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Fast ion conducting glasses: effect of preparation on conductivity and its correlation with surface analysis using SEM

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Glasses in the system $AgI–Ag_2O–As_2O_3$ and $AgI–Ag_2O–As_2O_5$ were prepared by three different methods and characterized by studying their transport and surface properties. A.c. conductivity studies performed on the samples with compositions (mol %) 66.6 AgI–33.3 ($xAg_2O–yAs_2O_3$) and 66.6 AgI–33.3 ($xAg_2O–yAs_2O_5$) for $y/x = 0.20$ to 5.0 revealed that the glasses are very good ionic conductors. The highest ionic conductivity was observed for the compositions $66.6AgI–16.66Ag_2O–16.66As_2O_3$ and $66.6AgI–16.66Ag_2O–16.66As_2O_5$, when prepared by the open-air crucible melting and rapid quenching method and $66.6AgI–16.66Ag_2O–16.66As_2O_3$ and $66.6AgI–22.2Ag_2O–11.11As_2O_5$, when prepared by the vacuum-sealed quartz tube melting and zone-controlled quenching method. The observation of high ionic conductivity for different glass former/glass modifier ratios in the $AgI–Ag_2O–As_2O_5$ system and its dependence on the method of preparation was explained by correlating the observed surface properties. The contribution of electronic conductivity to the total conductivity was estimated by Wagner's d.c. polarization technique. The surface of the bulk specimens belonging to the highest conducting composition in both the systems was studied using a scanning electron microscope to observe the formation of precipitated β- and α-AgI in the form of colloids which are assumed to be responsible for high ionic conductivity.

1. Introduction

The many diverse and novel properties possessed by glassy ternary fast-ionic conductors of the general formula $AgI–Ag_2O–M_nO_m$ ($M_nO_m = As_2O_3$, B_2O_3, V_2O_5, P_2O_5, As_2O_5, MoO_3, CrO_3 and WO_3) have given rise to the rapid growth of research activity into their ionic and electronic transport properties, surface analysis and application to solid state ionic devices [1–5]. Although the ionic conductivity is the most important factor that influences the application of an electrolyte to a particular device, electronic structures of glassy materials also influence all the above-mentioned properties and hence a knowledge of electronic structures is fundamental to the understanding of transport, chemical and dielectric properties. Nevertheless, these studies on glasses are still in an early stage of development compared to the other areas of solid state sciences.

In glasses, the surface composition is frequently quite different from that of the bulk form. This surface segregation phenomenon appears to be so important in glasses that extensive work on it has to be carried out. The essential driving force for segregation is believed to be the lowering of total free energy. However, in solidification phenomena, there is a segregation mechanism that can cause surface segregation even when the total free energy does not favour the formation of an enriched surface layer. This is due to the solid redistribution that occurs at the liquid–solid boundary. It can cause the solute to accumulate on the surface during freezing. Hence in silver-based fast-ion conducting glasses, a non-linear behaviour of ionic conductivity with different glass former (GF) to glass modifier (GM) ratio might be due to the formation of different natured segregation layers [6, 7]. In rapidly quenched glasses, the segregation behaviour can be explained in terms of a dendrite segregation and their known differences in solidification characteristics. As-quenched structures vary greatly ranging from fine dendrite structures to featureless grains: surface analysis supplements the transport data. It seems to be clear by now that the cooling rate is the most significant factor that determines the quenched structure [8]. As the cooling rate increases, the quenched structures change from branch dendrites via cellular structures to featureless grains. In fact, it will be very interesting

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to observe all the above structures using a scanning electron microscope.

With this new hypothesis, a study of transport and surface analysis on silver-based arsenate glasses was attempted. The availability of arsenic oxide in the form of As_2O_3 (trivalent cation) and As_2O_5 (pentavalent cation) is the factor that is responsible for this glass former to prove the above hypothesis. Also the decomposition of As_2O_5 to As_2O_3 above 350 °C necessitated the need to develop a new method of preparation in which segregation layers can be created artificially.

2. Preparation

The starting materials AgI, Ag_2O, As_2O_3 and As_2O_5 were obtained from Aldrich Inc., USA, and the crucibles used for melting were specially designed and made from high-quality quartz material from Corning Inc., USA. The chemicals were handled carefully in an argon glove box because As_2O_5 is highly hygroscopic and toxic in nature.

