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Phase Transition and Complex Impedance Studies of Mechano-Chemically Synthesized AgI-CuI Solid Solutions

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Solid solutions of AgI_x-$Cu_{1-x}I$ ($0.1 < x < 1.0$) were prepared using mechanochemical technique. XRD measurement shows the AgI-CuI phase system at room temperature. DSC traces show that the superionic phase transition temperature increases from 149°C to 376°C upon addition of Cu. The semicircle of impedance spectra is depressed at higher temperature. Arrhenius plots show a sudden jump in the conductivity around the phase transition temperature.

Keywords: Solid solutions; fast ionic conductor; Phase transition temperature; Ionic conductivity; mechanochemical technique

1. INTRODUCTION

Silver Iodide (AgI) is a remarkable compound due to its superionic α phase and high Ag^+ conductivity [1]. At ambient conditions, AgI occur as a mixture of Wurzitic (β-phase) and zinc blende (γ-phase). This material undergoes a first order superionic transition at 420K from the low temperature β-AgI to the α-AgI phase at higher temperature. The α phase exhibits a highly disordered cation distribution and a rigid crystal framework provided by the anion sublattice. Silver ions move easily through this structure with low activation energy giving rise to high ionic conductivity values in the order of $1.0\ \Omega\ cm^{-1}$ [2,3]. In α phase, the cation sublattice is diffusive while the anion remains localized in a BCC lattice [4]. The ionic conduction in γ-AgI is promoted by the migration of Frenkel defects. However, the physics of ionic conductivity in the low temperature phase (β-AgI) is not so well understood. There is no evidence for pre-transition behavior near the β to α phase transition which defies interpretation in terms of simple activated behavior [5]. In other words, it is not known yet how the disorder in the Ag^+ sublattice may develop and drive the transition to the fast ion conductivity phase with increasing temperature [6]. However, the bond fluctuation model has advanced considerably the understanding of the properties of superionic materials such as Ag-Cu-I system [7].

Study of the effects of chemical substitution on the superionic conductivity of AgI provides further insight into the complexities of this phase transition [8]. However, unlike alkali iodides, AgI does not easily admit impurities into its tetrahedrally bonded zinc blende structure, making it difficult to investigate the origin of phase transition and ion mechanisms. Studies have been made on doping AgI with alkali salts such as lithium to form other AgI type solid electrolyte compounds rather than form solid solutions [9]. Other salts like NaI do not dissolve in AgI eventhough doping with NaI was found to stabilize the $\beta \rightarrow \alpha$ phase bonding of AgI at 420K [10]. However, CuI is unique in that forms and a complete set of solid solutions with AgI and stabilize changes in the structure of the cation sublattice which control the phase stability and phase transition behavior [11]. Futhermore, the fact that CuI is an electronic conductor in the temperature range of investigation brings into play factors such as p-d hybridization to the conduction process. This unique feature is conducive for realizing metastable and new superionic phases by mechanochemistry. Thus the solid solution between AgI and CuI is expected to show a complex but interesting behavior in the temperature region 420 - 684 K where BCC and FCC structures compete for existence. Recently, mechanochemical reaction (MCR) has emerged as a variable method to produce solid solution materials [12]. This technique generally influences texture and structure leading to a decrease of the particle size and simultaneously increases the microstrain due to the contribution of the grain boundaries formed during the process [13]. In the present paper, we investigate experimentally the conductivity and phase transition behavior in nanoscale $Ag_x Cu_{(1-x)}I$. Unlike Kumar et al [11] which emphasized only on the Ag rich solid solution, our work is more comprehensive which covered Ag rich, Cu rich and intermediate solid solutions. We also prove that the Vegard's law is valid in the AgI – CuI system.

