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Structural, thermal and transport studies on $Ag_{1-x}Cu_xI$ ($0.05 \leqslant x \leqslant 0.25$) solid electrolyte

M. K. P. SEYDEI, S. A. SUTHANTHIRARAJ
Department of Energy, University of Madras, Guindy Campus, Madras 600 025, India

Preparation and characterization studies on polycrystalline samples of $Ag_{1-x}Cu_xI$ where $x = 0.05$, 0.1, 0.15, 0.2 and 0.25, respectively, have been reported. Samples were analysed using powder X-ray diffraction (XRD) and differential scanning calorimetric (DSC) techniques in order to identify the compositions and phase transition temperatures. A.c. electrical conductivity studies were carried out on pelleted specimens of various compositions in the frequency range 65.5 kHz to 1 Hz and over the temperature range 293–412 K. DSC results obtained in the temperature range 373–473 K have shown that the β- to α-phase transition temperature is enhanced from 426 K to 438 K when x is increased from 0.05 to 0.25. XRD results have indicated that there is a shift in d-spacing when the CuI content is increased, suggesting changes in the crystal structure. Typical XRD patterns recorded for the composition $Ag_{0.95}Cu_{0.05}I$ at three different temperatures (room temperature, 373 and 473 K, respectively) have confirmed that both face-centred cubic and hexagonal phases would be present at room temperature and at 373 K as well, whereas at 473 K the structure would be purely body-centred cubic in nature. A.c. impedance analysis of the above samples appears to suggest that their electrical conductivity, predominantly due to the migration of Ag^+ ions, lies in the order of $10^{-4}\ S\,cm^{-1}$ at room temperature.

1. Introduction

Synthesis of high conductivity solid electrolytes suitable for solid-state electro-chemical devices has been the recent trend in the field of solid state ionics. There have been a number of reports concerning modifications in compositions of silver iodide by suitable substitution within the lattice in various forms such as K^+, Rb^+, NH_4^+, $(CH_3)_4N^+$, $[C_5H_5NH_3]^+$, WO_4^{2-}, etc. [1–4].

Schmidt *et al.* [5] have examined the system AgI–CuI with different Ag/Cu ratios and observed that a compound with a lower copper content would be stable only when it is in contact with metallic silver and that $CuAg_3I_4$ (i.e. Cu : Ag = 1 : 3) would behave as a pure silver ion conductor lying in a zone in which the crystal structure is that of AgI, favourable for the movement of silver ions. It has been reported that when the CuI content is more than 47 mol % the structure would correspond to that of CuI and the material would exhibit Cu^+ ionic conduction. In this context, the present investigation concerning preparation, structural, thermal and transport studies on $Ag_{1-x}Cu_xI$ where $0.05 \leqslant x \leqslant 0.25$ has been undertaken. The main objectives of this work include identification of phase-transition temperature of various compositions in the above system and separation of their bulk electrical properties from electrode effects by carrying out temperature-dependent a.c. impedance analysis in order to evaluate their transport properties.

2. Experimental procedure

2.1. Sample preparation

Polycrystalline samples of $Ag_{1-x}Cu_xI$ ($x = 0.05$, 0.1, 0.15, 0.2 and 0.25) were prepared using Analar grade $AgNO_3$, $Cu(NO_3)_2 \cdot 3H_2O$ and KI as starting materials. Aqueous solutions of $AgNO_3$ and $Cu(NO_3)_2 \cdot 3H_2O$ were initially taken in appropriate amounts and mixed together. To this, an aqueous solution of KI was added in excess and the precipitate so obtained was washed several times with doubly distilled water and then with acetone. It was then filtered and dried in the dark at 373 K for nearly 3 h to obtain the final product.

2.2. X-ray diffraction analysis

All the powder samples were analysed using a Philips X-ray generator unit (Model PW 1130) with a CuK_α radiation ($\lambda = 0.154\,18$ nm) in order to identify and confirm their stoichiometry.

2.3. Differential scanning calorimetry (DSC) analysis

DSC measurements were made on all polycrystalline samples of $Ag_{1-x}Cu_xI$ using a Perkin–Elmer DSC 7 differential scanning calorimeter in conjunction with a Perkin–Elmer 3700 data station over the temperature range 373–473 K at the scanning rate of $10\ K\,min^{-1}$.

