The superionic AgI–Ag$_2$O–V$_2$O$_5$ system: electrical conductivity studies on glass and polycrystalline forms

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Superionic conducting glasses in the AgI–Ag$_2$O–V$_2$O$_5$ system were prepared by heating the appropriate amounts of raw materials at 723 K and quenching in liquid nitrogen. The polycrystalline materials were prepared by slowly cooling the melt to room temperature. X-ray diffraction was used for material characterization. The electrical conductivity of the pulverized samples, pressed together with an electrode mixture of silver and electrolyte (1 : 2 by weight) under 5000 kg cm^{-2} pressure to form pellets 10 mm in diameter and 2 to 3 mm in thickness, was measured in the temperature range 300 to 365 K at 1 kHz. The ionic conductivities of the glasses were always higher than those of their polycrystalline counterparts, while their activation energies were also slightly higher. Conductivity measurements on annealed glassy samples indicated that the conductivity decreases with the time of annealing, and reaches a constant value which is nearly the same as that of the polycrystalline sample. Electronic conductivities of both types of sample were obtained by using Wagner's polarization cell technique, which showed that the electronic conductivity for both types was five orders of magnitude less than the total conductivity. Typical galvanic cells having the configuration Ag,electrolyte/electrolyte/C,electrolyte,I$_2$ were constructed and the silver ion transport number was calculated by the e.m.f. method.

1. Introduction
Till about two decades ago, high conductivity electrolytes suitable for the preparation of solid-state electrochemical devices were found to have a peculiarly definite crystalline structure [1, 2]. However, now large values of ionic conductivity have been reported for vitreous phases obtained from AgI–Ag oxysalt systems [4]. These glasses have some fundamental advantages over the polycrystalline materials, e.g. isotropy, the possibility of being continuously modified in a wide composition range, and a relatively simple preparation method, especially as thin film and homogeneous blocks. Considering all these advantages the extension of the previous studies to an unexplored system seems justified.

In the preliminary investigation [3] it was seen that there were no differences in the results obtained from the ternary system AgI–Ag$_2$O–V$_2$O$_5$ when compared with the pseudo-binary system, AgI–Ag$_3$VO$_4$. It was also seen that the activation energy for silver ion migration in the polycrystalline Ag$_7$I$_4$VO$_4$ corresponding to the ternary proportions (mol%) of 66.67 AgI–25 Ag$_2$O–8.33 V$_2$O$_5$ was the same as the heat of transport as determined by the thermoelectric power studies. This paper deals with the preparation, characterization, electrical conductivity study and transport number determination of the silver ions in glasses and polycrystalline materials of different compositions in the ternary systems AgI–Ag$_2$O–V$_2$O$_5$ with Ag$_2$O/V$_2$O$_5$ = 3.

2. Experimental procedure
2.1. Sample preparation
Analar grades of AgI, Ag$_2$O, and V$_2$O$_5$ were used as raw materials for the sample preparation. The mixed raw materials of different compositions were sealed in Pyrex glass ampoules at a vacuum of 10^{-5} torr. The ampoule was then heated to 623 K for 24 h. The melt was then cooled in two ways. In the first instance, the tubes were dropped into liquid nitrogen while in the second case the material was slowly allowed to reach room temperature [3]. The compounds obtained in both ways were characterized by using a Philips X-ray generator Model 1140.

2.2. Electrical conductivity
The electrical properties of pulverized glasses and polycrystalline material were carried out in the range 300 to 365 K at 1 kHz using a General Radio Co. impedance bridge (GR 1650). The pulverized material was pressed together using an electrode mixture of silver and electrolyte (1 : 2 by weight) under 5000 kg cm^{-2} pressure to form a pellet 10 mm in diameter and 2 to 3 mm thick.

