Full Paper

Preparation and Calculation of Variour Ionic Transport Properties in a Superionic Mixed Composite System [Cu$_2$HgI$_4$:0.2 AgI]:0.xCuI

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Abstract- A new superionic mixed composite system, [Cu$_2$HgI$_4$:0.2 AgI]:0.xCuI, (x=0.2, 0.4, 0.6 mol. wt. %), was prepared by conventional solid state reactions and [Cu$_2$HgI$_4$:0.2 AgI] mixed system was used as the host. Electrical conductivity was measured to study the transition behavior at frequencies of 100 Hz, 120 Hz, 1 kHz, and 10 kHz in the temperature range 90°-170 °C by a Gen Rad 1659 RLC Digibridge. Conductivity increased sharply during the β-α phase transition. As a result of increase in the dopant-to-host ratio, the conductivity of the system exhibited Arrhenius (thermally activated)-type behavior. The phase transition temperature increased with an increase in the dopant concentration. Activation energies for the system in eV both for the pre-transition and post-transition phase transformations are reported. The addition of CuI to [Cu$_2$HgI$_4$:0.2 AgI] shifted the phase transition of the host [Cu$_2$HgI$_4$:0.2 AgI], due to an interaction between [Cu$_2$HgI$_4$:0.2 AgI] and CuI.

Keywords-Ionic Conductivity, Composites, Doping, Halides, Batteries

1. INTRODUCTION

Composite electrolytes are multiphase (mostly two phase) solid systems in which two or more materials are mixed together to achieve some desirable material properties, namely an enhancement in the ionic conductivity at room temperature. Composite electrolytes are also

called heterogeneously doped materials or dispersed solid electrolytes. Conductivity enhancement in two-phase composite systems was known for about 75 years [1], however, the research activity in this area gained impetus only after 1973, when C. C. Liang [2] reported approximately 50 times enhancement in LiC ion conduction at room temperature simply by dispersing ultrafine particles of inert Al_2O_3 in LiI. Since then, a large number of two-phase composite systems have been investigated with the conductivity enhancement of about one to three orders of magnitude compared with those of constituent phases [3-16]. Two-phase composite electrolyte systems are prepared, in general, by dispersing submicrometre-size particles of insulating and chemically inert materials (called second phase dispersoids) into a moderate-ionic conducting solid (called first phase host-matrix) [8,14]. The conductivity increases with increasing dispersoid concentration, attains a peak value, then decreases. The peak is generally sharp, except for few systems, such as HgI_2–Al_2O_3, AgI–predried Al_2O_3. Furthermore, the conductivity maxima may be different in different composite systems and depends on the nature of the second phase dispersoid. In some composite systems, dispersion has not altered/increased the conductivity of the host-matrix. The nature of dispersoid decides the order of enhancement in composite electrolyte systems. For instance, highest conductivity enhancements were reported in AgI–Al_2O_3 and LiCl–Al_2O_3 systems with´-Al_2O_3 dispersoid. In general, larger enhancements are reported with Al_2O_3 in many composite electrolyte systems as compared with other dispersoids [17]. The conductivity enhancement in composite electrolyte systems is strongly particle-size dependent of the dispersoid. It has been found that the conductivity of the composite system increases with decreasing particle size [18]. Temperature influences conductivity enhancement in composite electrolyte systems. The enhancement is highest only at low temperatures. As the temperature increases the enhancement decreases. This in turn lowers the activation energy as compared with the host-matrix. A detrimental effect is observed at high temperatures [19]. AgI-doped superionic composites have attracted much attention because of their high ionic conductivity at room temperature [20]. Silver-based glasses have been found to exhibit excellent ionic conductivity at ambient temperature [21]. More recently, development of a new solid electrolyte system involving, a number of compositional variations of AgI, CuI, KI and K_2SO_4 with ternary solid electrolytes [M_2HgI_4] have been attempted by some researchers [22-25].

