

Different effects of nickel and cobalt additions on the electronic conduction of copper tellurite glasses

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Measurements of the d.c. electrical conductivity were made on $65\text{TeO}_2-(35-x)\text{CuO}-x(\text{MO})$ (mol%) glasses where $x = 0, 0.5, 1, 2, 3, 4$ and M represents nickel or cobalt. A variation in the conductivity and activation energy of the glasses is observed as CuO is replaced by NiO and by CoO. It is found that with $x = 0.5$ to 3 mol% of NiO, the conductivity increases and the activation energy decreases due to the decrease in effective electron hopping distance between the transition metal (TM) ions. The conductivity is found to decrease with the substitution of 4 mol% of NiO and 0.5 to 4 mol% of CoO and this is attributed to the decrease in relative concentration of hopping centres because of the decrease in the hopping transitions between ions of the same element (e.g. Cu^+ and Cu^{2+} ions) and between the ions of different TM elements (e.g. Cu^+ and Ni^{2+} , Cu^+ and Co^{2+}). This decrease in conductivity has also been described due to the formation of Ni-O-Ni, Cu-O-Ni and Co-O-Co, Cu-O-Co bridge bonds in NiO- and CoO-doped glasses respectively. The CoO-doped glasses have been found to be of a more insulating nature.

1. Introduction

There have been many investigations of oxide glasses containing two transition metal (TM) oxides simultaneously with the purpose of understanding the transport properties of semiconducting glasses [1-13, 15-19, 22-24]. The general condition for electronic conduction in oxide glasses having TM oxides arises through electron hopping between two TM ions in different valency states, that is from lower to higher valency state ions which are formed during melting due to the loss of oxygen. The consequences of the presence of two TM ions include:

- (i) a reduction-oxidation (or redox) interaction between the two transition metals in the melts,
- (ii) a change in the activation energy due to the additional distortion of lattice sites, and
- (iii) a phase change

Different arguments have been given about the variation of electrical conductivity of oxide glasses. Bogomolova and Glassova [2] and Singh [3] have reported an initial rise and then fall in the electrical conductivity whereas Sayer and Lynch [4], Caley and Murthy [5], Bogomolova *et al.* [6] and Chomka *et al.* [7] all have predicted the initial decrease and then increase in conductivity when one TM oxide is replaced by the other TM oxide in glasses. They [3, 5, 7, 8] have all suggested that electrical conductivity increases because of hopping of electrons between TM ions of different elements in addition to the hopping of electrons between ions of the same elements while it decreases due to the decrease of the redox ratio [4] and also due to the possible formation of bridge bonds which comprise one ion from each TM ion with one

ligand oxygen, due to which the hopping is inhibited. Recently Bruckner [14] reported that the electrical conduction in mixed TM oxide glasses is closely related to the redox shift. For glasses containing double redox pairs there exists a mutual interaction, not at the melting temperature, but only during cooling from the melting temperature to a fictive temperature at which the redox reactions are frozen in, so the increasing or decreasing conductivity by partial substitution of one redox pair by another one can be observed and will depend widely on the redox ratio of the starting materials and on the efficiency of the dominant type of hopping process of the two redox pairs.

Electrical conductivity of binary copper tellurite glasses has been reported by Ivanova *et al.* [23] and by Hassan and Hogarth [24]. Dimitriev *et al.* [22] have found that the temperature dependence of the conductance of the ternary $\text{TeO}_2-\text{V}_2\text{O}_5-\text{CuO}$ system can be described better by the Arrhenius equation above 100°C and they calculated the activation energy to lie within the limits of 0.4 to 0.8 eV. Sunandana and Rao [13] have reported the increase in conductivity of $x(\text{CuO})-(0.55-x)\text{V}_2\text{O}_5-0.45\text{TeO}_2$ glasses in terms of changes in the $[\text{V}^{4+}]/[\text{V}^{5+}]$ ratio due to the electron exchange between V^{4+} and Cu^{2+} ions leading to a decrease of the V^{4+} content and the formation of Cu^{2+} clusters which cause the conductivity to drop with the increase in CuO content. Khan *et al.* [19] explained the decrease of d.c. conductivity of sodium tetraborate glasses containing NiO by considering the blocking effect of NiO ions on the overall mobility of sodium ions, on the basis of recent investigations concerning the role of the nickel ion in the materials on Hubbard