2. EXPERIMENTAL

High purity of AgI was prepared by mixture of silver nitrate, $AgNO_3$ and potassium iodide, KI and heated at 45 °C for 2 hrs. AgI and CuI powders were mixed with different weight ratios using a planetary ball mill (pm 400, MA type, Retsch). The mixtures were milled for 6 hrs at 400 rpm in a zirconia jar with zirconia balls. Annealing of the green was performed under air atmosphere at 200 °C for duration of 30 min. Structural characterization of the samples was carried out using monochromatic Cu K α radiation on a Philips X-Ray diffractometer Model PW 3040. Phase transitions were investigated using Mettler DSC 820 Calorimeter at heating rate of 10 °C per min at selected temperatures in the range of 25-400 °C so as to cover all possible phase transitions in AgI and CuI. The powdered samples were then compressed at pressure of 4 ton in a stainless steel dye using a hydraulic hand press (Gates by Specac). These pellet thus obtained had an diameter of 8 mm and thickness of 5 mm. Impedance measurements in the frequency and temperature range, 50 to 1 MHz and 25-400 °C respectively, were carried out using HIOKI 3532-50 LCR Hi Tester. A chemically inert and commercial grade graphite paste was used as the electrode. It was applied on opposite parallel surfaces of the sample pellet to block the ion movement on the other side of the sample configuration.

Repeated temperature cycles above β/γ → α transition temperature was performed to confirm the reproducibility of the impedance data of these polycrystalline specimens.

3. RESULTS AND DISCUSSIONS

3.1 XRD analysis

The representative XRD patterns of the pure AgI and Cu-rich solid solution at the room temperature are shown in Fig.1. Undoped AgI sample (pattern (a)) contains two phases: the major γ-AgI (zincblende structure) and the minor β-AgI (wurtzite structure). It is observed that the patterns consist of three prominent Bragg peaks (111), (220) and (311) at angle 2θ around 25°, 42° and 50°, respectively. The prominent peaks are the characteristic of a substantial amount of γ-AgI and the presence of additional weak reflections are attributed to the co-existence of other polymorphs of AgI [10]. The main purpose of Cu doping is to stabilize the metastable zincblende structure of γ-AgI as γ-AgI cannot be stabilized easily at ambient [11]. A more subtle but important role of Cu+ ions (higher polarizability and smaller ionic size than Ag+) is probably to impede the crystal growth to a significant extent, thereby lowering the average crystallite size which calculated using Debye-Scherrer formula and shown in Table 1.

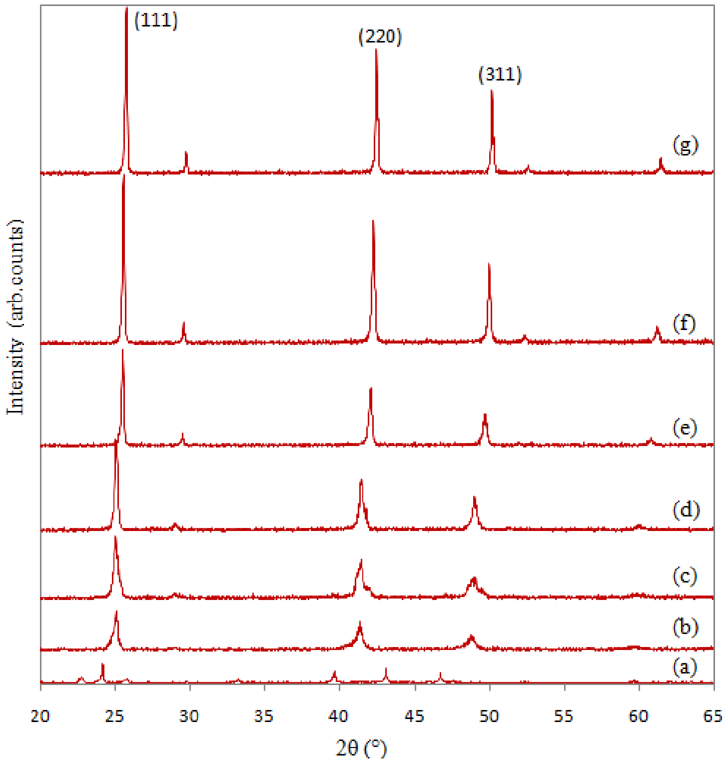

Figure 1. X-ray powder diffraction patterns for the various compositions of AgI-CuI solid solution: (a) 1.0 AgI; (b) 0.5AgI-0.5CuI; (c) 0.4AgI-0.6CuI; (d) 0.3Agi-0.7CuI; (e) 0.2AgI-0.8CuI; (f) 0.1AgI-0.9CuI; (g) 1.0CuI

