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Electrical conductivity of ion-exchanged oxide glasses

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Bulk glasses in the system Na_2O–CaO–Al_2O_3–B_2O_3–SiO_2 have been subjected to a sodium $\rightleftharpoons$ silver exchange reaction. The application of a suitable combination of electric field and temperature brings about switching to a high conducting state (HIE). The critical electric field, E_c, has a value in the range 2 to 20 V cm^{-1} and E_c values decrease as a function of temperature. The resistivity in the HIE state is of the order of 10 Ω cm and the activation energy is 0.01 eV. Wagner's asymmetric polarization cell measurements show that the conductivity is ionic in nature. No switching is observed in the case of glasses subjected to a sodium $\rightleftharpoons$ copper exchange reaction carried out on these glasses at 525° C for 12 h. This is ascribed to the microstructure exhibited by such exchanged samples which consists of copper-rich droplet phases dispersed within a copper-deficient matrix. The rather large inter-droplet separation makes it difficult for the copper-rich phase to grow to its percolation limit.

1. Introduction

Study of ionic conductivity in glasses has become an active area of research in recent years [1]. This interest has arisen due to the possibility of using suitable glasses as solid electrolytes in high energy density batteries [2]. Most of the fast ion conducting glasses contain either Ag^+ or Li^+ ions as the major species. These glasses have conductivities of the order of 10^{-2} to 10^{-3} S cm^{-1} at room temperature. The equivalent mole fraction in the glasses of the compounds containing the ionic species concerned are large, being of the order of 0.7 to 0.9. Some recent experiments in our laboratory have shown that high electrical conductivity in oxide glasses containing up to 30 mol % Na_2O can be induced by subjecting them to a sodium/silver ion exchange reaction followed by a suitable temperature/electric field treatment [3]. Typical room-temperature resistivity and activation energy in the high conductivity state of these glasses are found to be 50 Ω cm and 0.04 eV, respectively.

The above investigation was carried out on fibres of the glass system Na_2O–CaO–B_2O_3–Al_2O_3–SiO_2. Electrical measurements were made on a bunch of ion-exchanged glass fibres mounted between two electrodes. Fibres were chosen as the sample form to ensure almost complete exchange between sodium and silver ions after a 36 h ion-exchange treatment. However, from the point of view of practical application, a bulk form of the glass possessing high conductivity would be more suitable. In the present study, therefore, bulk glasses have been used having compositions similar to those investigated earlier in the fibre form.

It was found that bulk glasses after a sodium/silver ion-exchange reaction can also be switched to a high conductivity state by applying a suitable electric field. The results are reported in this paper. We have also explored the possibility of using a sodium/copper ion-exchange reaction to enhance the ionic conductivity of the parent glass. The latter investigation has been prompted by the fact that Cu^+ ions are reported to contribute to fast ion conduction in certain crystalline materials [4].

2. Experimental details

Table I gives the composition of the glasses investigated. The glasses are prepared from reagent grade chemicals, Na_2O is introduced as sodium carbonate, CaO as calcium carbonate, B_2O_3 as boric acid and the other ingredients as their respective oxides. Glasses are melted in alumina crucibles in an electrically heated furnace at temperatures ranging from 1250 to 1450° C. The melts are poured into an aluminium mould to obtain rectangular blocks which are annealed in a furnace at 500° C for 6 h. The samples are then allowed to cool within the furnace. Samples for ion exchange are prepared by polishing them with silicon carbide grits of different mesh sizes to an approximate dimension of 3 mm × 3 mm × 1.5 mm. The rather small size chosen is to ensure that most of the sodium ions are exchanged with silver (or copper as the case may be) after the duration of reaction as specified below.

TABLE I Compositions of glasses investigated (mol %)

Glass	Na_2O	CaO	B_2O_3	Al_2O_3	SiO_2
1	15.0	13.0	8.0	4.0	60.0
2	20.0	13.0	4.0	3.0	60.0
3	25.0	13.0	4.0	3.0	55.0
4	30.0	12.0	–	3.0	55.0

