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Anomalous ionic conduction in AgI–AgBr–CuI solid solutions

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The d.c. electrical conductivity of AgI–AgBr–CuI solid solutions has been investigated for the first time. Five samples of different molar compositions are considered for this study in the temperature range 25 to 300° C. It is found that the addition of AgBr and CuI in equal mole percentage with AgI results in a decrease in conductivity, in comparison with that of the AgI–AgBr system, for the same range of temperature. The possible reasons for such behaviour have been analysed on the basis of lattice distortion of the materials and polarizability of the ions.

1. Introduction

Measurement of electrical conduction helps greatly in understanding the defect properties of ionic materials. The so-called "superionic conductors" (SIC) such as α-AgI, $Ag_7I_4PO_4$, $Ag_{19}I_{15}P_2O_7$, Na-β-Al_2O_3 etc. are characterized by their high ionic but very low electronic conductivity at room temperatures. These materials, if at the same time they turn out to be electronic insulators, can be used as solid state electrolytes (SE) in solid state batteries, fuel cells, gas monitoring systems etc. [1]. Since they play promisingly a dominant role in technological applications, they have received a great deal of attention from the scientific community [2–12].

Sai Babu and Chiranjivi [13] have reported that the study of ionic conductivity on undoped crystals may not give conclusive evidence regarding the nature of the ion transport mainly responsible for the measured conductivity. Hence, the study of conductivity on crystals doped with suitable aliovalent impurities such as CaO · ZrO_2 are allied work like self- and impurity-diffusion, etc. would greatly help their understanding. At the same time, it must be remembered that the single crystals contain no grain boundaries at all. But these grain boundaries are present in polycrystalline materials, which are prepared more easily than single crystals. Also, in most applications, they have far-reaching practical implications.

Schmidt *et al.* [14] have studied the co-ionic conductivity in Cu–Ag halide compounds. They have observed from their total conductivity against $10^3/T$ plots that the ionic conductivity of the copper conductors increases as their copper content diminishes. Takahashi *et al.* [15] and Brightwell *et al.* [16] have also studied the conductivity of the AgI–CuI system. It was found that the addition of CuI to AgI, in general, has produced a marked decrease in the value of conductivity. Hariharan [17] has reported that the addition of CuI to synthesized solid, $RbAg_4I_5$ resulted in partial compensation of electron conductivity and an increase in the self-life of the solid state battery. Karpov *et al.* [18] have also found a decrease in conductivity of the solid electrolyte with increase in copper.

α-AgI has been considered to be the best known superionic conductor at its melting point (557° C). Recently, Shahi and Wagner have investigated very extensively the ionic conductivity, σ, of AgI–AgBr [19] and AgBr–AgI [20] polycrystalline materials in the form of pellets. They have found considerable increase in σ of β-AgI and a relatively small decrease for the α-phase. Among the various techniques generally employed for the enhancement of σ of the materials, the study of ionic conduction in solids containing homovalent ions would furnish more useful and valuable information.

Shahi and Wagner [20] have pointed out that the substitution of I^- ions for Br^- ions in AgBr or vice versa did not involve the existence of any excess charge, and so any change in the value of σ should directly reflect the effect of size and polarizability etc. of the substituted homovalent ions. Besides, the anomalous large increase in σ, due to substitution of homovalent ions, could not be explained simply in terms of the classical charge compensating mechanizm. Only a few, similar investigations [21–24] on such mixed solids have been done before. Nevertheless, they did indicate an appreciable contribution due to homovalent ions towards ionic conduction.

A survey of the literature has revealed that investigations had been done for the measurement of ionic conductivity and hence the calculation of activation energy for the AgI–CuI and the AgI–AgBr system, but no reported work was available for the AgI–AgBr–CuI system. This, in fact, has stimulated the authors to carry on the present work.

