Phase transition study in a [Cu₂HgI₄ : 0·xAgI] mixed composite system

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Abstract. A novel composite superionic system, [Cu₂HgI₄ : 0·xAgI], (x = 0·2, 0·4, 0·6 mol wt.%), was prepared. A [Cu₂HgI₄] system was used as the host. Electrical conductivity was measured to study the transition behaviour at frequencies of 100 Hz, 120 Hz, 1 kHz and 10 kHz in the temperature range 90–170°C using a Gen Rad 1659 RLC Digibridge. Conductivity increased sharply during the β–α phase transition. Upon increasing the dopant-to-host ratio, the conductivity of the superionic system exhibited Arrhenius (thermally activated)-type behaviour. DTA, DTG, TGA and X-ray powder diffraction were performed to confirm doping effect and transition in the host. The phase transition temperature increased with an increase in the dopant concentration. Activation energies in eV for pre- and post-transition phase behaviour are also reported. Due to an interaction between [Cu₂HgI₄] and AgI, the addition of AgI to [Cu₂HgI₄] shifted the phase transition of the host [Cu₂HgI₄].

Keywords. Chemical synthesis; electrical conductivity; phase transition; X-ray diffraction; thermal analysis.

1. Introduction

Interest in the phenomenon of fast-ion transport in solids has grown rapidly over the past decades (Bates and Farington 1981). Fast-ion conductors (also referred to as superionic conductors or solid electrolytes) are of continuing interest not only for their high ionic mobilities and technological promise, but also solid-state systems for the study of a wide range of problems (LeDuc and Coleman 1985). The design of electric batteries and potential optical devices requires an understanding of the role of the electronic structure in superionic conductors (Wakamura 2002). A number of these solids undergo a solid phase transition to a high temperature phase accompanied by a sharp jump in ionic conductivity by a factor of $\sim 10^4$, as well as a structural change (Secco and Sharma 1995). The ternary solid electrolyte, M_2NI_4 (M = Ag, Cu′, N = Hg, Cd), undergoes a phase transition at moderate temperatures (Nair and Ahmad 1997). Electrical conductivity and structural correlation for M_xHgI_4 type compounds were studied by Negoiu and Tador (1994). In this study, they have explained structural modifications of complex compounds, M_xHgI_4, by the application of 5·30 MPa to its powder. These modifications were confirmed by X-ray diffraction and by measurement of electrical conductivity. Diffraction, thermal analysis of compound, Ag_2HgI_4, Cu_2HgI_4, Tl_2HgI_4, $PbHgI_4$ and $CdHgI_4$ have been compared (Negoiu and Tador 1994) and the results thus obtained lead to the idea of using DTA and electrical

conductivity as methods for accessing the thermochromic transition in these compounds [M_xHgI_4, where M = Ag, Cu, Tl, Pb, and Cd, x = 1, 2]. Copper mercury iodide, Cu_2HgI_4, is unique amongst the superionic conductors in having a tetragonal unit cell and very complex electrical properties, first studied by Ketelaar (1934) that has an order–disorder transition at $\sim 76°C$, above which α phase displays mixed ionic and electronic conductivity (Shibata *et al* 1974). To attain optimum conductivity, a number of compositional variations of the ternary solid electrolytes with different cation dopants have been attempted using Cu_2HgI_4 as the host. Several theoretical models have been suggested (Suchow *et al* 1953; Akopyan and Novikov 1996; Nair *et al* 1996a) to explain the conductivity mechanisms in these systems but as yet no general agreement has been reached. Silver-based glasses have been found to exhibit excellent ionic conductivity at ambient temperature (Ingram 1987). Such fast ionic conducting (FIC) glasses have, therefore, been considered as potential candidates for solid state microbatteries and other device applications (Minami and Tanaka 1980; Minami 1986).

In the present study, we investigated a [Cu_2HgI_4 : 0·xAgI] mixed system, with different compositional variations of same cation dopant of AgI (Agrawal *et al* 1994; Swenson *et al* 1996). AgI is known as a typical superionic conductor (Mellander 1982). The superionic phase of AgI appears at 420 K. The value of the ionic conductivity is as high as about $1 \, \Omega^{-1} \, cm^{-1}$ (Secco and Usha 1994). It has been observed that a much better solid electrolyte composite system can be prepared with the host [Cu_2HgI_4] (Agrawal *et al* 1995).

