

*Full Paper*

## **Synthesis, Characterization, Fast Ion Transport and Phase Transition In a [Ag<sub>2</sub>HgI<sub>4</sub>:0.x AgI] Type Superionic Mixed Composite Materials (x = 0.2, 0.4, 0.6 mol. wt. %)**

**Noorussaba Afaq Ahmad\***

*Department of Chemistry, Aligarh Muslim University, Aligarh-202002, India*

\*Corresponding author: Tel: +91-9411983056, +91-9368515196; Fax: 0571-2703515

Email: [afaqahmad21@gmail.com](mailto:afaqahmad21@gmail.com) , [sabaamu@gmail.com](mailto:sabaamu@gmail.com)

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**Abstract-** Experimental investigations concerning the preparation and characterisation of the system [Ag<sub>2</sub>HgI<sub>4</sub>:0.x AgI] (x=0.2, 0.4, 0.6 mol. wt. %),, have been undertaken with a view to evaluate the transport properties of the mixed system and to identify the fast ion conducting compositions. Powder samples of various compositions containing 0.2, 0.4 and 0.6 mol. wt. % [Ag<sub>2</sub>HgI<sub>4</sub>:0.x AgI] (x=0.2, 0.4, 0.6 mol. wt. %), were synthesized by solid state reaction. Samples were analyzed using powder X-ray diffraction (XRD), differential thermal analysis (DTA) and thermo-gravimetric analysis techniques in order to determine their crystal structure and phase transition temperatures. These studies have revealed the formation of new substances having phase transition temperatures similar to that of AgI. Detailed electrical conductivity measurements carried out in the frequency range 100 Hz-10 kHz and over the temperature range 90°-170 °C by a Gen Rad 1659 RLC Digibridge have identified the best conducting composition namely 4 mol. wt.% [Ag<sub>2</sub>HgI<sub>4</sub>:AgI], exhibiting an electrical conductivity of 1.14×10<sup>-1</sup> S cm<sup>-2</sup> K at 393 K and an activation energy of 1.6 eV for Ag<sup>+</sup> ion migration within the solid. The occurrence of fast ion transport due to silver ion migration in several compositions of the above mixed system has been explained on the basis of “hard and soft acids and bases” principle and ion exchange chemistry.

**Keywords-** Electrical Conductivity, Phase Transition, X-ray Diffraction, Thermal Analysis, Composite Electrolytes

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## 1. INTRODUCTION

Interest in the phenomenon of fast-ion transport in solids has grown rapidly over the past decades [1], because of the great technological incentives for the development of more effective and efficient ways of converting and storing energy. Much of the attention given to fast ion conductors or solid electrolytes at the present time is either directly or indirectly related to their potential use in new types of solid state batteries and fuel cells for power source applications.

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 for the study of a wide range of problems [2]. The present trend in searching superionic conductors for battery material and other devices is two-fold in nature, (1) to find new materials showing high values of ionic conductivity in the vicinity of room temperature, and (2) to use known ionic conductors with other materials in the form of mixed systems to increase the conduction efficiency [3-6]. The later procedure attracted considerable attention in recent years as it not only lowers the phase transition temperature but also gives relatively higher values of conductivity. Generally these solids undergo a 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 structural changes [7].

The ternary solid electrolytes  $M_2HgI_4$  ( $M = Ag, Cu, \text{ and } Cd$ ) undergoes a phase transition at moderate temperatures [8]. Electrical conductivity and structure correlation for  $M_xHgI_4$  type compounds were studied by Negoiu et al. and Rasu et al. [9,10].

Several theoretical models have been suggested [11-13] 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 temperatures [14]. Such fast ionic conducting (FIC) glasses have therefore been considered as potential candidates for solid state micro batteries and other device applications [15-17]. Various silver-based FIC glasses have been synthesized with the general formula  $AgI-Ag_2M_xO_y$  (where  $M = Mo, Se$  etc. in pseudo binary systems). All these glasses have silver ion conductivity of the order of  $0.01 \text{ Scm}^{-1}$ , and the conductivity strongly depends on the concentration of AgI. Swenson et al. [18] investigated the structures of two fast-ion conducting molecular glasses; AgI doped  $Ag_2MoO_4$  and  $Ag_2WO_4$  by neutron and x-ray diffraction. Both molybdate and tungstate glasses show a fast diffraction peak (FSDP) at very low Q-values ( $0.65$  and  $0.55 \text{ \AA}^{-1}$  respectively) in the neutron data. However, only weak peaks are observed at similar Q-values in the X-ray data. Malugani et al. [19] found that in  $MI_2-Ag_2PO_3$  ( $M = Cd, Hg$  and  $Pb$ ), the introduction of  $Ag^+$  ions in the form of AgI rather than as  $AgPO_3$  caused a rapid increase in the conductivity. Here the conductivity rise is attributed to the formation of AgI due to the exchange of  $Cd^{2+}$  or  $Pb^{2+}$  with  $Ag^+$  ions and formation of  $\alpha$ -AgI like structures in glasses.

Rao and Karthikeyan [20] made a molecular dynamics study on the structure and dynamics of silver ion conducting AgI-Ag<sub>2</sub>MoO<sub>4</sub> glasses, Noorussaba and Ahmad [21] prepared AgI-Cu<sub>2</sub>HgI<sub>4</sub> composite system over a wide range of compositions and identified AgI like aggregates only in AgI rich glasses/composites. Increase in silver ion conductivity was seen with an increase in AgI content in glass. The dynamics of ion transport suggests that Ag<sup>+</sup> ion transport occurs largely through paths connected by silver ion sites of mixed iodide-oxide coordination. In recent years, significant work has been carried out on AgI, silver oxysalts and some of these show glass-type structures with high ionic conductivity at ambient temperature [22,23].

