

Full Paper

Preparation, Electrical Conductivity and Phase Transition in [Ag₂HgI₄:0.2 AgI]:0.x KBr Type Mixed Composite System (x=0.2, 0.4, 0.6 mol. wt. %)

Noorus Saba, and Afaq Ahmad*

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

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

E-Mail: afaqahmad21@gmail.com , sabaamu@gmail.com

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Abstract- A novel mixed composite system, [Ag₂HgI₄:0.2 AgI]:0.x KBr, (x=0.2, 0.4, 0.6 mol. wt. %), was prepared and [Ag₂HgI₄:0.2 AgI] composite 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 of 90-170 °C using a GENRAD 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 behavior. X-ray powder diffraction, DTA, DTG and TGA were performed to confirm the doping effect and transition in the host. The phase transition temperature decreased with an increase in the dopant concentration. Activation energies in eV for pre- and post- transition phase behavior are also reported .

Keywords- Powders-Solid State Reaction, Composites, Electrical Conductivity, Halides, Batteries, etc

1. INTRODUCTION

A few types of ionic solid, generally referred to as superionics or fast-ion conductors, have values of σ in the solid state comparable with that found in the melt and, as a consequence, have practical application e.g. in solid-state batteries [1]. Solid electrolytes composed of ionic salts which are insulating, chemically inert, have attracted a great deal of

attention and may be regarded as a new class of solid electrolytes. Some of these composite solid electrolytes exhibit high ionic conductivity and good mechanical properties and are found to be promising materials for solid state batteries, electrodes, fuel cells, sensors, etc. [2]. These composite solid electrolytes are also termed as heterogeneously doped materials or dispersed solid electrolyte systems. The research in this field was ignited in 1973 when Liang [3] first reported nearly 50 times enhancement in ionic conductivity at room temperature by dispersing ultra fine particles of insulating fine β - 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 to those of constituent phases [4] and [5]. A substantial change in conductivity and thermodynamic parameters of the ionic component were observed in $\text{AgI-Cu}_2\text{HgI}_4$, [6], $\text{Ag}_2\text{HgI}_4\text{-AgI-KI}$ [7], $\text{Ag}_2\text{HgI}_4\text{-AgI-CuI}$ [8], $\text{CdHgI}_4\text{-AgI-KI}$ and $\text{CdHgI}_4\text{-AgI-K}_2\text{SO}_4$ [9]. Such silver ion conducting composite solids are interesting materials specially to develop solid-state electrochemical devices such as batteries, fuel cells, sensors, super capacitors, electro chromic display devices, etc. [10]. These materials have recently attracted widespread attention mainly due to their high isotropic ionic conductivity (σ 25 °C $\sim 10^{-2}$ – 10^{-3} S cm^{-1}) as well as ease of material handling and synthesization [11].

Therefore, in the present study, the investigations is focused on an alternative novel composite compound, $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]:0.x \text{ KBr}$ ($x=0.2, 0.4, 0.6$ mol. wt. %) with KBr as the dopant, and $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]$ as a host. The composition of the host was kept constant in all the composite samples [7] and [8]. AgI is known as typical superionic conductors, the superionic phase of AgI appears at 420K. The value of the ionic conductivity is as high as about $1 \Omega^{-1} \text{ cm}^{-1}$ [12]. It has been observed that a much better solid electrolyte composite system can be prepared with the host $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]$ [8].

2. EXPERIMENTAL

2.1. Materials

Silver iodide and mercury [I] iodide were of CDH Analar grade and potassium bromide was obtained from Qualigens, each of which had a purity of 98%, 99% and 99% respectively.

2.2. Preparation and characterization of pure and doped samples

2.2.1. Preparation and characterization of pure host composite $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]$ samples

Ag_2HgI_4 was prepared by the solid state reactions between AgI and HgI_2 [13] and [14]. 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 AgI 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 deep red color compound was formed which changed to yellow color on

cooling, (Ag_2HgI_4 is yellow below 52 °C and red above 52 °C [15]). X-ray diffraction studies showed this yellow color compound to be single phase $\beta\text{-Ag}_2\text{HgI}_4$.

$[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]$ solid solutions were prepared by mixing 2 g Ag_2HgI_4 and 0.2 g AgI in an agate mortar at room temperature with intermittent grinding adopting the procedure reported earlier [6].