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2. Experimental

2.1 *Material*

Mercury [I] iodide (HgI_2), silver iodide (AgI) obtained from CDH Analar grade and cuprous iodide (CuI), obtained from S.d. fine-chem with stated purity of 99%, respectively were used.

2.2 *Synthesis of host and mixed composite system of* Cu_2HgI_4

The samples were prepared by precipitation using previously described techniques as well as by solid-state reaction (Ketelaar 1931; Wagner 1936; Mellander and Friesel 1987). Cu_2HgI_4 was prepared by solid state reaction between CuI and HgI_2. Both were mixed thoroughly in a requisite composition in an Agate mortar (each above 300 mesh size). The fine ground stoichiometric mixture of the binary components was sealed in an ampoule and placed in an air oven (CE 0434 NSW-144) at ∼ 100°C for 5 days. After cooling, the maroon colour changed to dark red. Cu_2HgI_4 is dark red below 76°C and maroon after 76°C.

X-ray diffraction studies showed that the dark red compound was single β-phase Cu_2HgI_4. It showed the typical diffraction pattern of Cu_2HgI_4 and the *d* values matched well with the ASTM Powder Diffraction file of Cu_2HgI_4 (ASTM 18-0450).

Mixed composite samples were prepared by adding AgI to the host, Cu_2HgI_4, in different ratios of *x* (*x* = 0·2–0·6), mixed thoroughly in an Agate mortar at room temperature using previously reported procedures (Agrawal and Kumar 1994).

2.3 *X-ray analysis*

The X-ray diffraction studies were performed for the pure hosts Cu_2HgI_4, AgI and the mixed composite systems [$Cu_2HgI_4 : 0·2AgI$], [$Cu_2HgI_4 : 0·4AgI$], and [$Cu_2HgI_4 : 0·6AgI$] after the reaction was completed using Rigaku-ultima D/Tex-25 with a K-beta filter with $CuK\alpha$ (λ = 0·154060 Å) radiation at room temperature. The angle range for measurement was 10–70° and the scanning speed was 1°/min.

2.4 *Thermal analysis*

Thermal analysis was carried out by DTA, DTG and TGA analysis using the Pyris Diamond (Perkin Elmer) in nitrogen atmosphere (200 ml/min) at a heating rate of 5°C per min and a temperature range of 20–250°C. For each experiment, 10·23 mg of samples were used. The reference was 10 mg alumina powder.

2.5 *Conductivity measurement*

Pellets (2·4 cm diameter, 0·1 cm thick) for the conductivity measurement were prepared by pouring the requisite amount of the compound into a stainless steel die at a pressure of 5 tons/cm^2 using a hydraulic press (Spectra Lab Model SL 89). Conductivity measurements were obtained 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 from the sample holder by Teflon sheets. The electrical conductivity of the samples was measured in the temperature range of 90–170°C using a Gen Rad 1659 RLC Digibridge in the frequency range 100 Hz–10 kHz at 30 min intervals. The rate of heating was maintained at 1°C/min (figure 1).

3. Results and discussion

3.1 *Compositional variation in conductivity*

The variations in the conductivity as a function of mol wt% *x* for the mixed composite system [$Cu_2HgI_4 : 0·xAgI$] at different temperatures ranging from 90–170°C are shown in figure 1. The conductivity sharply increased with an increase in *x*, attaining a peak value for *x* = 0·4, then decreased at temperatures in the range 90–150°C. Variations in the composition of the dopant in the host affected the phase change (β–α) within the temperature range of 120–150°C. This phenomenon is usually observed in a glass electrolyte/composite system. In the $\log\sigma T - x$ plot (figure 1), this mixed composite system looks qualitatively similar to those reported in the literature (Magistris *et al* 1976), but the σ values differ quantitatively at different temperature ranges (Agrawal and Kumar 1996).

3.2 *Temperature variations in conductivity*

The electrical conductivity of the pellets depended upon the pelletizing pressure. There was a linear increase in conductivity with a pelletizing pressure up to 5 tons/cm^2 and then it became almost constant. The temperature dependence of ionic conductivity is given by the following Arrhenius expression:

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

$$= ne^2\lambda^2 v\gamma/kT \exp(\Delta S^*/k - \Delta H^*/kT), \tag{2}$$

where *n* is the number of ions per unit volume, *e* the ionic charge, λ the distance between two jump positions, v the jump frequency, γ the intersites constant, *k* the Boltzmann's constant and ΔG^*, ΔS^*, ΔH^* are thermodynamic activation terms.