C. P. Versamis et al. [24] Investigated nature of copper ion sites in the superionics glasses xCuI.(1-x)CuMoO (x=0.4, 0.5), T. Tsurui [25] made CuI-Cu<sub>2</sub>MoO<sub>4</sub> superionic glasses. Earlier work on CdHgI<sub>4</sub>-CuI mixed composite system made by Khalid [26].

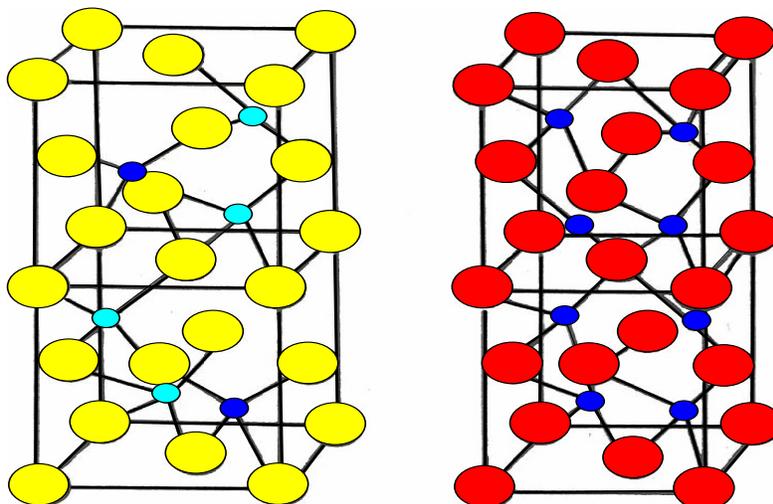
### 1.1. These results motivated us to undertake an investigation of AgI doped Ag<sub>2</sub>HgI<sub>4</sub>

Ag<sub>2</sub>HgI<sub>4</sub> is a well known superionic conducting material first studied by Ketelaar [27]. Many investigations have been reported on the electrical conductivity [28, 29], thermoelectric power [30], heat capacity, x-ray diffraction [31] and Raman scattering [32] of this material. This compound undergoes a phase transition from  $\beta$  to  $\alpha$  phase at 323.7 K. The transport number of Ag<sup>+</sup> in Ag<sub>2</sub>HgI<sub>4</sub> is 0.94.

The frequency dependence of the conductivity of Ag<sub>2</sub>HgI<sub>4</sub> observed by Shibata et al. [33] shows the similar behaviour as found for CuCl [34] and AgBr [35]. They also attempted to determine the transport number of the electronic components in Ag<sub>2</sub>HgI<sub>4</sub> and the results indicated that for the  $\beta$ -phase the conductivity could have a smaller electronic contribution, 1-10% of the total conductivity. These values of electronic conductivity are much smaller than those reported by Weil and Lawson [13] and Webb [36], suggesting that the Ag<sup>+</sup> ion is still the dominant charge carrier in the  $\beta$ -phase.

Though the  $\alpha$ -phase of Ag<sub>2</sub>HgI<sub>4</sub> shows exceptionally high ionic conductivity, the activation energy for ionic motion is much larger than those of other superionic conductors, such as AgI or  $\beta$ -alumina. This can be due to the fcc arrangement of I<sup>-</sup> sublattice so that the Ag<sup>+</sup> ion was forced to go through the high energy octahedral interstices in the transport process [37]. Therefore, the free-ion model proposed for the transport process by Rice et al. [38] is inappropriate. The microwave complex conductivity of Ag<sub>2</sub>HgI<sub>4</sub> [39] suggest hopping as the basic transport mechanism in the  $\alpha$ -phase.

Structures of Ag<sub>2</sub>HgI<sub>4</sub> based on x-ray powder diffraction were proposed by Ketelaar [40]. Later Kasper and Browell employed single crystal x-ray crytallography to obtain refined structure for the  $\alpha$  (disordered) [41] and  $\beta$  (ordered) [42] phases of Ag<sub>2</sub>HgI<sub>4</sub>. The structure of  $\alpha$  and  $\beta$  phase are shown in Fig. 1.



**Fig. 1.** The structure of  $\beta$ - and  $\alpha$ - phases of  $\text{Ag}_2\text{HgI}_4$ .

In the  $\beta$  phase, the iodide form a face centered cubic (fcc) lattice with two silver ions and one mercury ion occupying three of the four available tetrahedral sites, leaving one quarter of the tetrahedral sites empty. The primitive Wigner-Seitz cell shows  $S_4$  symmetry and the lattice parameters as  $a=6.3 \text{ \AA}$  and  $c=12.6 \text{ \AA}$  at room temperature, but above  $323.7 \text{ K}$ ,  $\text{Ag}_2\text{HgI}_4$  transforms from the yellow  $\beta$ -phase to the brick red  $\alpha$ -phase with the three cations randomly distributed among the four tetrahedral sites provided by the fcc sublattice of the  $\text{I}^-$  ions.

## 2. EXPERIMENTAL

### 2.1. Materials

Silver iodide and mercury [I] iodide were of CDH Analar grade, each of which had purity 98% and 99% respectively.

### 2.2. Synthesis of pure host and doped materials

#### 2.2.1. Synthesis of pure host [ $\text{Ag}_2\text{HgI}_4$ ] material

$\text{Ag}_2\text{HgI}_4$  was prepared by the solid state reactions between  $\text{AgI}$  and  $\text{HgI}_2$  [43, 44]. 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  $\text{AgI}$  and  $\text{HgI}_2$ ; was sealed in a glass ampoule and was placed in an air oven (CE 0434 NSW-144) at  $100 \text{ }^\circ\text{C}$  for 5 days. A deep red color compound was formed which changed to yellow color on cooling, ( $\text{Ag}_2\text{HgI}_4$  is yellow below  $52 \text{ }^\circ\text{C}$  and red above  $52 \text{ }^\circ\text{C}$  [45]). X-ray diffraction studies showed this yellow color compound to be single phase  $\beta$ - $\text{Ag}_2\text{HgI}_4$ .