2. Experimental details

2.1. Preparation of the pellets

The materials used in this study were already prepared, the preparation of which has been detailed elsewhere [25]. The sieved powders thus available were pelletized in a nickel-plated steel die at a pressure of 5000 kg cm^{-2} at room temperature, 25° C. This pressure was uniformly applied for all the samples. From

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the cylindrical pellets thus obtained, regular rectangular slabs of different sizes were cut and the faces were polished on silicon carbide paper. The flat faces of the samples were then silvered using high purity silver paint so as to ensure the solid/electrode contact resistance to be a minimum. Moreover, it is found that the silver paint resulted in better contact and yielded more reproducible results than silver tablets, particularly at low temperatures. The utmost care was taken to avoid contamination of the sample due to the organics present in the paint or silver diffusion, if any. X-ray analysis, before and after the experiments, also confirmed the absence of any such contamination or silver diffusion.

2.2. d.c. conductivity studies

The conductivity measurements were done for five different samples, using a two-probe technique. For that, the sample was held under spring pressure between a stainless steel (s.s.) plate at the top and a s.s. platform at the bottom. This platform rests on another s.s. plate, supported by s.s. rods, screwed to an aluminium ring resting on the top of a furnace. This s.s. rod serves as an electrode. A small s.s. rod, loosely fitted into the longitudinal cavity drilled into a brass cylinder serves as the other electrode. Thermal and electrical insulations were maintained using asbestos and Teflon discs over the aluminium ring. This set-up was kept inside a muffle furnace, powered from a constant voltage transformer, and the temperature was maintained steady correct to $\pm 0.5°$ C. A Chromel–Alumel thermocouple and a Philips d.c. microvoltmeter PP9004 were used for measuring the temperature of the samples. At each temperature, about 20 min were allowed for the same to attain the steady state.

Though polarization effects are avoided by using alternating currents, the use of direct current is never ruled out [26]. The applied voltage was kept constant at 10 V throughout the present investigation. The resistance measurements were made using a BPL Million Megohmmeter Model RM160 MK111A. The accuracy of the measurement was 1%. Extreme precautions were taken to avoid electrical leakage current so that the meter reading gave only the sample current. The samples were annealed at 225° C while loaded in the conductivity cell for 6 h. Heating and cooling cycles were also performed twice for each sample before taking any readings. It was found that such thermal cyclings improved the reproducibility of the data.

As anticipated for ionic conductivity, the electronic polarization effect was observed when d.c. voltage was applied. This time-dependent polarization was treated as a dielectric relaxation phenomenon and hence the final steady-state value was taken to be the true value. The temperature was varied from room temperature to 300° C and the observations were made while cooling the sample. After thermal cyclings, the experiment was repeated three to four times, for each sample, till the data were reproducible within the experimental error of 3%. Then the mean of the last two sets of readings was taken. The experiment was carried out in a dust-free air-conditioned room.

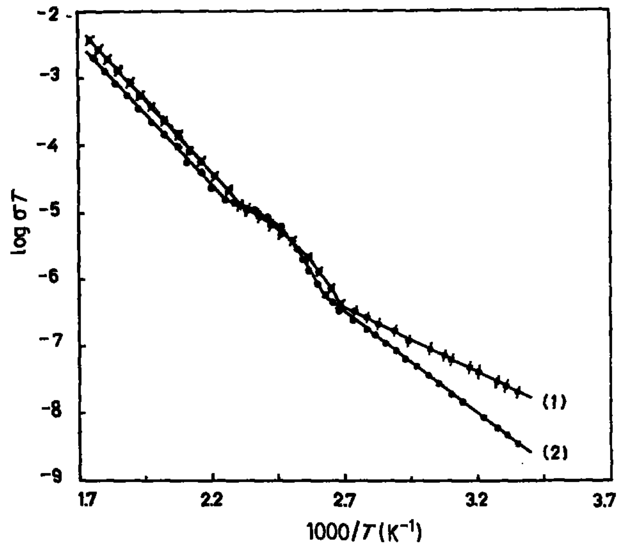

Figure 1 Temperature dependence of the conductivity of the AgI–AgBr–CuI system. Curves are labelled with the sample numbers.

3. Results

Figs 1 and 2 represent the log(σT) against $10^3/T$ plots. The conductivity is found to increase with increase in the mole percentage of AgBr and CuI with AgI throughout the temperature range studied, excepting the case of 80 : 10 : 10 mol % composition of AgI, AgBr and CuI. These curves have most of their length and fitting portions with straight-line segments, yielding two or three regions. Samples 1 and 2 yield two regions, one at low temperature and the other at high temperature. Samples 3, 4 and 5 yield two regions at low temperature and one at high temperature. A "knee" is found to appear between the high- and low-conducting regions in all the samples. It is also found to be gradually shifted towards the high temperature region, when the concentration of AgBr and CuI is increased. Of all the five samples, Sample 5 has the highest ionic conductivity. The conductivity increases at a slower rate at low temperatures but at a faster rate at high temperatures.