The electronic contribution to the total conductivity of the best conducting composition, both in the glassy and polycrystalline forms, was determined from the current–potential curves for the cell configuration Ag/electrolyte/C using Wagner's polarization technique [5].
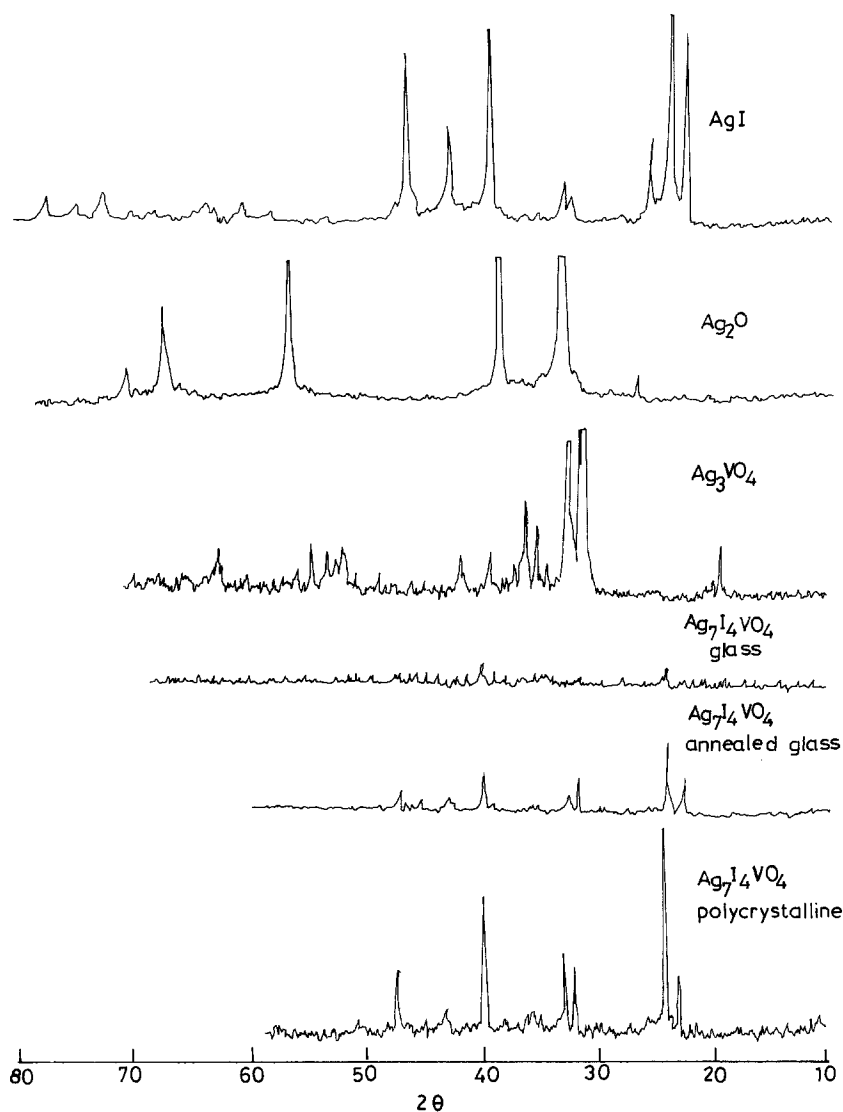
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Figure 1 X-ray diffraction patterns of the raw materials, and glassy and polycrystalline $Ag_7I_4VO_4$ (2θ).

2.3. Transport number measurement

The transport number of silver ions in the glassy and polycrystalline electrolytes was measured by the e.m.f. method. A cell of the type Ag,electrolyte/electrolyte/I_2,C,electrolyte was used. The transport number of the silver ions, t_r, can be found by the relation $t_r = E/E_0$, where E is the e.m.f. measured and E_0 is the standard e.m.f. corresponding to the cell reaction obtained from thermodynamical calculations.

3. Results and discussions

Fig. 1 shows typical X-ray diffraction patterns of $AgI-Ag_2O-V_2O_5$ (66.67 : 25 : 8.33) samples prepared by quenching in liquid nitrogen, by slow cooling, and by annealing the quenched samples at 315 K, along with the patterns for AgI, Ag_2O and Ag_3VO_4. The peak-free X-ray diffractogram of the quenched samples indicates that the sample is in glassy form. Among the polycrystalline samples, the compound corresponding to the proportions 66.67 : 25 : 8.33 was found to have the composition $Ag_7I_4VO_4$ when compared with the standard available data [6].

3.1. Variation of conductivity with composition

Fig. 2 shows the variation of conductivity with the composition of the electrolyte, both in the amorphous and polycrystalline forms for the $AgI-Ag_2O-V_2O_5$

system. It is seen that the conductivity of the amorphous form is about five times greater than that of the corresponding polycrystalline material for all compositions, and also that log σT for the amorphous form increases almost linearly with the AgI content. It is seen that the composition (mol %) 66.67 AgI–25

