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Electrical conductivity of ion-exchanged oxide glasses containing aluminium dispersoids

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The effect of sodium ⇌ silver exchange on the electrical properties of glasses in the systems $Na_2O–B_2O_3–SiO_2–Al$ and $Na_2O–B_2O_3–Al$ have been investigated. In general, the ion-exchange step lowers the resistivity as well as the activation energy for conduction. The glasses have a highly inhomogeneous structure. The ion-exchanged glasses are characterized by a semi-continuous silver-rich phase. These glasses can be switched to a highly conducting state by subjecting them to a critical electric field which varies from 0.2 to $5\,\mathrm{v\,cm^{-1}}$ depending on temperature and the virgin glass composition. The resistivities in the highly conducting state have values in the range 3 to $10\,\Omega\,\mathrm{cm}$ with activation energies varying from 0.002 to 0.008 eV. Wagner's asymmetric polarization cell measurements show that such high conductivity is electronic in nature.

1. Introduction

Ionic conduction in oxide glasses has been an active field of research in recent years [1, 2]. Some recent experiments have shown that fairly high conductivity in certain alkali-containing oxide glasses can be induced by subjecting them to an alkali ⇌ silver exchange reaction followed by the application of a suitable electric field at an appropriate temperature [3, 4]. Typical values of room-temperature resistivity are in the range 50 to $1000\,\Omega\,\mathrm{cm}$, and the activation energies encompass a wide range—0.03 to 0.36 eV. The ion-exchange route of electrical conductivity enhancement has also been applied successfully to silicate glasses containing aluminium dispersoids [5]. The latter work was carried out on fibres of the glass system $Na_2O–CaO–B_2O_3–SiO_2–Al$. An interesting feature of the results obtained was the effect of the amount of metallic aluminium on the conductivity of the switched ion-exchanged glasses. The activation energy in the latter state was found to show a minimum (~ 0.03 eV) at the composition which had 5 mol % aluminium metal in the starting mix. Although this work was carried out on glass fibres to ensure near-complete exchange of silver ions with sodium, the bulk form of the glass would be necessary for any practical application. We have therefore carried out experiments on related glass compositions in the bulk form and with an aluminium content higher than that explored earlier.

2. Experimental procedure

Table I gives the compositions of the glasses studied. The glasses were prepared from reagent grade chemicals. Na_2O and B_2O_3 were incorporated as Na_2CO_3 and H_3BO_3, respectively. Aluminium powder (99.9% pure, Sarabhai Merck, India) with a particle size distribution of 1.0 to 4.5 μm, was used directly while melting the glasses. Glasses were melted in alumina crucibles in an electrically heated furnace at temperatures ranging from 1000 to 1200 °C. The melts were poured onto an aluminium mould and cast into a rectangular block. The latter was annealed at 500 °C for 6 h. Polished samples of approximate dimensions $10 \times 10 \times 2$ mm were used for electrical measurements in the virgin state. Ion exchange was carried out on polished specimens of approximate dimensions $3 \times 3 \times 3$ mm by immersing them in a molten bath of silver nitrate contained in a pyrex boat at 325 °C for 48 h. The small size was chosen to ensure that most of the sodium ions were exchanged with silver [6]. The microstructures of various samples were investigated using a JEM 200 CX transmission electron microscope operated at 100 kV.

For electrical resistivity measurements, silver paint electrodes (supplied by NPL, New Delhi) were applied on two opposite faces. The measuring cell used has been described earlier [6]. The a.c. conductance and capacitance of each specimen were measured over the frequency range 100 Hz to 100 kHz with a General Radio 1615-A capacitance bridge for temperatures

TABLE I Compositions of glasses investigated (mol %)

Glass no.	Na_2O	B_2O_3	SiO_2	Al
1	25	10	45	20
2	30	10	40	20
3	20	60	–	20
4	30	50	–	20

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varying from 60 to 300 °C. The value of the d.c. resistivity was determined by the complex impedance analysis as described earlier [3]. The switching studies were carried out by connecting the sample in series with a voltage source and a standard resistance. The voltages across the sample and the latter were displayed on an X–Y recorder (model 2000, Digital Electronics Ltd, Bombay, India) which delineates the V–I characteristics of the specimen. Wagner's asymmetric cell configuration [7] was used to study the nature of charge carriers in the high-conductivity (HIE) state of the ion-exchanged samples. Silver paint served as the reversible electrode and graphite paint (Polaron Ltd, Watford, UK) as the blocking electrode.