That is the grain size of synthesized powder decreases with the Cu^+ concentration increases. This reinforces the cation sublattice to stabilize the zincblende phase γ-AgI, which has smaller unit cell than that of the wurtzite of β-AgI. However, the grain size starts to increase when the concentration of Cu^+ at 0.7 and above. This XRD results hint the different crystallite size is more likely to be an effect of different nucleation rates.

It is observed that a continuous shift in the Bragg angle in all Bragg peaks of Ag-rich system as it moves towards pure Cu region upon progressive addition of Cu. Undoped CuI (pattern (g)) shows clearly the more fully developed Bragg reflections of γ-CuI lines. The lattice parameter (a in pm) decreases linearly with increasing Cu as shown in Fig. 2 due to the radius of Cu^+ (0.096 nm) is smaller than that of Ag^+ (0.126 nm) [11].

As a result, the lattice distortion has occurred and become more significant as the concentration of CuI substitution increases.

This indicates a continuously uniform stabilization of static cation disorder in the zincblende AgI lattice brought about by the mechanochemical processing. Finally, Vegards's law is valid in AgI-CuI system [14].

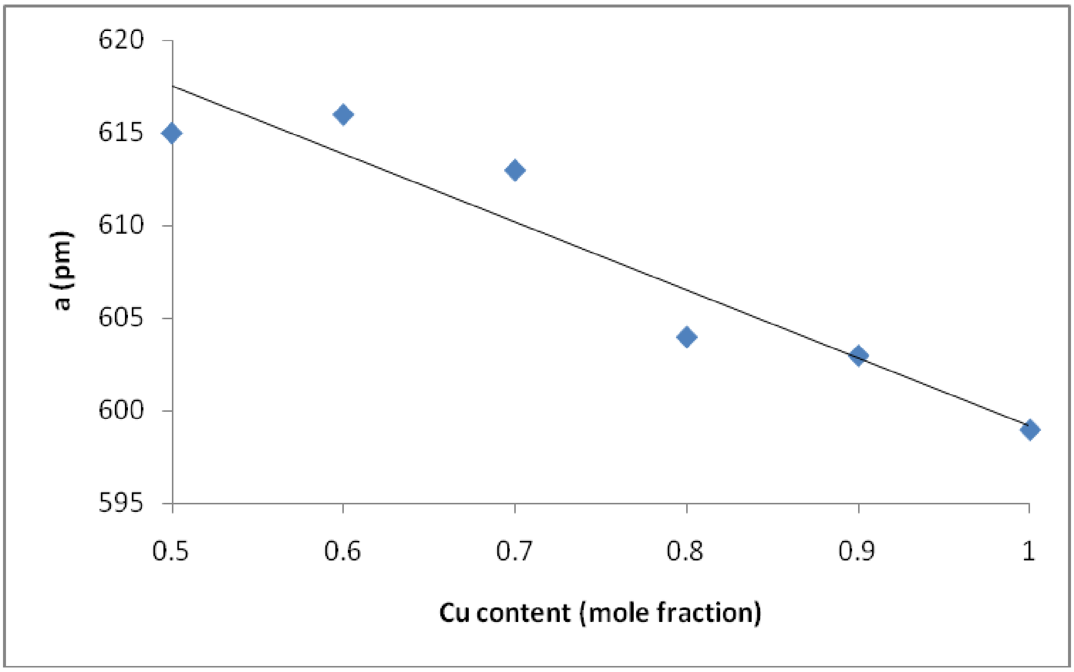

Figure 2. Plot of lattice parameter (a) vs Cu composition in the AgI-CuI of solid solution

3.2. DSC analysis

Fig. 3 shows the thermal response of AgI-CuI solid solution. On heating pure AgI, a sharp and intense endothermic peak, γ→α phase transition (T_t) observed at 149 °C (147 °C is in commercial AgI).

