition of cobalt. The frequency variation of a.c. conductivity can be approximated as

$$\sigma_{\text{a.c.}} = \sigma_{\text{total}} - \sigma_{\text{d.c.}} = A\omega^s \qquad (6)$$

where A is complex and $s < 1$. The values of s calculated from the slopes of curves in Figs 3 and 4 for the corresponding glassy systems at different temperatures are recorded in the Table II. The value of s is only dependent on the glass composition to a small extent and is found to decrease smoothly with increase in temperature. The values of s for cobalt-doped copper tellurite glasses in the temperatures range 293–458 K lie between 0.77 and 0.64 while for the binary glassy system, s has values between 0.75 and 0.72. The variations of s with temperature for binary and ternary glasses are shown in Fig. 5. Such behaviour can be explained by assuming a wide distribution of relaxation times due to the variation in jumping distances and barrier heights [10, 15, 16]. In the present systems under study, Co^{2+} ions make the hopping distances shorter by blocking the ionic movements thereby causing a rapid decrease in the values of s with the increase of temperature. From Fig. 5, it can be deduced that $d \log \sigma_{\text{a.c.}}/d \log f = -AT + B$ where A and B are constants, f is the measuring frequency and T is the absolute temperature.

This superposition of a wide distribution of relaxation times [8] gives an almost frequency independent dielectric loss ε_r'' (see Figs 6 and 7) which has only a weak dependence on temperature (see Figs 8 and 9) resulting in a frequency dependent and almost temperature independent a.c. conductivity. The variation of ε_r'' with frequency at different temperatures for binary and ternary glassy systems is shown in Figs 6 and 7, respectively. For binary, ε_r'' decreases slightly with the increase in frequency while for the ternary system, the dependence of ε_r'' on frequency is found to be strong even at higher temperatures.

On the basis of the measurements it can be noted that the incorporation of CoO in copper tellurite glasses is very effective in enhancing the loss factor ε_r'' at low frequency and high temperature. This may also indicate that the presence of Co^{2+} ions in the glassy structure creates hindrances to the carrier hopping process. Their interaction with Cu^{2+} ions must involve various relaxation times and hence their superposition

TABLE II Values of s at five different temperatures

Temperature (K)	TeO_2–CuO	TeO_2–CuO–CoO
293	0.73	0.77
339	0.74	0.74
378	0.75	0.73
416	0.72	0.67
458	0.71	0.64

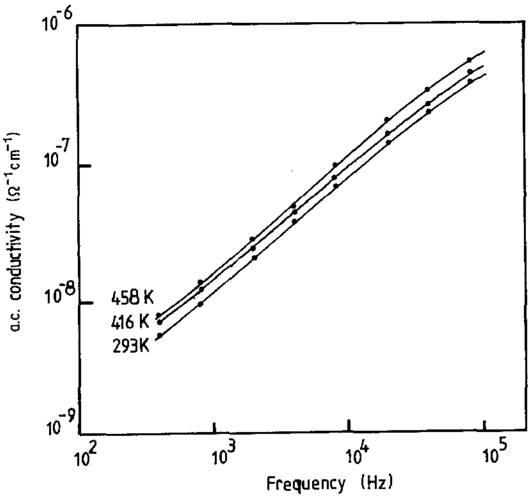

Figure 3 Variation of a.c. conductivity with frequency at different temperatures for $65TeO_2$–$35CuO$ (mol %) glass.

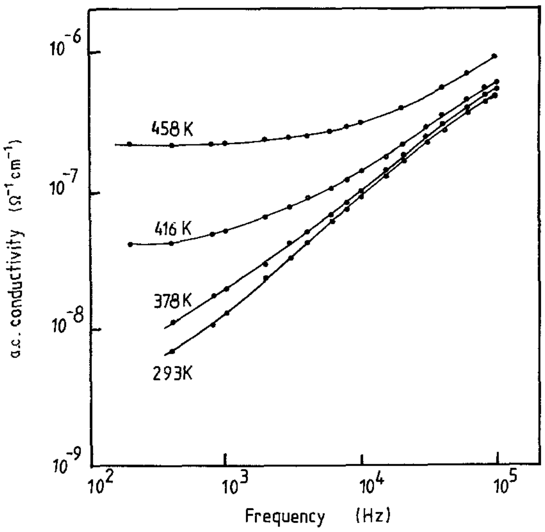

Figure 4 Variation of a.c. conductivity with frequency at different temperatures for $65TeO_2$–34CuO–1CoO (mol %) glass.