3. Results

Resistivity variation as a function of temperature for glasses 1–4 is shown in Figs 1–4, respectively. Each figure shows three curves delineating the resistivity variation for the virgin, ion-exchanged and high-conductivity states. The resistivities of all glasses in different states obey the Arrhenius equation. The activation energies and the pre-exponential factors are summarized in Table II. The ion-exchanged and high-conductivity states are referred to as $(\mathrm{IE})_n$ and $(\mathrm{HIE})_n$, respectively, where n represents the glass number. In general, it is found that the ion-exchanged samples exhibit a lower activation energy than that shown in their virgin states. This is consistent with the results reported earlier in other systems [3]. However, in the

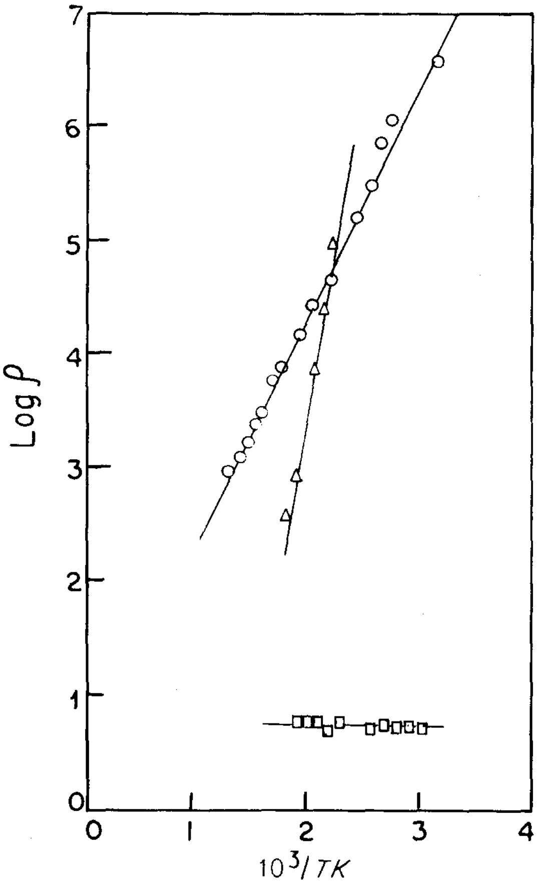


Figure 2 Resistivity variation as a function of temperature for glass no. 2. ○, Virgin; △, ion-exchanged; □, switched (HIE) state.