To create different layers of segregation and study the transport and surface analysis, the two ternary systems AgI–Ag_2O–As_2O_3 and AgI–Ag_2O–As_2O_5 were prepared by three different methods. The first is the open-air crucible melting and rapid quenching method (OCM) and the second, the vacuum-sealed quartz tube melting and quenching method (ZCQ) [9]. The third method of preparation is similar to the second but with a modification in the process of quenching. Instead of rapid quenching, a difference in quenching rates of the order of 10^3 K sec^{-1} was artificially created by heating the quartz tube at the bottom in a vertical position with a high-temperature flame from a gas burner. A coiled tube was wound around the crucible for the passage of liquid nitrogen at a controlled pressure. After the melting of the compound in the quartz crucible, the gas burner was extinguished and liquid nitrogen was passed through the circulating quartz tube from a nitrogen-refrigerated-liquid cylinder (Cryogenics Services Inc., Canton, Georgia, USA, model UN-1977). Hence a temperature gradient of 2000 K was created and thus different quenching rates. Owing to the high-temperature, AgI–Ag_2O–As_2O_5 decomposes, and on cooling at different quenching rates segregated layer compounds with traces of As_2O_3, As_2O_5 mixed with α-AgI were observed. Then corresponding compositions were also prepared by the other two methods and a comparative study of transport and surface analysis was attempted.

3. Experimental procedure

The glasses prepared by the three different methods were checked for glassy nature by recording the X-ray diffractograms using a Phillips X-ray generator model PW 1140. Ionic conductivity measurements were carried out on pulverized samples by pressing the samples with silver powder and electrolyte (1:2 ratio) together to form the electrodes under a pressure of 6000 kg cm^{-2} using a Perkin–Elmer hand press. Studies on pulverized samples were undertaken to investigate the effect of pressing pressure on ionic conductivity. Then four different pellets were made with varying thickness (by varying the weight content and constant pressure) to find the electrode–electrolyte interfacial resistance of the sample for zero thickness. The samples were annealed just below the glass transition temperature for a protracted period in order to allow mechanical stress relaxation and configurational relaxation to take place on which there is a reduction in volume, because the glass relaxes to a more stable state after which the charge carriers will be homogenized.

The ionic conductivity was measured with the configuration (Ag)/(glassy sample)/(Ag) on a GR 1689 precision RLC digibridge model operating at a fixed frequency of 1.0 kHz. The electronic conductivity with a cell configuration (Ag)/(glassy sample)/(graphite) was measured using Wagner's d.c. polarization technique employing a Kiethley 617 model with a digital data station and an X–Y recorder to plot the I–V characteristic curves at a constant gain for all the samples.

Small amounts of the glasses were pulverized, dispersed in KBr powder and polyethylene powder to be made into thin pellets to record infrared and Fourier infrared spectra in the regions 400 to 4000 and 20 to 400 cm^{-1}, respectively, using a Perkin–Elmer model 918 and a Polytec model 30, respectively. The presence of arsenate groups or arsenate structures in the glassy samples was confirmed from the spectra and will be shown elsewhere [10]. The surface of the glass sample was scanned using a scanning electron microscope model Phillips EM-200 at a maximum accelerating voltage of 100 kV and a magnification ranging from ×25,000 to ×100 000.

4. Transport analysis

4.1. A.c. conductivity studies

At room temperature (25 °C) the a.c. conductivity, σ_i, for all the samples was evaluated by measuring the impedance of the pellet at 1.0 kHz. Polycrystalline traces were observed in both the systems AgI–Ag_2O–As_2O_3 and AgI–Ag_2O–As_2O_5 when prepared by the conventional vacuum-sealed method. On the observation of low ionic conductivities of the order of magnitude $10^{-4}\,\Omega^{-1}\,cm^{-1}$ and high activation energies, the polycrystalline nature was confirmed and hence the room-temperature variation of ionic conductivity with GF/GM ratio is not shown here. Only data related to the samples prepared by OCM and ZCQ methods were plotted and are presented for a discussion.

