

Ionic transport in the (AgI:AgCl) mixed-system

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Ionic mobility, conductivity, number of charge carriers and transference number are reported for annealed and rapidly quenched $[x\text{AgI}:(1-x)\text{AgCl}]$ mixed systems, these results are compared with AgI. Of these three materials the quenched mixed-system had the highest Ag^+ ion conductivity. Further, preliminary studies are reported where the high conductivity system (i.e. quenched 0.75 AgI:0.25 AgCl) has been used as host material for the preparation of Ag^+ ion conducting glasses and composites. Detailed thermal/phase diagram studies have also been carried out on the quenched composition. The conductivity enhancement in the quenched system is attributed to the formation of new disordered phases and the introduction of amorphisity, the simple space-charge model applicable to the annealed system failed to explain these results.

1. Introduction

Silver ion conducting solid electrolytes in the glassy/amorphous and composite phases have attracted widespread interest in recent years due to their possible applications in solid state electrochemical devices [1–3]. The majority of these solids have been prepared with AgI as the host compound, where the high conducting α -phase ($> 147^\circ\text{C}$) of AgI has been partially stabilized or preserved at lower temperatures, either by quenching with various glass formers and glass modifiers [4–6] or by dispersing different second phase dispersoids [7–9]. Very few attempts have been made to replace AgI with an alternative host compound. It is suggested here that a quenched-in mixed-system of AgI:AgCl, in the mol wt (%) of 75:25, is an alternate host, exhibiting transport properties superior to AgI, having an indentical $\beta \rightarrow \alpha$ -like transition at ca. 135°C .

Conductivity anomalies in the AgI/AgCl two phase composite system have recently been studied by Lauer and Maier [10]. To prepare the composites, these authors melted the AgI/AgCl composition and left it to anneal at ca. 200°C for 24 h before cooling it to room temperature. They reported that the maximum enhancement in conductivity (σ ca. $3 \times 10^{-5} \text{ S cm}^{-1}$ at 30°C) for the melt and the annealed AgI:AgCl composite occurred at the 75:25% ratio. The conductivity enhancement was attributed to the increased silver ion vacancy conduction in the space-charge region of the AgI/AgCl interface. However, detailed studies on the ionic transport properties (mobility, number of charge carriers etc.) of this mixed-system have not been done. Further, the effect of different thermal treatments of the samples has also not been investigated.

In this paper results of the following experimental investigations on the $x\text{AgI}:(1-x)\text{AgCl}$ mixed-system are reported:

1. the effect of the rate of thermal cooling (slow and rapid quenching) of the melt on the room temperature conductivity values as a function of molar ratio, x ;
2. DTA studies to construct the phase diagram;
3. temperature variation of conductivity;
4. direct measurement of silver ion mobility, μ , as a function of temperature;
5. evaluation of mobile ion concentration, n , [from (3) and (4)] at different temperatures.
6. the use of the best composition of (AgI:AgCl) as host (instead of AgI) in the preparation of Ag^+ ion conducting glass and composite.

2. Experimental procedure

AgI and AgCl [Reidel (India) Ltd] were used as supplied. The homogeneous mixtures of $x\text{AgI}:(1-x)\text{AgCl}$ in the molar proportion x were heated to ca. $600\text{--}700^\circ\text{C}$ to a uniform melt. A portion of the melt was quenched rapidly at ca. $10\text{--}20^\circ\text{C}$ and the other portion was annealed at ca. 200°C for 24 h and then cooled slowly. Samples were ground separately to fine powders, then pressed at ca. 2 ton cm^{-2} to form pellets of dimensions 1.185 cm in diameter and 0.75–2 mm in thickness. Colloidal silver was painted on as electrodes for the electrical conductivity measurements. The bulk resistance was calculated from the complex impedance plots taken at different temperatures with the help of a computer controlled HIOKI Hi Tester LCR meter (model 3520–01) in the frequency range of 40 Hz to 100 kHz. Ionic mobility as a

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function of temperature and transference number were measured following the transient ionic current (TIC) technique [11–13] and Wagner's d.c. polarization method, respectively. A Graphtec $X-Y-t$ recorder (model WX 2300-IL) was used for these measurements. Differential thermal analysis (DTA) was carried out for the quenched composition at different molar ratios, x . The DTA was done in the Linseis TGA/DTA unit (model 2045).