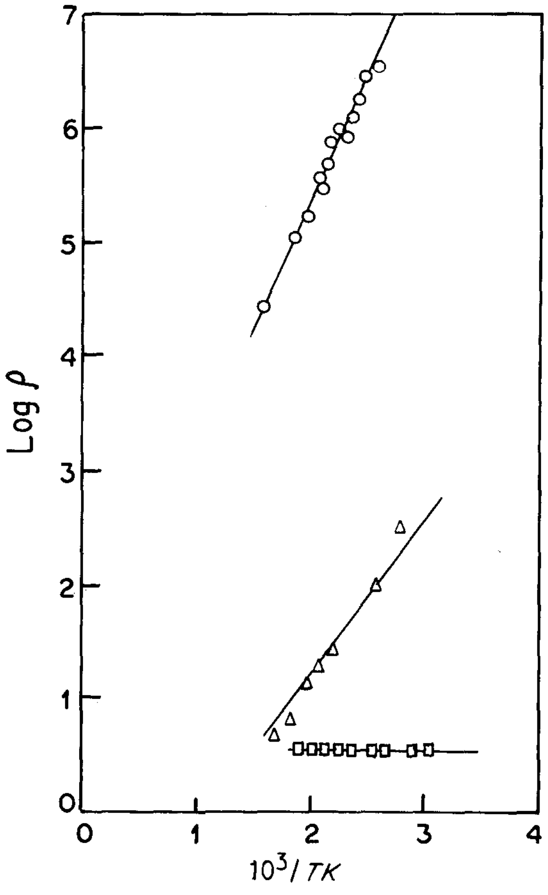


Figure 1 Resistivity variation as a function of temperature for glass no. 1. ○, Virgin; △, ion-exchanged; □, switched (HIE) state.

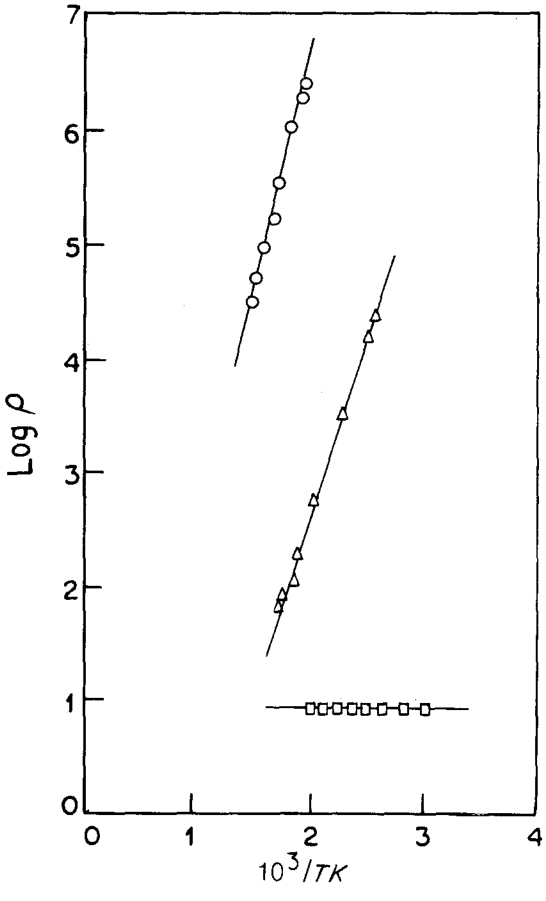


Figure 3 Resistivity variation as a function of temperature for glass no. 3. ○, Virgin; △, ion-exchanged; □, switched (HIE) state.

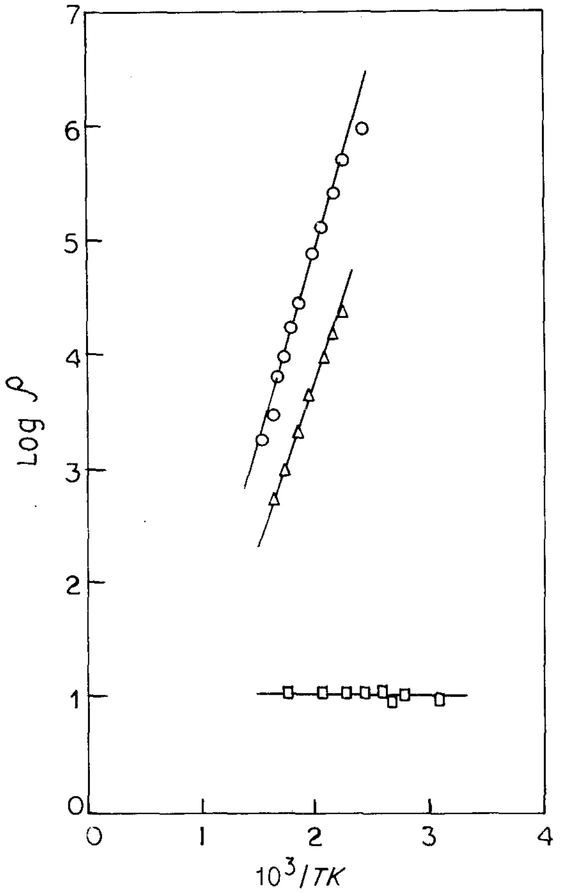


Figure 4 Resistivity variation as a function of temperature for glass no. 4. ○, Virgin; △, ion-exchanged; □, switched (HIE) state.