Fig. 1a shows the variation of ionic conductivity with GF/GM ratio ranging from 0.33 to 3.0. The highest ionic conductivity was observed for the (mol %) 66.6 AgI–22.2 Ag_2O–11.1 As_2O_5 glass, with a value of $5.2 \times 10^{-2}\,\Omega^{-1}\,cm^{-1}$ when the glass was prepared by the ZCQ method. Lower values of ionic conductivity were observed for 66.6 AgI–16.6 Ag_2O–16.6 As_2O_3 and 66.6AgI–16.6Ag_2O – 16.6As_2O_5 glasses with values of $2.0 \times 10^{-2}\,\Omega^{-1}\,cm^{-1}$ and $2.6 \times 10^{-2}\,\Omega^{-1}\,cm^{-1}$, respectively, when prepared by

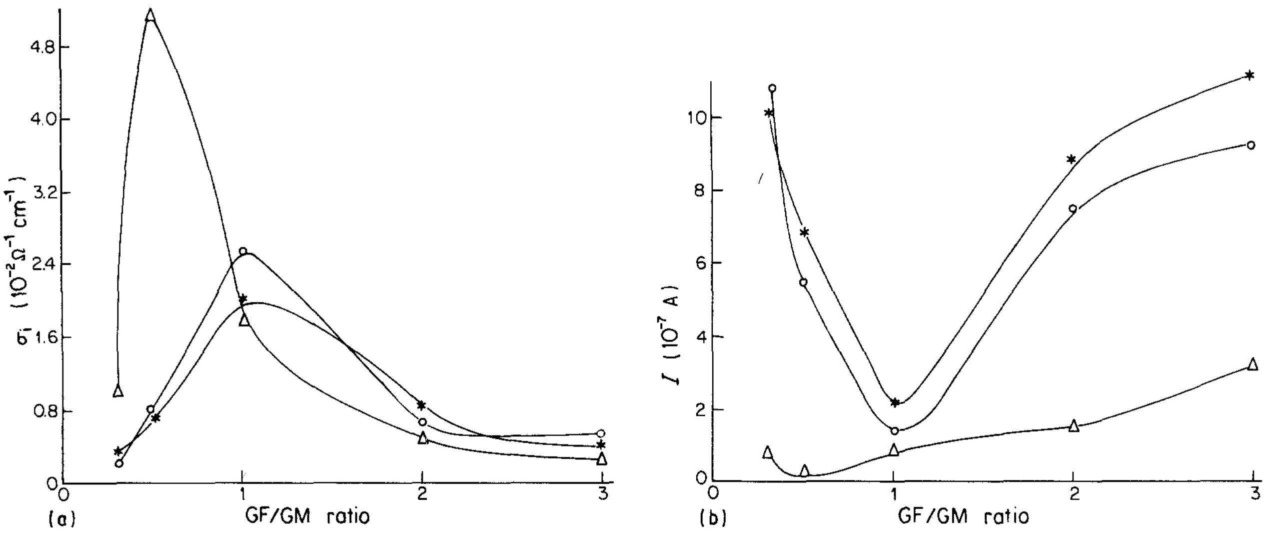

Figure 1 Variation of (a) ionic conductivity and (b) electronic current at 23° C with different glass former to glass modifier ratio (GF/GM). (∗) AgI–Ag_2O–As_2O_3, OCM; (○) AgI–Ag_2O–As_2O_5, OCM; (△) AgI–Ag_2O–As_2O_5, ZCQ.

the OCM method. Hereafter the above-mentioned highest conducting glasses are referred to as As_2O_3 and As_2O_5 glasses preceded by their method of preparation in order to compare the observed properties. Both As_2O_3 and As_2O_5 glasses prepared by the OCM method show maximum ionic conductivity for the same GF/GM ratio of 1.0, whereas As_2O_5 glass prepared by the ZCQ method has a maximum ionic conductivity for a GF/GM ratio 0.50. The observation of highest ionic conductivity in both As_2O_3 and As_2O_5 by the OCM method for the same GF/GM ratio is attributed to the possibility of decomposition of As_2O_5 to As_2O_3 in the process of heating the melt in the open air. Hence, although the starting material is As_2O_5, the glass former reduces to As_2O_3 and thus behaves similar to the As_2O_3 glass. The high ionic conductivity in the As_2O_5 glass when prepared by the ZCQ method was believed to be due to the presence of segregated layers of As_2O_3 and As_2O_5 polyhedral structures as assumed in the hypothesis. Also, the GF/GM ratio (0.50) having the highest ionic conductivity was in true conformity with the other glass formers of the same type with pentavalent cation oxides V_2O_5 and P_2O_5 [11, 12]. Both AgI–Ag_2O–As_2O_3 and AgI–Ag_2O–As_2O_5 glasses prepared by the OCM method follow the same pattern as observed in the case of other trivalent cation glass forming oxide B_2O_3 [13] and hexavalent oxides CrO_3, MoO_3 and WO_3 [14–16], where the highest conducting compositions were obtained for GF/GM ratio of 1.0. Thus it can be concluded that the arsenic cation exists in the 3+ valence state in both AgI–Ag_2O–As_2O_3 and AgI–Ag_2O–As_2O_5 glasses prepared by the OCM method. The observation of slightly higher values of ionic conductivities for the same GF/GM ratio in the As_2O_5 system when compared to the As_2O_3 system prepared by the OCM method is proof of the fact that As_2O_5 is a better glass former, although it is highly hygroscopic, toxic and decomposes above 350 °C.

