

Full Paper

Investigation of the Effect of Ionic Transport Properties on Phase Transition in a [CdHgI₄:xAgI] Type Mixed Composite System

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Abstract- An experimental investigations concerning the preparation and characterization of the superionic composite system [CdHgI₄:xAgI], (x=0.2, 0.4, and 0.6 mol. wt. %), have been undertaken with a view to evaluate the ionic transport properties of the mixed composite system, and to identify the phase transition. Powder samples of various compositions containing x mol. wt. %AgI were synthesized by solid state reactions, where [CdHgI₄] system was used as host. Samples were analyzed using powder X-ray diffraction, thermal gravimetric analysis (TGA) techniques. These studies have revealed the formation of new substance having phase transition temperature similar to that of AgI. Detailed electrical conductivity measurement carried out at frequencies of 100 Hz, 120 Hz, 1 kHz, and 10 kHz in the temperature range 150-250 °C by a Gen Rad 1659 RLC Digibridge, have identified the best conducting composition namely 4 mol. wt. %, exhibiting an electrical conductivity of $1.88 \times 10^{-1} \text{ Scm}^{-2}\text{K}$ at 543 K and an activation energy of 1.66 eV for Ag⁺ ion migration within the solid host. Activation energies for the system in eV both for the pre-transition and post-transition phase transformations are reported .

Keywords- Ionic Transport, Composites, Electrical Conductivity, X-ray Diffraction, Thermo-gravimetric Analysis

1. INTRODUCTION

Solid electrolytes composed of ionic salts and insulating, chemically inert, ultrafine particles 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. [1]. Since the discovery of superionic mixed conducting composite materials by Noorussaba et al., [2-9], AgI-doped superionic mixed conducting composite systems have attracted much attention because of their high ionic conductivity at room temperature. AgI-doped composite systems have several common features. Firstly, the ionic conductivity exponentially increases with increasing AgI concentration. The extrapolation of the composition dependence of the ionic conductivity to a composition of 100% AgI produces a value that agrees closely with the conductivity for α -AgI extrapolated back to room temperature. The activation energy for ionic conduction decreases with AgI content. Secondly, AgI addition to the host composites does not induce the disruption of composite network structure. These facts suggest AgI-like microdomain exists among the composites matrices [10]. It is supposed that doped AgI is homogeneously dispersed into the host matrix in low AgI concentration region, and then doped AgI tends to aggregate with increasing AgI concentration. Such a variation of the structure and resulting conduction mechanism cause the change from linear increase of the ionic conductivity at around the intermediate AgI concentration. No significant change in the slope for the logarithm of ionic conductivity versus AgI content plot is, however, observed in AgI–AgPO₃ glasses [11]. The effect of AgI addition on the ionic conduction of Ag₂O–V₂O₅ glass system has been investigated, because AgI–Ag₂O–V₂O₅ system has wide glass-forming ability [12]. Therefore, In the present investigation, focused on an alternative novel composite conducting compound, [CdHgI₄:xAgI] (x=0.2-0.6 mol. wt. %) mixed composite solid, with AgI as the dopant, and [CdHgI₄] as a host. The composition of the host was kept constant in all the composite samples [2,6]. AgI is known as typical superionic conductors, the superionic phase of AgI appears at 420 K. The value of the ionic conductivity is as high as about 1 $\Omega^{-1}\text{cm}^{-1}$ [13]. It has been observed that a much better solid electrolyte composite system can be prepared with the host [CdHgI₄] [2,6].

2. EXPERIMENTAL

Cadmium tetra iodomercurate [CdHgI₄] was prepared from CdI₂ (LOBA Chemie) and HgI₂ (CDH Analar grade) by the conventional solid state reaction. Both CdI₂ and HgI₂ were mixed in the requisite compositions in an agate mortar and were heated at 200 °C for 48 h in a silica crucible with intermittent grinding. The yellow product so formed was single phase according to X-ray powder diffraction studies.

Mixed composite doped samples [CdHgI₄:xAgI] were prepared by taking the starting materials, namely [CdHgI₄] and AgI respectively, in different ratios of x (x=0.2 to 0.6 mol. wt. %) by procedures reported elsewhere [2,6]. The powder mixture, were ground thoroughly in an agate mortar and collected in a silica crucible which is then kept in an air oven (CE 0434 NSW- 144) for 24 h at 200 °C. The resulting powdered sample were pressed into pellets (2.4 cm diameter, 0.1 cm thick) 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). The electrical conductivity was measured using a GENRAD 1659 RLC Digibridge in the temperature range of 150-250 °C over two cycles of heating and cooling, at different frequencies (viz., 100 Hz, 120 Hz, 1 kHz, and 10 kHz) at 30 min intervals [14].