### 2.2.2. Synthesis of doped materials

Different solid solutions were prepared by mixing 2 gm [ $\text{Ag}_2\text{HgI}_4$ ] and 0.x gm AgI where ( $x = 0.2, 0.4, 0.6$  mol. wt. %) in an agate mortar at room temperature with intermittent grinding, adopting the procedure reported earlier [21].

## 2.3. Characterization of the composite materials

### 2.3.1. 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/cm<sup>2</sup> 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 90°-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 /minute. 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 are reported to be affected by the change of frequency [46].

### 2.3.2. X-ray analysis

The x-ray diffraction studies were performed for the pure host  $\text{Ag}_2\text{HgI}_4$ , AgI, and all the mixed composite samples [ $\text{Ag}_2\text{HgI}_4:0.2$  AgI], [ $\text{Ag}_2\text{HgI}_4:0.4$  AgI], and [ $\text{Ag}_2\text{HgI}_4:0.6$  AgI] using Rigaku-ultima D/TeX-25 with a K-beta filter with  $\text{CuK}\alpha$  ( $\lambda = 1.54060 \text{ \AA}$ ) radiation at room temperature. The angle range for measurement was 10° to 70° and the scanning speed was 1°/ min.

### 2.3.3. Thermal analysis

Thermal analysis were carried out by DTA and TGA analysis using the Pyris Diamond (Perkin Elmer) in nitrogen atmosphere (200 ml/min) at a heating rate of 5° C per minute and a temperature range of 20 °C to 250 °C. For each experiment, 10.23 mg of samples was used. The reference sample was 10 mg alumina powder.

### 3. RESULTS AND DISCUSSION

#### 3.1. Conductivity studies

##### 3.1.1. Temperature dependence of conductivity

The electrical conductivity of the pellets depends upon the palletizing pressure. We observed a linear increase in conductivity with palletizing pressure up to pressure 5 tones/cm<sup>2</sup>, and after that it becomes almost constant. The temperature dependence of the ionic conductivity can be described by the Arrhenius relation

$$\sigma = ne^2\lambda^2\nu\gamma / k_bT \exp(-\Delta G^* / k_bT) \quad (1)$$

$$= ne^2\lambda^2\nu\gamma / k_bT \exp(\Delta S^* / k_b - \Delta H^* / k_bT) \quad (2)$$

where  $n$  is the number of ions per unit volume,  $e$  the ionic charge,  $\lambda$  the distance between two-jump positions,  $\nu$  the jump frequency,  $\gamma$  the intersites constant,  $k_b$  is Boltzmann's constant and  $\Delta G^*$ ,  $\Delta S^*$ ,  $\Delta H^*$  are thermodynamic activation terms.

The equation can be written in a simpler form as;

$$\sigma = \sigma_o \exp(-E_a / k_bT) \quad (3)$$

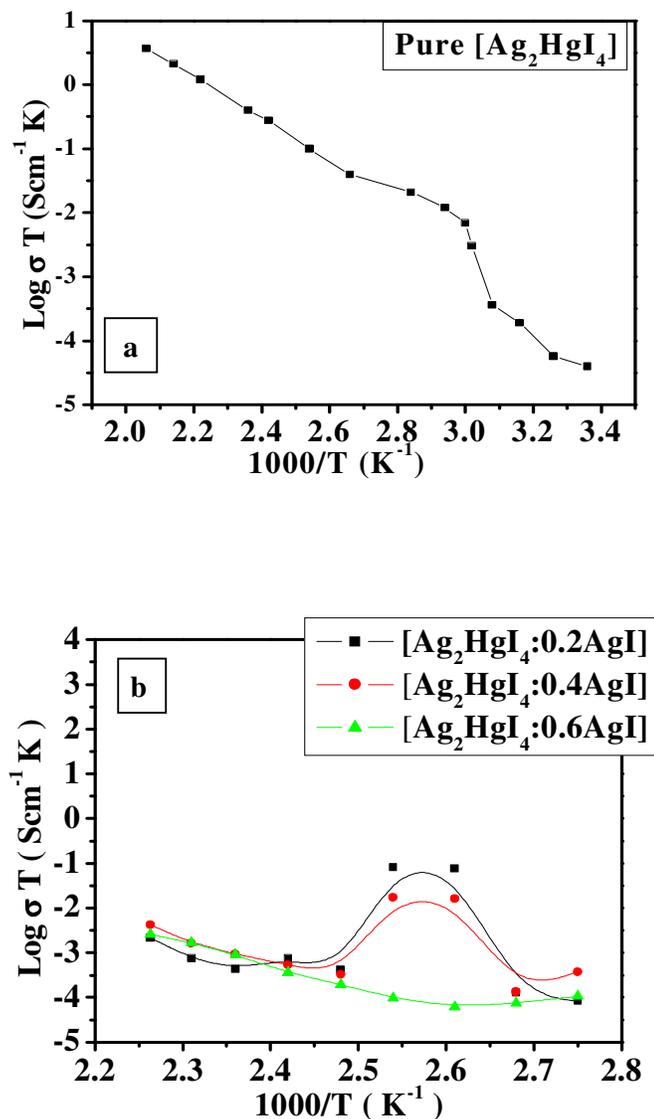
$$\text{Log } \sigma T = \text{Log } \sigma_o - E_a / 2.303 k_bT \quad (4)$$

$$\text{where } \sigma_o = ne^2\lambda^2\nu\gamma / k_b \exp(\Delta S^* / k_b)$$

$$\Delta H^* = \Delta H^*_{\text{migration}} + 1/2 \Delta H^*_{\text{defect}} \quad (5)$$

where  $\Delta H^* = E_a$ , i.e., the activation enthalpy equals the experimental activation energy for ionic motion, which may include a defect formation enthalpy contribution [47].