The variation of log σT with reciprocal of temperature as shown in Fig. 2 for both As_2O_3 and As_2O_5 glasses prepared by the OCM method were almost the same, indicating that arsenic exists only in the 3+

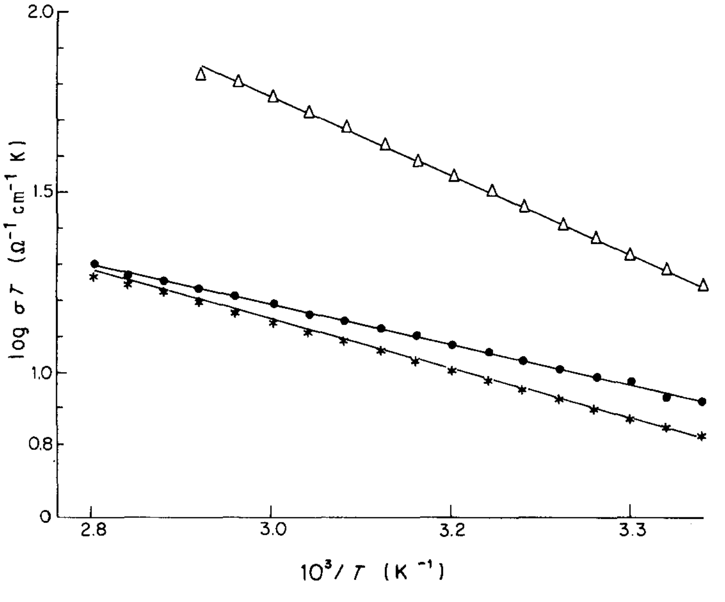

Figure 2 Log σ T–$10^3/T$ for the highest conducting As_2O_3 and As_2O_5 glasses prepared by (∗, ●) OCM and (△) ZCQ. (∗) 66.67 AgI–16.66 Ag_2O–16.66 As_2O_3, (●) 66.67 AgI–16.66 Ag_2O–16.66 As_2O_5; (△) 66.67 AgI–22.22 Ag_2O–11.11 As_2O_5.

TABLE I Values of ionic and electronic conductivities for different GF/GM ratios in the two systems AgI–Ag_2O–As_2O_3 and AgI–Ag_2O–As_2O_5 prepared by OCM and ZCQ methods

Sample	Method of preparation	GF/GM ratio	$\sigma_i(\times 10^{-3})$	$\sigma_e(\times 10^{-7})$
AgI–Ag_2O–As_2O_3	OCM	0.33	3.0	10.1
		0.50	6.9	6.8
		1.00	20.0	2.1
		2.00	8.1	8.9
		3.00	4.0	11.6
AgI–Ag_2O–As_2O_5	OCM	0.33	2.0	10.8
		0.50	8.0	5.3
		1.00	25.0	1.01
		2.00	6.8	7.4
		3.00	4.9	9.1
AgI–Ag_2O–As_2O_5	ZCQ	0.33	10.01	0.50
		0.50	52.0	0.1–8
		1.00	18.0	0.80
		2.00	5.3	0.144
		3.00	2.5	0.213

state. The low activation energy in the OCM As_2O_5 glass further supports the statement that As_2O_5 is a better glass former with easier Ag^+ ion migration through the As_2O_3 glassy network with As_2O_5 as starting material. This might be due to the availability of more bridging oxygen atoms in As_2O_5, due to partial decomposition of As_2O_5 to As_2O_3. On similar grounds of argument, the observation of high ionic conductivity in the ZCQ As_2O_5 glasses can be substantiated by the assumption of segregated layers of As_2O_3 and As_2O_5 as the liberated oxygen cannot escape out of the vacuum-sealed quartz tube. Thus, it has to react chemically when quenched to form partial covalent bonds that bridge As^{3+}–O–As^{4+} or As^{3+}–O–As^{3+} or As^{5+}–O–As^{5+} macromolecular chains that break and segregate as branch dendrites via cellular structures to featureless grains. This phenomenon takes place due to the lowering of total free energy in the whole of the system. The high activation energy which seemingly contradicts the above hypothesis can be explained on the basis of polycrystalline traces that were observed when the X-ray diffractogram was recorded. This observation was also in conformity with similar observation in the AgI–Ag_2O–V_2O_5 system [11], where an explanation was not given. This observation strongly supports the existence of arsenic in the 5+ valence state.