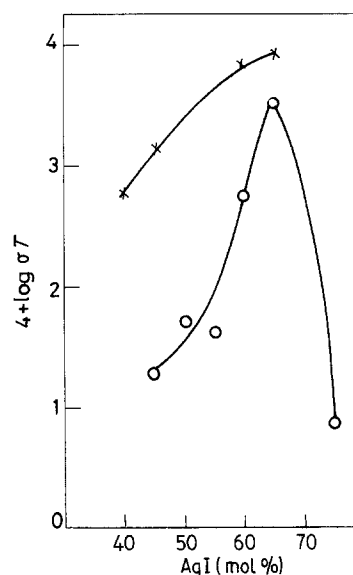*Figure 2* Plot of log σT against AgI content for (×) glassy and (O) polycrystalline materials in the system $AgI-Ag_2O-V_2O_5$.
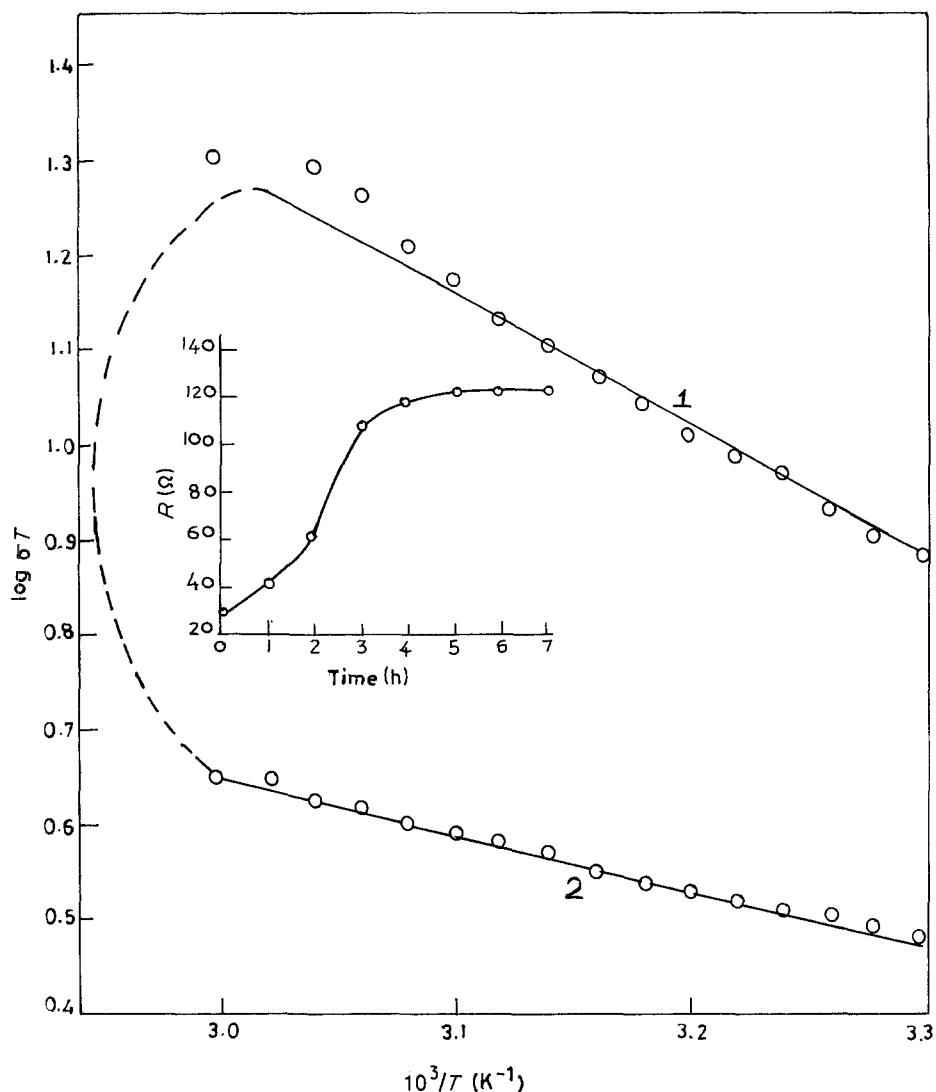
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Figure 3 Log σT against $10^3/T$ plot for 66.67 AgI–25 Ag$_2$O–8.33 V$_2$O$_5$ (mol%) for glass (Curve 1) and annealed glass (Curve 2). Inset shows the variation of sample resistance with time while the sample was being annealed at 338 K.

Ag$_2$O–8.33 V$_2$O$_5$ gives the highest conductivity at room temperature. Also the polycrystalline compound of this composition corresponds to Ag$_7$I$_4$VO$_4$ as confirmed by the X-ray diffraction data. Table I compares the room-temperature conductivities and activation energies of the various polycrystalline compositions with those of the corresponding glasses.

3.2. Variation of conductivity with temperature

Fig. 3 compares the variation of conductivity with temperature for amorphous and annealed glass

samples. It is seen that the variation below 330 K is along Curve 1 which denotes the glassy state. Above this temperature the conductivity decreases, and after a sufficient annealing period (5 h) the conductivity varies along a different path (Curve 2). This shows that the material retains its glassy state until 330 K, after which ordering starts to take place. The room-temperature conductivity of the annealed glass is less than that of the material prepared in polycrystalline form. The transition temperature of each composition is given in Table I.