3. Results and discussion

3.1. Compositional variation of room temperature conductivity and the effect of the rate of cooling (slow and fast)

Fig. 1 shows the variation of room temperature conductivity as a function of the mol wt ratio, x , for the slowly cooled (annealed) and rapidly cooled (quenched) melt of the $x\text{AgI}:(1-x)\text{AgCl}$ mixed-system. Flat conductivity maxima were obtained for both systems in the region of $x = 0.7-0.8$. The annealed samples were prepared in a similar manner to those of Lauer and Maier [10]. Theirs and the present conductivity variation with composition results are qualitatively similar but quantitatively different, due to the different purity of starting materials used. No measurements on quenched samples exist in the literature and so direct comparison was not possible. It is obvious from Fig. 1 that quenched samples show a high conductivity. A $0.75\text{AgI}:0.25\text{AgCl}$ composition was prepared for these studies. The conductivity values for annealed and quenched samples are ca. $1.3 \times 10^{-4} \text{ S cm}^{-1}$ and ca. $3.1 \times 10^{-4} \text{ S cm}^{-1}$, respectively at 27°C . The conductivity enhancement in the annealed composition from the constituent compounds was attributed by Lauer and Maier [10] to the increased mobile ion concentration in the space-charge region of the AgI/AgCl interface. The addi-

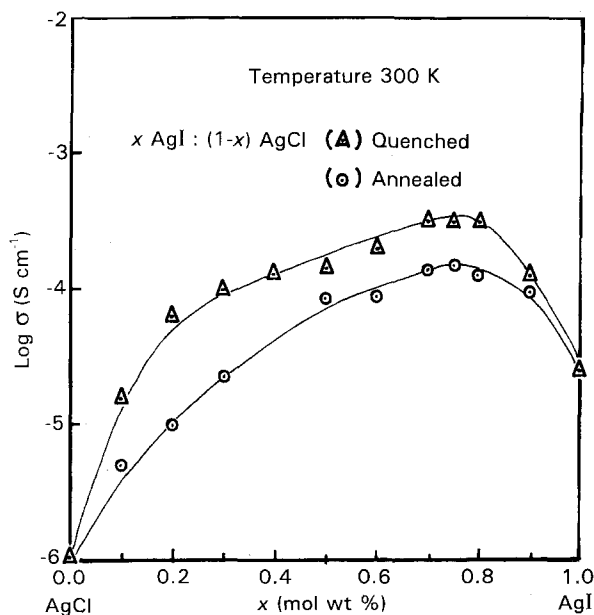


Figure 1 Compositional variation of room temperature conductivity of annealed and quenched $[x\text{AgI}:(1-x)\text{AgCl}]$ mixed-system.

tional enhancement of conductivity for the quenched samples of this study is attributed to the formation of new disordered phases. The formation of these phases, along with the presence of fractional amorphisity, are also indicated by the preliminary XRD results. To support this, a detailed thermal (DTA) study on the quenched samples was carried out, the results are discussed below.

3.2. Thermal/phase diagram study on quenched $x\text{AgI}:(1-x)\text{AgCl}$

Fig. 2 shows the DTA curves of $x\text{AgI}:(1-x)\text{AgCl}$ quenched samples where $x = 0, 0.1, \dots, 0.9, 1$. As the mol wt ratio, x , was increased, the following changes were observed in the DTA curves:

1. The well-defined, intense melting peak of pure AgCl ($x = 0$) at ca. 455°C became smaller and broader, and the peak gradually shifted towards the lower temperature region. The peak positions for $x = 0.1, 0.2$ and 0.3 occurred at $417, 396$ and 343°C , respectively. The peak finally disappeared to higher values of x . However, some new broad and deconvoluted small peaks started to appear in this temperature region, as indicated in Fig. 2.