The glass transition temperatures for As_2O_3 and As_2O_5 glasses prepared by the OCM method are in the region of 85 °C, and for As_2O_5 glasses prepared by the ZCQ method in the region of 66 °C. The low glass transition temperature further supports the assumption that arsenic is in pentavalent state in accordance with the other pentavalent cation glass-former oxides V_2O_5 and P_2O_5 [12]. One interesting observation is that, whether arsenic exists in the 3+ or 5+ state, the variation of log σT with reciprocal of temperature was found to be Arrhenius like in nature, with the glass transition temperature obeying the equation

$$\sigma = (\sigma_0/T)\exp(-E/RT)$$

as in the case of other silver ion conducting glasses [17, 18] where σ_0 is the pre-exponential factor, E is the activation energy for Ag^+ ion migration, T the absolute temperature and R the universal gas constant.

4.2. D.c. conductivity studies

The electronic conductivity of the glasses having maximum ionic conductivity were determined by Wagner's d.c. polarization technique. The order of magnitude of electronic conductivity was the same in both OCM As_2O_3 and As_2O_5 glasses. The observation of low electronic conductivity for a GF/GM ratio of 1.0 in both As_2O_3 and As_2O_5 glasses prepared by the OCM method further supports the conclusion from the a.c. conductivity studies that arsenic exists in the 3+ state in both the systems. Also, the nature of the variation of electronic current for both As_2O_3 and As_2O_5 glasses prepared by the OCM method as shown in Fig. 1b is similar, which also supports the above statement. The variation of electronic current for ZCQ As_2O_5 glasses was observed to be different from the OCM method, which explains the formation of polycrystalline or segregated layers whose electronic current does not follow the usual behaviour as observed in the case of fast-ion conducting glasses.

Fig. 3a, shows the I–V characteristics of highest conducting compositions. The saturation of current at higher applied potentials for all the above three samples indicates that the contribution was only from electrons and not from holes. Thus the total current, I, passing through the polarization cell, under steady state is given by

$$\begin{aligned} I &= I_e + I_h \\ &= (RTA/LF)\{\sigma_e[1 - \exp(-EF/RT)] \\ &\quad + \sigma_h[\exp(EF/RT) - 1]\} \qquad (1) \end{aligned}$$

where I_e and I_h represent the currents due to electrons and holes, respectively, A is the area of cross-section, L the thickness of the sample, R the gas constant, F the Faraday constant, E the applied potential and T the absolute temperature. As the conductivity is due to electrons, the above equation reduces to

$$I \sim I_e \sim (RTA/LF)\sigma_e \qquad (2)$$

From Fig. 3a, it can be observed that at higher potentials, the electronic current saturates with applied potential. Both As_2O_3 and As_2O_5 glasses prepared by the OCM method have almost equal saturation potentials and were high when compared to that of As_2O_5 glasses prepared by the ZCQ method. As_2O_5 glass prepared by the ZCQ method has a very low electronic conductivity of the order of $\sim 10^{-8}\,\Omega^{-1}\,cm^{-1}$ whereas As_2O_3 and As_2O_5 prepared by the OCM method have relatively high electronic conductivities. Fig. 3b shows the current, I, against $[1-\exp(-EF/RT)]$ plots for the As_2O_3 and As_2O_5 glasses. From the above I–V characteristic curves, it was concluded that conduction was due to electrons only. With this the current (I) was found to vary linearly with $\exp(-EF/RT)$. From the slope of the straight lines in Fig. 3b, σ_e was evaluated by calculating the slope and substituting for RTA/LF.