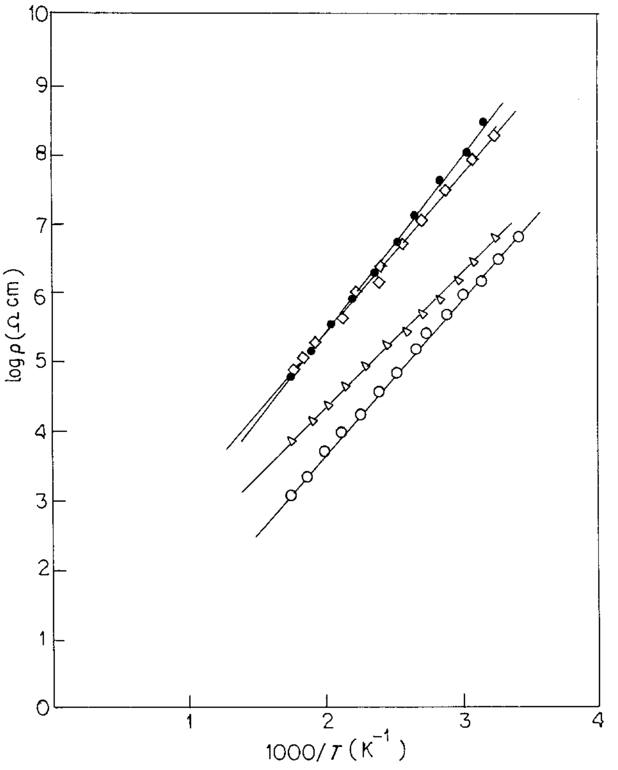

Figure 1 Resistivity variation as a function of temperature for different ion-exchanged ($Na^+ \rightleftharpoons Ag^+$) glasses. Glasses (△) 1, (□) 2, (○) 3, (●) 4.

The $Na^+ \rightleftharpoons Ag^+$ ion-exchange reaction is carried out by immersing the sample in a molten silver nitrate bath contained in a pyrex boat maintained at a temperature of 330° C for 48 h. The sample is taken out and then treated in boiling water for 2 h to remove any excess $AgNO_3$ adhering to the specimen surfaces.

For the $Na^+ \rightleftharpoons Cu^+$ ion exchange the sample is kept in a silica boat containing molten CuCl at 525° C for 12 h. The treatment is carried out in an argon gas atmosphere. The ion-exchanged sample is treated with dilute nitric acid to remove any CuCl adhering to the sample surfaces. The samples are finally washed with water and then acetone.

For electrical measurements, two opposite faces of the sample are coated with silver paint (NPL, New Delhi). The specimen cell used has been described elsewhere [5]. A General Radio 1615-A capacitance bridge is used to measure the a.c. conductance and capacitance of each sample over the frequency range 100 Hz to 100 kHz. The bulk electrical resistivity is determined by the complex impedance analysis of the data obtained [3]. The switching characteristics of the ion-exchanged samples are studied by recording the voltage–current curves on an x–y recorder (model 2000, Digital Electronics Ltd, India).

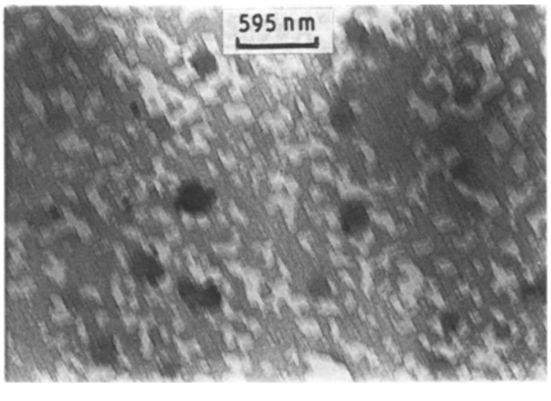

Figure 2 Electron micrograph of ion-exchanged glass 3.

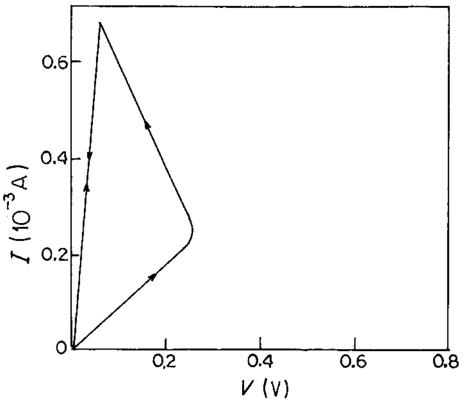

Figure 3 Voltage–current characteristics for ion-exchanged ($Na^+ \rightleftharpoons Ag^+$) glass 3 at 264° C.

To delineate the nature of conductivity in the switched state of the silver-enriched glasses Wagner's asymmetric cell configuration [6] is used to study the nature of current variation as a function of time when a d.c. voltage is applied across the specimen. Silver paint is used as the reversible electrode and graphite paint (Polaron Equipment Ltd, Watford, Hertfordshire UK) serves as the blocking electrode in our experiment.