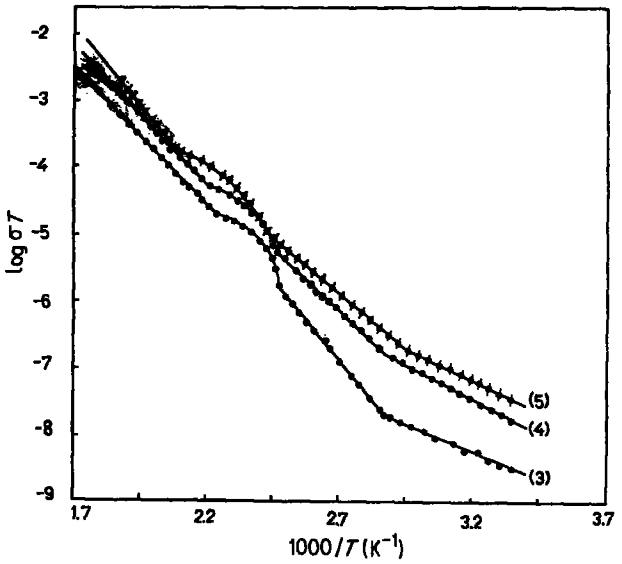

Figure 2 Temperature dependence of the conductivity of the AgI–AgBr–CuI system. Curves are labelled with the sample numbers.

TABLE I Some physical parameters of the AgI AgBr CuI system

Sample No.	Mole percentage			Lattice parameter (nm)	Area (cm^2)	Melting point (°C)	Molecular weight	Density ($g cm^{-3}$)
	AgI	AgBr	CuI					
1	85	7.5	7.5	0.64715	0.0745	541	227.9	1.2008
2	80	10.0	10.0	0.64738	0.1563	532	225.64	1.1495
3	60	20.0	20.0	0.64153	0.1386	460	216.51	1.1915
4	45	27.5	27.5	0.63713	0.2220	438	209.66	1.1881
5	40	30.0	30.0	0.63475	0.2189	415	207.37	1.2128

4. Discussion

It is found from the literature [27] that the pressure of pelletization has varied the σ value of a material to a great extent. In fact, σ increases with increasing pressure of pelletization. Hence, for a genuine interpretation of the results, a uniform pressure of $5000 \, kg \, cm^{-2}$ was applied in preparing the pellets.

The value of σ is found [13, 28, 29] to depend on the annealing temperature. Hence the samples were annealed at 225° C for 6 h in order to relax any stresses that may have occurred during pelletization and to homogenize the charge carriers in the samples. It is to be noted that the quenched sample may contain some supersaturated metastable solid solutions which on thermal cycling lead to a precipitation of the respective phases, which in turn causes a gradual increase in σ. Hence, additional care was taken to ensure that the samples were in thermodynamic equilibrium and to obtain reproducible data. In fact, heating and cooling cycles were performed twice for each sample before taking any readings to get stabilized values later. No hysteresis effect occurred between these heating and cooling cycles. Then, readings were taken and compared. The experiment was repeated till two sets of readings were consistent. So, each point in the conductivity plots is the average of two such sets of readings.

Table I gives an idea about some physical parameters of the samples tested. The lattice parameters of the samples were taken from our previous paper [25]. Table II gives the σ values of pure AgI, pure AgBr and the samples of the present work at room temperature, 25° C. The σ data for the AgI–AgBr system are also presented [19, 20] for comparison purposes. The σ values of both pure AgI and AgBr agree closely with the previously reported values [30–32] for polycrystalline materials.