In the present study, we investigated an alternative mixed composite solid [Cu_2HgI_4:0.2 AgI]:0.xCuI (x=0.2, 0.4, 0.6 mol. wt. %) where CuI is the dopant, [Cu_2HgI_4:0.2 AgI] is a host and the composition of host kept constant in all the composite samples [23] It has been observed that a much better solid electrolyte composite system can be prepared with the host [Cu_2HgI_4:0.2 AgI] [23,24]. Here we report the results of studies performed with the [Cu_2HgI_4:0.2 AgI] mixed system.

2. EXPERIMENTAL

2.1. Material

Silver iodide and mercury [I] iodide were of CDH Analar grade, copper [I] iodide was obtained from S.d.fine-chem (India), each of which had a purity of 98%, 99%, 99% respectively. They were used as such.

2.2. Preparation and characterization of pure and doped samples

2.2.1. Preparation of [Cu_2HgI_4:0.2 AgI] host composite samples

Cu_2HgI_4 was prepared by the solid state reactions between CuI and HgI_2 [22]. Both were mixed thoroughly in a requisite composition in an Agate mortar (each above 300-mesh size). The finely ground stoichiometric mixture of the binary components CuI and HgI_2; was sealed in a glass ampoule and was placed in an air oven (CE 0434 NSW-144) at 100 °C for 5 days. A maroon color compound was formed which changed to dark red color on cooling, (Cu_2HgI_4 is dark red below 76 °C and maroon above 76 °C [26]). X-ray diffraction studies showed this dark red color compound to be single phase β- Cu_2HgI_4.

The host [Cu_2HgI_4:0.2 AgI] was prepared by mixing 2 g Cu_2HgI_4 and 0.2 g AgI in an Agate mortar at room temperature with intermittent grinding adopting the procedure reported earlier [22].

2.2.2. Preparation and characterization of doped samples

Mixed composite doped samples [Cu_2HgI_4:0.2 AgI]:0.xCuI, were prepared by taking [Cu_2HgI_4:0.2 AgI] and CuI, in different ratios of x (x=0.2 to 0.6 mol. wt. %) following procedure reported elsewhere [23]. The powder mixtures were ground thoroughly kept in silica crucible in an air oven for 24 h. The resulting material at room temperature was used for further studies [24].

2.3. Electrical conductivity measurements

Specific conductivity as a function of temperature was measured on pellets (2.4 cm diameter, 0.1 cm thick) prepared by pouring the requisite amount of the compound into a stainless steel die at a pressure of 5 tons/cm² using a hydraulic press (Spectra Lab Model SL-89). In effect of pressure on pellets was also studied prior to making measurements, samples were cycled to above and below the transition temperature two or three times in order to relieve strains and improve their homogeneity. Conductivity measurements were measured using the two probe method. The pellet was mounted on a stainless steel sample holder assembly between copper leads using two polished platinum electrodes. The copper leads were electrically insulated by Teflon sheets. The electrical conductivity of samples in the temperature range of 80°-170 °C was measured by a Gen Rad 1659 RLC Digibridge at different frequencies (100 Hz, 120 Hz, 1 kHz, and 10 kHz) at 30 min intervals. The rate of

heating was maintained at $1°C/min$. Usually, conductivity is frequency dependent. Therefore, it was thought proper to investigate the effect of frequency on the conductivity behavior. The different frequencies were used to see the effect of frequency, if any, on the conductivity. Conductivity of solids is reported to be affected by the change of frequency [27].