Fig. 3 shows the variation of the sample resistance

TABLE I Conductivities and activation energies of samples

| Composition (mol %)			Polycrystalline samples		Glassy samples		T_g
AgI	Ag$_2$O	V$_2$O$_5$	σ_{305} (Ω^{-1}cm^{-1})	E_a (eV)	σ_{305} (Ω^{-1}cm^{-1})	E_a (eV)	(K)
75	18.75	6.25	1.34×10^{-4}	0.33	2.14×10^{-4}	0.29	–
70.84	21.88	7.29	3.07×10^{-4}	0.23	2.3×10^{-3}	0.29	330
66.67	25.00	8.33	1.05×10^{-3}	0.17	5.3×10^{-3}	0.27	330
62.50	28.13	9.38	6.26×10^{-4}	0.20	2.53×10^{-3}	0.30	332
58.33	31.25	10.42	1.79×10^{-4}	0.25	2.18×10^{-3}	0.26	332
50.00	37.50	12.50	1.19×10^{-5}	0.27	1.9×10^{-3}	0.27	334
41.67	43.75	14.58	4.18×10^{-6}	0.35	1.45×10^{-3}	0.32	339
33.33	50.00	16.67	4.91×10^{-6}	0.35	7.9×10^{-4}	0.29	–
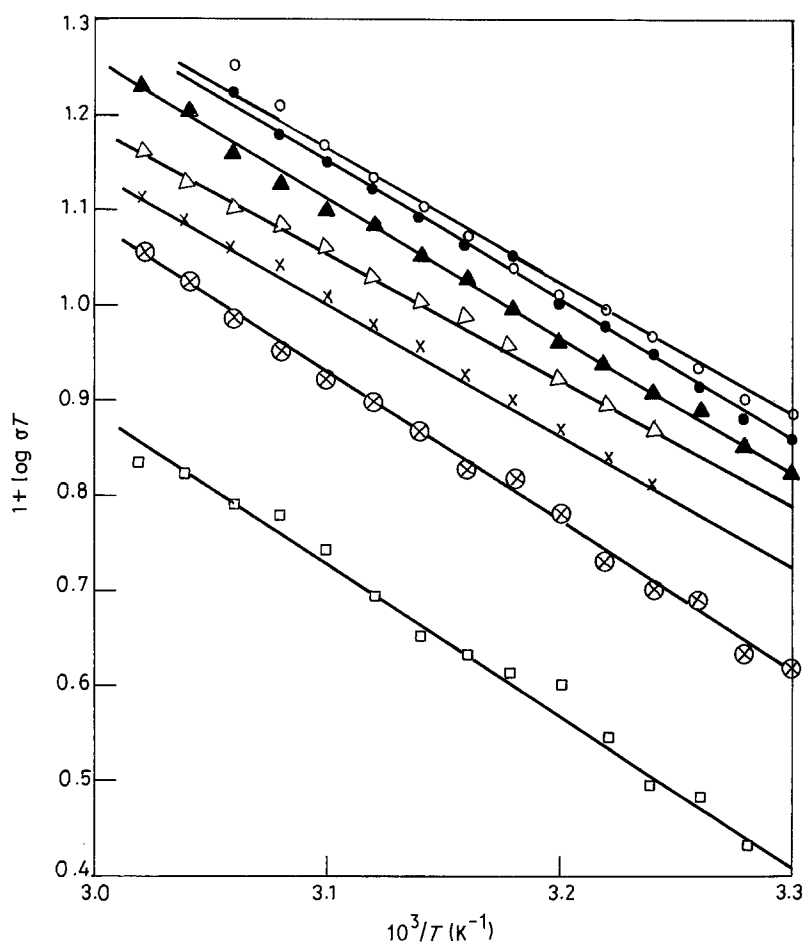
Figure 4 Plots of log σT against $10^3/T$ for different compositions of $AgI-Ag_2O-V_2O_5$ glasses. Proportions of $AgI : Ag_2O : V_2O_5$ as follows: (▲) 70.80 : 21.88 : 7.29, (○) 66.67 : 25.00 : 8.33, (●) 62.50 : 28.13 : 9.38, (△) 58.33 : 31.25 : 10.42, (×) 50.00 : 37.5 : 12.5, (⊗) 41.67 : 43 75 : 14.58, (□) 33.33 : 50.00 : 16.67.

with time when it was being annealed at 350 K. The resistance of the sample increases and attains a constant value after about 5 h.