2.2.2 Preparation and characterization of doped composite $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]:0.x \text{ KBr}$ samples

Mixed composite doped samples $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]:0.x \text{ KBr}$, were prepared by taking $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]$ and KBr, in different ratios of x (x=0.2 to 0.6 mol. wt. %) following procedure reported elsewhere [8]. 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.

2.3. Conductivity measurement

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 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 /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 are reported to be affected by the change of frequency [16].

2.4. X-ray analysis

The X-ray diffraction studies were performed for the pure host Ag_2HgI_4 , AgI, and all the mixed composite samples $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]:0.2 \text{ KBr}$, $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]:0.4 \text{ KBr}$, and $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]:0.6 \text{ KBr}$ 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.

2.5. Thermal analysis

Thermal analysis were 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 °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. Compositional variation in conductivity

The variations in the conductivity as a function of mol. wt. % x for the mixed composite system $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]:0.x \text{ KBr}$, at different temperatures in the range 90-170 °C are shown in Fig. 1. The conductivity sharply increased with an increasing in x , attaining a peak value for $x=0.4$ mol. wt. % and thereafter, decrease in between the temperature, 90-170 °C except at 100-110 °C. Variations in dopant composition in the host affected the phase change within the temperature range of 120- 150 °C (Fig. 1). This phenomenon is usually observed in some mixed composite system [6], [7], [8] and [9]. In the $\log \sigma T$ vs. x plot (Fig. 1), this mixed composite system looks qualitatively similar to those reported in the literature [8] and [17] but the σ values differ quantitatively at different temperature range [18].

Horizontally flat conductivity maxima was obtained for the systems in the region $x=0.4$ mol. wt. %. The conductivity variations with composition are 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 19 to the increased mobile ion concentration in the space charge region of the $\text{M}_x\text{HgI}_4/\text{AgI}$ interface. The additional enhancement of conductivity for the composite samples is attributed to the formation of new disordered phases (Fig. 1).

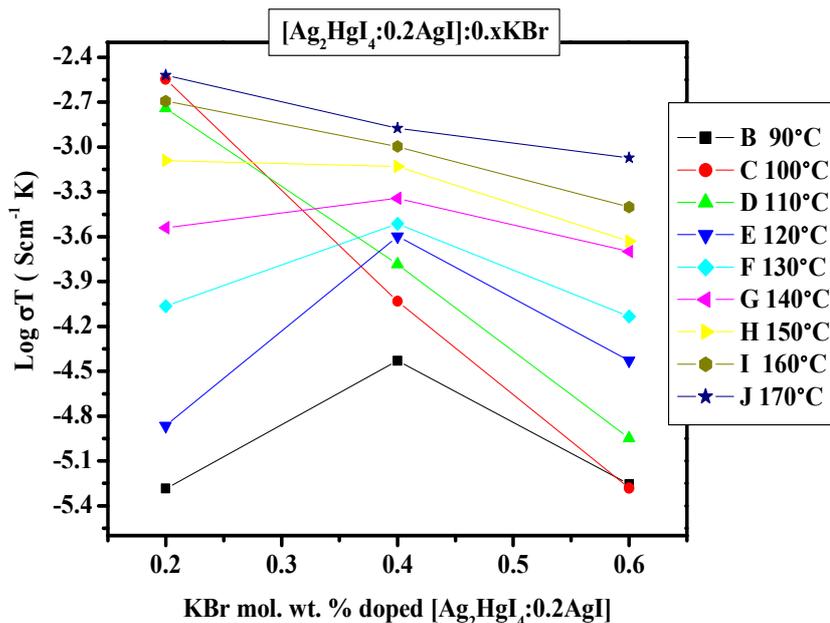


Fig. 1. $\text{Log}\sigma T$ vs. x plot for all mixed composite system $[\text{Ag}_2\text{HgI}_4:0.2 \text{AgI}]:0.x \text{KBr}$

3.1.2. Temperature dependence of 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;

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

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

Where n is the number of ions per unit volume, e the ionic charge, λ the distance between two-jump positions, ν 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:

$$\sigma = \sigma_0 \exp(-E_a / k_B T) \quad (3)$$

where $\sigma_0 = ne^2\lambda^2\nu\gamma / k_B \exp(\Delta S^* / k_B)$

and $\Delta H^* = \Delta H^*_{\text{migration}} + \frac{1}{2} \Delta H^*_{\text{defect}}$ (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 [12].