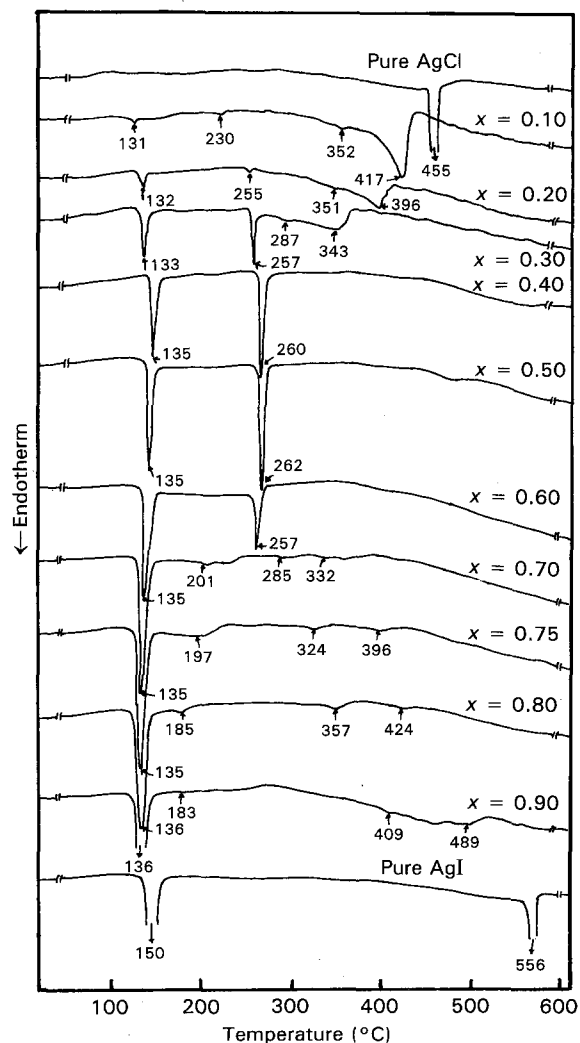


Figure 2 DTA curves for $[x\text{AgI}:(1-x)\text{AgCl}]$ quenched composition.

2. A relatively small, but well-defined, peak appeared at ca. 132°C for $x = 0.1$. The intensity of this peak increased as the fractional amount of AgI increased. This peak is similar to the $\beta \rightarrow \alpha$ transition of AgI with a reduced transition temperature. It should be noted that AgI appeared to become modified in the quenched system, since the characteristic $\beta \rightarrow \alpha$ transition of pure AgI is ca. 147°C.
3. A new well-defined peak appeared at ca. 257°C for the composition of $x = 0.3$. The intensity of this peak increased as x increased to 0.5, then decreased for $x = 0.6$. This peak corresponded to the melting of a newly formed compound, AgI_xCl_y . For higher compositions small and broad deconvoluted peaks appeared in the higher temperature region, as indicated in Fig. 2.
4. In the compositional region $0.7 < x < 0.9$ a very broad and diffused peak was observed just after the $\beta \rightarrow \alpha$ transition peak of modified AgI, as shown in Fig. 2. This broad peak was indicative of the presence of fractional amorphisity in this compositional region.

On the basis of the above study a phase diagram was drawn, which is shown in Fig. 3. AgI was modified (denoted as AgI*) with a reduced $\beta \rightarrow \alpha$ transition temperature, as the AgCl content increased a new compound, AgI_xCl_y , was partially formed. The amorphisity in the compositional region $0.7 < x < 0.9$, as discussed in (4) above, is shown in the diagram. It has been reported that the conductivity enhancement is directly related to the amorphisity in some glass systems [5, 6, 14], hence the enhancement in conductivity from the constituent compounds is expected to be more in the above compositional region. Maximum enhancements with flat maxima in the ratios for $x = 0.7-0.8$, as shown in Fig. 1, were obtained in this study.