bands as reported by Mott [20]. Harani and Hogarth [16] explained their results about the increase and decrease of conductivity in terms of redox ratio as well as due to the transitions between ions of two different TM oxides in copper phosphate glasses doped with NiO and CoO. Recently Khan *et al.* [17] have compared the d.c. conductivity of 50 GeO₂-(50-x)TeO₂-x(TM) (in mol %) glasses (where TM is for TiO₂, V₂O₅, NiO, CuO and ZnO at x = 10) and have reported that the d.c. conductivity in this system containing the same amount of V₂O₅ is larger than that of other glasses containing a similar amount of other TM oxides, and is due to the hopping between the localized states.

In the present work we report our experimental results of the electrical conductivity of ternary copper tellurite glasses containing NiO or CoO and up to now— according to our information— no electrical studies have been performed on these glassy systems. The object of the present investigation is to look into the effect of CoO or NiO on the electrical properties of the TeO₂-CuO glass system.

2. Experimental work

Reagent grades of NiO, CoO, TeO₂ and CuO were used as starting materials for making glasses in the system 65TeO₂-(35-x)CuO-x(TMO) mol % where TM is for nickel or cobalt and x = 0, 0.5, 1, 2, 3, 4. The alumina crucible containing the mixture was heated at 300°C for 1 h to minimize the material volatilization and then transferred to a melting furnace maintained at a temperature between 900 to 950°C and left for 2 h with frequent stirring. The homogenized melt was poured on to a steel plate and cast into a disc-shaped sample with diameter 1.5 cm and thickness about 1.2 to 2 mm. The disc-shaped samples were immediately transferred to an annealing furnace preheated at 300°C and left for 1 h in order to remove mechanical stresses. The furnace was then switched off to cool down to room temperature.

For electrical measurements, the annealed samples were ground smoothly on both sides and were then polished using diamond paste. The samples were cleaned carefully with acetone to remove the greasy layer. The gold electrodes were deposited by vacuum evaporation on both sides of each sample at a pressure below 10⁻⁴ torr. One side had a gold electrode of diameter more than 1 cm while the other side had a smaller circular electrode of diameter 0.5 cm surrounded by an annular guard ring electrode to minimize the effect of the relatively low surface resistance. The electrical measurements were made by standard techniques. A Keithley 240 A high voltage supply was used to provide a voltage source and the circulating currents were measured using a Keithley 610 C electrometer. The temperature of the sample was monitored using a chromel-alumel thermocouple attached to it. All the measurements were taken more than once, with samples maintained at an ambient pressure of 10⁻⁵ torr, over the temperature range 293 to 478 K. The limitation in the temperature range utilized was the experimental difficulty of measuring currents of less than 10⁻¹⁴ A with the equipment available.

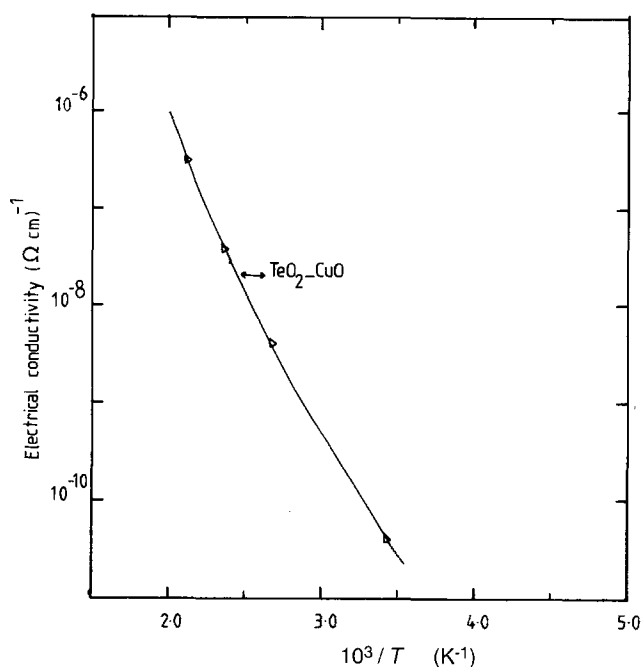


Figure 1 Conductivity plotted against inverse temperature for a 65TeO₂-35CuO glass.