Fig. 2 shows the $\log \sigma T$ vs. $(1/T)$ plots for the pure host $[\text{Ag}_2\text{HgI}_4:0.2 \text{AgI}]$ and all the mixed composite systems $[\text{Ag}_2\text{HgI}_4:0.2 \text{AgI}]:0.x \text{KBr}$, respectively.

The activation energy of Ag_2HgI_4 , host $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]$, and all mixed composite systems are shown in Table 1.

The phase transition temperature for the mixed composite system, $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]$, increases as compared to Ag_2HgI_4 (Fig. 2). The β -phase has thermal activation up to 110 °C. Fig. 2 shows that the highly conducting α -phase of the host (approximately $T_c=110$ °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 [18]. The $\log \sigma T$ values of the mixed composite systems are also intermediate between Ag_2HgI_4 [20] and dopant AgI.

The $\log \sigma T$ vs. $1/T$ plot shifts from a lower temperature to a high temperature is responsible for the phase transition from β - Ag_2HgI_4 (yellow) to α - Ag_2HgI_4 (red) 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 $[\text{Ag}_2\text{HgI}_4]$ [21]. Therefore, in the host $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]$ 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 K^+ doped samples (Fig. 2), decrease in the mobile charge carriers, Ag^+ , that is proportionate with the increased 0.x mol. wt. % in the host mixed system $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]$. This may be explained in terms of extra free volumes produced by larger guest ions [$r_{\text{K}^+}=152$ pm and $r_{\text{Ag}^+}=129$ pm] for CN=6 [22].

In $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]$, additional free volume is generated, permitting greater Ag^+ ion mobility and therefore enhancing ionic conductivity. The enhanced conductivity (Fig. 2) can also result from an increased number of activated mobile Ag^+ ions resulting from weaker lattice bonding forces. The above effect is known as “lattice loosening” in a mixed cation composition [12]. Secco et al. reported parallel ionic conductivity behavior for Rb^+ -doped Na_2SO_4 based compounds [23].

Another important feature observed in the K^+ -doped $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]$ was the erratic conductivity in the post transition region. After the phase transition, the conductivity increased smoothly and thereafter tended to decrease with an increase in 0.x mol. wt. %. The drop in the conductivity may be due to the collapse of the iodide framework at temperatures above 140 °C. Upon cooling, however, the higher conductivity was regained. This argument of lattice collapse and its subsequent recovery on cooling implies restructuring of the sublattice. A similar type of decrease in conductivity was reported for Na_2SO_4 [24] and K_2SO_4 [20].

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 [25], consistent with the conductivity behavior.

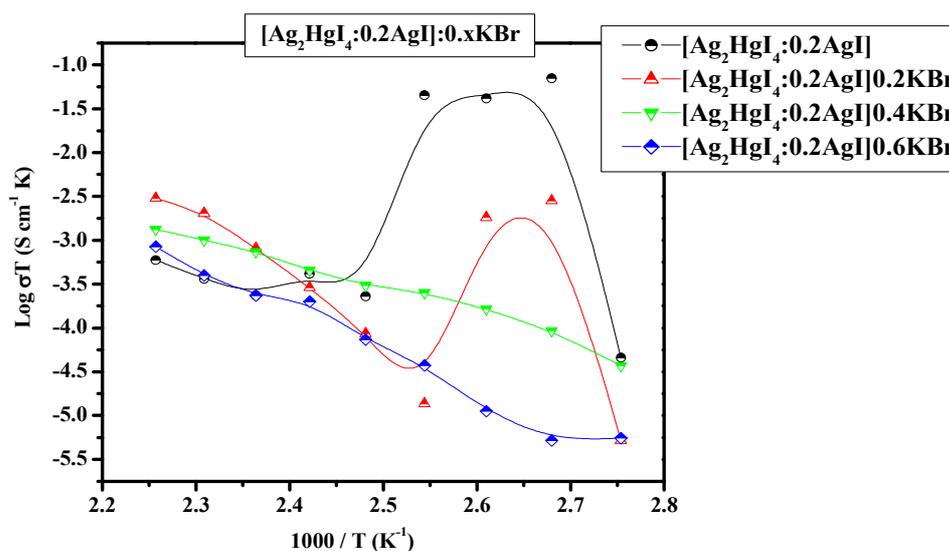


Fig. 2. Log σ vs. $(1000/T)$ plot for pure host and the entire mixed composite

Table 1. Comparative activation energies for ionic conductivity of pure $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]$ and KBr doped $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]$