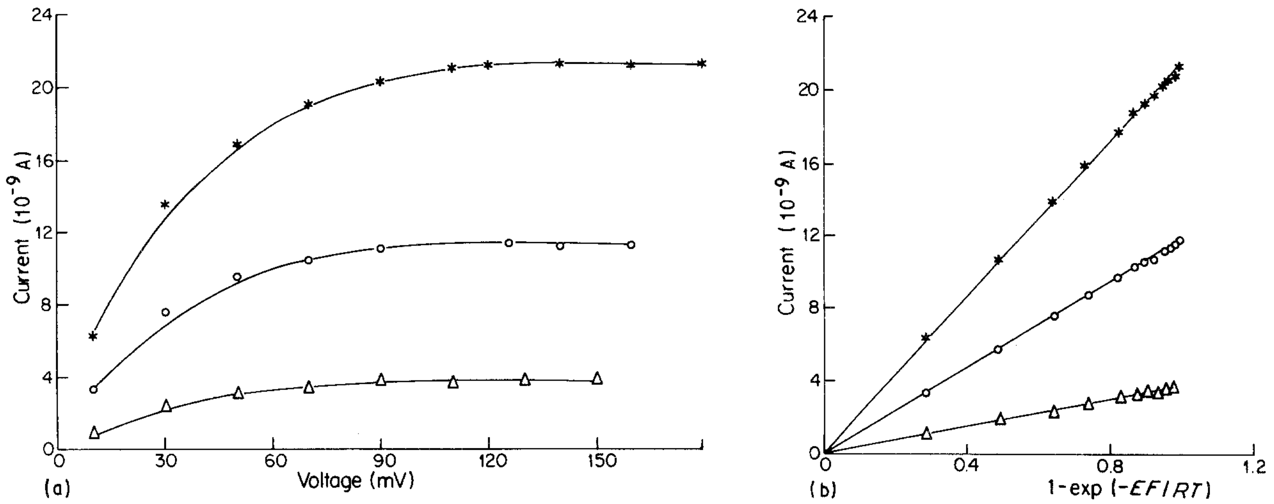

Figure 3 (a) I–V characteristics, and (b) I–$[1 - \exp(-EF/RT)]$ plots for the highest conducting As_2O_3 and As_2O_5 compositions. For key, see Fig. 1.

Thus from the d.c. conductivity studies it can be concluded that the contribution of d.c. conductivity is from electrons and was low enough to be negligible. Thus the materials can be used as glassy electrolytes in solid state ionic devices.

5. Surface analysis

The surfaces of three bulk samples As_2O_3, As_2O_5 prepared by the OCM method and As_2O_5 prepared by the ZCQ method were scanned to observe the difference in the nature of surfaces and to relate this to the observed differences in conductivity. When the amount of Ag_2O exceeds a certain value (GF/GM = 2.0), then the capability of the glass to harden decreases and soft glasses form. This condition may be related to the formation of ionic clusters or open channel-like structures, as can be seen in the photographs shown in Figs 4 and 5. Fig. 4 shows a photograph of the As_2O_3 glass prepared by the OCM in which ionic cluster-like features can be seen. As the same area is magnified further, a single unit of the ionic cluster (polyhedral structures) is seen to have an open channel-like structure for easy ion migration as shown in Fig. 5. The formation of ionic clusters due to the partial valency of As_2O_3 and As_2O_5 in the glass-forming network with the existence of open cage-like structures with iodine polyhedra linked to metal ions of the glass former, and the presence of both As_2O_3 and As_2O_5 in the same glass as-layered structures, decreases the enthalpy of glass due to evolution of oxygen. Thus the observation of low T_g, when compared to that of semiconducting vitreous As_2O_3 [19] is in conformity with the previously observed microphase separation in K_2O–P_2O_5–WO_3 glasses [20]. Whereas when the surface layer was scanned with a magnification of 3×10^6, bright and dark spots were observed which were assumed to be ion polyhedral structure or cellular dendrites as can be seen in the photograph of Fig. 6. This could not be observed on the surface of glasses with low ionic conductivities as in the case of As_2O_3 and As_2O_5 glasses prepared by the OCM method as shown in Fig. 7. Also the silver metal colloids that exist in the glass due to rapid quenching change to the brittle condition as can be observed from the photograph shown in Fig. 8, where small amounts of metallic silver can be observed in the As_2O_5 glasses prepared by the ZCQ method, which have very high ionic conductivity. The observed physical changes on the surface of the glasses with As_2O_5

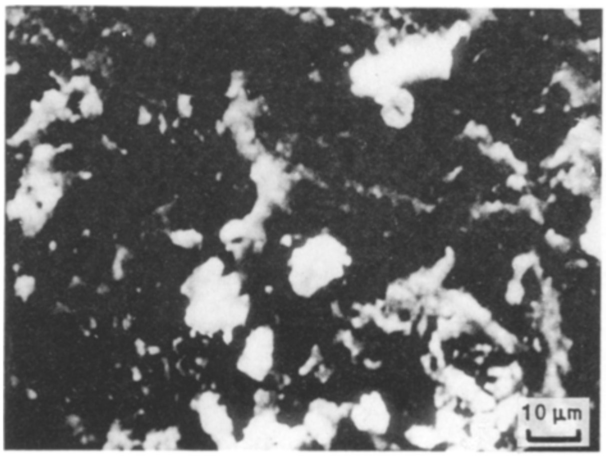

Figure 4 Photograph showing the ionic cluster-like features.