causes the loss factor to increase because of the motion of the ions backwards and forwards across the low frequency barriers along with the appearance of the exchange charge polarization. It is also noted from Figs 6 and 7 that the energy loss per cycle varies with frequency, depending upon the glass composition. The energy loss per cycle of the material is proportional to the tangent of the loss angle δ. The variation of tan δ and ε_r'' with temperature at different frequencies for binary and ternary glasses is shown in Figs 8 and 9, respectively. It is observed that in both cases, the values of tan δ and ε_r'' show a slight dependence at low temperatures but vary sharply for low frequencies at higher temperatures and this variation is found to be greater for the ternary glassy network. The rate of increase is not so rapid at higher frequencies and the temperature dependence is only approximately linear. The major part of the increase in tan δ in the present glasses corresponds to the conduction losses. The value of tan δ at 400 Hz in the present glassy systems is found to be very small and to lie between 10^{-3}–10^{-2}. The present results for the variation of tan δ with temperature are in accordance with the following law of Stanworth [17] for the dependence of loss tangent of glasses upon the temperature T which is generally valid for frequencies $< 10^6$ Hz and is expressed as

$$\tan \delta = k \exp (\alpha T) \qquad (7)$$

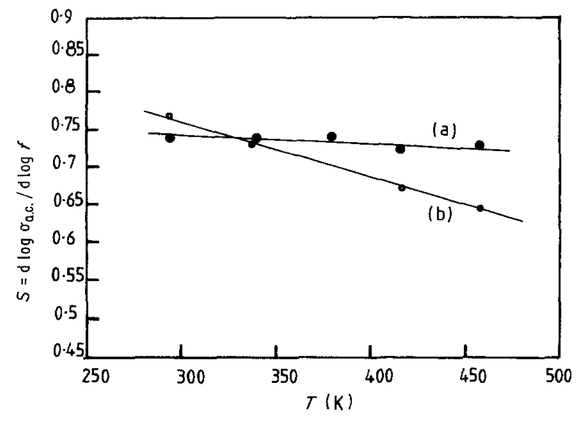

Figure 5 Temperature dependence of the slopes of the conductivity against frequency curves of Fig. 3 of $65TeO_2$–35CuO (mol %) glass.

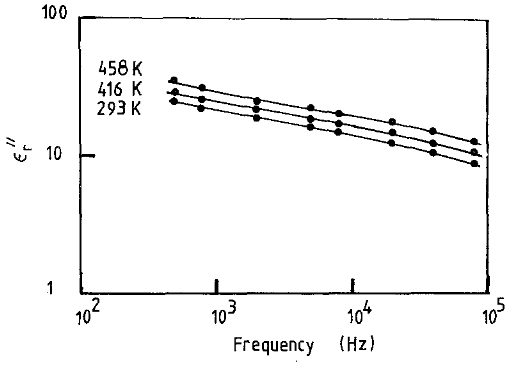

Figure 6 Variation of dielectric loss with frequency at different temperatures for $65TeO_2$–35CuO (mol %) glass.

where k and α depend upon the glass composition and frequency and the parameter α decreases with the frequency. It is necessary to state here that the maximum in the loss curve required by the theory and normally observed in dielectric measurements is not observed in the present binary and ternary glasses at the measuring frequencies. In the present range of temperatures and glass compositions, it can be suggested that the hopping of carriers within a range kT of the Fermi level may dominate and the conventional Debye type loss peaks may lose their significance. Typical plots of the variation of capacitance with frequency for the binary and ternary systems of glasses are shown in Figs 10 and 11. The capacitance in the binary glass is found to be less than that of cobalt-doped copper tellurite glasses in the same range of temperatures and frequencies. This decrease in capacitance with increase in frequency could be associated with the increasing leakage current with increasing frequency which is found to be greater in the ternary glasses.