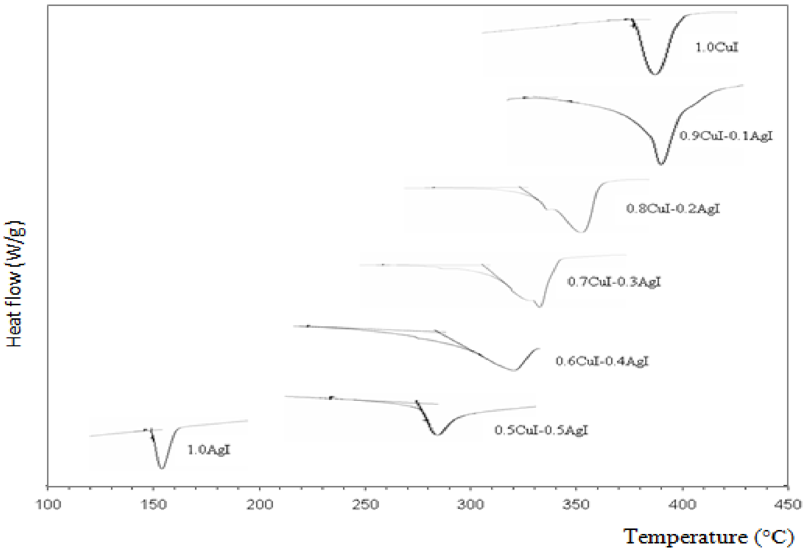

Figure 3. DSC traces of Cu rich solid solution

In Cu-rich region, all plots show diffuse endothermic peak in contrast to a much sharper peak in pure AgI. The mixed phase region corresponds to an increasingly asymmetric endotherm as Cu content increases. AgI is weakly covalent bonded structure and also cation disordered even at room temperature. The addition of Cu^+ resulted in a decrease in the number of Frenkel defects at the $\gamma \rightarrow \alpha$ phase transition leading to a broad and increased asymmetric endothermic peak. The zinc blende phase of AgI apparently retards the phase transition of AgI to the superionic phase. As far as Ag^+ transport is concerned, this means partial blocking of conducting paths in the AgI structure. In Cu-rich region, AgI bond is further strengthened by the Cu substitution. So that MCR of (Ag-Cu) I extends the transition temperature range over which the γ-phase is stable (Table 1). The increased T_t arises from the relatively strengthened Ag-I bond, due to an effect induced by MCR process as shown in Fig. 4. This extended thermal stability is important in view of the potential applications.

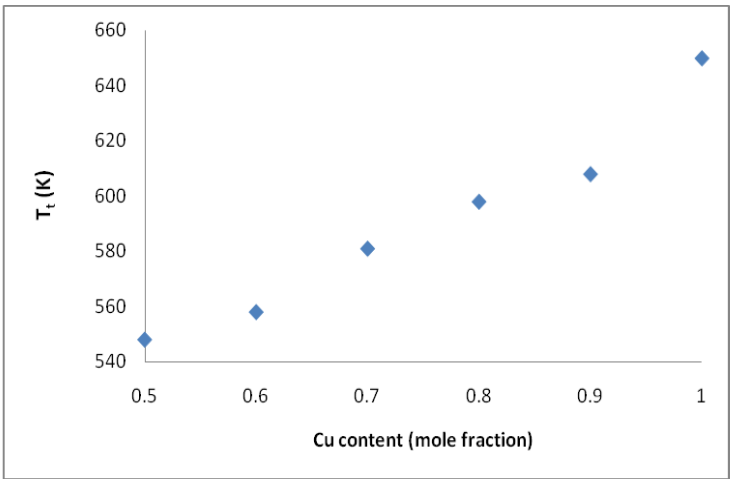

Figure 4. Phase transition temperature of AgI-CuI system

3.3. Impedance spectroscopy analysis

The effect of temperature on impedance behavior becomes more prominent at higher temperature. The impedance spectrum is characterized by the appearance of semicircular arcs, whose pattern of evolution changes with a rise in temperature (Fig. 5). At the higher temperature, the semicircle is being depressed due to a distribution of relaxation times. The presence of a single semicircular arc indicates that the electrical process contribution is from a bulk material (grain interior) which can be modeled as an equivalent circuit comprising of a parallel combination of bulk resistance (R_b) and bulk capacitance (C_c).