Figs 4 and 5 show the log σT against $10^3/T$ plots for the glassy and polycrystalline samples studied in the $AgI-Ag_2O-V_2O_5$ system. The conductivities below the glass transition temperature are expressed by the relation $\sigma = (\sigma_0)/T \exp(-E/kT)$ as in the case of other silver ion conducting glasses [4], where σ_0 is a constant, T is the absolute temperature, k is the Boltzmann constant and E is the activation energy for Ag^+ ion conduction. The activation energies calculated from the slopes of the plots show that those for the glassy samples are slightly larger than their corresponding polycrystalline counterparts (Table I). Such variations are also reported in the case of $AgI-Ag_2O-P_2O_5$ glasses [7]. For polycrystalline samples, the room-temperature conductivity shows a sharp peak at the 66.67 : 25 : 8.33 composition, whereas for the glasses it was seen that log σT varies almost linearly with increasing AgI content up to 66.67 mol %, after which glass formation was not observed. The almost linear variation of room-temperature conductivity with increasing AgI content for glasses indicates that there is a strong partial covalency existing between Ag^+ ions (introduced in the form of Ag_2O) and non-bridging oxygen (NBO). These Ag^+ ions can be considered to be less mobile as compared to the Ag^+ ions surrounded by I^- ions [4] (introduced in the form of AgI).

3.3. Electronic contribution to conductivity

Wagner's polarization cell, of configuration $(-)Ag/$ electrolyte$/C(+)$, was used to determine the electronic contribution to the total conductivity of the highest conducting glassy and polycrystalline composition (66.67 : 25 : 8.33) of the $AgI-Ag_2O-V_2O_5$ system. On applying a d.c. potential below the decomposition voltage of the silver electrolytes to the above configuration (graphite $+$ve w.r.t. silver), at equilibrium conditions the flow of the silver ions due to the electrical gradient will equal the flow due to the chemical gradient and the total current will be carried by the electrons and/or electron holes only. In a cationic conductor this current is given by [5]

$$I = I_e + I_h = \frac{RTA}{LF} \left\{ \sigma_e \left[1 - \exp\left(\frac{-EF}{RT}\right) \right] + \sigma_h \left[\exp\left(\frac{EF}{RT}\right) - 1 \right] \right\} \quad (1)$$

where I_e and I_h represent the currents due to the electrons and holes, respectively, A is the area of cross-section, L the thickness of the electrolyte, R the gas constant, F the Faraday constant and T the absolute temperature. Dividing Equation 1 by $[\exp(EF/RT) - 1]$,

$$\frac{I}{\exp(EF/RT) - 1}$$

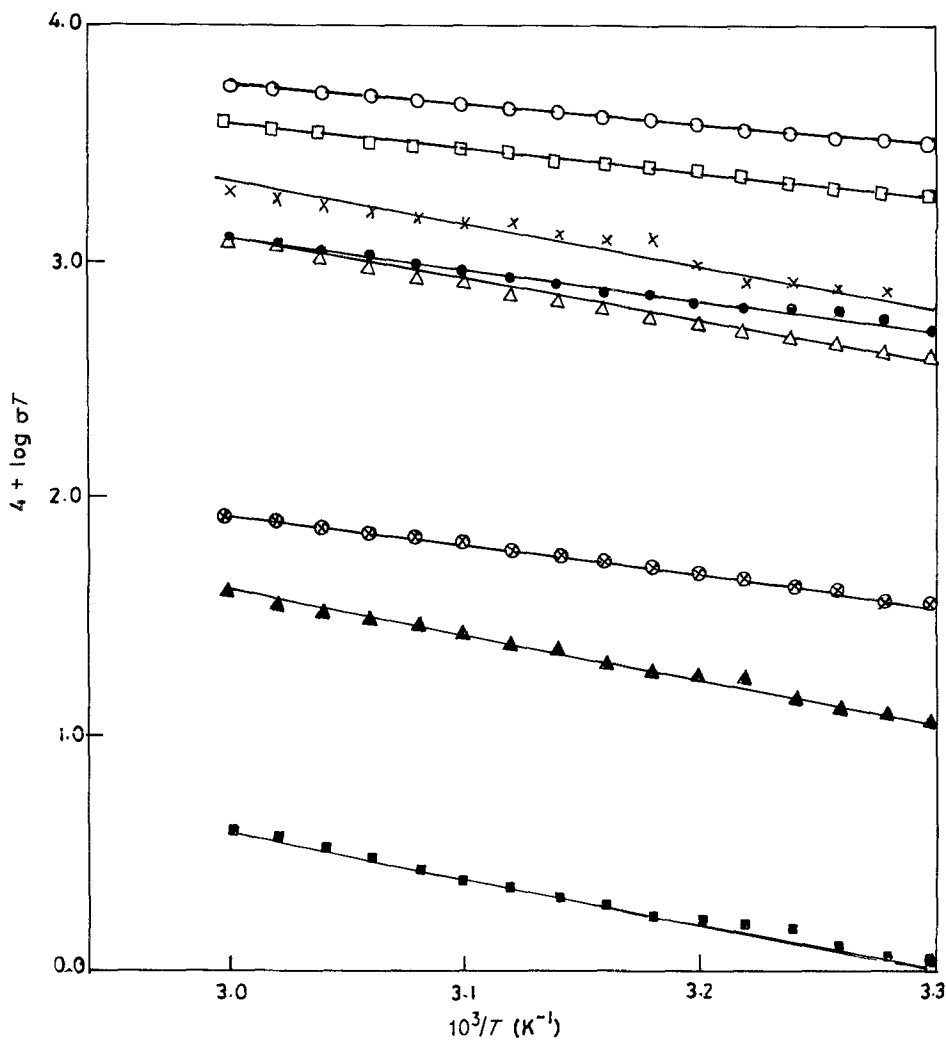$$= \frac{RTA}{LF} \left[\sigma_e \frac{1 - \exp(-EF/RT)}{\exp(EF/RT) - 1} + \sigma_h \right]$$