TABLE II Activation energy ϕ and pre-exponential factor ρ_0 for glasses in different states

Glass no.	ϕ (eV)	ρ_0 (Ωcm)
1	0.4	7.9
2	0.4	2.0
3	0.8	4.5×10^{-2}
4	0.7	1.1×10^{-2}
$(\text{IE})_1$	0.3	3.2×10^{-2}
$(\text{IE})_2$	1.1	2.5×10^{-6}
$(\text{IE})_3$	0.6	1.8×10^{-3}
$(\text{IE})_4$	0.5	1.8×10^{-2}
$(\text{HIE})_1$	0.004	3.5
$(\text{HIE})_2$	0.008	5.6
$(\text{HIE})_3$	0.002	8.9
$(\text{HIE})_4$	0.005	11.2

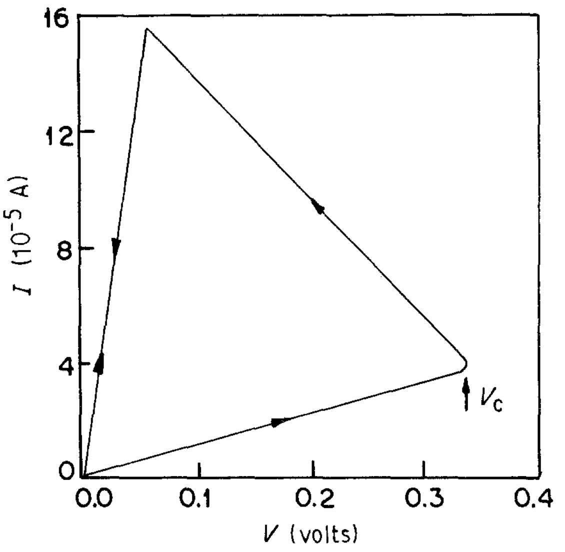


Figure 5 *V–I* characteristics for ion-exchanged glass no. 4 at 152 °C.

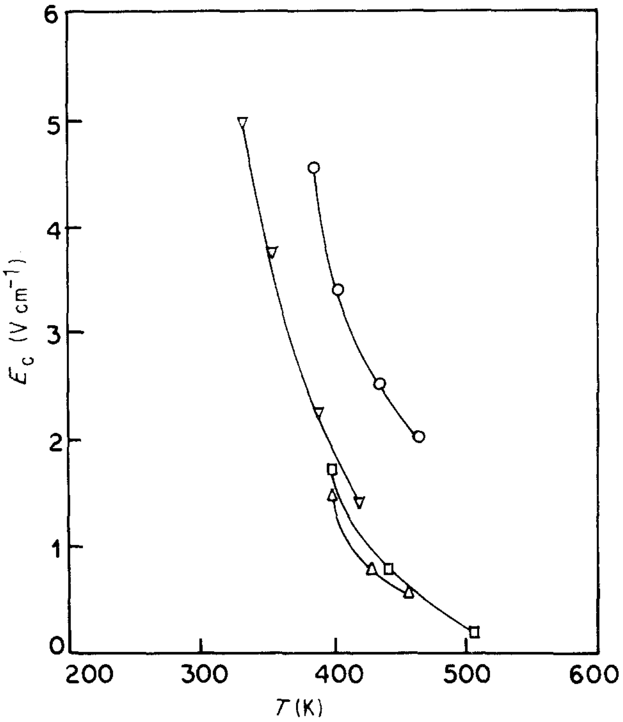
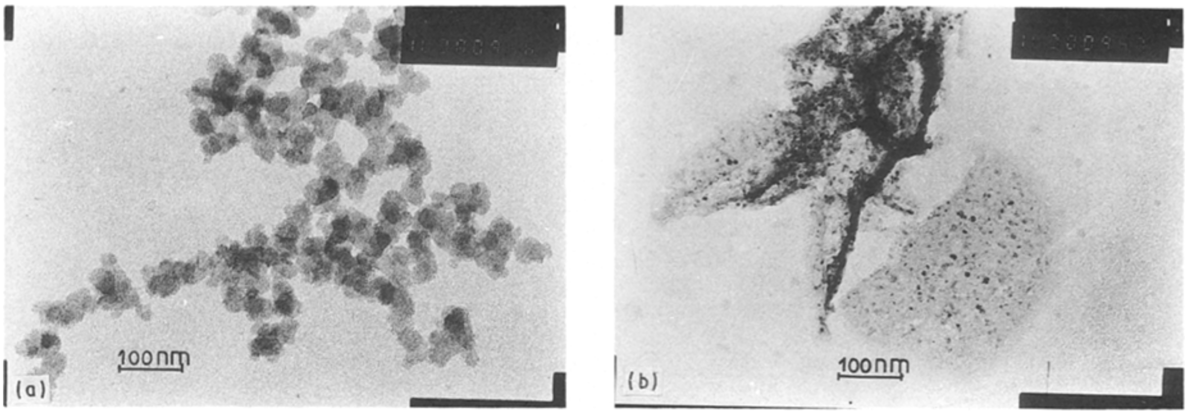