The σ values of AgI–AgBr–CuI polycrystalline materials have been investigated as a function of temperature and the results are shown in Figs 1 and 2. The curves follow the well-known exponential relation, $\sigma T = \sigma_0 \exp(-E/kT)$, but with two slopes for Samples 1 and 2, and three slopes for Samples 3, 4 and 5. The activation energies (E) are calculated from the slopes of the corresponding segments and are listed in Table III. The activation energy ranges from 0.3243 to 0.4145 eV in the extrinsic (low-temperature) region, where the ionic conductivity is due to defects created by the presence of impurities. But in the intrinsic (high-temperature) region, where thermally generated defects dominate, the activation energy ranges from 0.8154 to 0.9714 eV. A "knee" is present in all the plots, which is found to be gradually shifted towards the high-temperature region, when the concentration of AgBr and CuI has been increased. The reason for such behaviour is not immediately known.

On comparing the σ data for the AgI–AgBr system [19, 20] with the present system in the same temperature range, it is observed that the σ of the former is much greater than for the latter. In other words, the addition of AgBr and CuI in equal mole percentage with AgI has produced a sudden decrease in the overall σ value of the system. However, the increase in concentration of AgBr and CuI has very interesting results on the σ of the samples, to varying magnitude.

The possible reasons for such behaviour can be qualitatively discussed as follows. It is greatly believed

TABLE II Conductivity, σ, data for pure AgI, pure AgBr and for the present AgI–AgBr–CuI system at room temperature, 25° C. σ data for AgI–AgBr [20] are also presented for comparison purposes

Mole percentage			Conductivity, σ ($\Omega^{-1} cm^{-1}$)	Quantum of increase	Quantum of reduction	Reference
AgI	AgBr	CuI				
100	–	–	1306×10^{-10}	–	–	This work
–	100	–	645×10^{-10}	–	–	This work
85	15	–	1×10^{-4}	766	–	[20]
85	7.5	7.5	0.621×10^{-10}	–	2103	This work
80	20	–	2.806×10^{-4}	2148	–	[20]
80	10	10	0.090×10^{-10}	–	14463	This work
60	40	–	1.215×10^{-4}	930	–	[20]
60	20	20	0.109×10^{-10}	–	12025	This work
45	55	–	5.180×10^{-5}	397	–	[20]
45	27.5	27.5	0.570×10^{-10}	–	2292	This work
40	60	–	3.957×10^{-5}	303	–	[20]
40	30	30	1.191×10^{-10}	–	1097	This work

TABLE III Activation energy and the occurrence of "knee" region for the AgI–AgBr–CuI system

Sample No.	Activation energy, E (eV)	Temperature range (° C)	Knee region (° C)
1	0.3907	25 to 105	105 to 162
	0.8709	162 to 300	
2	0.6316	25 to 120	120 to 170
	0.8686	170 to 300	
3	0.3243	25 to 72	
	0.9674	72 to 132	132 to 178
	0.8154	178 to 300	
4	0.4145	25 to 85	
	0.80	85 to 135	135 to 182
	0.8296	182 to 300	
5	0.3636	25 to 65	
	0.68	65 to 144	144 to 203
	0.9714	203 to 300	

and strongly supported by X-ray studies that the incorporation of a foreign ion, generally having a different size, into the lattice of a host material would cause a strain in the lattice. The effect of such a strain is evidently to produce lattice distortion or "lattice loosening". This lattice distortion would be larger for impurity ions having much larger or much smaller ionic radii than the respective host ion. Ultimately, the melting point of the material is reduced, leading to an increased concentration of Frenkel defects and hence increased conductivity.

The magnitude of the lattice strain depends on $|1 - (r_h/r_i)|$, where r_h and r_i are the ionic radii of the host and impurity ions respectively. The substituted ions having larger values of $|1 - (r_h/r_i)|$ would then cause greater lattice distortion and hence an appreciable increase in σ. For instance, in the case of the AgCl–AgBr system the value of $|1 - (r_h/r_i)|$ is 0.076. But the value of $|1 - (r_I/r_{Br})|$ is 0.122 and that of $|1 - (r_{Br}/r_I)|$ is 0.109. As the value of $|1 - (r_h/r_i)|$ is small in the case of substitution of a Br^- ion for a Cl^- ion or vice versa, it is found to have a relatively small effect on the conductivity. On the other hand, the substitution of a Br^- ion for an I^- ion or vice versa will have a greater impact on σ, because their sizes are very dissimilar. Moreover, the effect of "wrong size" would become significant at higher concentrations and higher temperatures where the effect of "wrong charge" is less important [20]. Our experimental findings have supported this view very well.