Compounds	PhaseTransition	Activation Energy (eV)	
	Temperature (°C)	Pre-transition (β) (E_{a1})	Post-transition (α) (E_{a2})
$[\text{Ag}_2\text{HgI}_4]$	50	0.6852	0.558
$[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]$	110	0.6338	0.5073
$[\text{Ag}_2\text{HgI}_4:0.2\text{AgI}]:0.2 \text{ KBr}$	100	0.8839	0.4255
$[\text{Ag}_2\text{HgI}_4:0.2\text{AgI}]:0.4 \text{ KBr}$	120	0.6363	0.4378
$[\text{Ag}_2\text{HgI}_4:0.2\text{AgI}]:0.6 \text{ KBr}$	140	0.4698	0.9545

3.1.3. Time variations in conductivity

The conductivity behavior of host and all the mixed composite system versus time at a 30 min interval in the temperature range 90–170 °C for different dopant ratios were calculated (Fig. 3). 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 (Fig. 3) decays at elevated temperature with the loss in conductivity being most pronounced at temperatures at or higher than 150 °C in air [26] and [27]. The conductivity degradation rate constants as well as the apparent activation energies were extracted from the curve slopes (Fig. 3) and a standard Arrhenius analysis [13] reported in Table 2.

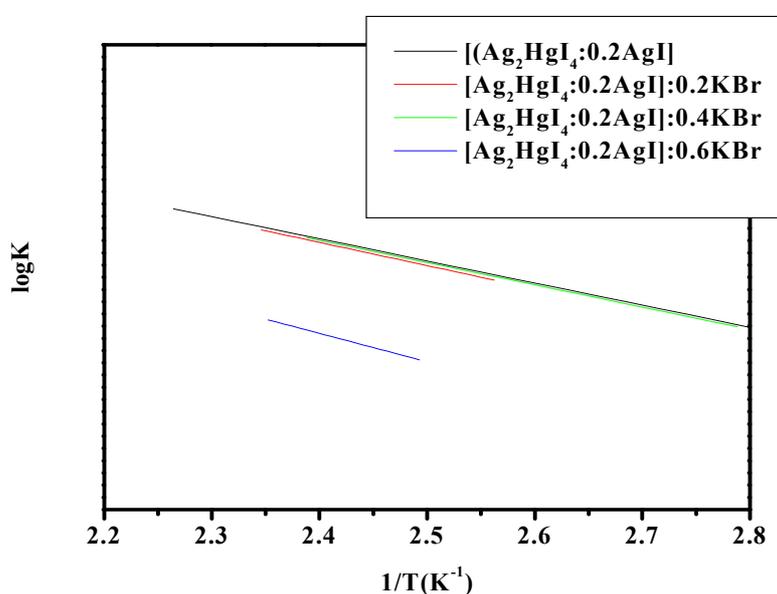


Fig. 3. Plot of $\log k$ vs. $1000/T$ (K^{-1}) for all mixed composite system $[Ag_2HgI_4:0.2 AgI]:0.x$ KBr

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

Compounds	Average Activation Energy (eV)
$[Ag_2HgI_4:0.2AgI]$	0.3592
$[Ag_2HgI_4:0.2AgI]:0.2 KBr$	0.3759
$[Ag_2HgI_4:0.2AgI]:0.4 KBr$	0.3620
$[Ag_2HgI_4:0.2AgI]:0.6 KBr$	0.2881

3.2. X-ray diffraction

The structure of the stable β -phase of Ag_2HgI_4 , which is not superionic, under ambient conditions is tetragonal with space group [28]. Iodide adopt, a slightly distorted face centered cubic (fcc) arrangement and the cations occupy $3/8$ of the tetrahedrally coordinated positions in an ordered manner derived from the chalcopyrite ($\text{A}_2\text{B}_2\text{X}_4$) structure by the accumulation of cation vacancies. The first superionic α -phase appears at 325 K, and the transition is classified as type I in the nomenclature of Boyce and Heberman [29].