3. Results and discussion

The d.c. conductivity is a negative exponential function of inverse temperature and can be represented by the usual equation

$$\sigma = \sigma_0 \exp(-W/kT) \quad (1)$$

where W is the activation energy. Semilogarithmic plots of d.c. conductivity against inverse temperature for binary TeO₂-CuO glass and ternary TeO₂-CuO-NiO and TeO₂-CuO-CoO glassy systems are shown in Figs 1, 2 and 3 respectively. The conductivity, plotted as described above, is found to decrease with decrease in temperature in a slightly non-linear manner for nearly all the compositions investigated. It can be suggested that this is due to the changes in both mobility and the

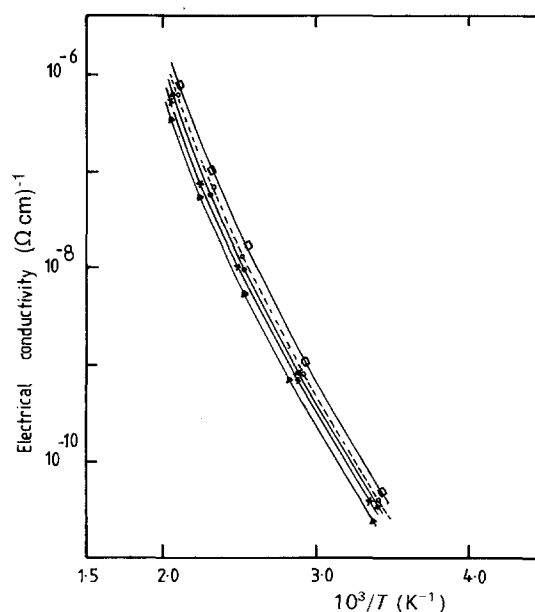


Figure 2 Conductivity plotted against inverse temperature for five samples of TeO₂-CuO-NiO glass. (□ 0.5 mol % NiO; ● 1 mol % NiO; ● 2 mol % NiO; ○ 3 mol % NiO; ▲ 4 mol % NiO).

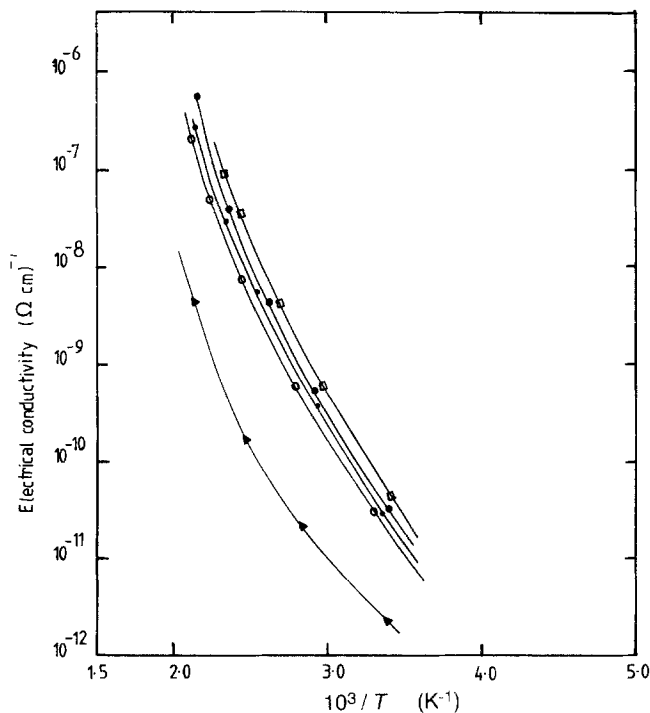


Figure 3 Conductivity plotted against inverse temperature for five samples of $\text{TeO}_2\text{-CuO-CoO}$ glass. (\square 0.5 mol % CoO; \bullet 1 mol % CoO; \bullet 2 mol % CoO; \circ 3 mol % CoO; \blacktriangle 4 mol % CoO).