3.3. Measurement of conductivity, mobility and mobile ion concentration as a function of temperature

Fig. 4 gives the $\log \sigma$ versus $1/T$ plots for quenched and annealed composition [0.75AgI:0.25AgCl]. Similar plots for AgI and AgCl are also drawn on the figure to allow direct comparison. It is obvious from the figure that the quenched composition exhibits the highest conductivity ($\sigma = 3.1 \times 10^{-4} \text{ S cm}^{-1}$ at 27°C) as compared to other materials. The conductivity of both annealed and quenched compositions initially increased slowly with temperature, followed by abrupt jumps at ca. 140°C and ca. 135°C, respectively, which were identical to the $\beta \rightarrow \alpha$ transition behaviour of AgI. The activation energy values were calculated in both regions of the transition. Table I lists the room temperature conductivity and activation energy values for quenched and annealed compositions, and AgI and AgCl [13]. The ionic transference number measurements was done using Wagner's d.c. polarization method. Table I also gives the transference number, ionic mobility and mobile ion concentration values at room temperature for all four systems. The trans-

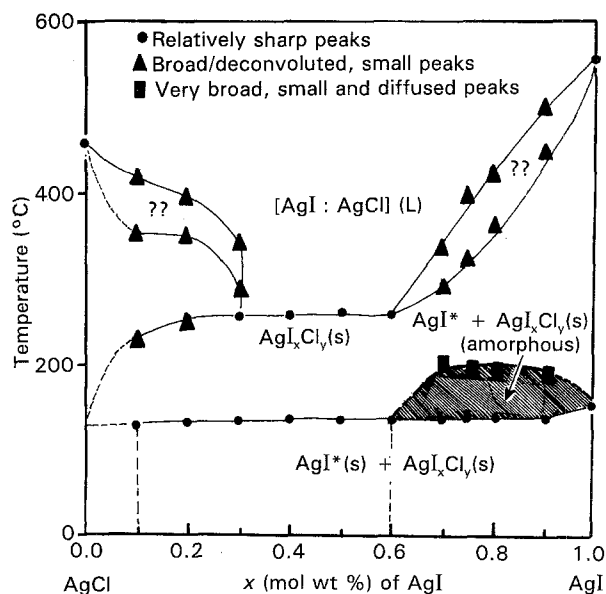


Figure 3 Phase diagram of $[x\text{AgI}:(1-x)\text{AgCl}]$ quenched composition.

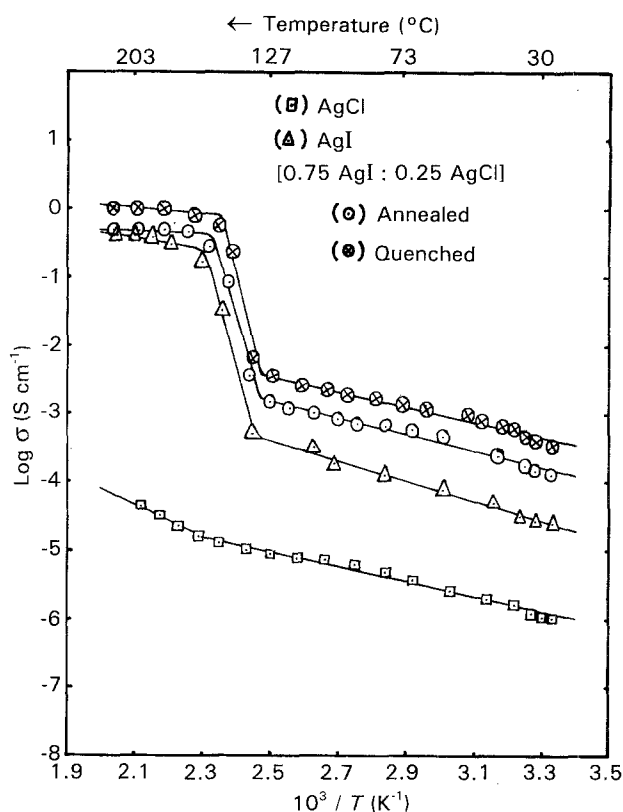


Figure 4 $\log \sigma$ versus $1/T$ plots for [0.75AgI:0.25AgCl] quenched (\otimes) and annealed (\circ) compositions, AgI (Δ) and AgCl (\square).

ference number t_{Ag^+} ca. 1 indicated that the total current in the system was carried only by Ag^+ ions.