3. Results

Fig. 1 shows the resistivity variations as a function of temperature for the ion-exchanged glasses 1, 2, 3 and 4 (designated IE_n, where $n = 1$ to 4). The resistivities evidently obey an Arrhenius equation. The activation energies for all the ion-exchanged glasses are found to be identical. This is in conformity with the results obtained in the case of ion-exchanged fibres of the same glass system reported earlier. Also, the activation energies for ion-exchanged glasses obtained for bulk samples (present study) are in agreement with those of specimens in the fibre form. Fig. 2 is an electron micrograph of glass 3 ion-exchanged with silver. It is evident that the silver-rich phase is semi-continuous, having a width of 60 nm. The microstructure is typical of other ion-exchanged glass compositions.

Fig. 3 is a typical V–I plot for the ion-exchanged glass 3 at 264° C which shows the switching to a high conductivity state designated HIE_3. In Fig. 4 the variation of critical electric fields, E_c, as a function of temperature for different ion-exchanged glasses is shown. It is evident that the critical field decreases as the temperature is increased. The reason for rather small E_c values for IE_1 compared to the other glasses is discussed in the following section. The variation of resistivity with temperature for the IE_4 and HIE_4 states of glass 4 are drawn in Fig. 5. This is typical of the behaviour exhibited by other glass compositions. Table II summarizes the pre-exponential factors and activation energy values for different glasses in their IE and HIE states, respectively. The small activation energies obtained in the HIE state for all the compositions studied are in agreement with the corresponding

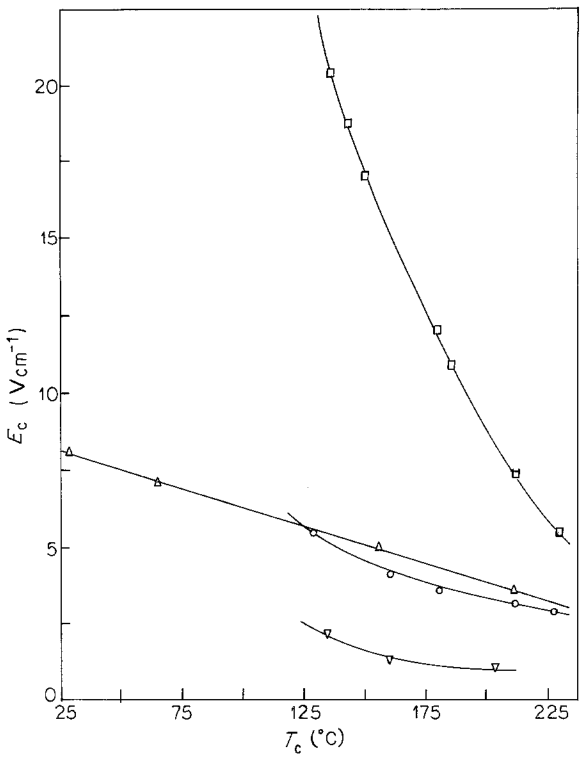

Figure 4 Variation of critical electric field as a function of temperature for different ion-exchanged ($Na^+ \rightleftharpoons Ag^+$) glasses. Glasses (▽) 1, (□) 2, (○) 3, (△) 4.

values found in the case of ion-exchanged glass fibres. The room-temperature (27° C) resistivity values in the HIE states of different glasses are also indicated in column 4 of Table II. The polarization experiments using the electrode assembly Ag/HIE glass/C^+ show that the conductivity in the HIE state of the silver-exchanged specimens is ionic in nature. In a typical run with 10 mV applied across the sample HIE_1, the resistance changes from 10 to 10^4 Ω in 15 sec.

Fig. 6 shows the resistivity variation as a function of temperature for glass 2 ion-exchanged with copper. The data for the virgin sample are also plotted in this figure for comparison. It is seen that the copper-exchanged glass has a smaller activation energy than that of the original sample. This behaviour is also typical of other glasses. Table III summarizes the pre-exponential factor, ρ_0 and activation energy, ϕ, for both the virgin and ion-exchanged ($Na^+ \rightleftharpoons Cu^+$) glasses of different compositions.

It has, however, not been possible to switch the copper-exchanged glasses by applying an electric field up to 50 Vcm^{-1}. The implication of this result is discussed in the following section.