A surprising feature of the present study of copper tellurite glasses, with or without cobalt, is the unexpectedly large value of the relative dielectric constant of the order of 10^3 (see Table I) which is not normally

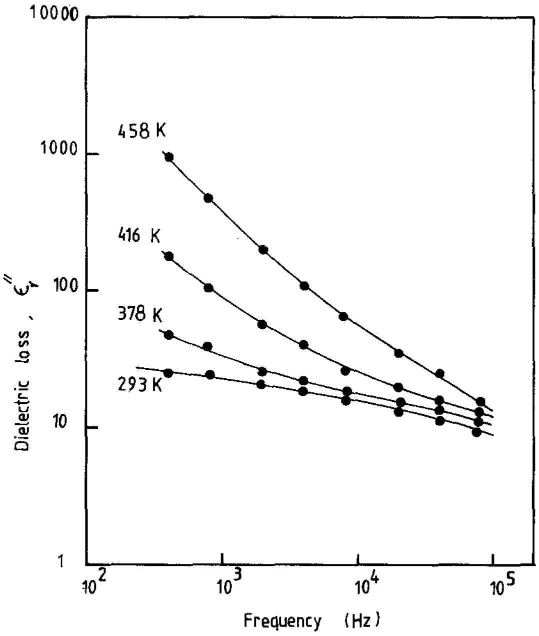

Figure 7 Variation of dielectric loss with frequency at different temperatures for $65TeO_2$–34CuO–1 CoO (mol %) glass.

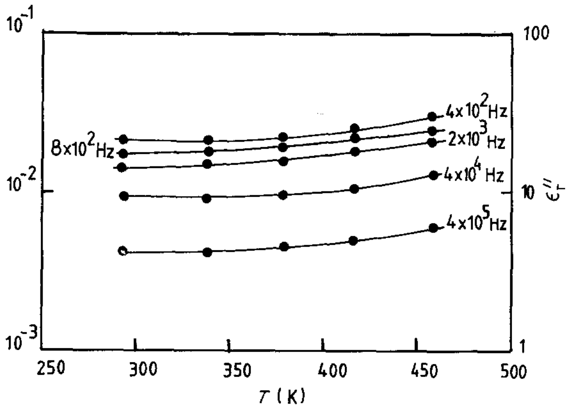

Figure 8 Variation of tan δ and ε_r'' with temperature at different frequencies for $65TeO_2$-35CuO (mol %) glass.

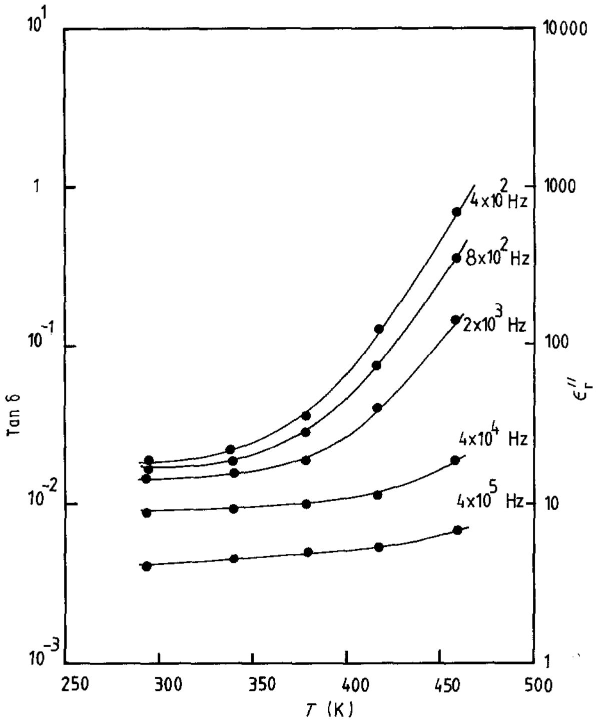

Figure 9 Variation of tan δ and ε_r'' with temperature at different frequencies for $65TeO_2$-34CuO-1CoO (mol %) glass.

found in oxide glasses except in those ferroelectric glasses where the values of relative dielectric constant may exceed 10^5 in some cases [6]. The variation of dielectric constant ε_r' with temperature at fixed frequencies as well as with frequency at various temperatures, for both the glassy systems are shown, respectively, in the Figs 12 and 13 and in Figs 14 and 15. The dependence of dielectric loss on the glass composition is larger in cobalt-doped copper tellurite glasses. The dielectric constant ε_r' appears to increase with increase in temperature and decrease in frequency as shown in Figs 14 and 15. It is noted that as the frequency increases, the real part of the dielectric constant tends to become independent of the temperature and frequency. These somewhat higher values of the derived dielectric constant at the lower frequencies suggest that some orientational polarization may be occurring in our samples at these frequencies and that the present glassy systems are behaving more or less ferroelectrically. It is known that tellurium does