The structure of $\alpha\text{-Ag}_2\text{HgI}_4$ is similar to that of the β -phase, except that the iodide sublattice is an ideal face centered cubic arrangement. X-ray diffraction studies show the cation to be disordered in over half of the tetrahedrally coordinated positions [28]. Crystallography revealed that $\alpha\text{-Ag}_2\text{HgI}_4$ is in the cubic space group $F\bar{4}3m$ with each cation site having an average occupancy of $1/2$ Ag and $1/4$ Hg.

The primitive Weigner-Seitz cell shows S_4 symmetry and the lattice parameters as $a=6.3$ Å and $c=12.6$ Å at room temperature [30]. The structure of AgI is a hexagonal wurtzite and zinblende-type structure [31], where the structure of KI is a cubic NaCl-type structure, where each of the two atom types forms a separate face-centered cubic lattice, with the two lattices interpenetrating so as to form a 3D checkerboard pattern [32]. The space group of this structure is called "Fm3m"

Room temperature X-ray diffractogram for all the doped composite systems [$\text{Ag}_2\text{HgI}_4:0.2$ AgI]: $0.x$ KBr are shown in Fig. 4. The X-ray diffractogram of [$\text{Ag}_2\text{HgI}_4:0.2$ AgI] consist of Ag_2HgI_4 peaks and, in addition a number of peaks for the K^+ -doped host composite system. The appearance of two tiny peaks (reflections at 27.10° and 38.66°) observed for the $x=0.2$ K^+ doped composite system shifted to (27.06° , 38.66°) and (27.10° , 38.69°) in the $x=0.4$ and $x=0.6$ K^+ doped composite systems, respectively, and the corresponding peaks (Fig. 4) were more intense upon doping.

Therefore a significant structural change occurs with small compositional changes of KBr (Fig. 4) in the host composite system [33]. It is, therefore, concluded that the phase composition is influenced by the presence of the dopant [34] and [16].

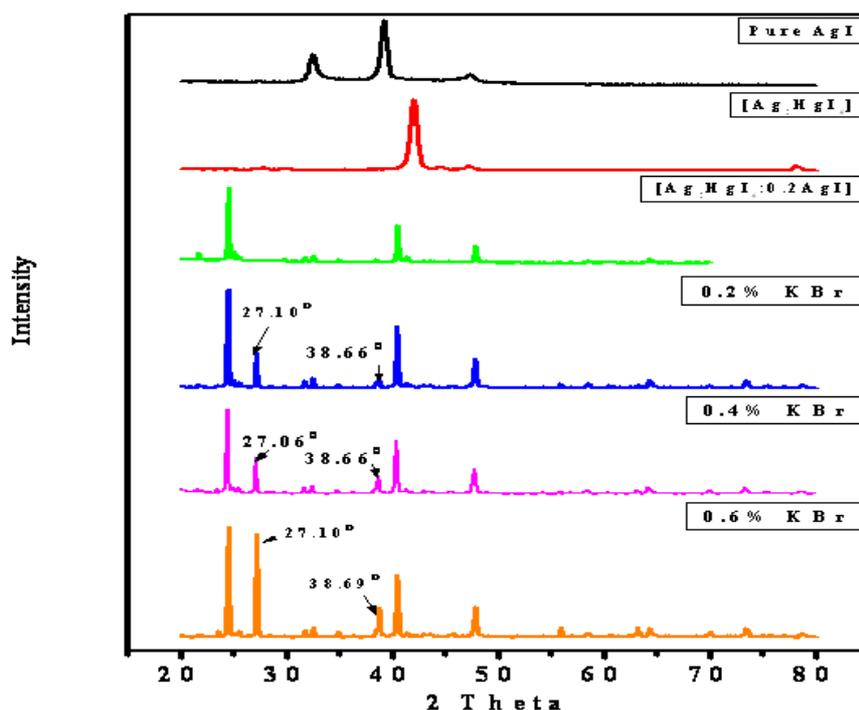


Fig. 4. X-ray diffractograms for all mixed composite system $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]:0.x \text{ KBr}$

3.3. Thermal analysis

3.3.1. DTA analysis

DTA curves for $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]:0.x \text{ KBr}$ are shown in Fig. 5. All the DTA curves contained two endothermic peaks, the first endotherm corresponded to a $\beta - \alpha$ transition (at approximately $50.1 \text{ }^\circ\text{C}$ for Ag_2HgI_4) and the second endotherm corresponded to melting of the material [35]. The DTA curve (Fig. 5) of the pure host shows a sharp endothermic peak at $55.52 \text{ }^\circ\text{C}$ due to the gradual phase transition of Ag_2HgI_4 from room temperature tetragonal $\beta - \alpha$ transition. There is clear evidence that the phase transition (Fig. 5) temperature decreases and then increases as K^+ -dopant concentration increases. This indicate the (Fig. 5) significant interaction between host $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]$ system with dopant KBr content and host $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]$ system with dopant KBr content respectively.