3. RESULTS AND DISCUSSION

3.1. Compositional variation in conductivity

The variations in the conductivity as a function of mol. wt. % x (where x=0.2–0.6 mol. wt. %) for the mixed composite system $[Cu_2HgI_4:0.2\ AgI]:0.xCuI$, at different temperatures in the range 80°-170 °C are shown in Fig. 1. The conductivity sharply increased with an increase in x, attaining a peak value for x=0.2 to x=0.4 mol. wt. % and thereafter decrease in between the temperature, 80°-110 °C. Variations in dopant composition in the host affected the phase change within the temperature range of 90°-100 °C. This phenomenon is usually observed in a solid electrolyte composite system [22]. The log σT-x plot (Fig. 1) of the mixed composite system looks qualitatively similar to those reported in the literature [23] but the σ values differ quantitatively in different temperature range [28].
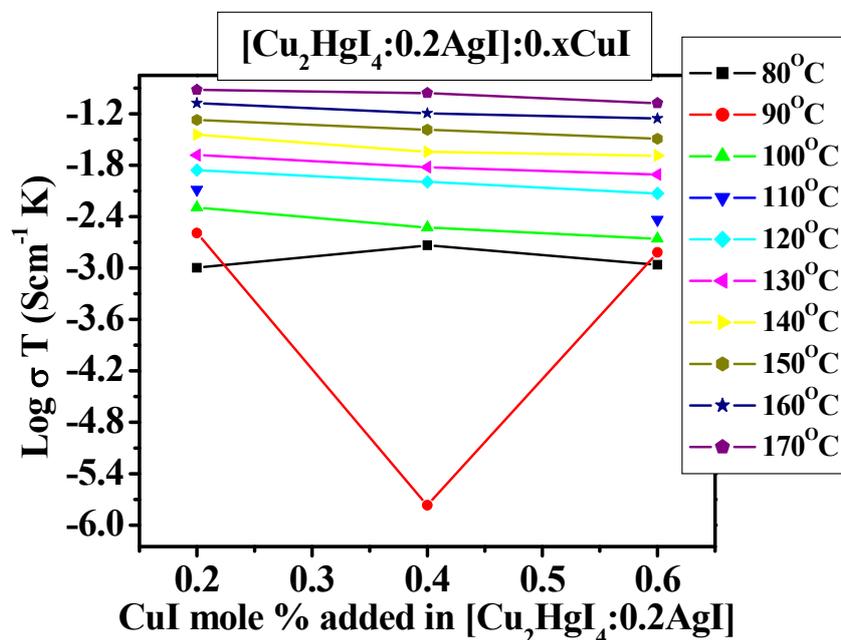

Fig. 1. Log σT *vs.* the x mol. wt. % plot of CuI in the $[Cu_2HgI_4:0.2\ AgI]:0.xCuI$ at different temperature, where (x=0.2, 0.4, 0.6 mol. wt. %)

Horizontally flat conductivity maxima was obtained for the systems in the region x=0.2-0.4 mol. wt. %. The conductivity variation with composition is qualitatively similar but quantitatively different, due to the different purity of starting materials used. No measurements on composite samples exist in the literature and so direct comparison was not possible. It is obvious from Fig. 1, that composite samples showed conductivity-composition dependence. The conductivity enhancement in the composite composition from the constituent compounds was attributed by Lauer and Maier [29] to the increased mobile ion concentration in the space charge region of the M_xHgI_4/AgI interface. The additional enhancement of conductivity for the composite samples is attributed to the formation of new disordered phases.

3.2. Temperature variations in conductivity

The electrical conductivity also depended upon the palletizing pressure. There was a linear increase in conductivity with a palletizing pressure up to 5 tons/cm^2, after this, there was no dependence on pressure. The temperature dependence of the ionic conductivity can be described well by the Arrhenius relation;

$$\sigma = ne^2\lambda^2\upsilon\gamma \, / \, k_BT \exp(-\Delta G^* / k_BT) \tag{1}$$

$$= ne^2\lambda^2\upsilon\gamma \, / \, k_BT \exp(\Delta S^* / k_B - \Delta H^* / k_BT) \tag{2}$$

where n is the number of ions per unit volume, e the ionic charge, λ the distance between two-jump positions, υ the jump frequency, and γ the intersite geometry constant, k_B is Boltzmann's constant and ΔG^*, ΔS^*, ΔH^* are thermodynamic activation parameters. The equation can be written in a simpler form as;

$$\sigma = \sigma_o \exp(- E_a / k_BT) \tag{3}$$

where $\qquad \sigma_o = ne^2\lambda^2\upsilon\gamma \, / \, k_B \exp(\Delta S^* / k_B)$

and $\qquad \Delta H^* = \Delta H^*_{migration} + \tfrac{1}{2} \Delta H^*_{defect} \tag{4}$