Table 1.

Sample	Transition temperature (T_t) in ^oC	Conductivity, σ (Scm^{-1}) (room temperature)	Activation Energy, E_a in eV ($<150^oC$)	Activation Energy, E_a in eV ($>150^oC$)	Crystallite size (nm)
1.0AgI					
	149	1.24 $x10^{-6}$	0.54	0.04	63
0.5AgI-0.5CuI					
	275	1.08 $x10^{-3}$	0.10	0.27	25
0.4AgI-0.6CuI					
	285	5.41 $x10^{-4}$	0.08	0.04	18
0.3AgI-0.7CuI					
	308	3.38 $x10^{-4}$	0.06	0.55	28
0.2AgI-0.8CuI					
	325	1.76 $x10^{-4}$	0.11	1.15	36
0.1AgI-0.9CuI					
	334	7.63 $x10^{-5}$		0.05	43
1.0CuI					
	376	2.00 $x10^{-7}$		0.38	62

Arrhenius plots of the dc conductivity, σ were extracted from the analysis of above impedance spectra are shown in Fig.6. It is observed that the conductivity obey the Arrhenius law throughout the region. However, there are also sudden changes in the conductivity in pure AgI at 111 and 147^{o}C due to the (γ→β) and (β→α) phase transition respectively. The composition of 0.5AgI−0.5CuI and 0.4AgI−0.6CuI have a sharp conductivity jump at 250 °C compare to its transition temperature at 275 and 285 °C, respectively.

While the composition of 0.3AgI−0.7CuI and 0.2AgI−0.8CuI have a sharp conductivity jump at 250 and 350 °C, which are nearly to their transition temperature at 308 and 325 °C, respectively. However, there are no sharp conductivity jump for both compositions of 0.1AgI-0.9CuI and 1.0CuI. The addition of Cu content caused the average Ag-I bond became more covalent and the ionicity became less critical than pure AgI. Hence, this ensured that the high temperature conductivity of Cu-doped AgI was less than pure AgI. The activation energies of various compositions are tabulated in Table 1.

