Research Letter

Ionic Conductivity and Phase Transition Behaviour in $4\text{AgI}-(1-x)\text{PbI}_2-2x\text{CuI}$ System

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Samples of general formula $4\text{AgI}-(1-x)\text{PbI}_2-2x\text{CuI}$, $x = 0-0.4$, have been prepared and investigated by XRD, DSC, and temperature-dependent conductivity studies. X-ray diffractograms showed the presence of binary system consisting of AgI and PbI_2 in the sample $x = 0$. Cu-substituted samples showed very similar diffractograms to that of the pure compound which indicates that no effect for the substitution on the nature of the binary system. DSC curves showed the presence of phase transition whose temperature increased with Cu^+ ratio in the system. Ionic conductivity measurements confirmed the occurrence of the phase transition and showed that the high temperature phase is superionic conducting, whose conductivity increases with the increasing Cu^+ amount in the system.

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1. INTRODUCTION

Superionic conductors are solid compounds in which electric current is carried by charged atoms, that is, by ions. The passage of current is thus associated with mass transfer. Such ionic conductors are sometimes called “solid electrolytes,” by analogy to liquid electrolyte solutions, and have permitted development of a new scientific discipline, *namely*, solid state electrochemistry. The associated technology is termed solid-state ionics, in contrast to solid-state electronics.

AgI is the most investigated superionic conductor which has high ionic conductivity in its α -phase stable above 147°C . Below 147°C silver iodide exists in several modifications based on zinc blend and wurtzite structures, both of which favour ionic diffusion via face sharing polyhedra. Many attempts have been made to stabilize this high conducting phase at room temperature by substitution leading to a growing group of silver ion conductors in which the transitions temperatures to the superionic phase are lower or higher than that of the α -AgI.

$(\text{AgI})_x(\text{PbI}_2)_{1-x}$ is one such system which has been studied extensively owing to the improved transport properties of AgI. The phase diagram of the system was studied by many workers [1–4]. The recent work by Hull et al. [5]

has shown that the system contains a superionic phase of composition $4\text{AgI}-\text{PbI}_2$ stable at $T \geq 400\text{ K}$. This phase has the ionic conductivity of 0.1 Scm^{-1} . The structure of the phase has been resolved and was found to have an fcc Structure I^- sublattice with majority of cations (over 90%) located in octahedral 4(b) cavities and the remainder within tetrahedral 8(c) interstices. Extensive work has been done to study the effect of substitution of mobile cation on the ionic conductivity of AgI-based superionic conductors. However, not much work seems to have been done on the substitution of immobile cations. The present work is an attempt to study the effect of substitution of immobile cation Pb^{+2} by Cu^+ on the ionic conductivity, phase transition temperature, and dielectric constant of $4\text{AgI}-\text{PbI}_2$ system. Two Cu^+ ions replace each Pb^{+2} ion; therefore, the extra Cu^+ ion is expected to occupy interstitial position and participate in the conduction process thereby enhancing the ionic conductivity of the system.

2. EXPERIMENTAL

AgI was prepared by the precipitation from ammonical silver nitrate solution by the addition of ammonium iodide solution. PbI_2 was prepared by the precipitation from lead

nitrate solution by potassium iodide. CuI was taken from Otockemi, India, with stated purity of 99%. Appropriate amounts of the starting materials were mixed to produce the series $4\text{AgI}-(1-x)\text{PbI}_2-2x\text{CuI}$ where $x = 0-0.4$. The materials were then heated for 20 hours at 480 K with intermittent grinding.

Pellets for conductivity and capacitance measurements were prepared by pouring different molar ratio mixtures into stainless steel die and pressed under the pressure of 4 tonnes/cm² with the help of a hydraulic press. All the samples were annealed at 310 K for 6 hours to eliminate any grain boundary effects. The pellet was mounted on stainless steel sample holder between two copper leads using two polished platinum electrodes. The copper leads were electrically insulated from the holder by Teflon sheets. The electrical conductivity and capacitance of samples were measured in the temperature range of 300 K–470 K using Gen Rad 1659 RLC Digibridge at a single frequency of 1 KHz. The heating rate was maintained at 2°C/min.

Impedance measurements were performed using HIOKI3532-50 LCR meter in the frequency range of 40 Hz–5 MHz. DSC scanning was traced by Perkin Elmer instrument using alumina as a reference. XRD were recorded using RIGAKU D/MAX-B diffractometer with CuK_α radiation.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction and DSC

X-ray diffractograms of the pure and substituted samples are shown in Figure 1. Two phases can be identified in the diffractogram of the pure compound, namely, AgI and PbI_2 . This agreed with the previous studies which reported that the fcc high temperature phase whose formula is Ag_4PbI_6 dissociates to its primary compounds at temperatures below the phase transition temperature [5]. The substituted samples show very similar diffractograms to those of the pure system. Substitution by Cu^+ does not seem to affect the crystal structure of the final mixture and Cu^+ ions appeared to occupy the voids in the lattices of the binary system, since no peaks related to CuI can be identified in the diffractograms.

DSC curves of the pure and substituted samples are shown in Figure 2. The pure compound shows the expected thermal arrest at the temperature 130°C which was reported to be originated from the formation of the fcc superionic phase [5]. Substituted compounds showed gradual increase in the phase transition temperature with Cu^+ ratio without any saturation observed within the concentration range studied. The α - β transition temperature in AgI has also increased upon incorporating Cu^+ in its lattice [6]. No other peaks were observed in the DSC curve of these samples other than a very weak arrest which was detected at 177°C in the sample $4\text{AgI}-0.4\text{PbI}_2-0.8\text{CuI}$ which might have resulted from insignificance decomposition of the superionic phase at high concentrations of Cu^+ . The absence of any thermal arrest before the phase transition temperature indicates that the binary system persists below this temperature without any other phase formation.