Equation (2) can be written in a simpler form as

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

$$\log \sigma T = \log \sigma_{\mathrm{o}} - E_a / 2 \cdot 303 kT, \tag{4}$$

where $\sigma_{\mathrm{o}} = ne^2 \lambda^2 \nu \gamma / k \exp(\Delta S^*/k)$ and $\Delta H^* = E_a$, i.e. the activation enthalpy equals the experimental activation energy for ionic motion, which may include a defect formation enthalpy contribution (Nair and Ahmad 1997; Nair *et al* 1996b; Huang and Secco 1993).

The $\log \sigma T - (1/T)$ plots for pure Cu_2HgI_4 systems were reproduced based on the previous study as depicted in figure 2(a) (Nair *et al* 1996a; Akopyan and Novikov 1996).

Figure 2(b) shows the $\log \sigma T - (1/T)$ plots for the mixed composite systems, $[Cu_2HgI_4 : 0 \cdot 2AgI]$, $[Cu_2HgI_4 : 0 \cdot 4AgI]$ and $[Cu_2HgI_4 : 0 \cdot 6AgI]$, respectively. The activation energy of host, Cu_2HgI_4, and all the mixed composite systems are shown in table 1.

Based on the literature and the $\log \sigma T - (1/T)$ plot, pure $[Cu_2HgI_4]$ deviates from the Arrhenius linear plot at about 65–70°C, and transforms from the low temperature phase, β (dark red) with ordered tetragonal structure, to the high temperature phase, α (maroon) with disordered pseudocubic structure (Suchow and Pond 1953; Hahn *et al* 1955), with three cations (two copper and one mercury ions) randomly distributed among the four tetrahedral sites provided by the *fcc* sublattice of the I^- ions. The α phase shows exceptionally high ionic conductivity and activation energy because ionic motion is much greater than those of other superionic conductors, whereas in a mixed composite system, $[Cu_2HgI_4 : 0 \cdot xAgI]$, the phase transition temperature increases as compared to Cu_2HgI_4. The β phase has thermal activation up to 76°C, and just before the transition temperature, figure 2(b) shows that the highly conducting α-like phase of the host ($\sim T_c = $

76°C) is almost completely stabilized in the mixed composite system. Deviations from the linear behaviour of the $\log \sigma T - (1/T)$ plot were observed, however, at 120°C, a point at which there was a large increase in the conductivity and then slight increase in $x = 0 \cdot 2$ ratio; in the $x = 0 \cdot 4$ ratio, there was large increase in conductivity up to 130°C; and in the $x = 0 \cdot 6$ ratio, $\log \sigma T$ increased to 120°C and then slightly increased up to 170°C. The small jump in the conductivity was due to the $\beta - \alpha$ like transition of the system of fractional amounts of the unstabilized/unreacted host present in the system. The drop in conductivity was probably due to softening of the materials (Agrawal and Kumar 1996). The $\log \sigma T$ values of all the mixed composite systems are also intermediate between the host, Cu_2HgI_4 (Kumari and Secco 1985).

The $\log \sigma T - 1/T$ plot shift from a lower temperature to a high temperature is responsible for the dark red to
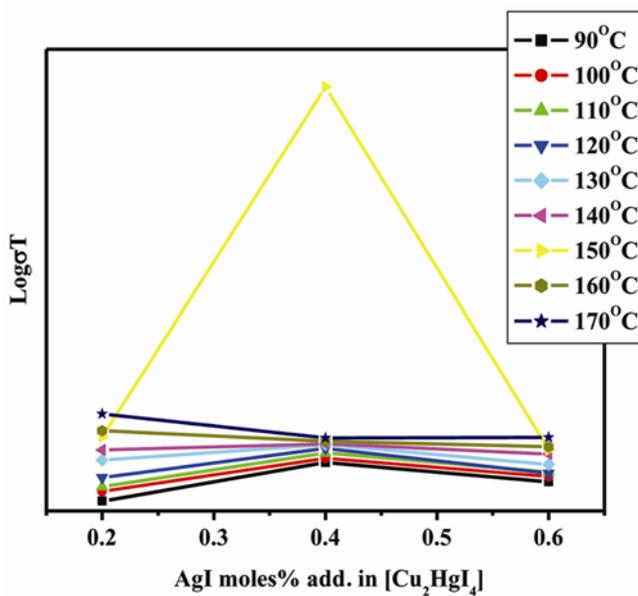