Ag^+ ion mobilities at different temperatures were measured by the transient ionic current (TIC) technique. A d.c. potential of 0.5 V was applied across the cell of the following configuration:

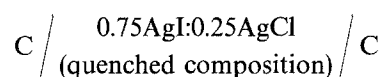


TABLE I Comparison of some important transport parameters of AgI, AgCl, and [0.75AgI:0.25AgCl] annealed and quenched

Material	Ionic conductivity $\sigma_{27^\circ\text{C}}$ (S cm^{-1})	Ionic mobility $\mu_{27^\circ\text{C}}$ ($\text{cm V}^{-1} \text{s}^{-1}$)	Transference number t_{Ag^+}	Activation energy E_a (eV)	Mobile ion concentration n (cm^{-3})	$\beta \rightarrow \alpha$ transition temp. ($^\circ\text{C}$)	Ref.
AgI	2.5×10^{-5}	$(2.5 \pm 1) \times 10^{-2}$	ca. 1	0.29 (β -phase) 0.049 (α -phase)	6×10^{15}	ca. 147	[13, 15]
AgCl	1×10^{-6}	$(3.1 \pm 1) \times 10^{-3}$	ca. 1	0.235	2×10^{15}	—	[13]
0.75AgI:0.25AgCl (annealed)	1×10^{-4}	$(1.5 \pm 1) \times 10^{-2}$	ca. 1	0.24 ($< 140^\circ\text{C}$) 0.025 ($> 140^\circ\text{C}$)	4×10^{16}	ca. 140	This work
0.75AgI:0.25 AgCl (quenched)	3.14×10^{-4}	$(2.4 \pm 1) \times 10^{-2}$	ca. 1	0.23 ($< 135^\circ\text{C}$) 0.05 ($> 135^\circ\text{C}$)	8×10^{16}	ca. 135	This work

where graphite (C) acted as blocking electrodes. The cell was first completely polarized and then the polarity was reversed. The current was recorded with time. The peak in the plot gives the time of flight, τ , i.e. the time taken by the Ag^+ ion to cross the thickness, d , of the sample. The ionic mobility was calculated by the following equation:

$$\mu = \frac{d^2}{V\tau} \quad \left(\frac{\text{cm}^2}{\text{V s}} \right)$$

To confirm the reliability of the above measurements, the ionic mobilities were calculated as a function of pellet thickness (0.05–0.2 cm) and applied voltage (ca. 0.2–0.7 V). The ionic mobility value [μ ca. $(2.4 \pm 1) \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 27°C] was independent of these variables within the experimental error limit. Using conductivity (σ) and mobility (μ) data, the mobile ion concentration (n) was calculated at different temperatures by the well-known expression:

$$n = \frac{\sigma}{q\mu} \quad (\text{cm}^{-3})$$

We obtained n ca. $8 \times 10^{16} \text{ cm}^{-3}$ at 27°C for the quenched composition, one order of magnitude higher than that for AgI (see Table I). Fig. 5 gives the plots of $\log \mu$ versus $1/T$ and $\log n$ versus $1/T$ for the quenched composition. The plot of $\log \sigma$ versus $1/T$ of Fig. 4 is redrawn in Fig. 5 to enable direct comparison. The mobility, μ , increased (ca. 10^1) as the temperature was increased to ca. 100°C , it then decreased sharply by more than two orders of magnitude. Whereas mobile ion concentration, n , initially increased slowly with temperature, it showed an abrupt jump (ca. 10^4) beyond ca. 100°C . The onset of these changes, well ahead of the β - α -like transition at ca. 135°C may be assigned to pre-transition effects. The decrease in mobility may be due to the structural-volume contraction [14], as also observed by this group for AgI after the β - α transition [15], which resulted in space narrowing for ion migration. The abrupt increase in the mobile ion concentration was due to the transition to an entirely new structure (assigned the α -phase, analogous to the average structure of α -AgI) where a large number of equienergetic Ag^+ ions became available for conduction. An apparent decrease in σ , due to the decrease in μ , was more than compensated for by the large number of mobile Ag^+ ions present in the α -phase. The Arrhenius equations governing the vari-