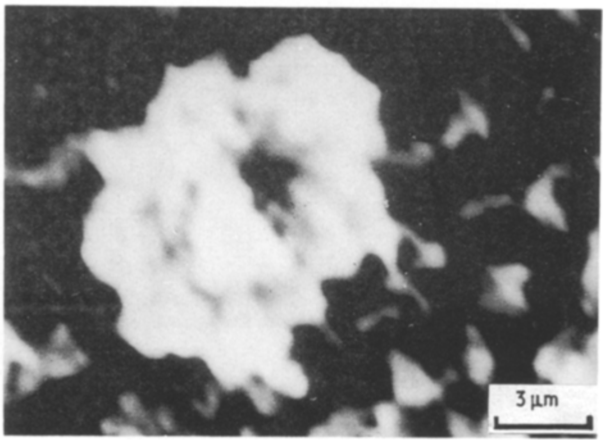

Figure 5 Photograph showing the open channel-like structures.

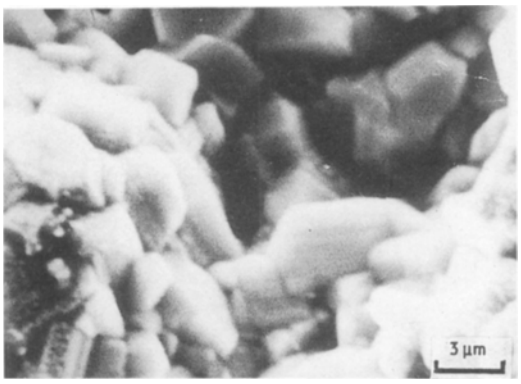

Figure 6 Photograph showing the cellular dendrites.

prepared by the ZCQ method lead to the conclusion that the criteria of inhomogeneities in glasses with high ionic conductivity when GF/GM = 1.0 cause local stress concentration. The formation of points or planes of defects in the form of fine points and layer-like structures, which are shown in Fig. 9a and b are attributed to the presence of silver ions in dual valency (Ag^+ and Ag^0). When the content of Ag_2O increases further for GF/GM ratio greater than 1.0, the already existing defects reach the dimensions of pits and etches covering an area of several square millimetres, as can be seen in Fig. 10. These trap the mobile cations which corresponds to the observation of low ionic conductivities.

6. Conclusions

$AgI–Ag_2O–As_2O_5$ glasses, when prepared by the open-air crucible melting method, reduce to $AgI–Ag_2O–As_2O_3$ and show analogous behaviour in the variation of ionic conductivity with GF/GM ratio. However, when the same $AgI–Ag_2O–As_2O_5$ is prepared by the zone controlled quenching method, it shows the highest ionic conductivity for a GF/GM ratio of 2.0 analogous to $AgI–Ag_2O–V_2O_5$ and $AgI–Ag_2O–P_2O_5$ and hence the existence of As_2O_5 can be confirmed. The observation of low electronic conductivities in the system $AgI–Ag_2O–As_2O_3$ when compared to $AgI–Ag_2O–As_2O_5$ is an indication of the nature of the glass former's ability to form bridging atoms of the configuration $As^{4+}–O–As^{5+}$ for the small polaron hopping to take place, as in the case of semiconducting oxide glasses. The observation of high ion conductivity in the glasses with As_2O_5 prepared by the vacuum-sealed quartz tube and zone-controlled quenching method is attributed to the formation of precipitated β- and α-AgI in the form of dendrites, as confirmed from the electron microscope pictures. The formation of layered or segregated structures with ionic clusters which act as pathways for ion migration in glass is believed to be responsible for the high silver mobility in $AgI–Ag_2O–As_2O_5$ glasses. The $AgI–Ag_2O–As_2O_3$ glasses prepared by the OCM method do not contain any traces of β- or α-AgI precipitates