number of charge carriers. Such behaviour is often observed for the hopping type semiconducting glasses. The activation energies of these present glassy systems were measured from the slopes of $\log \sigma$ against $1/T$ plots and above room temperature lie in the range 0.55 to 0.76 eV for $\text{TeO}_2\text{-CuO-NiO}$ and 0.76–0.83 eV for $\text{TeO}_2\text{-CuO-CoO}$ glasses depending upon their compositions. The values of activation energies and d.c. conductivity at a fixed temperature of 454 K (181°C) are summarized in the Tables I and II. The variations of activation energy with NiO and CoO content are shown in plots 4 and 5. From the present data (see Figs 4 and 5 and Tables I and II) it can be seen that the magnitude of the d.c. conductivity becomes smallest for those glasses which have the highest thermal activation energy. This behaviour is consistent with the general formula of Mott [10] and agrees with the previous results of Moridi *et al.* [9], Sayer and Mansingh [11] Hogarth and Jamel Basha [15], Harani and Hogarth [16] and Khan *et al.* [17] for other systems of oxide glasses. It may be observed in

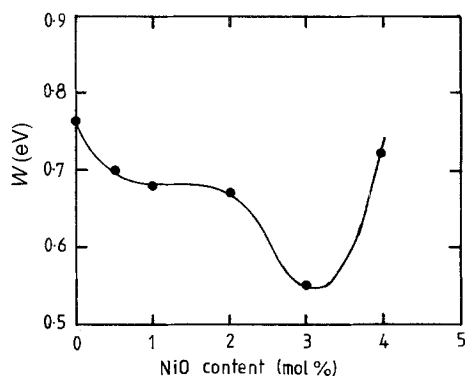


Figure 4 Variation of activation energy (W) with NiO content of $\text{TeO}_2\text{-CuO-NiO}$ glasses.

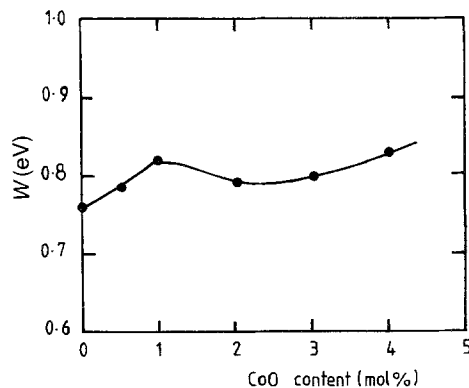


Figure 5 Variation of activation energy (W) with CoO content of $\text{TeO}_2\text{-CuO-CoO}$ glasses.

Figs 4 and 5 that the semiconducting oxides NiO and CoO when added to copper tellurite glasses show the opposite behaviour because with the incorporation of NiO up to 3 mol %, an initial increase and at 4 mol % of NiO a decrease in conductivity is observed as shown in Fig. 6. These results are different from the behaviour of NiO in copper phosphate glasses reported by Harani and Hogarth [16] where the substitution of NiO shows an initial decrease and then increase in conductivity and the addition of CoO shows the initial increase and then decrease in conductivity but such behaviour of CoO is not observed in the present copper tellurite glasses. It has been noted that 0.5 to 4 mol % of CoO in copper tellurite glasses decreases the d.c. conductivity continuously without showing any reverse trend and this is shown graphically in Fig. 7.

The type of conduction in the present glasses has been checked by measuring the resistance of all the glasses as a function of time. A fixed voltage of about 100 V was applied for 5 h and the value of current was recorded after each half hour. The resistance was calculated by Ohm's law and was found to be constant with time. The graphic representations of the results of this experiment for 0.5 mol % of NiO and 0.5 mol % of CoO glasses are shown in Figs 8 and 9 respectively. At room temperature there is a very short term initial variation with time; otherwise the resistance is constant over an extended period of time. This can be taken as evidence that the polarization effect in these glasses is minimal or absent and the electrical conduction in these glasses will be due to the transport of electrons rather than ions [21].