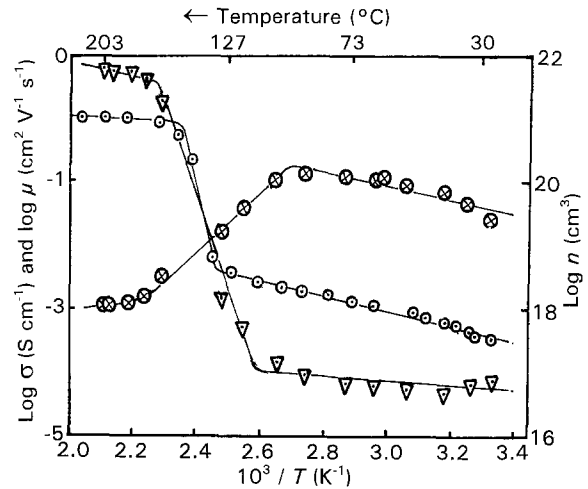


Figure 5 Arrhenius plots of $\log \mu$ versus $1/T$ (\otimes) and $\log n$ versus $1/T$ (∇) for [0.75AgI:0.25AgCl] quenched composition. Plot $\log \sigma$ versus $1/T$ (\circ) of Fig. 4 is redrawn.

ation of μ and n with temperature in the two regions of the phase transition are written as:

$$\left. \begin{aligned} \mu &= 32.8 \exp(-0.17/kT) \\ n &= 9.3 \times 10^{17} \exp(-0.07/kT) \end{aligned} \right\} \beta\text{-region} \quad (300\text{--}77 \text{ K})$$

and

$$\left. \begin{aligned} \mu &= 1.4 \times 10^{-5} \exp(+0.18/kT) \\ n &= 1.9 \times 10^{24} \exp(-0.24/kT) \end{aligned} \right\} \alpha\text{-region} \quad (446\text{--}76 \text{ K})$$

The energy of migration and formation are estimated from the above equations as 0.17 and 0.07 eV, respectively, in the β -region and $(-0.18$ and 0.24 eV, respectively, in the α -region; for AgI these values are 0.14 and 0.15 eV, respectively, in the β -phase and 0.05 and 0.006 eV, respectively, in the α -phase [15].

3.4. (0.75AgI:0.25AgCl): Quenched composition as host for the preparation of Ag^+ ion conducting glass and composite systems

AgI is used, in general, as a host material for the preparation of Ag^+ ion conducting glasses and composites. Very few attempts have been made to replace it with an alternative host. On the basis of above investigations, it can be observed that the $x\text{AgI}:(1-x)\text{AgCl}$ quenched composition in the compositional region $x = 0.7\text{--}0.8$ may be a good substitute for