Figure 6 Variation of critical electric field as a function of temperature for different ion-exchanged glasses. △, glass no. 1; ○, 2; □, 3; ▽, 4.

case of glass no. 2 an anomalously large activation energy is observed. This is explained below on the basis of the microstructural characteristics of the glasses concerned. The high-conducting states of all the glasses show a very low activation energy. Also the resistivities in the HIE state for all glasses are low, of the order of 10 Ωcm. These features are consistent with the results reported earlier on glass fibres [5].

The high-conductivity states referred to above for the different ion-exchanged glasses are induced in the samples by the application of a suitable combination of temperature and electric field [3]. A typical voltage–current characteristic which shows such a switching is seen in Fig. 5 for ion-exchanged glass no. 4 at 152 °C. In this figure, V_c represents the critical voltage at which switching occurs and the high-conducting state is attained after passing through a negative resistance region. The lower-conductivity state can be restored by heating the sample above the temperature of measurement. In Fig. 6, the variation of critical electric field as a function of temperature for different ion-exchanged glasses is shown. It is evident that the critical field decreases with an increase in temperature. This is consistent with the results obtained earlier in related glass systems [5]. However, an apparently anomalous result is indicated by the increase in the critical field value for glass no. 2 as compared to that for glass no. 1, which has a lower alkali content. This



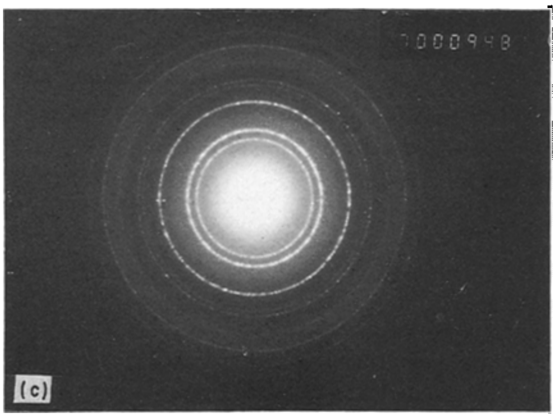


Figure 7 Electron micrograph of glass no. 1 showing (a) a co-continuous phase morphology and (b) metallic clusters. (c) Selected-area electron diffraction pattern of (b).