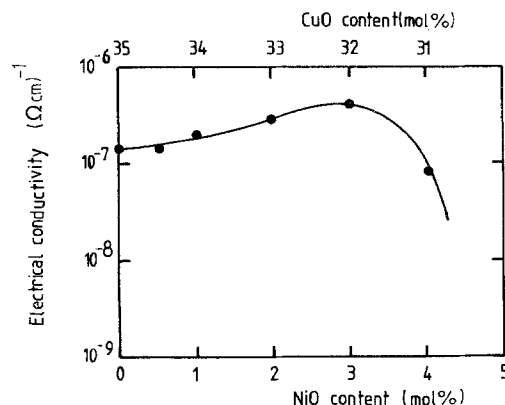


Figure 6 Variation of d.c. conductivity ($\sigma_{d.c.}$) with NiO content for $\text{TeO}_2\text{-CuO-NiO}$ glasses.

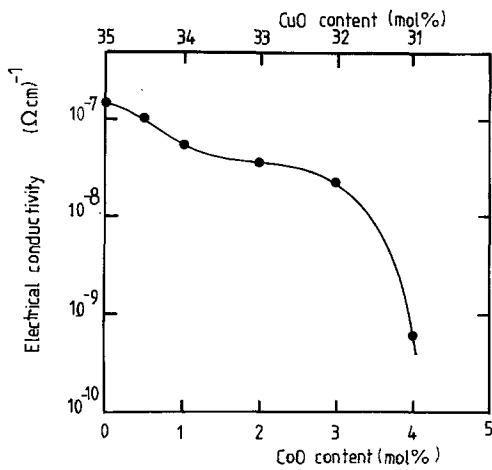


Figure 7 Variation of d.c. conductivity ($\sigma_{d.c.}$) with CoO content for TeO_2 -CuO-CoO glasses.

The present experimental results concerning the variation of conductivity of copper tellurite glasses doped with NiO and a continuous decrease of conductivity in CoO-doped copper tellurite glasses can be interpreted in terms of double redox pairs [14] as well as in the formation of bridge associates [3, 7, 18].

In NiO-doped glasses, the increase in conductivity can be attributed to the increase in the concentration of hopping centres which is consistent with the decrease in the effective distance between the hopping centres. This consideration is in good agreement with the results of Chomka *et al.* [7] on TeO_2 - V_2O_5 -FeO glasses.

The increase in the conductivity up to 3 mol % of NiO in copper tellurite glasses may be due to the increasing probability of hopping between the following pairs of centres: $\text{Cu}^+ \leftrightarrow \text{Cu}^{2+}$; $\text{Ni}^+ \leftrightarrow \text{Ni}^{2+}$; $\text{Cu}^+ \leftrightarrow \text{Ni}^{2+}$; $\text{Cu}^{2+} \leftrightarrow \text{Ni}^+$. As the NiO content is increased to 4 mol %, the conductivity decreases and this may be due to the relative decrease in the concentration of copper hopping centres with an effective increase in the distance between them. In this situation the following types of transitions take place among the TM ions: $\text{Ni}^+ \leftrightarrow \text{Ni}^{2+}$; $\text{Cu}^+ \leftrightarrow \text{Ni}^{2+}$; $\text{Cu}^{2+} \leftrightarrow \text{Ni}^+$

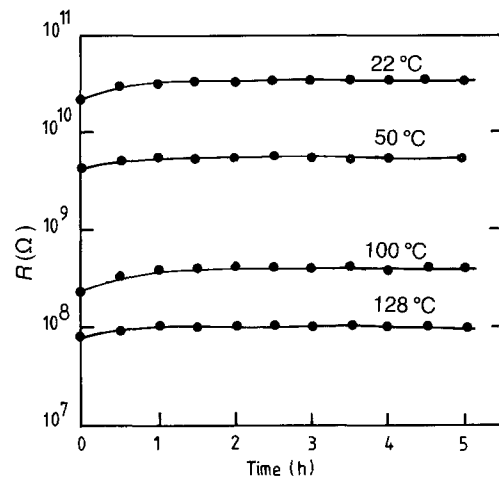


Figure 8 Variation of resistance (R) with time for a 65TeO_2 - 34.5CuO - 0.5NiO (mol %) glass at different temperatures.

but these transitions cannot compensate for the drop of conductivity due to the decreasing number of $\text{Cu}^+ \leftrightarrow \text{Cu}^{2+}$ transitions.