We have reported [25] that the addition of AgBr and CuI in equal mole percentage with AgI has really brought about a marked improvement in the gradual reduction of the lattice constant of AgI, excepting the 80 : 10 : 10 mol % combination of AgI, AgBr and CuI (present Sample 2). The X-ray powder diffractograms also revealed the formation of a continuous cubic solid solution throughout the different compositions of the system. It is found [33] that the lattice parameter is one of the important factors that largely influences the σ of a material. It seems rather inevitable that a decrease in lattice constant would cause an increase in σ. The decrease in σ for Sample 2 (Fig. 1) for which the lattice parameter increases suddenly (Table I) is a clear case of experimental evidence.

A clear understanding of the conduction mechanism of the present system will be possible only on carefully analysing Table II. The σ data from the work of Shahi and Wagner [20] and from the present work have been compared at room temperature. It is quite obvious [20] that the addition of AgBr with AgI increases enormously the σ of the system, where σ reaches a maximum for 20 mol % AgBr and then decreases for more than 20 mol % AgBr. The quantum of increase in σ has been calculated in terms of the ratio of the σ of the AgI–AgBr system to the σ of pure AgI, for samples containing 85, 80, 60, 45 and 40 mol % AgI. But, when the mole percentages of AgBr in the above cases are equally shared by both AgBr and CuI with the same mole percentage of AgI in each case, the effects are found to be dramatic. There is a drastic reduction in σ. The quantum of reducton in σ has been calculated in terms of the ratio of the σ of pure AgI to the σ of the AgI–AgBr–CuI system. From these ratios, namely, 2103, 14463, 12025, 2292 and 1097, it is found that the net effect, due to the addition of AgBr and CuI with AgI, is only a drastic reduction in the values of σ of the system.

Comparatively speaking, the drastic reduction has been maximum in the case of Sample 2, slightly less than the maximum for Sample 3, still less than 3 for Sample 4, and is the least for Sample 5. Accordingly, the σ of Sample 2 is minimum while that of Sample 5 is maximum. If R represents the resultant effect on the σ of the present system, then it may be symbolically written as $R_{\sigma 1} < R_{\sigma 2} > R_{\sigma 3} > R_{\sigma 4} > R_{\sigma 5}$, where $\sigma 1$, $\sigma 2$, $\sigma 3$, $\sigma 4$ and $\sigma 5$ are the respective conductivities of the samples, taken in order. It is true that the σ values of Samples 3 and 4 are less than 1. Our results fully acknowledge the observations of the previous workers [14, 15] where the quantum of reduction in σ of their systems first increases, reaches a maximum, and then decreases as the concentration of CuI has been increased.

Another possible reason for the drastic reduction in σ, due to the presence of CuI, can also be given on the basis of the polarizability of atoms. It is well known that AgI and CuI have similar physicochemical properties. CuI is a hole-type semiconductor [34]. It is likely that Ag^+ ions and Cu^+ ions are possible by the substitution of Br^- ions for I^- ions, present both in AgI and CuI. Hence, a mixture of these cations of different sizes will become ordered and it can be expected that the Cu^+ ion would tend to become oriented in a direction different from that of the Ag^+ ion. Since the radius of the Cu^+ ion is smaller than that of the Ag^+ ion, the polarizability of the Cu^+ ion is small. Hence, the mobility of the Cu^+ ion is high but the conductivity is small. Also, the presence of bigger Ag^+ ions may have provoked a partial deformation in the structure which has greatly helped the movement of the Cu^+ ions, leading to a decrease in conductivity, as suggested by Schmidt *et al.* [14]. The Ag^+ ions would have easy access to move through the lattice by an interstitial mechanism.

5. Conclusions

The addition of AgBr to AgI has so far resulted in the anomalous increase in the conductivity of AgI. But the addition of CuI to AgI has shown the opposite effect of decreasing the conductivity of AgI to varying magnitude. It is found in the present study that the addition of both AgBr and CuI in equal mole percentage has produced a drastic reduction in the σ of the system. Hence, it is concluded that the influence of CuI on conductivity is far greater than that of AgBr.

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