TABLE III Interplanar spacings d_{hkl} (nm) from electron diffraction pattern of glass no. 1

Observed	d_{hkl} (nm) ASTM
0.2338	0.2338
0.2025	0.2024
0.1427	0.1431
0.1215	0.1221
0.1165	0.1169
0.1008	0.1012
0.0897	0.0905
0.0820	0.0827

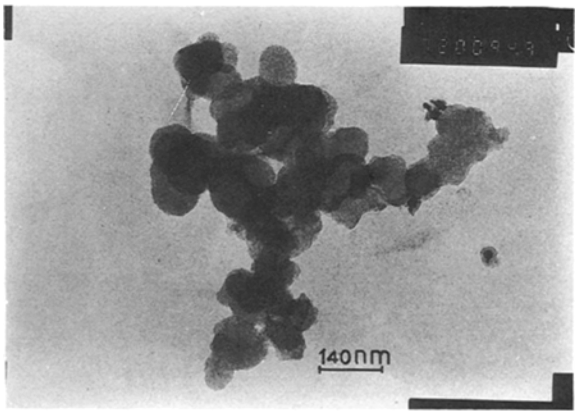


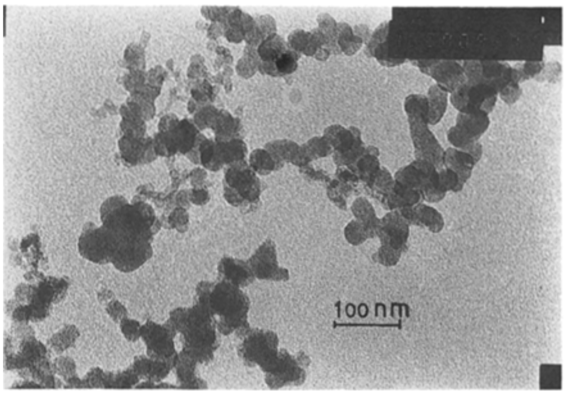
Figure 8 Electron micrograph of ion-exchanged glass no. 1.

can be explained on the basis of the microstructural features for these glasses as discussed below.

The microstructures of all the glasses indicate that they have an inhomogeneous phase structure. Fig. 7a shows a co-continuous phase morphology for glass no. 1, one phase being rich in silica and the other rich in alkali ions. The phase width is of the order of 20 nm. Clusters of metallic aluminium particles are also present in this glass as shown by Fig. 7b. The selected area electron diffraction pattern of the latter is shown in Fig. 7c. The interplanar spacings as calculated from the diffraction rings are given in Table III. The matching of these values with standard ASTM data confirm these particles to be metallic aluminium. The particle sizes are found to have a range from 2 to 10 nm. Fig. 8 shows the electron micrograph of ion-exchanged glass no. 1. A co-continuous silver-rich phase is observed which does not give any electron diffraction ring, indicating that this phase does not contain any metallic particles. The interconnected phase of the ion-exchanged sample has a width of ~ 70 nm.

The microstructural features of glasses 3 and 4 in their virgin as well as ion-exchanged states have characteristics similar to those described for glass 1 above. However, glass 2 shows a different behaviour. Fig. 9 is the electron micrograph of glass 2 in the virgin state. It has an interconnected phase morphology of approximate width 20 nm. Fig. 10a is the electron micrograph of ion-exchanged glass 2, and Fig. 10b is the selected area electron diffraction pattern for the same sample. The rings have been analysed and represent the interplanar spacings for metallic aluminium. It is evident from Fig. 10a that the ion-exchanged glass has a semi-continuous silver-rich phase of approximate width 27 nm within which aluminium metal particles with an average diameter of 3 nm are dispersed uniformly. The minimum distance of separation between the disjointed portions of the silver-rich phase is of the order of 10 nm.

Fig. 11 gives the current voltage characteristics for glass 3 in the HIE state at 110 °C by Wagner's asymmetric cell technique with the graphite paint electrode acting as the anode. The current saturates at around 30 mA and remains constant up to an applied voltage of 1.2 v before increasing exponentially. This behaviour is found to be typical of all the ion-exchanged samples in their HIE states.