Where $\Delta H^* = E_a$, the activation enthalpy equals the experimental activation energy for ionic motion, which may include a defect formation enthalpy contribution [30]. Fig. 2 shows the $\log\sigma T$ *vs.* (1/T) plots for the pure composite host [Cu_2HgI_4:0.2 AgI] and the mixed composite systems [Cu_2HgI_4:0.2 AgI]:0.xCuI, respectively.

The activation energy of Cu_2HgI_4, [Cu_2HgI_4:0.2 AgI], and all mixed composite systems are shown in Table 1.

The phase transition temperature for the mixed composite system, [Cu_2HgI_4:0.2 AgI], increases as compared to Cu_2HgI_4. The β-phase has thermal activation up to 120 °C. Fig. 2

shows that the highly conducting α-phase of the host (approximately T_c=120 °C) is almost completely stabilized just before the transition temperature. The small jump in the conductivity was due to the β–α transition in the host. The drop in conductivity was probably due to softening of the materials [28]. The logσT values of the mixed composite systems are also intermediate between Cu_2HgI_4 [31] and dopant AgI.
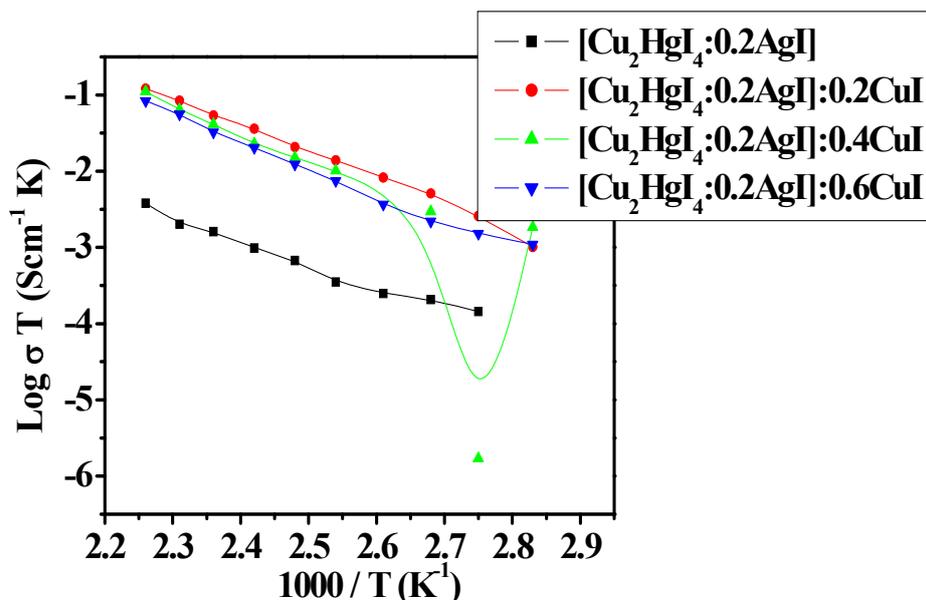

Fig. 2. Log σT *vs.* (1/T) plots for mixed composite systems, [Cu_2HgI_4:0.2 AgI]:0.xCuI where (x=0.2, 0.4, 0.6 mol. wt. %)

In Cu^+-doped sample, the prospects of cationic conductivity with smaller radii and lower masses i.e. Cu^+[rAg^+=1.26 Å and rCu^+=0.96 Å] [32] in the host [Cu_2HgI_4:0.2 AgI] structure, the enhanced conductivity as predicted for Cu^+ incorporation in the lattice is observed for each addition respectively. The highest conductivity is observed in the 0.2 mol. wt. % Cu^+-doped samples. In the mixed cation compounds, it would generally be the case that the smaller cations are the better mobile ions [33].