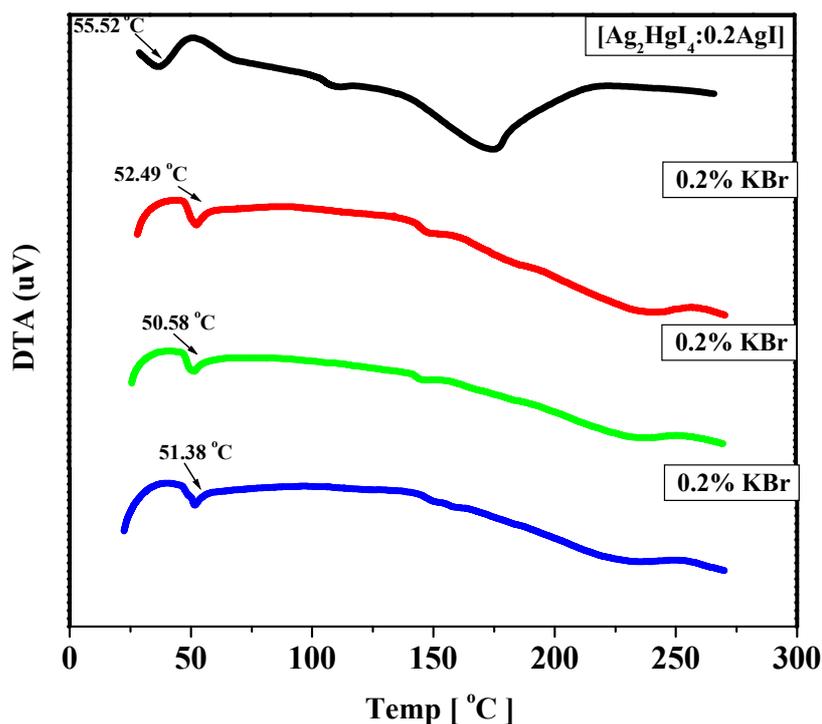


Fig. 5. DTA curves for all mixed composite system $[\text{Ag}_2\text{HgI}_4:0.2 \text{AgI}]:0.x \text{KBr}$

3.3.2. DTG Analysis

DTG curves for $[\text{Ag}_2\text{HgI}_4:0.2 \text{AgI}]:0.x \text{KBr}$ are shown in Fig. 6, whereas for K^+ -doped host samples, it shifted to a lower temperature because of the interaction between dopant KBr and the host $[\text{Ag}_2\text{HgI}_4:0.2 \text{AgI}]$. The shift decreased (Fig. 6) with an increase in the KBr content [6].

3.3.3. TGA analysis

TGA curves for $[\text{Ag}_2\text{HgI}_4:0.2 \text{AgI}]:0.x \text{KBr}$ are shown in Fig. 7, whereas for K^+ -doped host samples, it shifted to a lower temperature because of the interaction between dopant KBr and host $[\text{Ag}_2\text{HgI}_4:0.2 \text{AgI}]$. The shift decreased (Fig. 7) with an increase in the KBr content [8].