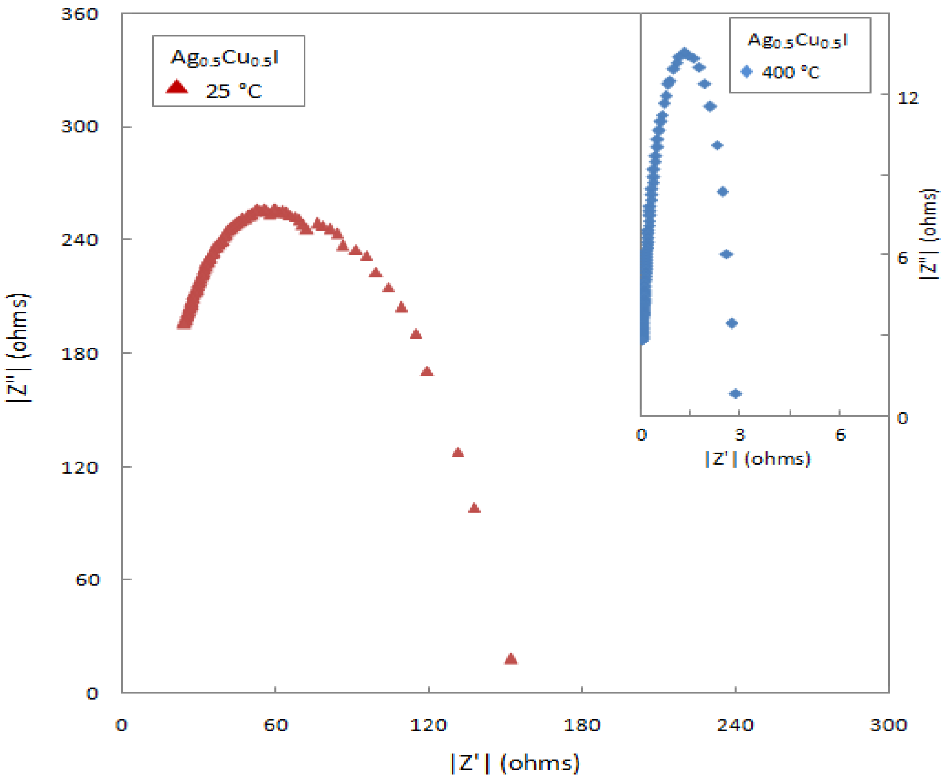

Figure 5. Variation of real and imaginary parts of impedance with temperature for 0.5 AgI-0.5 CuI sample.

The activation energies of 0.5AgI−0.5CuI composition, which has the highest conductivity at room temperature, are 0.10 eV and 0.27 eV for less and more 250 °C, respectively. The conductivity increases rapidly above 250 °C, correspond to the *β* →α phase transition. The composition dependence of activation energy for AgI−CuI solid solution at higher temperature phase is rather small. This is may attributed to the fact that even though both Ag and Cu ions have the same conduction paths, the amplitudes of their anharmonic thermal vibration are different [10]. Moreover, the Arrhenius plot in the high temperature is almost parallel to the T^{-1} axis, implying smaller activation energy.

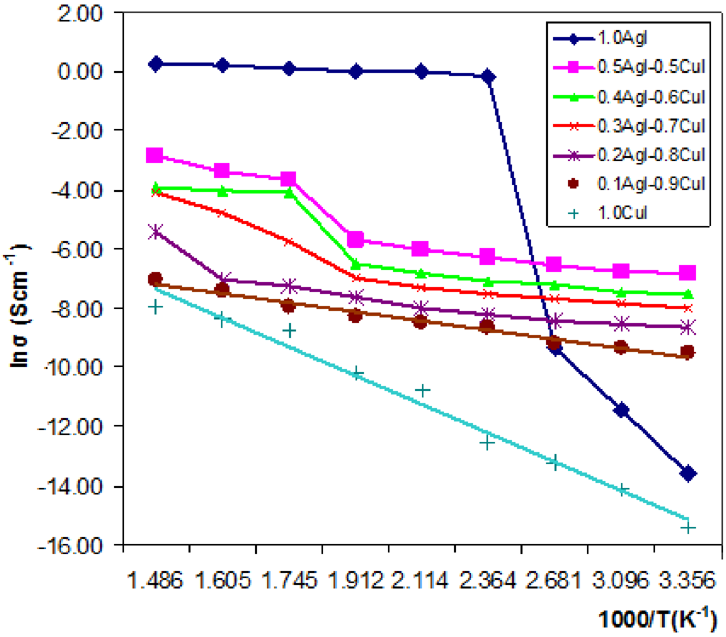

Figure 6. The temperature dependence conductivities of AgI-CuI solid solution.

4. CONCLUSION

A new polycrystalline AgI−CuI solid solution has been successfully prepared by mechano-chemically technique at ambient temperature. XRD measurements are reported on room temperature synthesized AgI-CuI system. With increasing Cu concentration, the phase transition temperature increases from 149 to 376 °C. The mixed phases are discussed in relation to Ag^+ conductivity behavior in the AgI-CuI system as well as the diffusion phase transition observed in DSC. The effect of temperature on impedance behavior was more prominent at higher temperature and semicircle being depressed due to a distribution of time relaxation. Arrhenius plots show a sudden jump of conductivity around the phase transition temperature. Microscopically, the fundamental change in ionicity of the Ag-I bond and increases in strength of *p-d* hybridization upon Cu-substitution are the two factors, which strongly determine the ionic conductivity of these solid solutions.

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