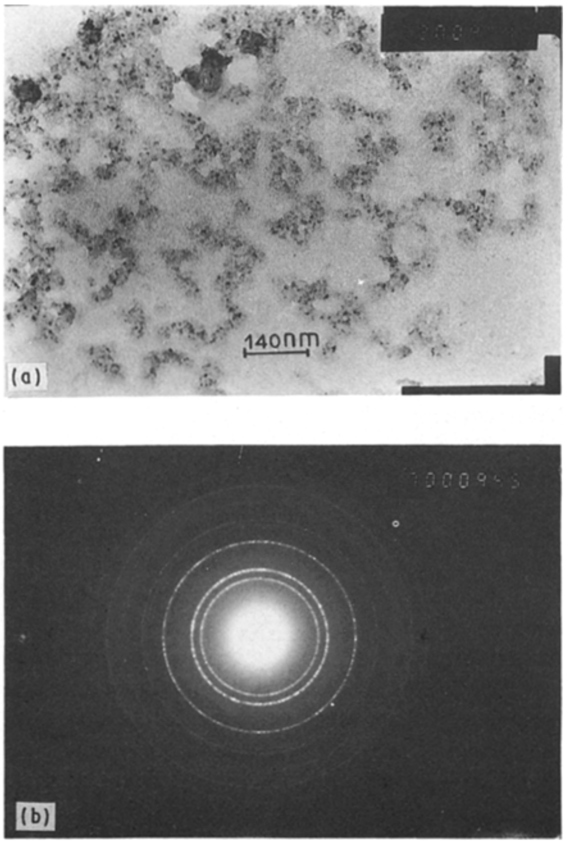


Figure 10 (a) Electron micrograph of ion-exchanged glass no. 2; (b) selected area electron diffraction pattern of (a).

4. Discussion

From the data presented above, it is evident that none of the glasses in its virgin state exhibits conductivity by an electron tunnelling mechanism between aluminium metal islands, as was to be expected in these systems [5]. The reason lies in the fact that the aluminium metal granules form clusters within the glasses and are not dispersed uniformly throughout the glass matrices. As shown above, only in the case of glass 2 are these particles seen to be present in the silver-rich phase after the ion-exchange operation.

The electrical resistivity of ion-exchanged glass 2 prior to switching is controlled by the silver ions within the co-continuous silica-rich phase, as shown by the electron micrograph in Fig. 12. The silica-rich phase therefore contributes to the high activation energy because of the rigidity of the glass network [8]. The disjointed silver-rich phase containing aluminium particles is the high-conducting phase which becomes co-continuous at a critical electrical field. The latter brings about a growth of the HIE phase to the percolation configuration, as discussed earlier [3]. This model predicts a decrease in the value of the critical electric field with an increase in temperature. The data shown in Fig. 6 are in agreement with this prediction. The rather high critical electric field for glass 2 can be explained on the basis of its microstructure in the ion-exchanged state. As mentioned above, its microstructure is characterized by a number of breaks of average width 10 nm in the otherwise semicontinuous form. The electrical field needed for the growth of the silver-rich phase to a percolation condition will therefore be higher than in the case of other glasses where the width of such possible breaks is much smaller. The exact value in the latter cases could not be determined because of the resolution limit of the electron microscope.

We analyse the voltage–current characteristics of the Wagner's polarization cell in terms of the electron and hole components of conductivity, σ^0_- and σ^0_+, respectively, as follows. The current density J is given by [7]