Similarly with CoO-doped copper tellurite glasses, the decrease in conductivity may be due to the increasing number of the following transitions which are also inadequate to compensate for the decreasing number of $\text{Cu}^+ \leftrightarrow \text{Cu}^{2+}$ transitions: $\text{Co}^+ \leftrightarrow \text{Co}^{2+}$; $\text{Cu}^+ \leftrightarrow \text{Co}^{2+}$; $\text{Co}^+ \leftrightarrow \text{Cu}^{2+}$. Again the decrease in the conductivity can also be explained by the possible formation of associates composed of one ion from each TM with one oxygen ligand as reported by previous workers [3, 18]. So the addition of NiO or CoO into the TeO_2 -CuO glassy network will break the Cu-O-Cu bridging bonds and new bridging bonds Cu-O-Ni, Ni-O-Ni in TeO_2 -CuO-NiO and Cu-O-Co, Co-O-Co in TeO_2 -CuO-CoO glasses will be formed and, as the new bridging bonds cannot be equivalent to the Cu-O-Cu bonds, they will inhibit the hopping of electrons and cause a decrease in the conductivity.

Our experimental data show that the formation of new bonds affects the conductivity for concentrations of more than 3 mol % NiO in TeO_2 -CuO-NiO glasses

TABLE I Chemical composition and derived parameters of TeO_2 -CuO-NiO glasses

No	Glass number	Composition (mol %)			d.c. conductivity at 454 K (Ωcm) ⁻¹	W (eV)
		TeO ₂	CuO	NiO		
1	a	65	35	0	1.41×10^{-7}	0.76
2	b	65	34.5	0.5	1.43×10^{-7}	0.70
3	c	65	34	1	1.89×10^{-7}	0.68
4	d	65	33	2	2.61×10^{-7}	0.67
5	e	65	32	3	4.0×10^{-7}	0.55
6	f	65	31	4	8.6×10^{-8}	0.72

TABLE II Composition and some derived parameters of TeO_2 -CuO-CoO glasses

No	Glass number	Composition (mol %)			d.c. conductivity at 454 K (Ωcm) ⁻¹	W (eV)
		TeO ₂	CuO	CoO		
1	a	65	35	0	1.41×10^{-7}	0.76
2	g	65	34.5	0.5	1.0×10^{-7}	0.78
3	h	65	34	1	5.3×10^{-8}	0.77
4	i	65	33	2	3.6×10^{-8}	0.79
5	j	65	32	3	2.3×10^{-8}	0.80
6	k	65	31	4	5.9×10^{-10}	0.83

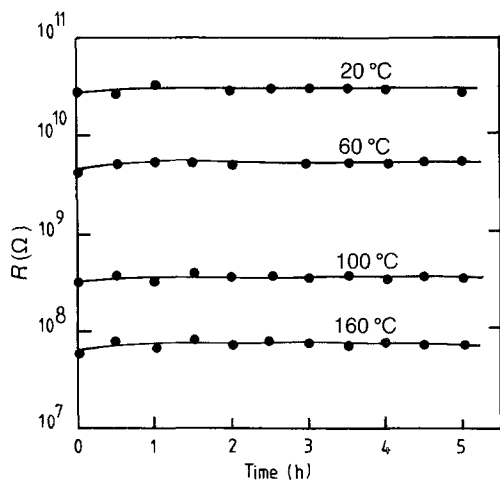


Figure 9 Variation of resistance (R) with time for a $65\text{TeO}_2-34.5\text{CuO}-0.5\text{CoO}$ glass at different temperatures.

while in cobalt-doped glasses, the effect is even more dominant from 0.5 to 4 mol % CoO and a continuous decrease in conductivity is observed. From the present investigation the following conclusions may be drawn.

(i) The transition metal oxide CoO is more dominant than NiO

(ii) Nickel and cobalt oxides when incorporated separately into copper tellurite glasses show different behaviours in their electrical properties.

(iii) Cobalt-doped copper tellurite glasses show more insulating behaviour than that of nickel-doped copper tellurite glasses.

(iv) The $\log \sigma$ against $1/T$ plots display a non-linear behaviour which is associated with the temperature variation of mobility and is similar to the results for other hopping type semiconducting glasses.

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