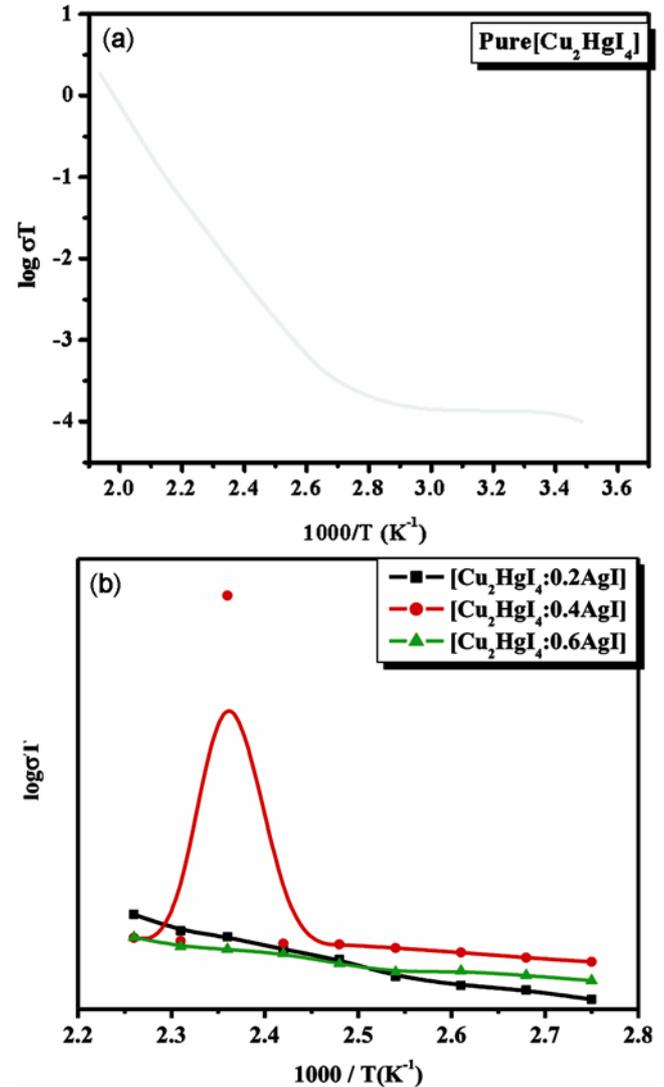**Figure 1.** Log σT–X plot for mixed composite system.

Figure 2. (**a**) Log $\sigma - (1/T)$ plot for pure Cu_2HgI_4 and (**b**) log $\sigma - (1/T)$ plot for pure host and all the mixed composite systems.

Table 1. Comparison of ionic conductivity and activation energy values for pure and doped [Cu_2HgI_4].

Compounds	Phase transition temp. (°C)	Activation energy (eV) Pre-transition (β) phase (E_{a1})	Activation energy (eV) Phase transition (α) phase (E_{a2})
[Cu_2HgI_4]	70	0·03759	0·88033
[$Cu_2HgI_4 : 0·2AgI$]	120	0·3549	0·7155
[$Cu_2HgI_4 : 0·4AgI$]	130	0·2094	0·5131
[$Cu_2HgI_4 : 0·6AgI$]	120	0·1068	0·4092

maroon colour change of Cu_2HgI_4 and 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 interaction 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 as a consequence of a structural distortion, because the Hg–I distance would increase and lead to the observed changes in pure [Cu_2HgI_4] (Fernandez *et al* 1986). Therefore, in the mixed system [$Cu_2HgI_4 : 0·2AgI$], 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 shifts to higher temperature up to 120°C. On further doping of Ag^+ in the host [Cu_2HgI_4], the fraction of mobile charge carriers, Ag^+, much increases proportionately leading to Ag–I distance increase and so phase transition shifts to high temperature up to 130°C with increased $x = 0·4$ in the host system [Cu_2HgI_4], therefore, increased ionic conductivity activated up to $T_c = 130°C$ in $x = 0·4$, this is due to Frenkel defects which dominated the electrical conductivities in Ag halides (Ono *et al* 2007), so more defects formed on further doping in host and transition shift to higher temperature but in $x = 0·6$ ratio Ag^+ increases but due to most of the defects filled by Ag^+ in host [Cu_2HgI_4], and activated only up to 120°C, so phase transition shifts to lower temperature up to 120°C. Secco *et al* reported parallel ionic conductivity behaviour for Rb^+-doped Na_2SO_4-based compounds (Yanjiu *et al* 1993).