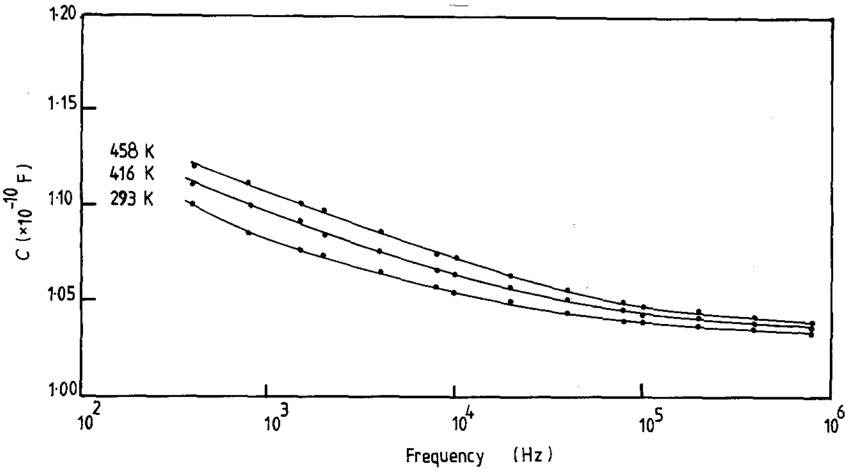

Figure 10 Variation of capacitance with frequency at different temperatures for $65TeO_2$-35CuO (mol %) glass.

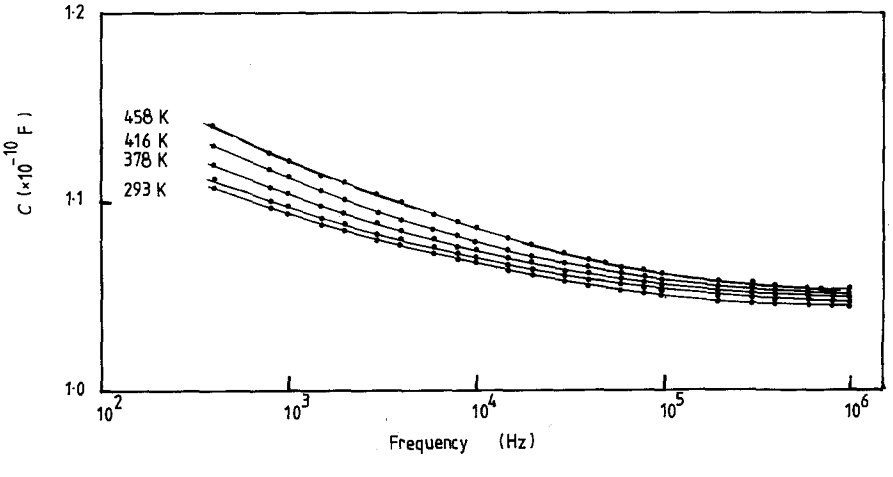

Figure 11 Variation of capacitance with frequency at different temperatures for $65TeO_2$-34CuO-1CuO (mol %) glass.

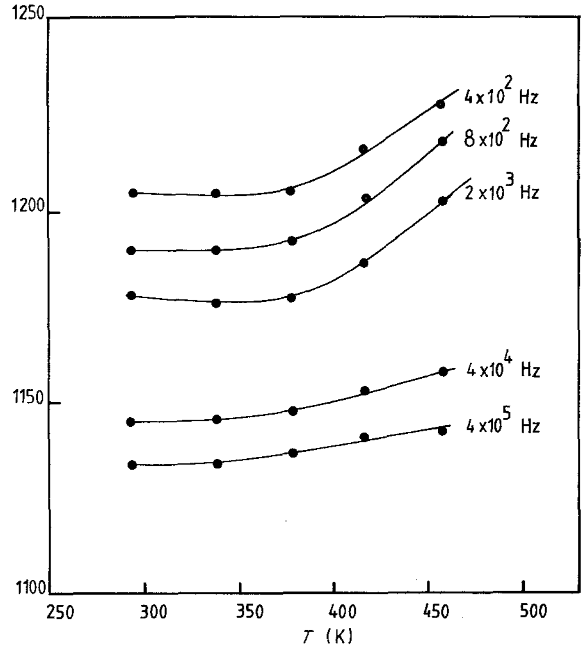

Figure 12 Variation of dielectric constant with temperature at different frequencies for $65TeO_2$–35CuO (mol %) glass.

