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Electrical conductivity studies of sodium tetraborate glasses containing copper

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In recent years many investigations have been reported on the semiconducting properties of borate based glasses [1, 2]. The general condition for semiconducting behaviour is that the transition metal ion should be capable of existing in more than one valency state, so that conduction can take place by the transfer of electrons from low to high valency states.

The purpose of the present letter is to study the electrical conductivity of sodium tetraborate glasses with varying CuO contents. Details about preparing the glasses and the experimental procedures can be found elsewhere [3]. Briefly, for preparing the glasses a mixture of sodium tetraborate $[(Na_2B_4O_7)_{100-x}$ and $(CuO)_x$ (chemical purity 99.99%); $x = 0$, 5, 10, 15 and 20 mol %] was used and circular glass discs of 2 cm diameter were obtained.

The d.c. conductivities of the samples were measured using a d.c. power supply and Keithley 610C electrometer in the temperature range 293–573 K. Evaporated aluminium electrodes with a guard-ring configuration were used. X-ray diffraction (XRD) measurements confirmed the glassy nature of all glass samples examined.

Fig. 1 shows the temperature dependence of d.c. conductivity, σ. The results of the temperature variations of σ showed that in the modest range investigated $\log \sigma$ was a linear function of $1/T$ for all glass samples. The values of the activation energies, shown in Table I, were calculated from the slopes of the curves, using the relation

$$\sigma = \sigma_0 \exp(-E_a/k_b T)$$

where E_a is the activation energy, k_b the Boltzmann constant, T the absolute temperature and σ_0 a constant. Addition of CuO to the glasses caused the electrical conductivity to increase and was associated with a decrease in the activation energy, E_a. Table I lists the derived values of E_a and relates them to the compositions.

The time dependence of current at a fixed applied field was studied for periods of up to 180 min for all glass samples at different temperatures. Fig. 2 illustrates the results obtained for a glass sample containing 20 mol % CuO (sample 5). It can be seen that the current remained constant over these extended periods at different temperatures, suggesting the conduction to be electronic rather than ionic. Further increases in time beyond 3 h revealed no significant changes in current. A similar behaviour has been observed in molybdenum phosphate glasses [4].

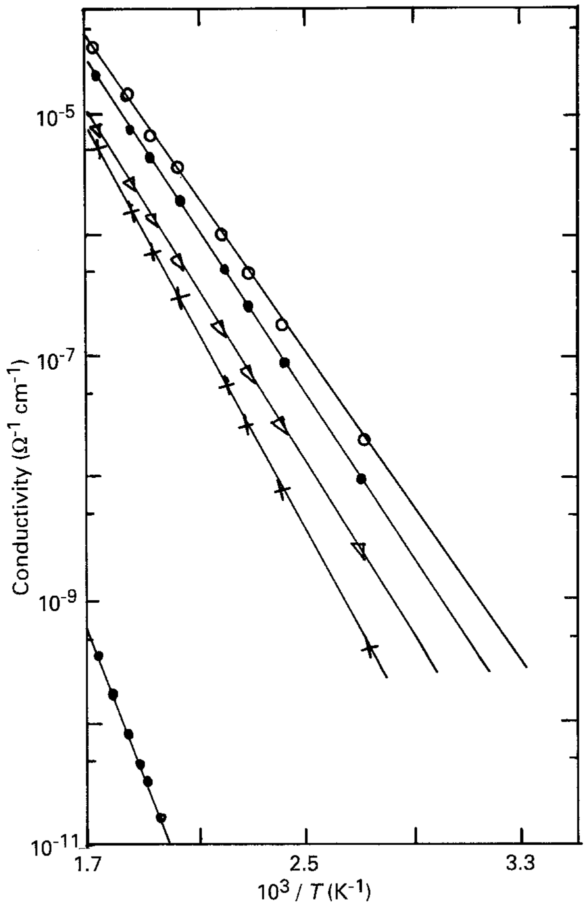

Figure 1 Electrical conductivity as a function of the reciprocal of temperature for a series of $(Na_2B_4O_7)$–(CuO) glasses listed in Table I. Sample: ●, 1 (bottom left-hand side); ×, 2; ∇, 3; ●, 4; O, 5.

TABLE I Composition data and electrical properties of glass in the system $(Na_2B_4O_7$–$CuO)$

Sample	Composition (mol %)	Electrical activation energy (E_a) (eV)
1	$(Na_2B_4O_7)_{100}$–$(CuO)_0$	1.35
2	$(Na_2B_4O_7)_{95}$–$(CuO)_5$	0.83
3	$(Na_2B_4O_7)_{90}$–$(CuO)_{10}$	0.80
4	$(Na_2B_4O_7)_{85}$–$(CuO)_{15}$	0.76
5	$(Na_2B_4O_7)_{80}$–$(CuO)_{20}$	0.69

A voltage–current characteristic is shown in Fig. 3 for a glass sample containing 20 mol % CuO (sample 5). It is clear that the conduction was ohmic and plots of $\log V$ versus $\log I$ gave straight lines.