Temperature-dependent variations in conductivity for all the samples were also studied at 10 kHz, 120 Hz and 100 Hz, and the change in frequency did not induce a change in electrical conductivity. Activation energies (E_{a1}) and (E_{a2}) for the pre-transition and post-transition regions are reported in table 1. A commonly accepted method to study non-linear Arrhenius behaviour 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 (Nair *et al* 1996b), consistent with the conductivity behaviour.

3.3 *Time variations in conductivity*

Figure 3 shows the conductivity behaviour of all the mixed composite systems vs time at 30 min intervals at

temperatures ranging from 90–170°C for different dopant ratios. In general, the conductivity of all the mixed composite systems decays at an elevated temperature with the loss in conductivity being most pronounced at temperatures of 150°C or higher in air. An apparent activation energy was extracted from the curve slopes and a standard Arrhenius analysis (Wang and Rubner 1990, 1992) was performed (figure 4, table 2).

3.4 *X-ray diffraction*

The structure of the stable β-phase of Cu_2HgI_4, which is not superionic, under ambient conditions is tetragonal with a space group of $I42m^-$. The iodine atoms adopt a slightly distorted face centred cubic (*fcc*) arrangement and the cations occupy 3/8 of the tetrahedrally coordinated positions in an ordered manner derived from the chalcopyrite ($A_2B_2X_4$) structure by the accumulation of cation vacancies. Upon heating, the first superionic α phase appears at 473 K. The structure of α-Cu_2HgI_4 is similar to that of the β phase, except that the iodine sublattice is an ideal *fcc* arrangement and diffraction studies show the cation to be disordered in over half of the tetrahedrally coordinated positions. Crystallography revealed that α-Cu_2HgI_4 is in the cubic space group $F^-43 m$ with each cation site having an average occupancy of 1/2 Ag and 1/4 Hg^{-2}.

Rietveld refinements of the diffraction data show the lattice parameters as $a = 6·0672$ Å and $c = 12·2266$ Å at room temperature (Hull and Keen 2000). The structure of AgI is a hexagonal wurtzite and zincblende-type structure (Burley 1962). X-ray diffraction patterns for pure AgI, Cu_2HgI_4 and all the mixed composite systems are shown in figure 5 at room temperature. The X-ray diffractogram values of the pure host corresponds to standard values of Cu_2HgI_4 and careful analysis revealed that in addition to standard peaks of Cu_2HgI_4, a number of peaks appeared for the Ag^+-doped host composite system. The appearance of three tiny peaks in host (reflections at 22·6041, 31·6041 and 48·7291) shifted to (25·1875, 33·4583 and 49·5), (25·0625, 33·625 and 49·04) and (25·2708, 33·125 and 49·104) in the $x = 0·2$, 0·4 and 0·6 Ag^+ doped composite systems, respectively and the corresponding peaks were more intense upon doping.

This finding indicated significant structural changes with only small compositional changes (Ya *et al* 2007) in the host composite system with a gradual increase in AgI.