2.4. A.c. impedance analysis

The powder specimens were ground and pressed together with electrodes on either side under a pelletizing pressure of 4000 kg cm^{-2} to form circular pellets of 12 mm diameter. The electrodes consisted of silver metal powder mixed with the sample in the weight ratio of 2 : 1. Schmidt *et al.* [5] have observed that the compound with low copper content in contact with metallic silver is stable, whereas the same compound in contact with metallic copper changes spontaneously to $CuAg_3I_4$. Similarly, a compound prepared with a lower silver content in contact with metallic silver undergoes a transformation into the same stable form. For the above reasons, the electrodes used for electrical conductivity studies during the present investigation were a mixture of metallic silver powder and sample powder.

A.c. electrical conductivity studies were carried out on the pelleted samples using a Solartron Model 1254 four-channel frequency response analyser and a Solartron Model 1286 electrochemical interface in conjunction with a BBC Model B$^+$ Microcomputer over the frequency range 65.5 kHz–1 Hz at different temperatures. The sample temperature was varied from 293–412K. A chromel–alumel thermocouple was employed to record the sample temperature.

3. Results and discussion

3.1. Structural characterization

Table I shows the powder X-ray diffraction data obtained at room temperature (RT) for the system $Ag_{1-x}Cu_xI$ where $x = 0.05$, 0.1, 0.15, 0.2 and 0.25, respectively, together with ASTM data reported for γ-AgI and γ-CuI. It is seen from Table I that the values of *d*-spacings obtained during the present study are different from those reported for pure AgI and CuI. This suggests that solid solutions are formed between AgI and CuI. Fig. 1 indicates the typical powder XRD patterns for the composition $Ag_{0.95}Cu_{0.05}I$ recorded

TABLE I Powder XRD data obtained for the system $Ag_{1-x}Cu_xI$ ($x = 0.05$, 0.1, 0.15, 0.2 and 0.25) and ASTM data for γ-AgI and γ-CuI

γ-AgI (ASTM data)		Present study										γ-CuI (ASTM data)	
		$x = 0.05$		$x = 0.1$		$x = 0.15$		$x = 0.2$		$x = 0.25$			
d(nm)	*I*(%)	*d*(nm)	*I*(%)	*d*(nm)	*I*(%)	*d*(nm)	*I*(%)	*d*(nm)	*I*(%)	*d*(nm)	*I*(%)	*d*(nm)	*I*(%)
0.375	100	0.392	23	0.386	100	0.387	72	0.391	6	0.390	6	0.349	100
0.230	60	0.372	100	0.233	100	0.234	100	0.369	100	0.369	100	0.303	12
0.195	30	0.228	93	0.163	33	0.199	60	0.227	67	0.227	59	0.214	55
0.162	6	0.222	15					0.194	8	0.194	32	0.182	30
0.149	8	0.194	46					0.161	5	0.148	7		
0.133	8							0.148	10	0.131	13		
0.125	6							0.131	7	0.124	5		
								0.124	5				