Fig. 2(a) shows the  $\log\sigma T$  vs.  $(1/T)$  plots for pure host  $\text{Ag}_2\text{HgI}_4$ , binary composite systems were reproduced from previous studies [48-50]. Fig. 2(b) shows the  $\log\sigma T$  vs.  $(1/T)$  plots for all the mixed composite systems,  $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]$ ,  $[\text{Ag}_2\text{HgI}_4:0.4 \text{ AgI}]$  and  $[\text{Ag}_2\text{HgI}_4:0.6 \text{ AgI}]$  respectively. The activation energy of host and all the mixed composite systems are shown in Table 1.



**Fig. 2 (a).**  $\log \sigma T$  vs.  $(1/T)$  plots for pure  $\text{Ag}_2\text{HgI}_4$  **(b).**  $\log \sigma T$  vs.  $(1/T)$  plots for mixed composite system,  $[\text{Ag}_2\text{HgI}_4:0.x\text{AgI}]$ .

From the literature and from the  $\log \sigma T$  vs.  $(1/T)$  plot, pure  $[\text{Ag}_2\text{HgI}_4]$  shows deviation from Arrhenius linear plot at about  $50^\circ\text{C}$ - $52^\circ\text{C}$ , representing transformation of  $\beta$  (yellow) –  $\alpha$  (brick red) phase with three cation randomly distributed among the four tetrahedral sites provided by the fcc sublattice of the  $\Gamma^-$  ions and  $\alpha$  phase shows exceptionally high ionic conductivity and activation energy for ionic motion is much larger than those of other superionic conductors [28].

In a mixed composite system  $[\text{Ag}_2\text{HgI}_4:0.x \text{AgI}]$ , the phase transition temperature increases as compared to host  $\text{Ag}_2\text{HgI}_4$  ( $T_c \approx 52^\circ\text{C}$ ). In mixed composite system  $[\text{Ag}_2\text{HgI}_4:0.2$

AgI], the  $\beta$ -phase has thermal activation upto 110°C temperature as compared to host  $\text{Ag}_2\text{HgI}_4$ . It can be clearly seen from the Fig. 2(b), that the highly conducting  $\alpha$ -phase of this mixed composite system [ $\text{Ag}_2\text{HgI}_4:0.2 \text{AgI}$ ], (about  $T_c=110$  °C) has been almost completely stabilized. However, deviation from the linear behavior of the  $\log\sigma T$  vs.  $(1/T)$  plot were observed at temperature 120 °C where a large jump in the conductivity occurred and then decreased for  $x=0.4$  ratio, however in  $x=0.6$  ratio, slight increase upto 100 °C and thereafter a drop in  $\log\sigma T$  occurred.

The  $\log\sigma T$  vs.  $1/T$  plot shift from lower temperatures to high temperatures is responsible for the respective color change of  $\text{Ag}_2\text{HgI}_4$  and is associated with a charge transfer process between electron levels of Hg and I. These observed change in the phase transition can be explained by assuming an increase of the interaction between I and Ag atoms above the phase transition, and consequent decrease of the I----Hg interaction. These changes would be induced by a decrease of the Ag----I distance above the phase transition, as a consequence of a structural distortion, consequently the Hg-----I distance would increase and lead to the observed changes in pure [ $\text{Ag}_2\text{HgI}_4$ ] [51].

Therefore in mixed system [ $\text{Ag}_2\text{HgI}_4:0.2\text{AgI}$ ], one may expect the fraction of mobile charge carriers,  $\text{Ag}^+$  increases leading to Ag----I distance increases and so phase transition shift to high temperature, on further doping of  $\text{Ag}^+$  ions in the host [ $\text{Ag}_2\text{HgI}_4$ ], the fraction of mobile charge carriers,  $\text{Ag}^+$ , increases proportionately leading to Ag----I distance increase and so phase transition shift to high temperature with increased  $x=0.4$  in the host system [ $\text{Ag}_2\text{HgI}_4$ ], therefore increased in ionic conductivity and activated upto  $T_c$  in  $x=0.4$ , this is due to Frenkel defects dominate the electrical conductivities in Ag halides [52] so more defects formed on further doping in host and transition shift to higher temperature but in  $x=0.6$  ratio  $\text{Ag}^+$  increases, but due to most of the defects occupied by  $\text{Ag}^+$  ions in host [ $\text{Ag}_2\text{HgI}_4$ ], phase transition shift to higher temp.

Secco et al. reported parallel ionic conductivity behavior for  $\text{Rb}^+$ -doped  $\text{Na}_2\text{SO}_4$  based compounds [53].

**Table 1.** Comparison of ionic conductivity activation energy values for pure and doped [ $\text{Ag}_2\text{HgI}_4$ ] host compound

Compounds	Phase Transition	Activation Energy (eV)	
	Temperature (°C)	Pre-transition ( $\beta$ ) Phase ( $E_{a1}$ )	Post-transition ( $\alpha$ ) Phase ( $E_{a2}$ )
[ $\text{Ag}_2\text{HgI}_4$ ]	50	0.69	0.56
[ $\text{Ag}_2\text{HgI}_4:0.2\text{AgI}$ ]	110	0.63	0.51
[ $\text{Ag}_2\text{HgI}_4:0.4\text{AgI}$ ]	120	1.60	0.43
[ $\text{Ag}_2\text{HgI}_4:0.6\text{AgI}$ ]	100	0.19	1.23

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 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, consistent with the conductivity behavior [49].