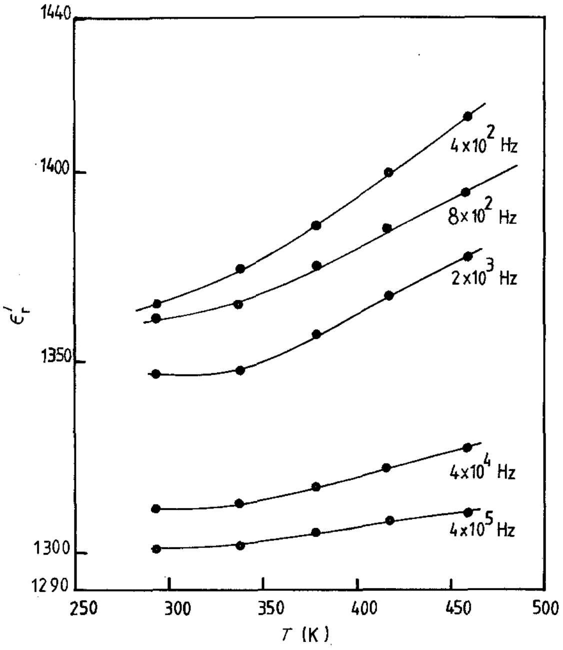

Figure 13 Variation of dielectric constant with temperature at different frequencies for $65TeO_2$–34CuO–1CoO (mol %) glass.

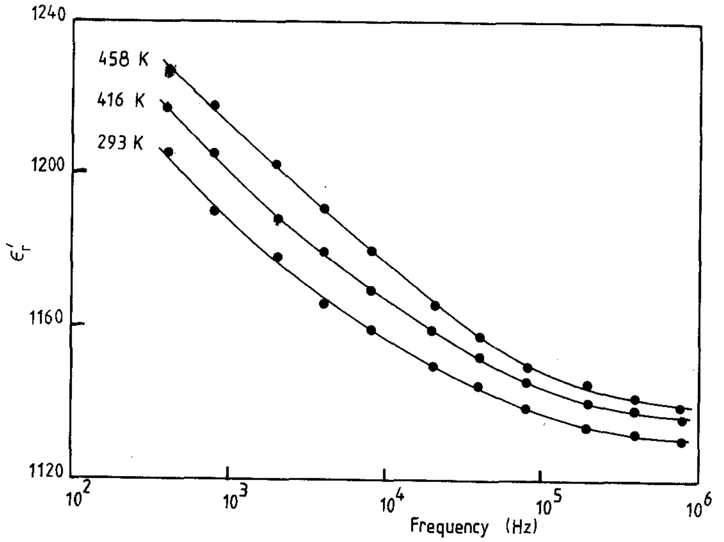

Figure 14 Variation of the dielectric constant with frequency at different temperatures for $65TeO_2$–35CuO (mol %) glass.

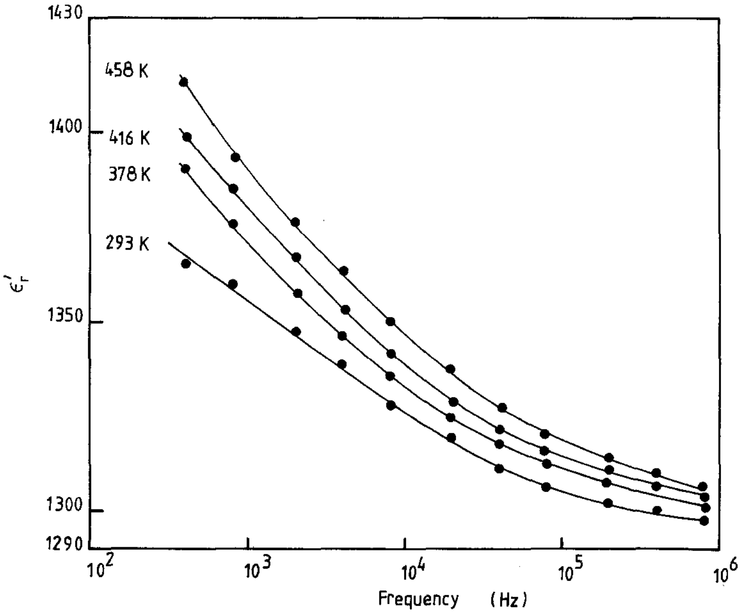

Figure 15 Variation of the dielectric constant with frequency at different temperatures for $65TeO_2$–34CuO–1CoO (mol %) glass.