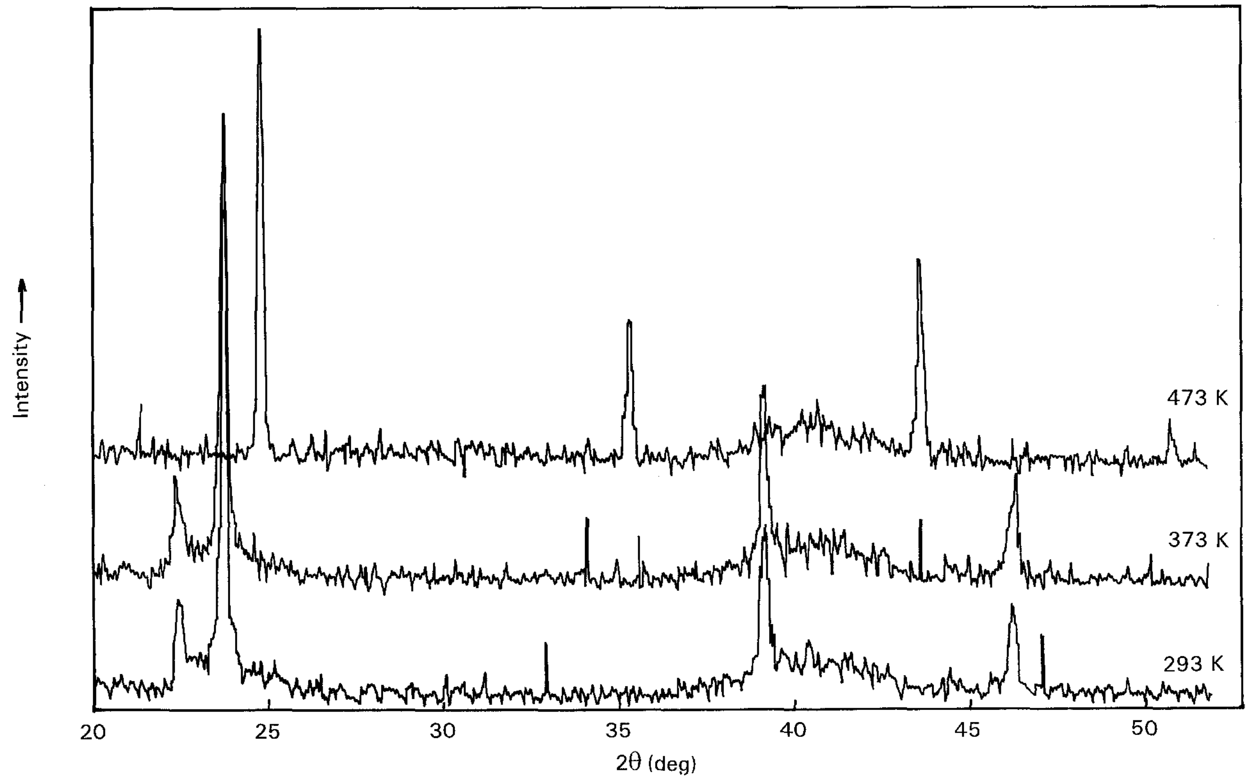

Figure 1 Powder XRD patterns for the composition $Ag_{0.95}Cu_{0.05}I$ recorded at 293, 373 and 473 K, respectively.

at 293 (RT), 373 and 473 K, respectively. It is clear from Fig. 1 that the crystal structure of $Ag_{0.95}Cu_{0.05}I$ remains the same from 293–373 K and is a mixture of both hexagonal and face-centred cubic (fcc) phases. On the other hand, at 473 K the crystal structure changes into body-centred cubic (bcc) type as indicated by the XRD data. These results tend to suggest that the phase-transition temperature of $Ag_{0.95}Cu_{0.05}I$ would certainly lie between 373 and 473 K. In fact, DSC experiments carried out on this specimen have identified the exact phase-transition temperature of these materials, the results of which will be discussed in the next section.

3.2. DSC results

DSC traces obtained during the present investigation for various compositions in the system $Ag_{1-x}Cu_xI$ have indicated endothermic peaks around 430 K for all the samples. Table II presents the endothermic peak positions seen in the DSC traces. It can be seen from Table II that the transition temperature changes from 426 K to 438 K when x is changed from 0.05 to 0.25. In other words, when the CuI content is increased, the phase-transition temperature of AgI is shifted from 420 K to higher temperatures. A comparison of the DSC results and temperature-dependent XRD data would suggest that changes in the crystal structure of $Ag_{1-x}Cu_xI$ solid solutions may be associated with the endothermic phase-transition temperatures observed for the respective composition.

3.3. A.c. conductivity results

Fig. 2 shows the typical complex impedance plots ($-z''$ versus z') obtained for the composition $Ag_{0.75}Cu_{0.25}I$ at six different temperatures (293, 316, 334, 343, 351 and 359 K). It is interesting to note that the points of intersection on the z' (real part of the impedance) axis would directly give the values of the bulk resistance of these specimens at these temperatures. The values of the bulk resistance have been found to decrease when the temperature is increased. From the value of bulk resistance estimated for various temperatures, the d.c. electrical conductivity, σ, values were calculated using the relation

$$\sigma = \frac{t}{RA} \tag{1}$$

where t is the sample thickness, R the bulk resistance and A is the area of cross-section of the pelleted specimen.