The logσT *vs.* 1/T plot shifts from a lower temperature to a high temperature is responsible for the phase transition from β- Cu_2HgI_4 (dark red) to α- Cu_2HgI_4 (maroon) which is associated with a charge transfer process between electron levels of Hg and I. These observed changes in the phase transition can be explained by assuming an increase in the reaction between I and Ag atoms above the phase transition, and a consequent decrease in the I-----Hg interaction. These changes would be induced by a decrease in the Ag-----I distance above the phase transition, a consequence of structural distortion, because the Hg------I distance would increase and lead to the observed changes in pure [Cu_2HgI_4] [34]. Therefore, in the host [Cu_2HgI_4:0.2 AgI] mixed system, one may expect that fraction of mobile charge

carriers, Ag^+, increases leading to an increase in the Ag-----I distance and thus the phase transition shift to higher temperature up to 110 °C. On the other hand, in the Cu^+ mixed samples, the partial replacement of the Ag^+ ions by smaller Cu^+ ions in the host $[Cu_2HgI_4:0.2$ AgI] lattice tends to open up more space for the Cu^+ ion to move freely through the host lattice framework.

Table 1. Comparative activation energies for ionic conductivity of pure and doped $[Cu_2HgI_4:0.2$ AgI]

Compounds	PhaseTransition Temperature (°C)	Activation Energy(ev) Pre-transition (β) Phase (Ea$_1$)	Activation Energy (eV) Post-transition (α) Phase (Ea$_2$)
$[Cu_2HgI_4]$	70	0.0375	0.8803
$[Cu_2HgI_4:0.2$ AgI]	120	0.3549	0.7155
$[Cu_2HgI_4:0.2$ AgI]:0.2 CuI	100	1.0410	0.6969
$[Cu_2HgI_4:0.2$ AgI]:0.4 CuI	110	0.2726	0.7435
$[Cu_2HgI_4:0.2$ AgI]:0.6 CuI	120	0.2984	0.8324

The ionic conductivity and the activation energy of conduction show strong dependence on the concentration of Cu^+ ion in the host lattice which confirms the argument of Cu^+ ion predominance in the conduction process. The transition temperature on doping with Cu^+ is essentially due to the reinforcement of the cation sublattice. At the most fundamental level, the average Ag----I bonds becomes more covalent and the ionicity becomes less critical than that deduced by Phillips for AgI [35]. This ensures that the high temperature conductivity of Cu^+-doped $[Cu_2HgI_4:0.2$ AgI] than that of undoped $[Cu_2HgI_4:0.2$ AgI].

Ionic conduction is determined by thermally activated defect. The increase of conductivity up-to 140 °C can be attributed to the extra enhancement of $\bar{I}$ orientational disorder. Upon cooling, however, the higher conductivity was regained. This argument of lattice collapse and its subsequent recovery on cooling implies restructuring of the sublattice.

The conductivity data show that the doped sample exhibit very high Cu^+ ion conductivity in the system of compound referred to as NASICON [36].

The proposed model of highly mobile Cu^+ ion in a fixed sublattice in host $[Cu_2HgI_4:0.2$ AgI] compound parallels the accepted model of highly mobile Ag^+ ion in the fixed network of $\bar{I}$ in AgI compound [37].