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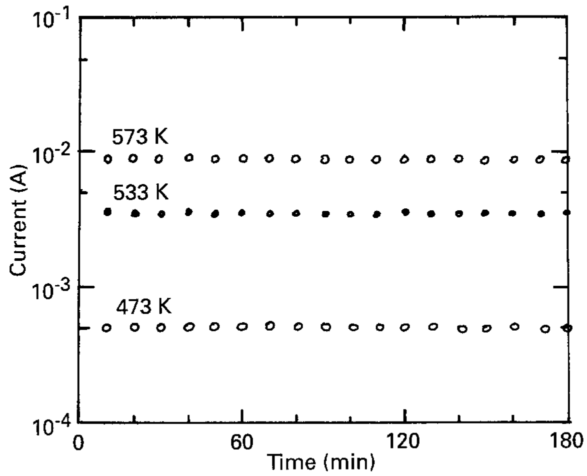

Figure 2 Time dependence of current for glass sample 5 (Table I).

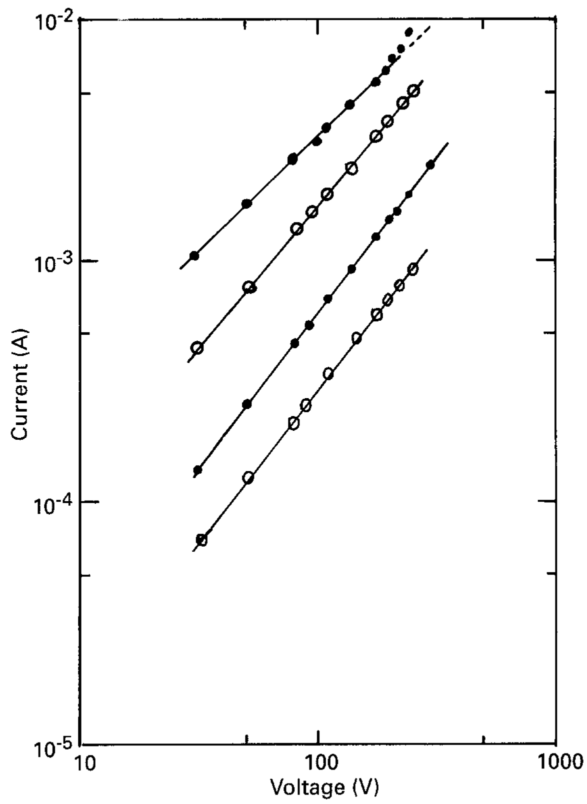

Figure 3 I–V characteristics for glass sample 5 at different temperatures. Temperature (K): ● (upper), 573; ○ (upper), 533; ● (lower), 503; ○ (lower), 473.

Increasing the temperature caused a non-ohmic behaviour and a departure from linearity occurred at fields below 1×10^3 V cm^{-1} at 573 K. Similar trends were found for $Na_2B_4O_7$ glass samples containing 20 mol % Pb_3O_4 [5].

The observed increase in the electrical conductivity of $Na_2B_4O_7$ glass (sample 1) with an increase in temperature could be due to the thermal agitation which facilitated the movement of Na^+ ions in the interstices of the boron network. The observed decrease in activation energies of $Na_2B_4O_7$ glasses with the addition of CuO was related to the change of BO_4 ions to BO_3 ions; the activation energy being the energy needed to activate the ion diffusion and separate one configuration of the borate unit from the other. This means that the activation energy is the interaction energy that couples the borate unit motion with the diffusion of the ions. CuO could also contribute to the observed increase in electronic conductivity since, when added, it began to enter into the network as a modifier and the conduction became partly ionic and partly electronic. Actually, the electronic conduction in oxide glasses is often due to the presence of transition metal ions of different valencies. Konstants and Vaivadal [6] suggested that if there are two elements in a system which form ions of variable valency, then interaction between them usually takes place. Mackenzie [7] reported that the oxide glasses can exhibit electronic conduction even when the concentration of the transition metal is > 10 mol %.

The electrical conductivity in $Na_2B_4O_7$–CuO glass samples may be assumed to be due to hopping of electrons from the low valence state Cu^+ to the higher state of Cu^{2+}. Thus, a change in the CuO content in the glass composition is expected to alter the ratio (Cu^+/Cu_{total}) and consequently control the transition probabilities of the conduction electrons and the electrical conductivity.

It is believed that the principle involved is one which could be applied to a range of glasses involving electron transition between ions of different valencies, for example between V^{4+} and V^{5+} ions in vanadate glasses and between Mo^{5+} and Mo^{6+} ions in molybdate glasses.

In the light of the above discussion, and because glass systems consist of large volumes of ionic species such as sodium, borate and copper ions, it appears that the copper ion predominates due to its high charge and small ionic radius. Thus, the decrease in the activation energy of $Na_2B_4O_7$–CuO glasses could be ascribed to the added copper which alters the ratio of the concentration of Cu^{2+}:Cu^+ ions in the glasses.

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