We, therefore, concluded that the phase composition is influenced by the presence of the dopant (Adamski *et al* 1999; Varshney *et al* 2006).
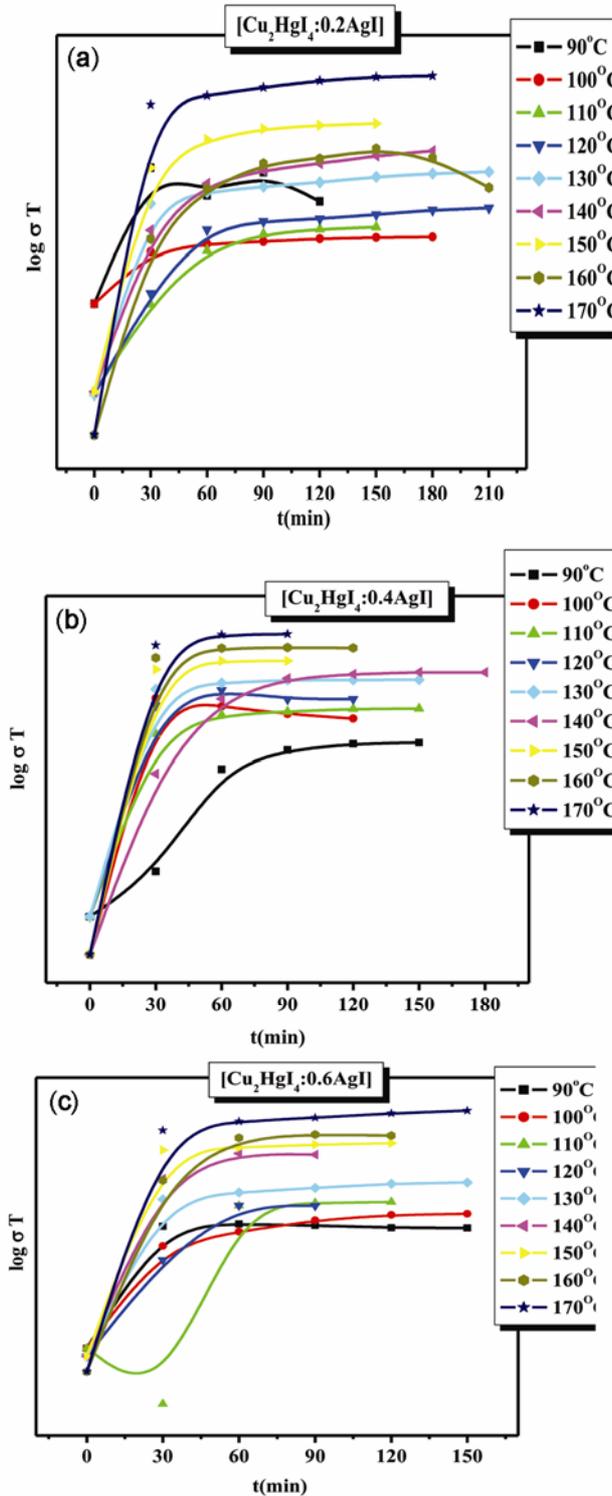
3.5 *Thermal analysis*

3.5a *Differential thermal analysis*: Thermal analysis was performed by DTA analysis. Parameters measured by means of DTA are transition temperature (Abenojar *et al* 2006). The DTA curves contain two endothermic peaks,
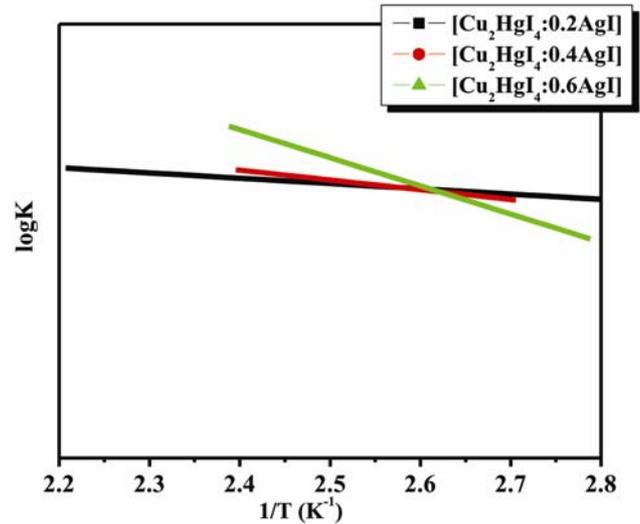

Figure 3. (**a**) Log σT – time (min) vs plot for host [Cu$_2$HgI$_4$: 0·2AgI] system, (**b**) log σT – time (min) vs plot for [Cu$_2$HgI$_4$: 0·4AgI] system and (**c**) log σT – time (min) vs plot for [Cu$_2$HgI$_4$: 0·6AgI] system.