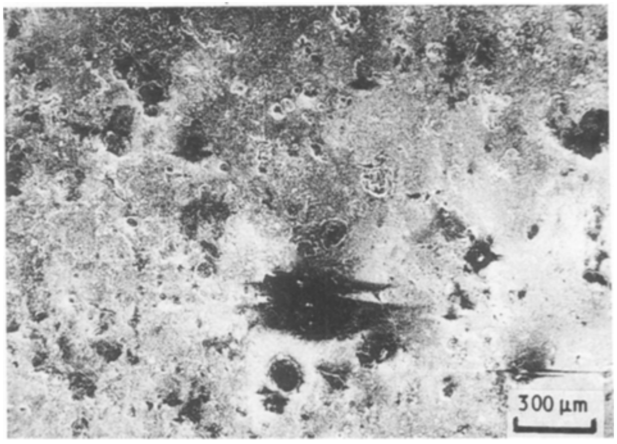

Figure 7 Photograph showing the absence of dendrites on the glass surface.

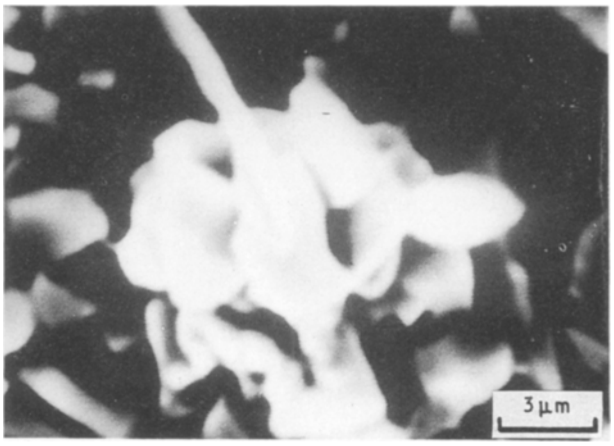

Figure 8 Photograph showing the existence of silver metal colloids.

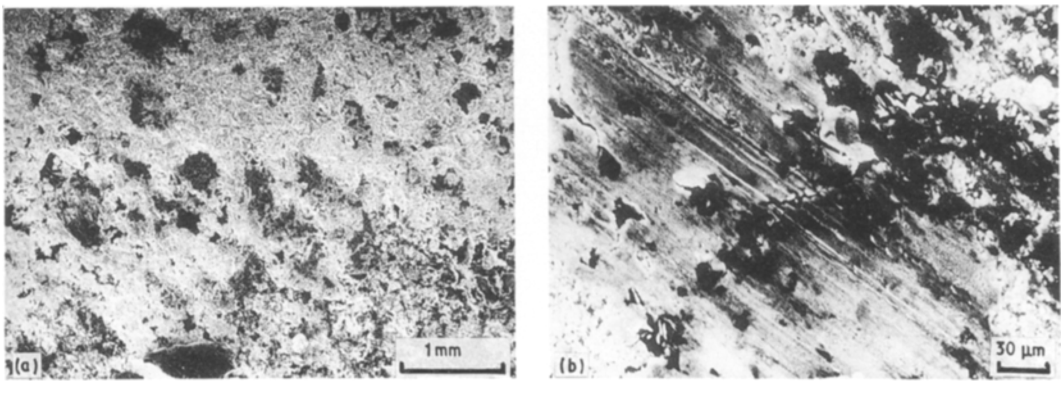

Figure 9 The existence of (a) point defects and (b) plane defects on the surface of the glasses.

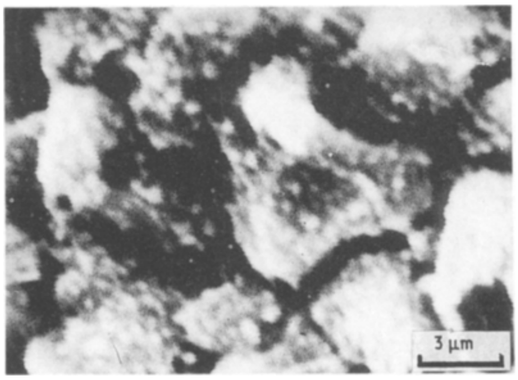

Figure 10 The presence of pits and etches on the surface of the glass.

and this is due to the uniform distribution of As_2O_3 as glass forming network. Glasses AgI–Ag_2O–As_2O_5 when vacuum sealed and quenched, might contain both As_2O_3 and As_2O_5 polymorphs which segregate into different layers and provide open channels for ion migration. In this process, the arsenic polyhedra, formed due to the slow cooling rate, are believed to be responsible for the high ion mobility. As these ionic clusters cannot be observed in X-ray diffractograms, further analysis using spectroscopic techniques was attempted and is being reported elsewhere [10].

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