### 3.1.2. Compositional variation in conductivity

Fig. 3 shows the  $\log \sigma T$  vs. mol. % of AgI in the  $[\text{Ag}_2\text{HgI}_4:0.x\text{AgI}]$ . Maximum conductivity values for a composition of  $x=0.4$  mol. wt. % AgI are obtained. As this conductivity values is higher than that of the parent compounds i.e., AgI and  $\text{Ag}_2\text{HgI}_4$ , the possibility of the formation of new intermediate compounds,  $(\text{Ag}, \text{Ag}) \text{HgI}_4$  at this composition may be concluded.

In all the composition there is a jump in conductivity at around 423K which may be due to the characteristic transition temperature ( $\beta-\alpha$ ) of AgI, formed as one of the reaction products. The proposed reaction in the solid-state for the system  $\text{Ag}_2\text{HgI}_4\text{-AgI}$  may be written as:



This is consistent with the reaction proposed by Vishwanathan et al. [54].

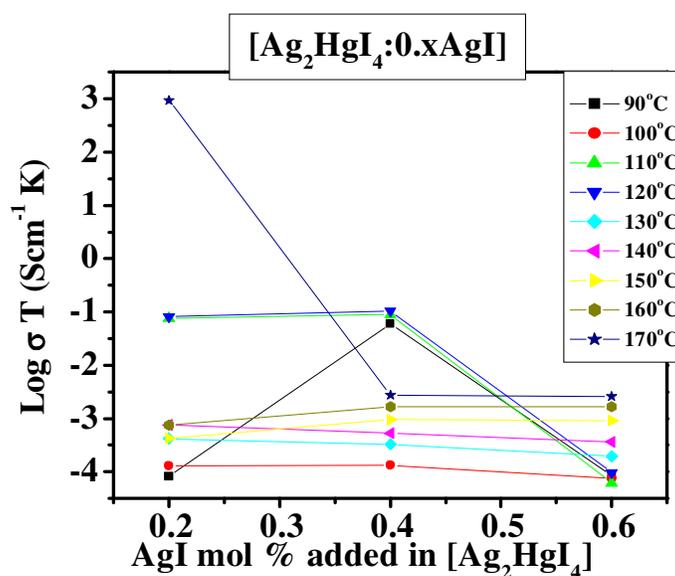


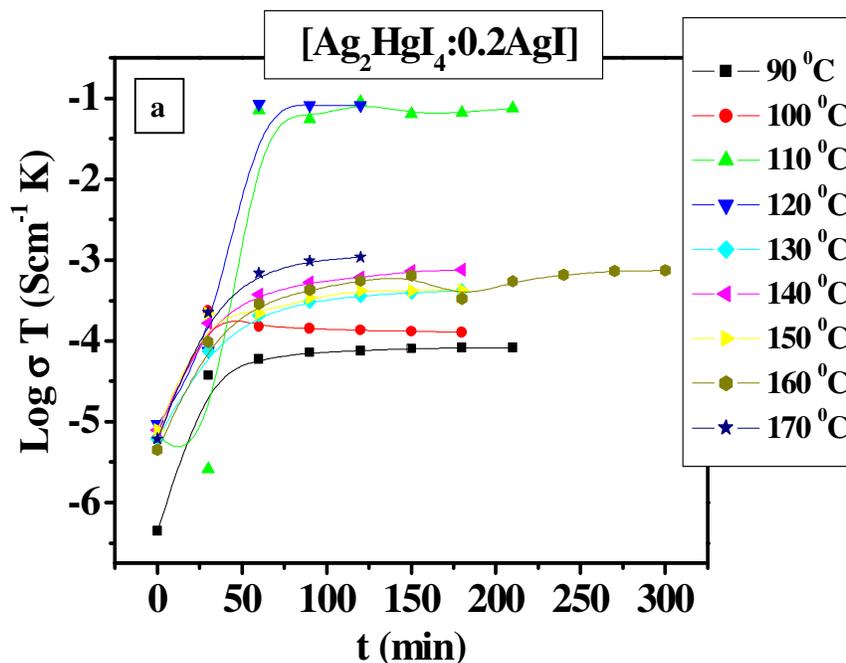
Fig. 3.  $\log \sigma T$  vs.  $x$  plots for mixed composite system,  $[\text{Ag}_2\text{HgI}_4:0.x\text{AgI}]$