Figure 5 Plots of log σT against $10^3/T$ for different compositions in $AgI-Ag_2O-V_2O_5$ polycrystalline system. Proportions of $AgI:Ag_2O:V_2O_5$ as follows: ($\triangle$) 75:18.75:6.25, ($\times$) 70.84:21.88:7.29, ($\bigcirc$) 66.67:25.00:8.33, ($\square$) 62.50:28.13:9.38, ($\bullet$) 58.83:31.25:10.42, ($\otimes$) 50.00:37.50:12.50, ($\blacktriangle$) 41.67:43.75:14.58, ($\blacksquare$) 33.33:50.00:1667.

when $EF \gg RT$,

$$\frac{I}{\exp (EF/RT) - 1}$$

$$= \frac{RTA}{LF} [\sigma_e \exp (-EF/RT) + \sigma_h] \qquad (2)$$

A plot of $I/[\exp (EF/RT) - 1]$ against $\exp (-EF/RT)$ will thus give a straight line, the slope of which gives the electronic conduction due to electrons, while the intercept on the y axis gives the contribution due to the electronic holes.

Usually the conductivity is due either to electron or to electronic holes only. Therefore

$$I = I_e = \frac{RTA}{LF} \sigma_e[1 - \exp (-EF/RT)]$$

when $\sigma_e \gg \sigma_h$ \qquad (3)

$$I = I_h = \frac{RTA}{LF} \sigma_h[\exp (EF/RT) - 1]$$

when $\sigma_h \gg \sigma_e$ \qquad (4)

When the applied d.c. potential is sufficiently high such that $EF \gg RT$, then Equations 3 and 4 reduce to

$$I = I_e = (RTA/LF)\sigma_e \qquad (5)$$

$$I = I_h = (RTA/LF)\sigma_h \exp (EF/RT) \qquad (6)$$

The above equations indicate that the electronic current will saturate, while the hole current will increase exponentially with the applied voltage.

Figs 6 and 7 show these plots for both the polycrystalline and glassy materials, respectively. The plateau on the I–V plot at 70 mV for polycrystalline material (Fig. 6b) and 80 mV for glassy material (Fig. 7b) indicates that the electrons are the majority carriers in the electronic conduction. This is further confirmed by the vanishing value of the intercept on the $I/[\exp (EF/RT) - 1]$ against $\exp (-EF/RT)$ plot, signifying the absence of hole conductivity. The above values for the electronic conduction were obtained from the I against $[1 - \exp (-EF/RT)]$ plots for both types of materials (Figs 6a and 7a), at three different temperatures. These plots are straight lines, the slopes of which are equal to $\sigma_e(RTA/LF)$. Since the quantities in the parenthesis are known, σ_e can be calculated. It is evident from the plots that the electronic contribution is mainly due to electrons only, the values of which for polycrystalline and glassy samples are 3.93×10^{-8} and $4.68 \times 10^{-8} \Omega^{-1} cm^{-1}$, respectively.