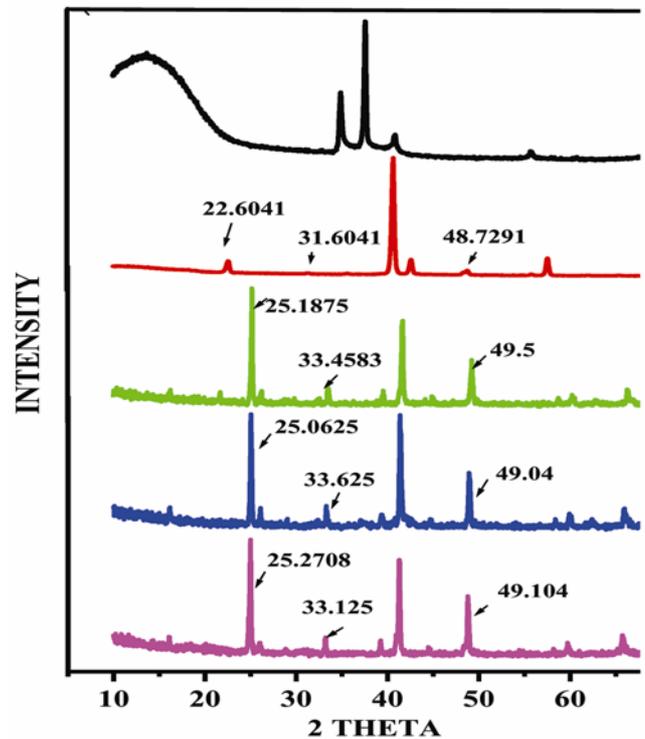
Figure 4. Plot of log K vs 1000/T (K^{-1}).

Figure 5. X-ray diffractogram of pure AgI, host and composite systems: (**a**) XRD of AgI, (**b**) XRD of pure Cu$_2$HgI$_4$, (**c**) XRD of [Cu$_2$HgI$_4$: 0·2AgI] mixed composite sample, (**d**) XRD of [Cu$_2$HgI$_4$: 0·4AgI] mixed composite sample and (**e**) XRD of [Cu$_2$HgI$_4$: 0·6AgI] mixed composite sample.

the first endotherm corresponds to a $\beta - \alpha$ transition (at about $\approx 70°C$ for Cu_2HgI_4) and the second endotherm corresponds perhaps to the melting of the material (Agrawal *et al* 1994). Figure 6 shows DTA curves of all

Table 2. Apparent activation energies were extracted from curve slopes by a standard Arrhenius analysis.

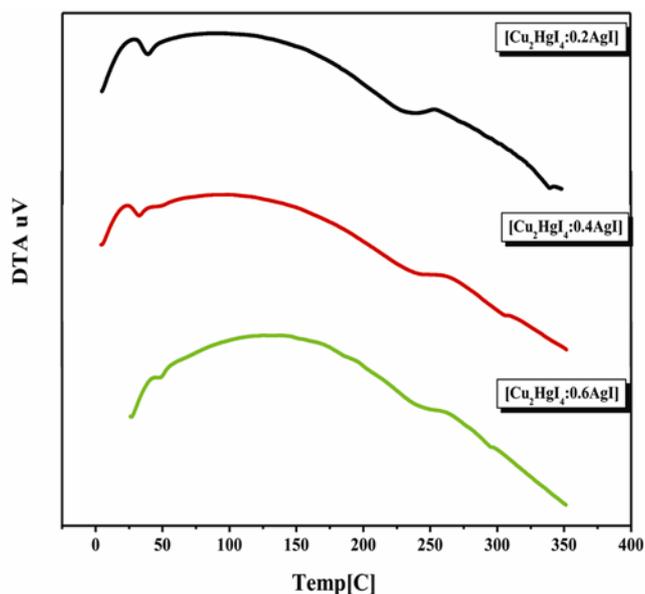| Compounds	Average activation energy (eV)
$[Cu_2HgI_4 : 0·2AgI]$	0·0820
$[Cu_2HgI_4 : 0·4AgI]$	0·1524
$[Cu_2HgI_4 : 0·6AgI]$	0·4385