TABLE II Pre-exponential factor, ρ_0, and activation energy, ϕ, for different glasses in IE and HIE states

Glass system	ρ_0 (Ω cm)	ϕ (eV)	$\rho_{27°C}$ (Ω cm)
IE_1	2.5	0.4	
HIE_1	3.2	0.01	3.2
IE_2	7.9	0.4	
HIE_2	6.3	0.02	5.0
IE_3	0.2	0.4	
HIE_3	14.1	0.02	10.0
IE_4	3.2	0.4	
HIE_4	2.5	0.01	6.3

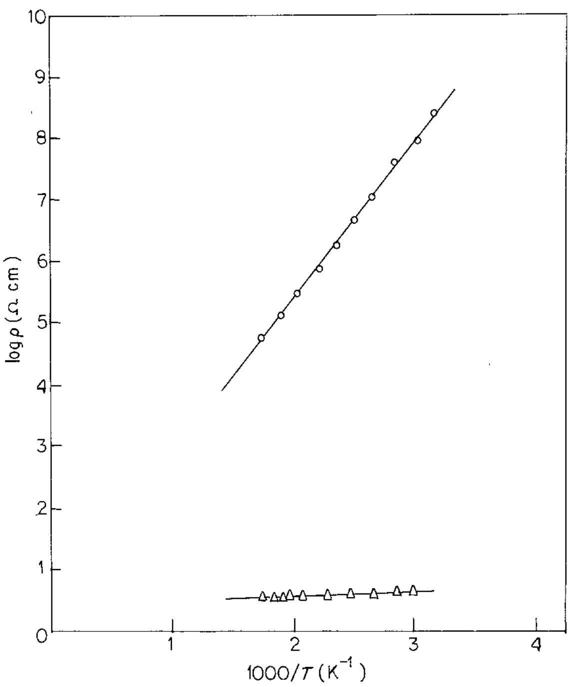

Figure 5 Variation of resistivity with temperature for glass 4 in ion-exchanged (IE) ($Na^+ \rightleftharpoons Ag^+$) and ion exchanged/switched (HIE) states. (○) IE, (△) HIE.

4. Discussion

The lowering of the activation energy of ionic conduction in the ion-exchanged state (after $Na^+ \rightleftharpoons Ag^+$ and $Na^+ \rightleftharpoons Cu^+$ reaction) in relation to that in the virgin state is ascribed to the larger size of silver and copper ions, respectively, compared to that of sodium ions [3]. As discussed in the earlier report, the electrostatic contribution to the activation energy of migration is reduced in the case of ions having diameters greater than that of sodium ions. The overall activation energy is controlled by this contribution because the mechanical barrier to ion movement is negligible in glasses having as high an alkali concentration as those in the present systems.

The silver-exchanged glasses switch to a high conducting state because of an electric field-induced growth of the silver-rich phase, the critical condition being reached when the latter attains a percolation configuration [3]. The decrease in the critical field value as the temperature rises (Fig. 3) confirms this model.

The critical electric field for switching is found to be the least for glass 1 whereas it is the highest for glass 2. Glasses 3 and 4 have nearly identical E_c values. This trend can be explained as follows.

The critical field, according to the present model, has been shown to be given by [3]

$$E_c = \frac{\Delta F}{e\lambda}\left[1 - \frac{T}{T_c}\right] \qquad (1)$$

TABLE III Pre-exponential factor, ρ_0, and activation energy, ϕ, for different glasses subjected to an $Na^+ \rightleftharpoons Cu^+$ exchange

Glass	ρ_0 (Ω cm)		ϕ (eV)	
	Virgin	Ion-exchanged	Virgin	Ion-exchanged
1	6.3×10^{-3}	20.0	0.9	0.5
2	1.4×10^{-3}	7.9	0.8	0.3
3	4.5×10^{-4}	0.1	0.8	0.4

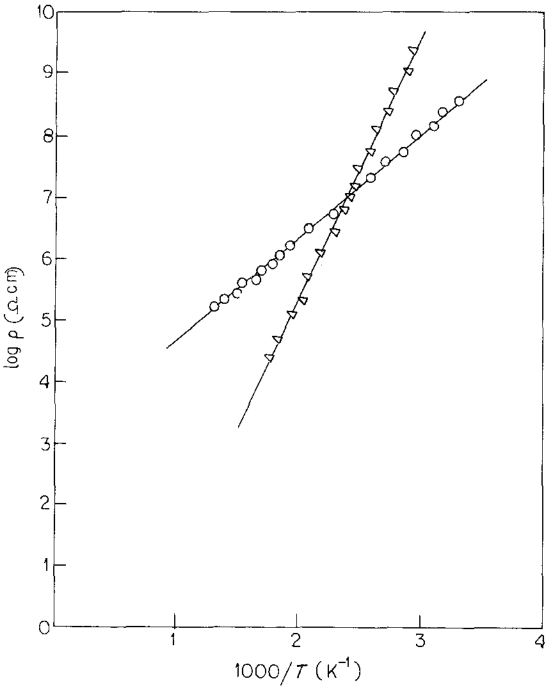

Figure 6 Variation of resistivity with temperature for glass 2 at different states. (●) Virgin, (○) ion-exchanged ($Na^+ \rightleftharpoons Cu^+$).