Fig. 3 depicts the variation of log T as a function of the reciprocal absolute temperature for different compositions in the systems $Ag_{1-x}Cu_xI$. The behaviour of their electrical conductivity is found to be Arrhenius type

$$\sigma T = \sigma_0 \exp(-E_a/kT) \tag{2}$$

where E_a is the activation energy for ionic migration within the solid solution, and k is the Boltzmann

TABLE II DSC results obtained for various compositions

Composition	Endothermic peak in DSC (K)
$Ag_{0.95}Cu_{0.05}I$	426
$Ag_{0.90}Cu_{0.10}I$	429
$Ag_{0.85}Cu_{0.15}I$	429
$Ag_{0.80}Cu_{0.20}I$	434
$Ag_{0.75}Cu_{0.25}I$	438

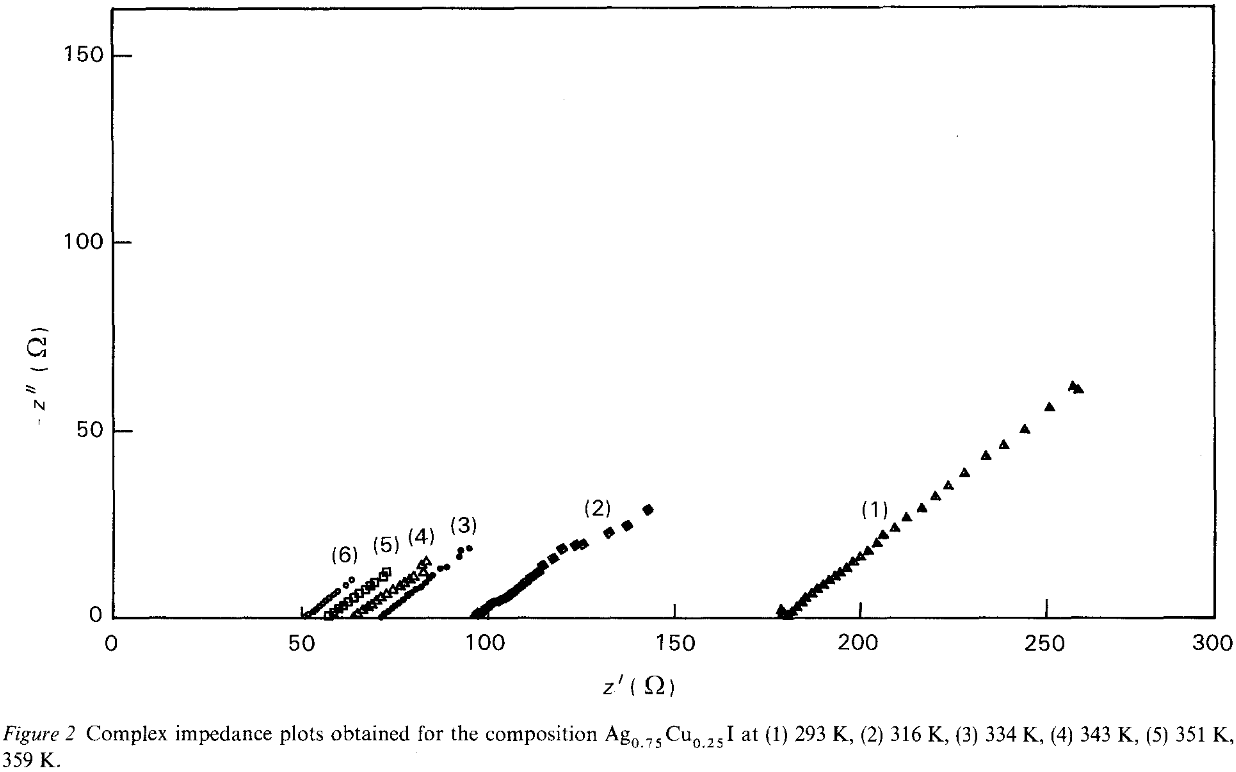

Figure 2 Complex impedance plots obtained for the composition $Ag_{0.75}Cu_{0.25}I$ at (1) 293 K, (2) 316 K, (3) 334 K, (4) 343 K, (5) 351 K, (6) 359 K.