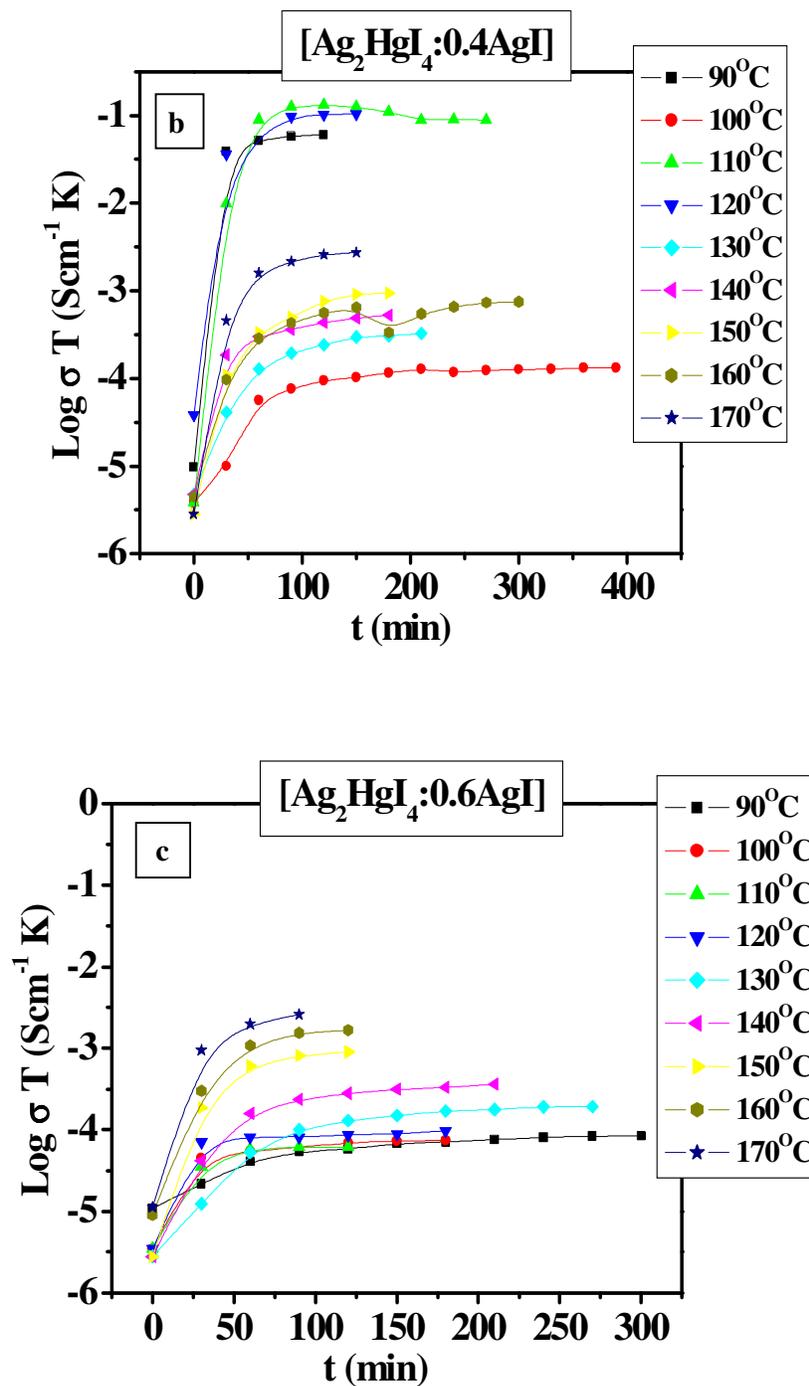
(Ag, Ag)HgI<sub>4</sub> possibly a new compound formed in the above reaction with a disordered structure may be responsible for the enhancement in the electrical conductivity in the case of compositions 0.4 mol% of AgI. Further increase in the concentration of AgI results in the decrease in conductivity which may be due to the formation of some other low conducting substance in addition to (Ag, Ag)HgI<sub>4</sub> and AgI. In samples having low concentration of AgI, there is also an increase in conductivity than the parent compounds which may be attributed to the formation of (Ag, Ag)HgI<sub>4</sub> by the higher concentration of Ag<sub>2</sub>HgI<sub>4</sub> consuming AgI appreciably.

Thus the best conductivity observed in the case of  $x=0.4$  mol. % AgI can be attributed to the possible disordered phase.

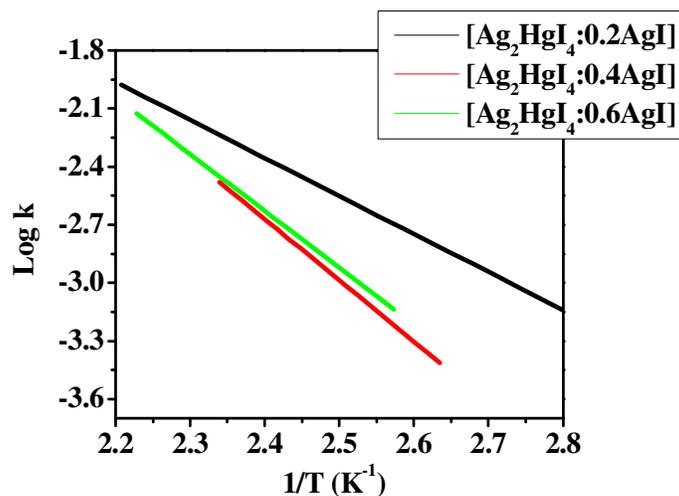
### 3.1.3. Time variation of conductivity

Fig. 4(a-c) displays the conductivity behavior of all the mixed composite system versus time at a 30 mint interval in the temperature range of 90 °C to 170 °C in [Ag<sub>2</sub>HgI<sub>4</sub>:0.x AgI] composite systems for different dopant ratios. In general, the conductivity of all the mixed composite systems decay at elevated temperatures with the loss in conductivity being most pronounced at temperatures at or higher than 150 °C in air. Fig. 5. displays the conductivity degradation rate constants as well as the apparent activation energies extracted from the curve slopes and a standard Arrhenius analysis [55, 56] reported in Table 2.





**Fig. 4 (a).** Log  $\sigma T$  vs. t (mint) plots for mixed composite system, [Ag<sub>2</sub>HgI<sub>4</sub>:0.2 AgI] **(b).** Log  $\sigma T$  vs. t (mint) plots for mixed composite system, [Ag<sub>2</sub>HgI<sub>4</sub>:0.4 AgI] **(c)** Log  $\sigma T$  vs. t (mint) plots for mixed composite system, [Ag<sub>2</sub>HgI<sub>4</sub>:0.6 AgI]



**Fig. 5.** Log  $k$  vs.  $1/T$  ( $K^{-1}$ ) plots for mixed composite system,  $[Ag_2HgI_4:0.x AgI]$

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

Compounds	Average activation energy (eV)
$[Ag_2HgI_4:0.2AgI]$	0.4793
$[Ag_2HgI_4:0.4AgI]$	0.6292
$[Ag_2HgI_4:0.6AgI]$	0.5828

### 3.2. X-ray diffraction

The structure of the stable  $\beta$ -phase of  $Ag_2HgI_4$  under ambient conditions, which is not superionic, is tetragonal with space group  $I\bar{4}$  [57]. The iodine atoms adopt a slightly distorted fcc arrangement and the cation occupy 3/8 Of the tetrahedrally coordinated positions in ordered manner derived from the chalcopyrite ( $A_2B_2X_4$ ) structure by the addition of cation vacancies. Upon heating, the first superionic  $\alpha$ -phase appears at 325K [58].