Temperature-dependent variations in conductivity for all the samples were also studied at 10 kHz, 100 Hz, and 120 Hz, and the change in frequency did not induce a change in electrical conductivity. The conductivity is therefore frequency independence. Activation energies (E_{a1}) and (E_{a2}) for the pre-transition and post-transition region are reported in Table 1. A commonly accepted method to study non-linear Arrhenius behavior is to fit the experimental data using two straight lines in the pre- and post-transition regions. The pre-transition phases have higher activation energy than the post-transition phase [38], consistent with the conductivity behavior.

3.3. Time variation of conductivity

Fig. 3 (a,b,c) displays the conductivity behavior of all the mixed composite system $[Cu_2HgI_4:0.2\ AgI]:0.xCuI$ *vs.* time at a 30 min interval in the temperature range 90°–170 °C for different dopant ratios. The 30 min time interval was selected in order that the structural changes, if any, would homogenize during this interval. The conductivity of all the mixed composite system decays at elevated temperature with the loss in conductivity being most pronounced at temperatures at or higher than 150 °C in air. The conductivity degradation rate constants as well as the apparent activation energies were extracted from the curve slopes Fig. 4 and a standard Arrhenius analysis [39, 40] reported in Table 2.
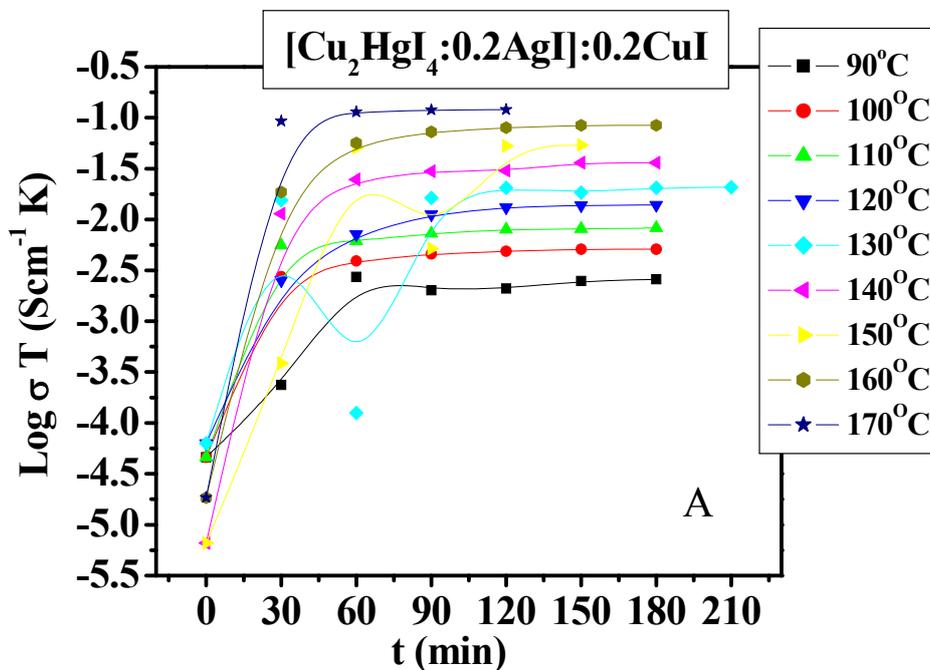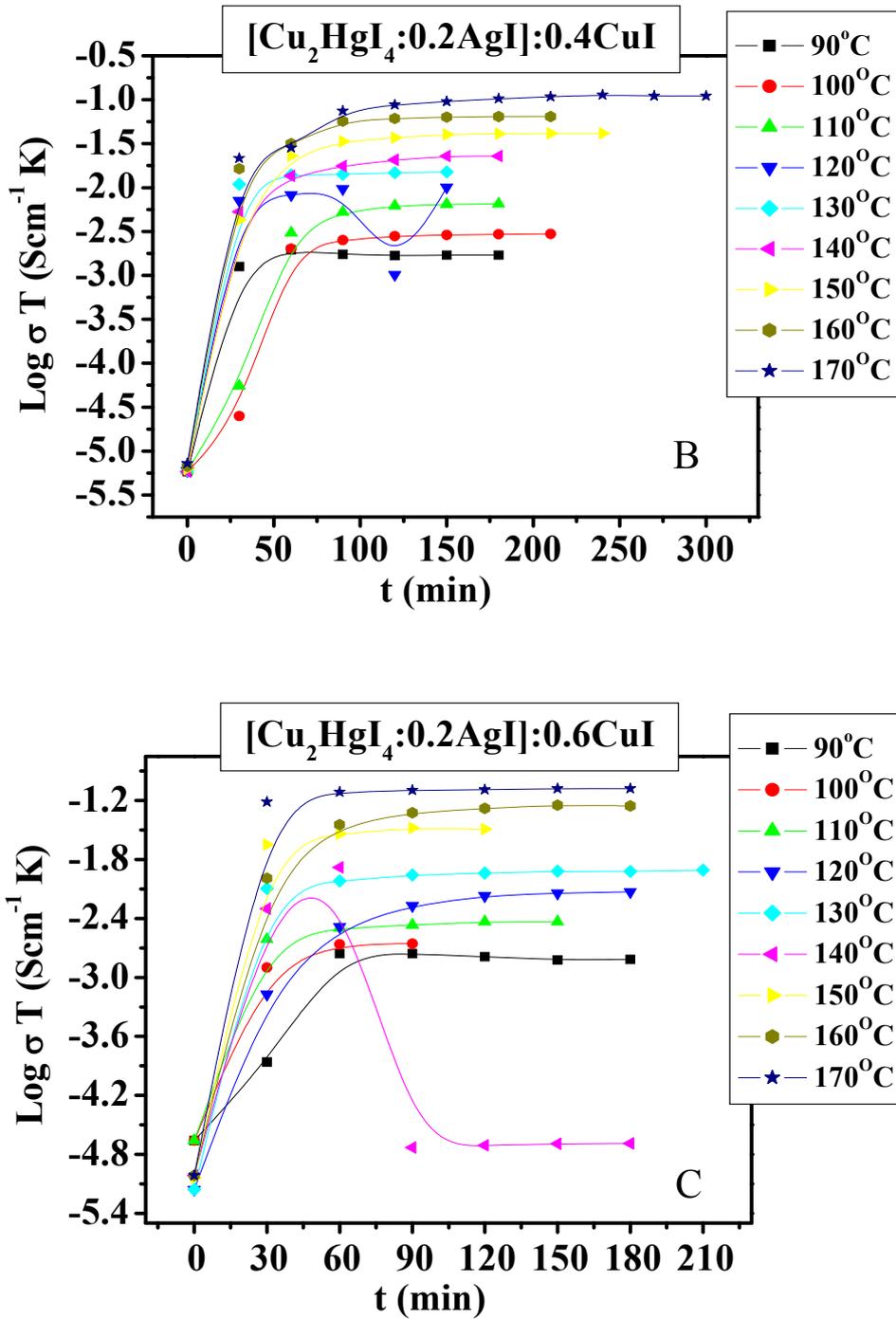
Fig. 3. (A) Log σT *vs.* t (min) plots for mixed composite system [Cu₂HgI₄:0.2 AgI]:0.2 CuI at different temperature (B) Log σT *vs.* t (min) plots for mixed composite system [Cu₂HgI₄:0.2 AgI]:0.4 CuI at different temperature (C) Log σT *vs.* t (min) plots for mixed composite system [Cu₂HgI₄:0.2 AgI]:0.6 CuI at different temperature

Table 2. Average activation energies extracted from the curve slopes by a standard Arrhenius analysis