TABLE III Summary of a.c. impedance analysis

Composition	Room-temperature electrical conductivity, $\sigma_{306\,\text{K}}$ $(10^{-4}\,\text{S cm}^{-1})$	Conductivity equation, $\log_{10}\sigma T = \log_{10}\frac{-E_a}{kT}$	Activation energy E_a(eV)
$Ag_{0.95}Cu_{0.05}I$	6.61	$\text{Log}_{10}\sigma T = 0.54–0.37(10^3/T)$	0.07
$Ag_{0.90}Cu_{0.10}I$	1.01	$\text{Log}_{10}\sigma T = 1.47–0.90(10^3/T)$	0.17
$Ag_{0.85}Cu_{0.15}I$	5.13	$\text{Log}_{10}\sigma T = 0.54–0.39(10^3/T)$	0.07
$Ag_{0.80}Cu_{0.20}I$	6.14	$\text{Log}_{10}\sigma T = 0.61–0.40(10^3/T)$	0.08
$Ag_{0.75}Cu_{0.25}I$	4.13	$\text{Log}_{10}\sigma T = 0.94–0.50(10^3/T)$	0.10

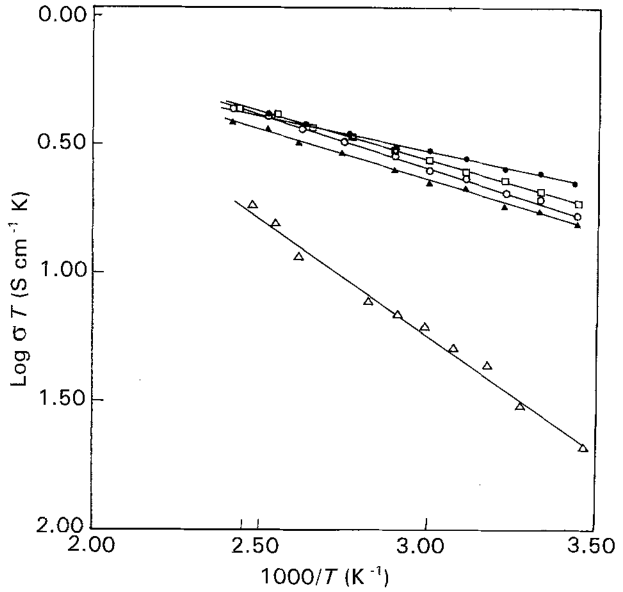

Figure 3 Variation of log σT with $1/T$ for different compositions in the system $Ag_{1-x}Cu_xI$ $(0.05 \leqslant x \leqslant 0.25)$. (□) 5 mol % CuI, (△) 10 mol % CuI, (▲) 15 mol % CuI, (○) 20 mol % CuI, (●) 25 mol % CuI.

constant, T the absolute temperature, and σ_0 the pre-exponential factor. The best-fit lines obtained for the plots of log σT against $1000/T$ for various compositions by the least-squares method, together with the values of activation energy obtained from the slope values are presented in Table III.

Fig. 3 shows that the electrical conductivity increases as the temperature is increased. From Table III it is seen that the room-temperature electrical conductivity ($\sigma_{306\,\text{K}}$) of all these specimens lies in the order of 10^{-4} S cm^{-1}, comparable to that of pure AgI [6]. It is interesting to note that all the compositions under investigation are stable solid electrolyte materials up to 412 K. These results are in good agreement with the phase diagram for the mixed system AgI–CuI, in view of the fact that the crystal structure of all these compositions has been reported to be suitable for silver ionic migration [5].

4. Conclusion

The present investigation concerning preparation and characterization of $Ag_{1-x}Cu_xI$ ($x = 0.05, 0.1, 0.15, 0.2$ and 0.25) solid solutions has indicated the formation of silver ion conducting solid electrolytes having electrical conductivity values comparable to that of pure AgI. Crystallographic phase-transition temperatures in these phases have also been determined through thermal characterization.

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