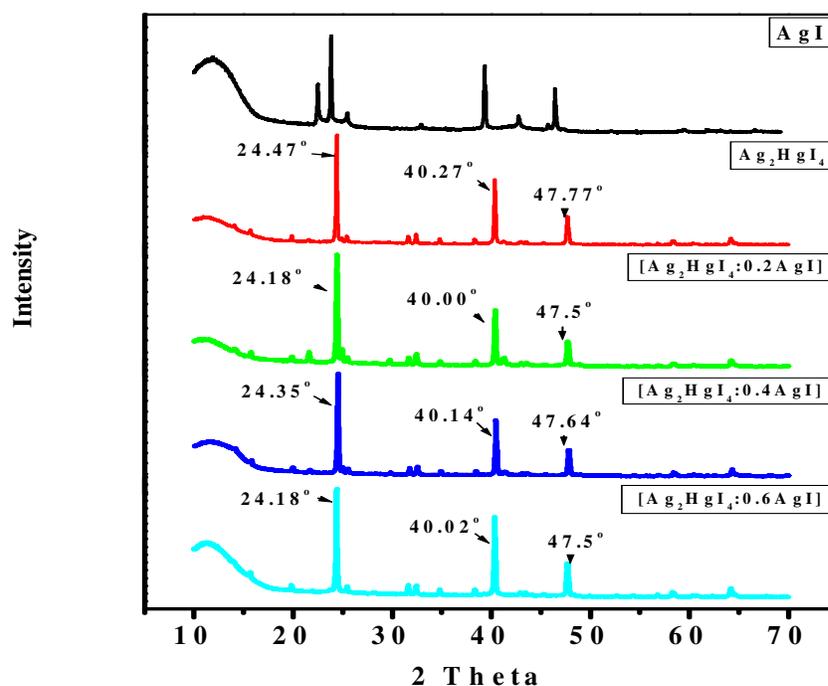
The structure of  $\alpha$ - $Ag_2HgI_4$  is similar to that of the  $\beta$ -phase, except that the iodine sublattice is now an ideal fcc arrangement and diffraction studies show the cation to be disordered over half of the tetrahedrally coordinated positions [57]. Crystallographically,  $\alpha$ - $Ag_2HgI_4$  is described in the cubic space group  $F\bar{4}3m$  with each cation site having an average occupancy of  $\frac{1}{2}$  Ag and  $\frac{1}{4}$   $Hg^{-2}$ . The primitive Wigner-Seitz cell shows  $S_4$  symmetry and the lattice parameters as  $a=6.3 \text{ \AA}$  and  $c=12.6 \text{ \AA}$  at room temperature [41]. The structure

of AgI is hexagonal wurtzite and Zinc blende type [59]. The structure of  $\alpha$ -AgI possesses a bcc lattice of iodide ions, while  $\text{Ag}^+$  ions are distributed over 42 crystallographic sites; 6(b) octahedral, 12 (d) tetrahedral, and 24 (h) trigonal. AgI might be expected to transform from the Zinc blende to Rocksalt [60].

The ideal wurtzite structure composed of regular tetrahedra, has a  $c/a$  axial ratio of 1.633. When this compound is dimorphous and exists also in the zinc blende structure the  $c/a$  ratio is close to the ideal value. The unit cell parameters were refined from powder diffraction data  $a=4.592 \text{ \AA}$ ,  $c=7.510 \text{ \AA}$ ,  $c/a=1.635$  [59]. Two space groups were  $P6_3$  (No.173) and  $P6_3mc$  (No. 186), as listed in the International Tables for X- Ray Crystallography [60].

X-ray diffraction patterns for pure AgI,  $\text{Ag}_2\text{HgI}_4$  and all the doped composite systems are shown in Fig. 6. Respectively at room temperature. The appearance of three tiny peaks occurs in host (reflections at  $24.47^\circ$ ,  $40.27^\circ$  and  $47.77^\circ$ ) shifted to ( $24.18^\circ$ ,  $40.0^\circ$ , and  $47.5^\circ$ ), ( $24.35^\circ$ ,  $40.14^\circ$  and  $47.64^\circ$ ) and ( $24.18^\circ$ ,  $40.02^\circ$  and  $47.5^\circ$ ) in the  $x=0.2$ ,  $0.4$  and  $0.6 \text{ Ag}^+$  doped composite systems respectively, and the corresponding peaks were more intense upon doping.

The x-ray diffractogram of the pure host corresponds to those of standard values of  $\text{Ag}_2\text{HgI}_4$  and careful analysis reveals that in addition to standard peaks of  $\text{Ag}_2\text{HgI}_4$  a number of peaks appear for  $\text{Ag}^+$ -doped composite system and these corresponding peaks were more intense or become very short upon doping.



**Fig. 6.** X-ray diffractogram for  $[\text{Ag}_2\text{HgI}_4:0.x \text{ AgI}]$  system

This indicated significant structural changes upon small compositional changes [61] in the host with gradual increase of AgI. It may therefore be concluded that phase composition is influenced by the presence of dopant [62].