3.4. Transport number measurement

To determine the transport number by the e.m.f. method, a galvanic cell of the configuration $Ag,Ag_7I_4VO_4/Ag_7I_4VO_4/I_2Ag_7I_4VO_4,C$ was constructed. The
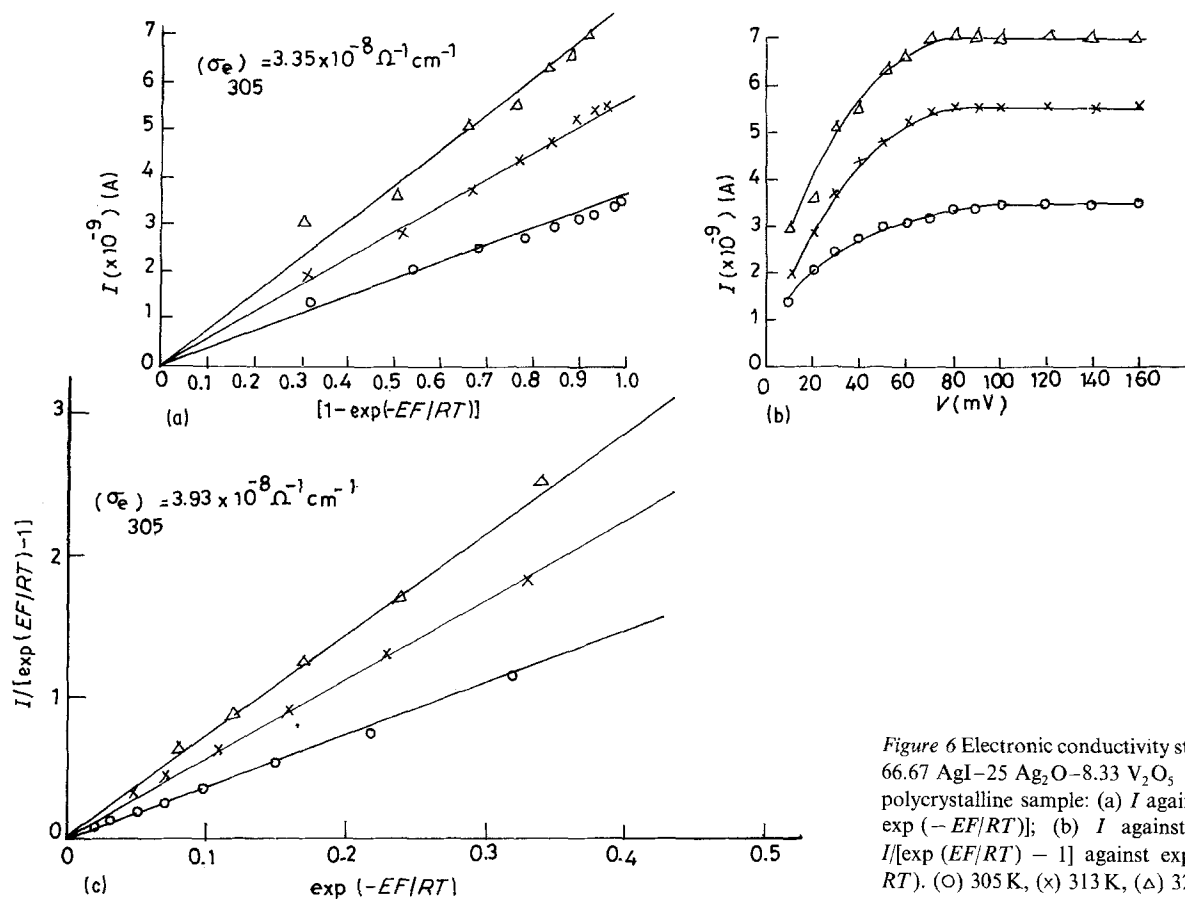
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Figure 6 Electronic conductivity studies on 66.67 AgI–25 Ag$_2$O–8.33 V$_2$O$_5$ (mol %) polycrystalline sample: (a) I against [1 – exp $(-EF/RT)$]; (b) I against V; (c) I/[exp (EF/RT) – 1] against exp $(-EF/RT)$. (O) 305 K, (x) 313 K, (Δ) 323 K.

weights of the anode, electrolyte and cathode were 0.58, 1.5 and 0.88 g, respectively. The battery was in the form of a cylindrical pellet, 2.5 mm thick and having a diameter of 13 mm. The open-circuit voltage for glass was found to be 0.682 mV. Taking the theoretical value of the OCV to be 0.687 mV, the ionic