FIGURE 1: Room temperature X-ray diffractograms of $4\text{AgI}-(1-x)\text{PbI}_2-2x\text{CuI}$ samples.

The variation in the phase transition temperature with the incorporation of substituent ion can be attributed to two reasons: (i) the distortion of the lattice due to the “wrong” sized substituent and (ii) the increased defect concentration in the lattice lead to the stronger defect-defect interaction which affects the phase transition temperature.

The relation between the defect-defect interaction and phase transition temperature is given [7] by

$$T = \frac{W - \lambda/2}{k(1 + \ln \nu)}, \quad (1)$$

where W is the energy difference between the interstitial position and the lattice sites, λ represents the defect-defect interaction parameter and $\nu = ((\omega_1/\omega_2)^3(N_1/N_2))$, ω_1 , and ω_2 are the vibration frequencies of the ions at interstitial positions and lattice sites, N_1 and N_2 are the number of interstitials and original lattice sites per unit volume and k is Boltzmann’s constant. However, the crucial role in affecting the phase transition temperature arises from lattice

FIGURE 2: DSC curves of 4AgI-(1-x)PbI₂-2xCuI samples. FIGURE 3: Room temperature complex impedance spectra of 4AgI-(1-x)PbI₂-2xCuI samples.

distortion which is proportional to size mismatch between the host and guest cation [8].

3.2. Electrical conductivity

Complex impedance plots of the investigated samples are shown in Figure 3. They are typical plots of ionic conductors showing a semicircle at high frequency side and a spike at lower frequency for all of the samples. Two overlapped semicircles are shown in case of Ag₄Pb_{0.7}Cu_{0.6}I₆ sample, the one at higher frequency resulted from bulk resistance while that at low frequency results from grain boundary resistance contribution. The relaxation times of the two contributions are very close in the other sample which results in a depressed semicircle. The spike in the lower frequency range is attributed to the blocking electrodes due to ion migration. The appearance of the spikes is an indication that the conduction in these materials is ionic in nature [9].

FIGURE 4: Arrhenius plots of 4AgI-(1-x)PbI₂-2xCuI samples.

The temperature dependence of ionic conductivity is given by the Arrhenius expression,

$$\sigma T = \sigma_0 \exp \left(- \frac{E_a}{kT} \right), \quad (2)$$

where σ_0 is the pre-exponential factor and E_a is the activation energy of ionic motion.

Arrhenius plots of the samples are shown in Figure 4. Ionic conductivity measurements showed higher phase transition temperature in Cu-substituted samples which is in agreement with the DSC results.

The ionic conductivity decreased gradually with increasing Cu⁺ ratio in the low temperature region while significant enhancement is observed at the high temperature phase. Cu⁺, which is less mobile than Ag⁺, accumulates in the vacancies available in the lattice of AgI and partially blocks Ag⁺ ions motion through these vacancies leading to the overall decrease in the ionic transport. While in the high temperature region, the conductivity results from the hopping of the interstitial Ag⁺ ions, hence the presence of Cu⁺ does not block the migration of these ions but enhances the ionic conduction through its mobility in the lattice.

The activation energies calculated from the slope of Arrhenius plot in the low and high temperature regions are presented in Table 1. Significant enhancement in the activation energies of Cu-substituted samples is observed in the low temperature region. This directly reflects the increase of the potential barrier which has to be overcome by the mobile ion to hop from one position to another. The increase in activation energy in the substituted samples is due to the restricted movement of Ag⁺ ions due to the substitution. The comparable values of the activation energies for the various substitutions suggest that an identical hopping mechanism is responsible for the transport in all the samples [10].

The activation energies in the high temperature region are much lower than those in the low temperature region which is explained by the greater disorder possessed by the high temperature phase. In general, Cu-substituted samples show higher activation energies compared to the pure one.

TABLE 1: Activation energies in the low and high temperature regions of $4\text{AgI}-(1-x)\text{PbI}_2-2x\text{CuI}$ samples.

$x/\text{mole fraction}$	Activation energies in prephase transition region/eV	Activation energies in postphase transition region/eV
$x = 0$	0.262	0.118
$x = 0.1$	0.420	0.304
$x = 0.2$	0.439	0.199
$x = 0.3$	0.457	0.195
$x = 0.4$	0.465	0.150

In spite of the enhancement of conductivity which results from the participation of Cu^+ in the conduction process, replacement of the larger size cation ($r_{\text{Pb}^{2+}} = 1.21 \text{ \AA}$) by the smaller one ($r_{\text{Cu}^+} = 0.67 \text{ \AA}$) leads to the contraction of the lattice of the high temperature phase and hence decreasing the bottle-neck size through which ion hopping takes place. Therefore, higher thermal energy is required by Ag^+ ion to overcome this potential barrier. Activation energy decreases in the high temperature region which is explained by the increasing importance of Cu^+ conduction at the higher concentrations of the ion.

4. CONCLUSION

The electrical conductivity and phase transition behaviour in the system $4\text{AgI}-(1-x)\text{PbI}_2-2x\text{CuI}$ were investigated. Formation of the fcc superionic phase at temperatures larger than 130°C in the pure and substituted compounds was confirmed by DSC as well as electrical conductivity measurements. X-ray measurements showed the presence of binary system at lower temperatures with no effect of the substitution. The ionic conductivity enhanced markedly in the high temperature phase with the incorporation of Cu^+ . Unfortunately, this enhancement comes at the expense of the increasing phase transition temperature beyond that of the unsubstituted system.

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