### 3.3. Thermal analysis

#### 3.3.1. DTA analysis

Thermal analysis was performed by DTA measurement. Parameters measured by means of DTA are transition temperature [63]. The DTA curves contains two endothermic peaks, the first endotherm corresponds to a  $\beta - \alpha$  transition ( $\approx 52^\circ\text{C}$  for  $\text{Ag}_2\text{HgI}_4$ ) and the second endotherm corresponds to the melting of the material [64]. Fig. 7 shows DTA curve of all doped samples. It shows three sharp endotherm, I endotherm corresponds gradual transition of  $\text{Ag}_2\text{HgI}_4$  from room temperature to tetragonal  $\beta - \alpha$  transition; II may be due to interaction of the  $\text{Ag}^+$  ions to the host and III one corresponds to the melting of materials. It is clear from the Fig. 7 that on the doping by  $\text{Ag}^+$  ions, transition shifts to lower to higher temperature because of the interaction between dopant AgI and host  $\text{Ag}_2\text{HgI}_4$ . The shift decreases and then increases on further doping with AgI content.

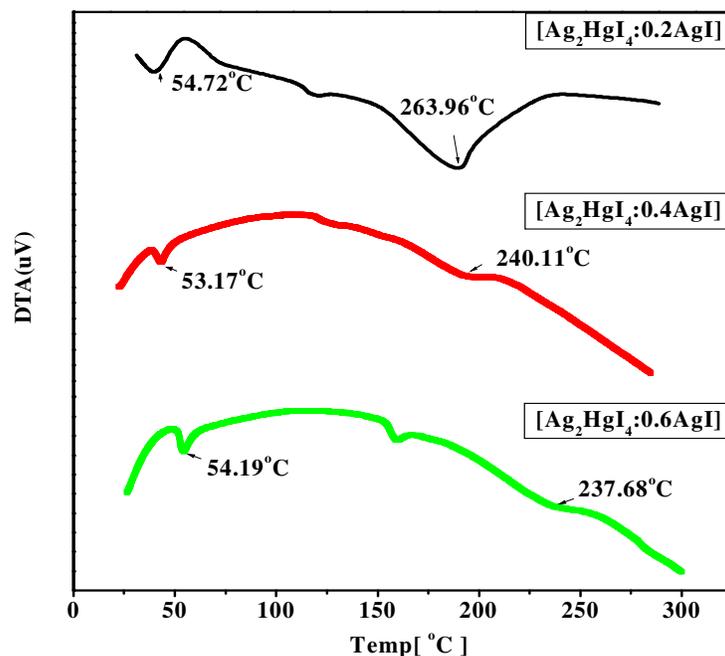
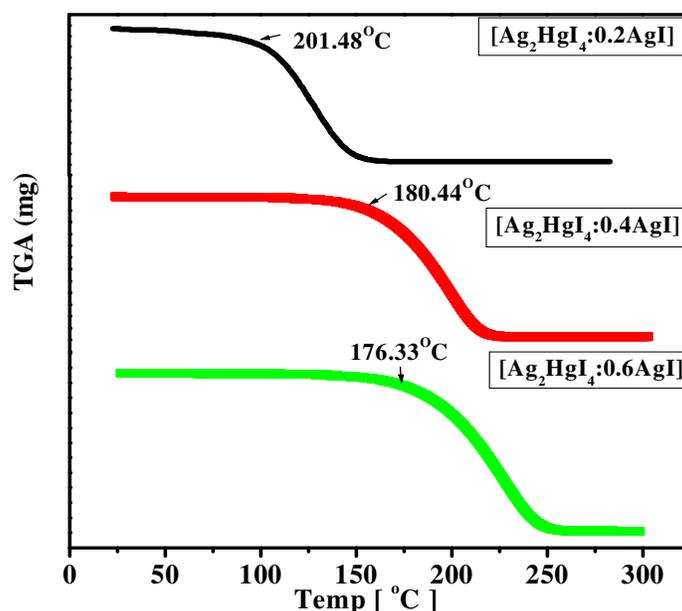


Fig. 7. DTA curves for  $[\text{Ag}_2\text{HgI}_4:0.x\text{AgI}]$  system

### 3.3.2. TGA analysis

Thermo-gravimetric analysis (TGA) is used to study the kinetics of the reactions [65]. TGA curves are shown in Fig. 8.

In  $\text{Ag}_2\text{HgI}_4\text{-AgI}$  system all the TGA curves are shifted to lower temperature. It may be expected that the reactions are constantly reached upto a particular temperature and then decreases to a lower temp. In 0.2  $\text{Ag}^+$  doped sample the reaction reached upto 201.48 °C temperature, on further doping of AgI it shifts to lower temperature upto 180.44 °C and 176.33 °C temperatures in 0.4 and 0.6  $\text{Ag}^+$  doped samples respectively due to the interaction between  $\text{Ag}^+$  ions and host  $[\text{Ag}_2\text{HgI}_4]$  the shift decreases with increasing AgI content (Fig. 8.).



**Fig. 8.** TGA curves for  $[\text{Ag}_2\text{HgI}_4:0.x \text{AgI}]$  system

## 4. CONCLUSION

A new composite superionic systems  $[\text{Ag}_2\text{HgI}_4:0.x \text{AgI}]$  has been investigated. The electrical conductivity of  $[\text{Ag}_2\text{HgI}_4]$  is found to be enhanced markedly in the temperature range 90 °C–130 °C and 150 °C–210 °C respectively, on doping with AgI. Initially the conductivity increases with temperature due to increase in rate of migration of Frenkel defects and interstitial  $\text{Ag}^+$  ions.

X-ray powder diffraction, DTA, DTG, DSC 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, doping effect and phase transition.

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