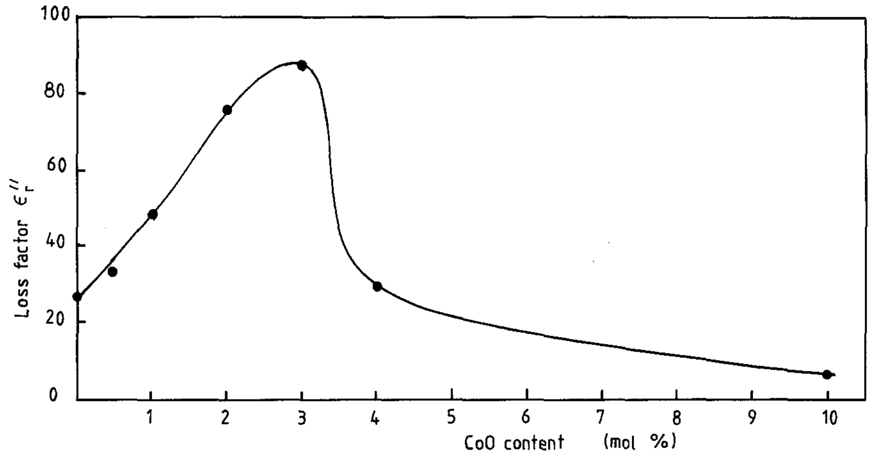

Figure 16 Variation of loss factor ε_r'' with CoO content at fixed frequency (4×10^2 Hz) and temperature (378 K).

increase the tendency of the glass to crystallize and furthermore this behaviour may be attributed to the deformation of the octahedral unit cell of TeO_2 as a result of the other oxide impurities supplying oxygens and permitting a structural change to corner-linked octahedra and a more or less random structure under the effect of the applied a.c. field. From Equation 3, it is evident that at fixed frequency, the loss parameter ε_r'' produces the same results as the measured electronic conductivity. An interesting behaviour of CoO in the a.c. conduction mechanism of copper tellurite glasses can be assessed from the variation of the loss factor ε_r'' with CoO content at fixed frequency (4×10^2 Hz) and temperature (378 K) as shown in Fig. 16. The values of ε_r'' and corresponding a.c. conductivity for different glass compositions are listed in Table II. The plot shows that with the increase of CoO concentrations from 0.5 to 3 (mol %), the loss factor increases linearly resulting from the exchange charge polarization. Above this limit the glassy structure shows a reverse trend and the loss factor ε_r'' decreases exponentially with increase in CoO content. This decrease is expected to be due to the higher concentrations of CoO causing the non-bridging oxygen ions to become more rigid thereby reducing their polarizability by decreasing the charge displacements where the oscillating ions face large barriers, and thereby causing the loss factor to decrease and the a.c. conductivity to drop. Another possible reason for the decrease of loss factor may be the reduced total amplitude of oscillations of the copper ions is used as a modifier, as its content in the glassy network decreases as well as the deformation of oxygen ligands around the metal ions where the mobile ions are inhibited from oscillating with the applied a.c. field, thus causing the loss factor to decrease to its minimum value. So from the comparative study and the above discussion, it can be said that the Co^{2+} ions are contributing markedly to the variation of loss factor as well as the a.c. conductivity in the present glassy systems.

TABLE III Values of loss factor and a.c. conductivity at fixed frequency (400 Hz) and temperature (378 K) for copper tellurite glasses containing CoO

No of glass	Composition (mol %) TeO_2	 CuO	 CoO	a.c. Conductivity (Ω^{-1} cm^{-1})	Loss factor
1	65	35	0	5.8×10^{-9}	26.0
2	65	34.5	0.5	7.4×10^{-9}	33.26
3	65	34	1	1.1×10^{-8}	49.0
4	65	33	2	1.6×10^{-8}	70.6
5	65	32	3	1.9×10^{-8}	88.09
6	65	31	4	6.5×10^{-9}	29.3
7	65	25	10	1.3×10^{-9}	5.7

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