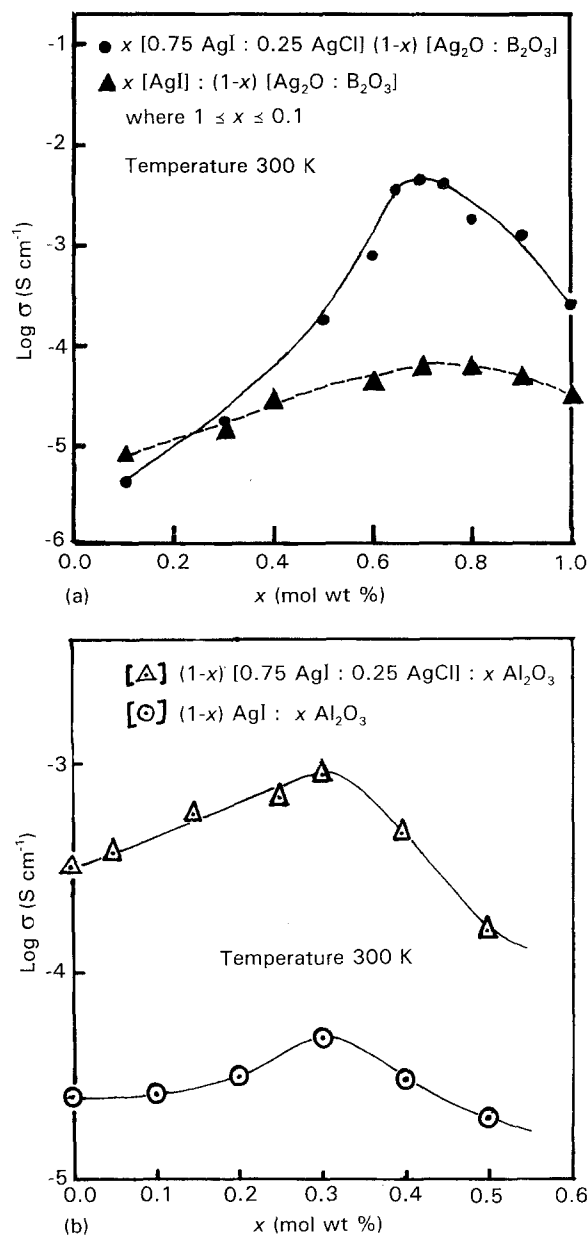


Figure 6 (a) Compositional variation of room temperature conductivity for quenched glass systems: ● $x[0.75\text{AgI}:0.25\text{AgCl}]:(1-x)[\text{Ag}_2\text{O}:\text{B}_2\text{O}_3]$ and ▲ $x[\text{AgI}):(1-x)[\text{Ag}_2\text{O}:\text{B}_2\text{O}_3]$. (b) Compositional variation of room temperature conductivity for the composite systems: △ $(1-x)[0.75\text{AgI}:0.25\text{AgCl}]:x\text{Al}_2\text{O}_3$ and ○ $(1-x)[\text{AgI}]:x\text{Al}_2\text{O}_3$.

AgI. This system has transport properties superior to AgI, see Table I. Using the $[0.75\text{AgI}:0.25\text{AgCl}]$ quenched composition as host, a glass system $[x(0.75\text{AgI}:0.25\text{AgCl}):(1-x)(\text{Ag}_2\text{O}:\text{B}_2\text{O}_3)]$ and a composite system $[(1-x)(0.75\text{AgI}:0.25\text{AgCl}):x\text{Al}_2\text{O}_3]$ were prepared [16, 17]. The variation of room temperature conductivity as a function of the mol wt (%) ratio, x , for these systems are shown in Fig. 6. Similar plots for $x\text{AgI}:(1-x)(\text{Ag}_2\text{O}:\text{B}_2\text{O}_3)$ and $(1-x)\text{AgI}:x\text{Al}_2\text{O}_3$ are also drawn for direct comparison. It can be seen that the glass and composite systems prepared with $(0.75\text{AgI}:0.25\text{AgCl})$ quenched composition exhibit better room temperature conductivity values than with AgI as host.

4. Conclusion

High ionically Ag^+ ion conductive compositions can

be prepared by rapidly quenching the molar $[x\text{AgI}:(1-x)\text{AgCl}]$ compositions. The $\beta \rightarrow \alpha$ transition of AgI becomes modified and some new phases appeared in the compositional phase diagram. Detailed investigations on transport properties of quenched composition $0.75\text{AgI}:0.25\text{AgCl}$ are reported. The mobility decreased sharply on going from the $\beta \rightarrow \alpha$ phase of this system (analogous to the $\beta \rightarrow \alpha$ transition of AgI), but a large increase in n not only compensated for but essentially gave a "net" increase in σ . The conductivity results are explained on the basis of phase diagram. Further, it is shown that $(0.75\text{AgI}:0.25\text{AgCl})$ quenched material can be a superior substitute for AgI in preparing Ag^+ ion conducting glasses and composites.

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