Compounds	Average Activation Energy (eV)
[Cu_2HgI_4:0.2 AgI]:0.2 CuI	0.2501
[Cu_2HgI_4:0.2 AgI]:0.4 CuI	0.1310
[Cu_2HgI_4:0.2 AgI]:0.6 CuI	0.3367
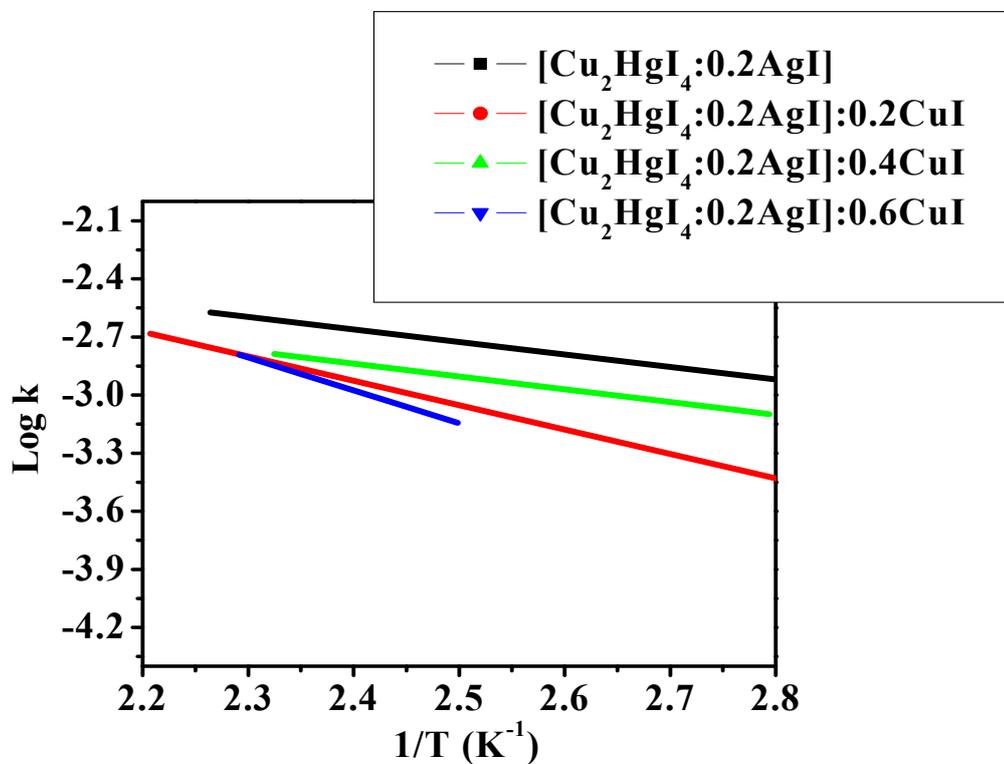
Fig. 4. Log k (rate constant) *vs.* 1/T (K^{-1}) plots for mixed composite systems, [Cu_2HgI_4:0.6 AgI]:0.xCuI, where (x=0.2, 0.4, 0.6 mol. wt. %)

4. CONCLUSION

A novel composite superionic systems [Cu_2HgI_4:0.2 AgI]:0.xCuI, was prepared and investigated. An alternative host [Cu_2HgI_4:0.2 AgI] mixed system was used in place of the traditional host [Cu_2HgI_4]. The electrical conductivity of [Cu_2HgI_4:0.2 AgI] is found to be enhanced markedly in the temperature range 80-110 °C, on the doping with CuI Initially the conductivity increases with temperature due to increase in rate of migration of frenkel defects

and interstitial Cu^+ ions, and then decrease becomes constant beyond 110-170 °C due to collapse of the iodide framework. The increase of conductivity upto 110 °C can be attributed to the extra enhancement of $\bar{I}$ orientational disorder. The enhanced conductivity as predicted for Cu^+ incorporation in the lattice is observed for each addition, in the host $[Cu_2HgI_4:0.2\ AgI]$.

The temperature dependence of various ionic parameters was determined to characterize the ion transport properties and doping effect .

Acknowledgements

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