transference number was calculated to be 0.993 and electronic transport number to be 0.007. For polycrystalline material the OCV was 0.683 V, which gives the silver ion transport number as 0.994 and the electronic transport number as 0.006. The transport number as determined by the polarization technique (Section 3.3)
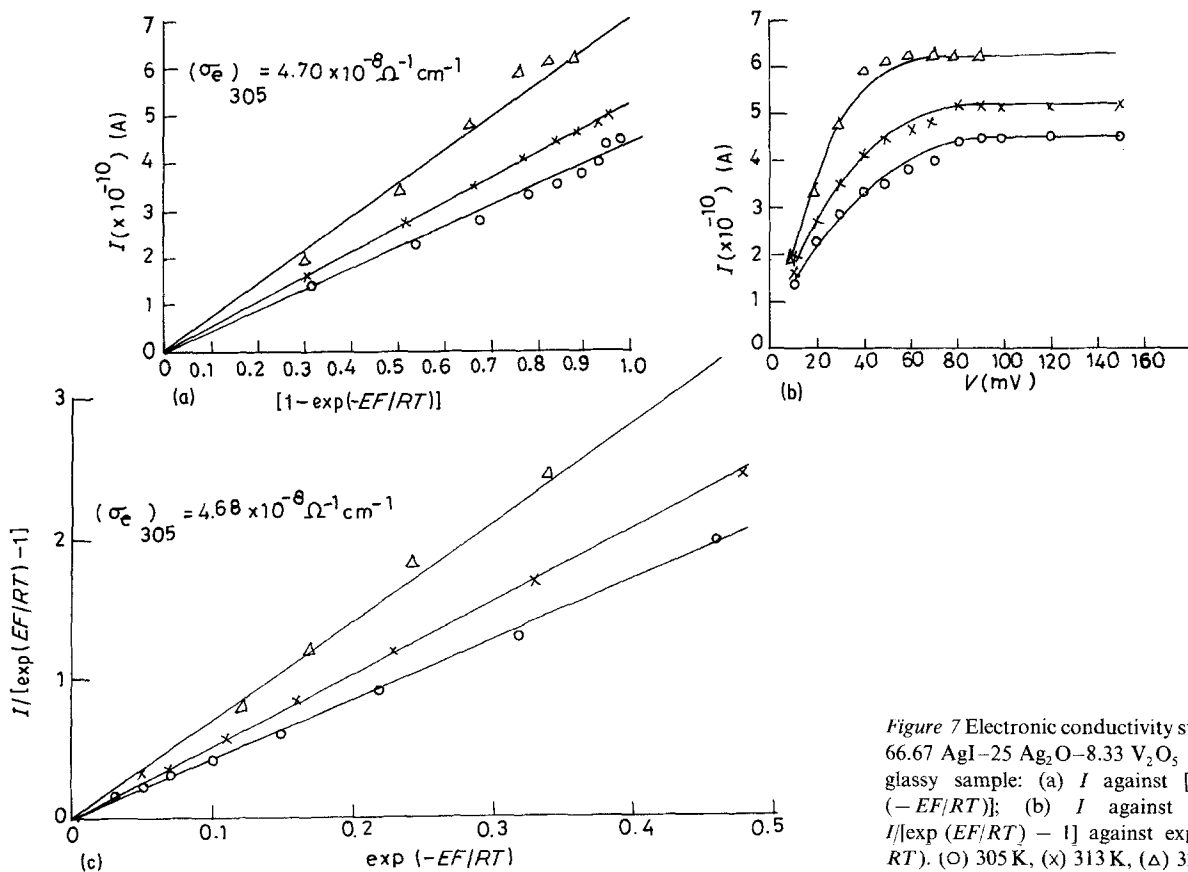

Figure 7 Electronic conductivity studies on 66.67 AgI–25 Ag$_2$O–8.33 V$_2$O$_5$ (mol %) glassy sample: (a) I against [1 – exp $(-EF/RT)$]; (b) I against V; (c) I/[exp (EF/RT) – 1] against exp $(-EF/RT)$. (O) 305 K, (x) 313 K, (Δ) 323 K.

was 0.999 for silver ions and 0.001 for electrons for both glassy and polycrystalline materials. In both cases the electron hole current was negligibly small and could thus be ignored. However, it is seen that the electron transport number for both glassy and polycrystalline materials as determined by the e.m.f. technique is about two orders of magnitude higher than those determined by polarization studies. This may be attributed to the increase in the concentration of electronic carriers because of the probable diffusion of I_2 (from the cathode material) into the electrolyte. These values are in close agreement with those obtained from the studies done on electrolyte prepared by using AgI and Ag_3VO_4 as raw materials [3].

4. Conclusions

1. $AgI-Ag_2O-V_2O_5$ glasses were prepared by heating different compositions of the above compounds at 450° C for 24 h and quenching them in liquid nitrogen. The highest conducting glass in the $AgI-Ag_2O-V_2O_5$ system for $Ag_2O/V_2O_5 = 3$ has the composition (mol %) 66.67 AgI–25 Ag_2O–8.33 V_2O_5.

2. For any particular ratio, the glassy form has a higher conductivity at any temperature as compared with polycrystalline samples.

3. Electronic conductivity measurements were undertaken using Wagner's technique. The electronic conductivity came out to be $4.68 \times 10^{-8}\,\Omega^{-1}\,cm^{-1}$ for glassy and $3.93 \times 10^{-8}\,\Omega^{-1}\,cm^{-1}$ for polycrystalline samples.

4. Transport number measurement was made using the e.m.f. technique. The silver ion transport number came out to be almost unity for glass and polycrystalline materials.

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