where ΔF is the activation energy for ionic diffusion across the interface between the growing and the matrix phases, respectively, e is the electronic charge, λ is the thickness of one atom layer of the growing phase and T_c is the critical temperature at which $E_c = 0$. Using Equation 1, E_c values for different glasses have been estimated substituting for ΔF the activation energy obtained for the ion-exchanged samples, extrapolating E_c–T curves to find the T_c values and putting $\lambda \sim 0.3$ nm. It turns out that the calculated values are of the order of 10^6 V cm^{-1}. The rather low experimental E_c values confirm that the silver-rich phase has broken interconnectivity and the effective thickness of the silver-deficient phase, in which most of the applied electric field is concentrated, will be of the order of a few nanometres. The effective thicknesses of the silver-deficient phase in the different ion-exchanged glasses as estimated from the observed E_c values are 0.5, 6.7, 1.4 and 1.8 nm for ion-exchanged glass numbers 1, 2, 3 and 4, respectively. From this analysis, therefore, the E_c value for IE_1 should be the smallest, whereas that for IE_2 should be the largest. This is consistent with the experimental data. The relative magnitudes of broken interconnectivity as represented by the above effective thickness values also explain the rather low value of resistivity in IE_1 compared to those of IE_2, IE_3 and IE_4, respectively, even though the alkali concentration is the least in glass 1 [5]. The absence of switching in copper-exchanged glasses can be explained on the basis of their microstructure, a typical one being shown in Fig. 7. It is evident that the copper-rich phase is dispersed within a copper-deficient phase. The separation between the copper-rich droplet phases is quite large, being of the order of a few tens of nanometres. The electric field needed to let this phase grow to a percolation configuration will therefore be much larger than those used in the present investigation. An interesting aspect of this result is that the original co-continuous microstructure of the parent glass undergoes substantial modification after the sodium $\rightleftharpoons$ copper exchange carried out at a temperature (525° C) around the glass transition point. This is not surprising, because the composition of the glass undergoes a drastic change after the ion-exchange reaction and the phase separation characteristics of the new glass composition are obviously different from those of the virgin glass system. Further work is in progress to investigate this point.

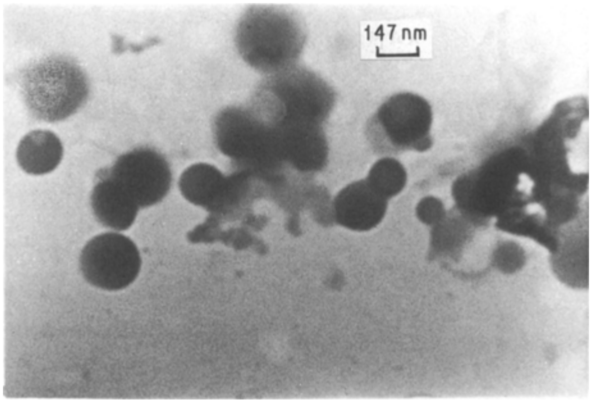

Figure 7 Electron micrograph for glass 1 subjected to $Na^+ \rightleftharpoons Cu^+$ exchange at 525° C for 12 h.

The pre-exponential factors for ion-exchanged samples (sodium $\rightleftharpoons$ silver) in their HIE states are much larger than those corresponding to their virgin states. This supports the general observation in fast ion conducting glasses thus indicating that the vibrational frequency of the mobile ionic species is very low [7]. The implication is, therefore, that these ions are located in shallow potential wells.

5. Conclusions

High electrical conductivity of the order of 10 Ω cm can be induced in glasses in bulk form of the system Na_2O–CaO–Al_2O_3–B_2O_3–SiO_2 which have been ion exchanged with silver and subsequently subjected to an electrical field at a suitable temperature. The activation energy in this high conducting state is 0.01 eV. The conductivity is ionic in nature. The switching to this state arises due to the growth of a silver-rich phase to percolation configuration due to the applied electric field. The sodium $\rightleftharpoons$ copper exchange carried out at 525° C on these glasses fails to exhibit the switching effect. This is due to the fact that the copper-rich phase is dispersed within the copper-deficient phase with a separation of the order of a few tens of nanometres.

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