$$J = (\sigma^0_- + \sigma^0_+ e^{VF/RT})RT/Fl \qquad (1)$$

where V is the voltage across the sample; F, Faraday

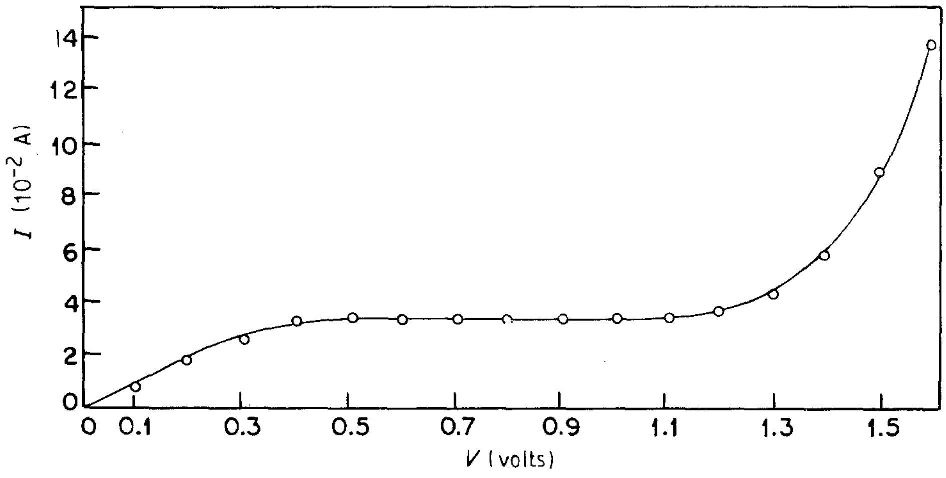


Figure 11 Current voltage curve in asymmetric cell Ag/(HIE)$_3$/C$^+$ at 110 °C.

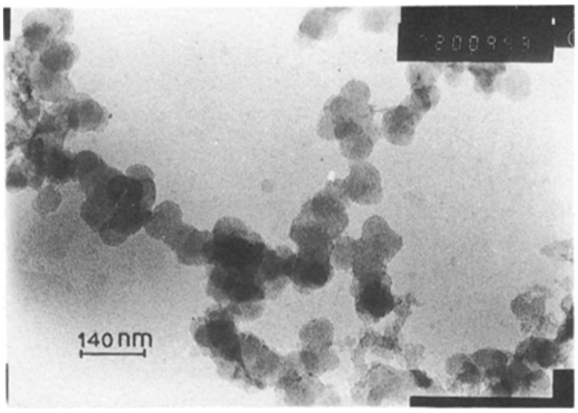


Figure 12 Electron micrograph of silica-rich phase in ion-exchanged glass no. 2.

constant; R, gas constant; T, temperature in K, and l, sample thickness.

Assuming $\sigma_-^0 \gg \sigma_+^0$, we can write Equation 1 for the constant current region of Fig. 11 as

$$J \approx \sigma_-^0 RT/Fl \qquad (2)$$

Using the values of different parameters as obtained from experimental data, we estimate a value of $\sigma_-^0 \sim 0.96\,\Omega\,\mathrm{cm}^{-1}$. The corresponding resistivity $\rho_-^0 \sim 1.0\,\Omega\,\mathrm{cm}$ is of the same order of magnitude, but smaller than the measured HIE resistivity of glass 2:9 Ω cm. Similar results are obtained for all the glasses investigated. It can therefore be concluded that the HIE state of the present series of glasses is controlled by an electronic conduction mechanism.

The above conclusion is apparently at variance with that drawn in an earlier investigation involving glasses of a different composition, but ion-exchanged with silver and subjected to an electric field [6]. It is likely that the conducting silver-rich glasses prepared by the ion-exchange technique act as an electrolyte and contribute to electrodeposition of silver on the cathode. If filaments of metallic silver form by this process and bridge the two electrodes, a highly conducting state with electrons as the predominant charge carriers will result. A detailed study of the microstructure of different ion-exchanged and switched glasses is necessary before any definite conclusion on the above model of the high-conducting state can be drawn. Such work is now in progress. It should be noted, however, that a continuous silver-rich phase must form first, before any electrodeposition mechanism of the type envisaged as above can set in.

5. Conclusions

High electrical conductivity has been induced in bulk glasses of the systems Na_2O–B_2O_3–SiO_2–Al and Na_2O–B_2O_3–Al, respectively, by subjecting them to a sodium silver-exchange treatment followed by a suitable electric field at different temperatures. The resistivities in the switched state are found to have values in the range 3 to 10 Ω cm. The microstructure of the ion-exchanged glasses, in general, consists of a silver-rich semi-continuous phase. Wagner's asymmetric cell measurements indicate that the conductivity in the switched state is electronic in nature.

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