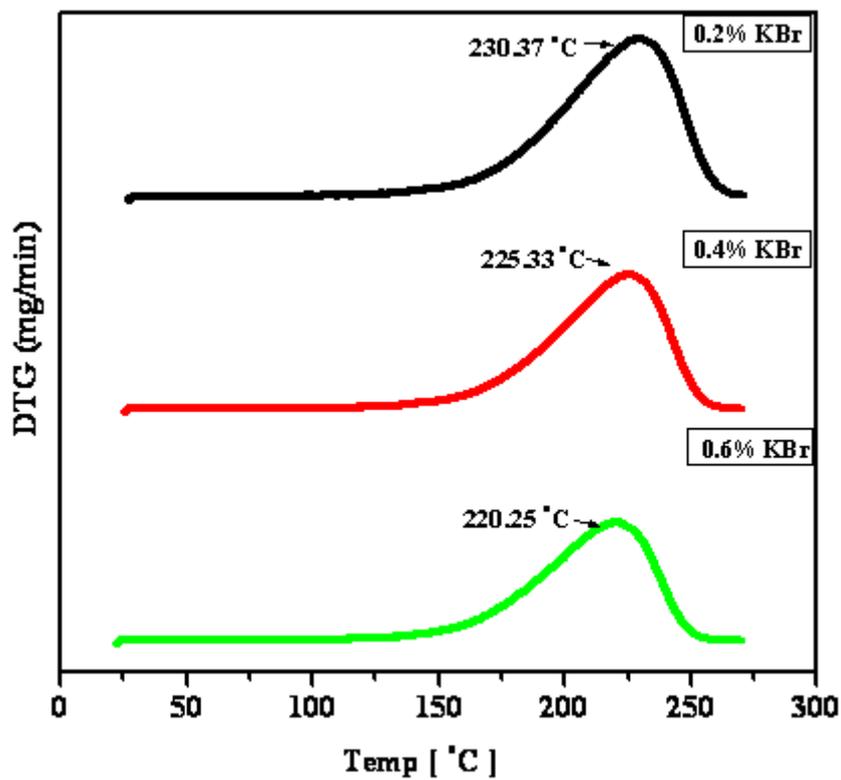


Fig. 6. DTG curves for all the composite system $[Ag_2HgI_4:0.2 AgI]:0.x KBr$

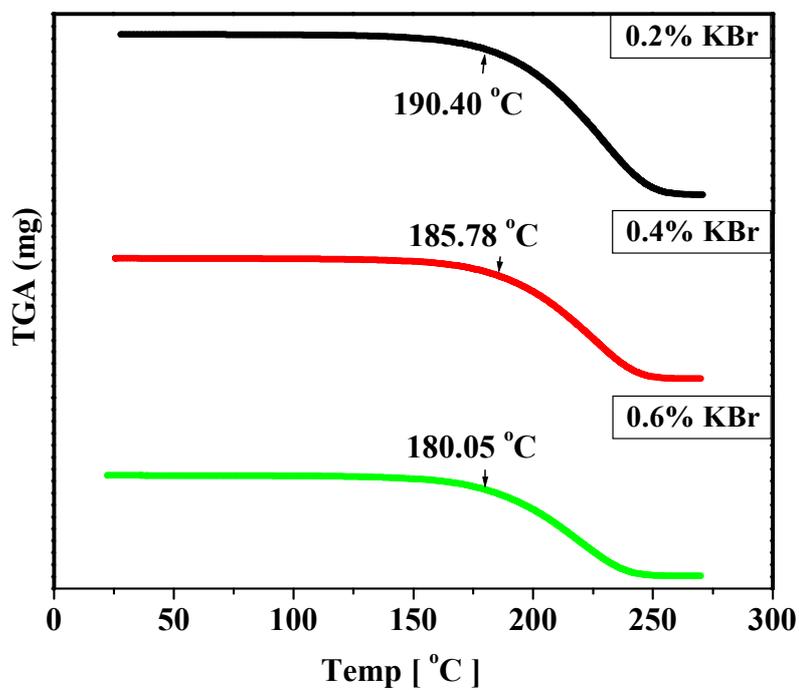


Fig. 7. TGA curves for all the composite system $[Ag_2HgI_4:0.2 AgI]:0.x KBr$

4. CONCLUSION

A novel composite superionic systems $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]:0.x \text{ KBr}$ were investigated. An alternative host mixed composite system $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]$ was used in place of the traditional host $[\text{Ag}_2\text{HgI}_4]$. The increase of conductivity upto 140°C can be attributed to the extra enhancement of I^- orientational disorder. In the host $[\text{Ag}_2\text{HgI}_4:0.2 \text{ AgI}]$ structure. Doping with K^+ in the host induces a decrease in the mobile charge carriers, Ag^+ ions, that is proportionate with the increased $0.x$ mol. wt. % in the host mixed system.

X-ray powder diffraction, DTA, DTG and TGA studies confirmed the formation of a superionic phase in the composite system. The temperature dependence of various ionic parameters was determined to characterize the ion transport properties and doping effect.

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