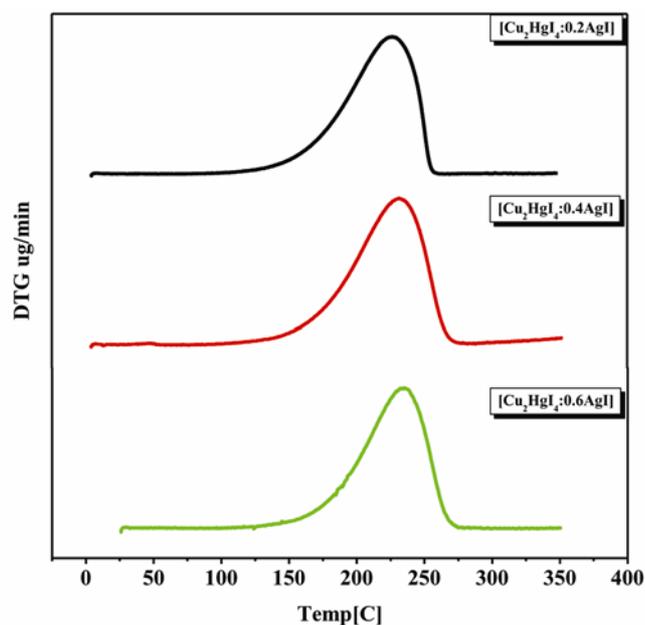**Figure 6.** DTA curves for all the composite systems.

Figure 7. DTG curves for all the composite systems.

doped samples, having three sharp endotherms, endotherm I corresponds to gradual transition of Cu_2HgI_4 from room temperature to tetragonal $\beta - \alpha$ transition, endotherm II perhaps due to interaction of the Ag^+ to the host and endotherm III corresponds to the melting of materials. It is clear from the figure that on doping of Ag^+ transition, it shifts to lower temperature because of the interaction between AgI and Cu_2HgI_4. The shift decreases with increasing AgI content.

3.5b *Differential thermogravimetry*: DTG curves are shown in figure 7, whereas for Ag^+-doped host samples, it shifted to a higher temperature because of the interaction between AgI and Cu_2HgI_4. The shift increased with an increase in the AgI content.

3.5c *Thermogravimetric analysis*: Thermogravimetric analysis (TGA) is used to study the kinetics of the reactions (Matsuura 1979). TGA curves are shown in figure 8. All the TGA curves are shifted to higher temperature. It may be expected that the reactions constantly reached up to a particular temperature and then decreased to a higher temperature. In $0·2 Ag^+$ doped samples the reaction reached up to $175·2380°C$ temperature, on further doping of AgI it shifted to higher temperature up to $179·6428°C$, $183·3333°C$ temperature in $0·4$, $0·6 Ag^+$ doped samples due to the interaction between Ag^+ and $[Cu_2HgI_4]$. The shift increases with increasing AgI content.

4. Conclusions

A new composite superionic system $[Cu_2HgI_4 : 0·xAgI]$ has been investigated. The electrical conductivity of
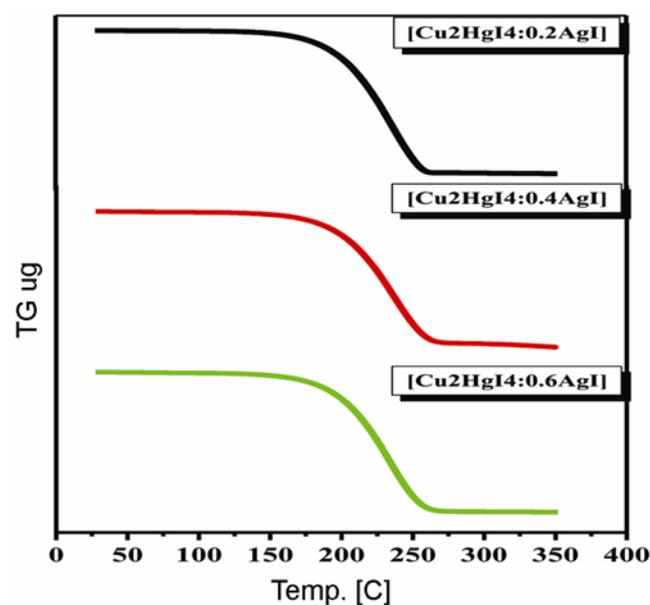

Figure 8. TGA curves for all the composite systems.

[Cu$_2$HgI$_4$] is found to be enhanced markedly in the temperature range 90–130°C, on doping with AgI. Initially the conductivity increases with temperature due to increase in rate of migration of Frenkel defects and interstitial Ag$^+$ ions. X-ray, DTA, DTG and TGA studies confirmed the formation of superionic phase in the composite systems. The temperature dependence of various ionic parameters has been carried out for the characterization of ion transport property and doping effect.

Acknowledgements

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