The X-ray diffraction studies were performed for all the samples using Rigaku-ultima D/Tex-25, Rigaku Rad B powder diffractometer and a Bruker AXS D8 Advance diffractometer with a K-beta filter with CuK α ($\lambda=1.54060$ Å) radiation at room temperature. The angle range for measurement was 10°-60° and the scanning speed was 1°/ min.

DTA, DSC and TGA analysis were performed by Perkin Elmer Pyris Diamond model in nitrogen atmosphere (200 ml/min) at a heating rate of 5 °C per min and a temperature range of 20 °C to 300 °C .

3. RESULTS AND DISCUSSION

3.1. Temperature dependence of conductivity

The temperature dependence of the ionic conductivity is shown in Fig. 1 (a, b) for pure host and all the mixed composite systems [CdHgI₄:xAgI] (where x=0.2, 0.4, 0.6 mol. wt. %) respectively.

In general, the conductivity increases with temperature and obeys the Arrhenius relation. The equation can be written in a simpler form as;

$$\sigma_{\text{ionic T}} = \sigma_0 \exp(-E_a / kT) \quad (1)$$

Where σ_0 is the pre-exponential-factor of the ionic conductivity, k the Boltzmann constant, T the absolute temperature and E_a is the activation energy for the ionic conductivity.

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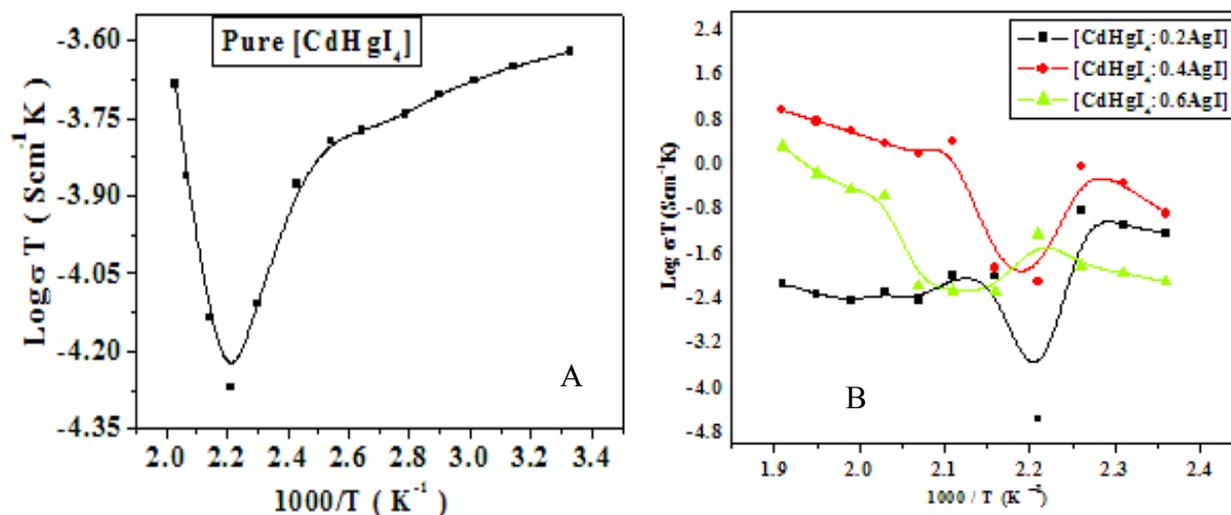


Fig. 1. The temperature dependence of electrical conductivity of mixed composite systems $[\text{CdHgI}_4:\text{xAgI}]$ (A) $\text{Log } \sigma T$ vs. $(1/T)$ plots for mixed composite system, $[\text{CdHgI}_4]$ (B) $\text{Log } \sigma T$ vs. $(1/T)$ plots for mixed composite system, $[\text{CdHgI}_4:\text{xAgI}]$

From the literature and from the $\text{log } \sigma T$ vs. $(1/T)$ plot, pure $[\text{CdHgI}_4]$ shows deviation from Arrhenius linear plot at about 180°C , representing transformation of β (light yellow) to α (dark yellow) phase change of CdHgI_4 with three cation randomly distributed among the four tetrahedral sites provided by the fcc sublattice of the I^- ions and α phase shows exceptionally high ionic conductivity and activation energy for ionic motion is much larger than those of other superionic conductors [6]. The $\text{log } \sigma T$ vs. $1/T$ plot shift from a lower temperature to a high temperature is responsible for the β (light yellow) to α (dark yellow) phase change of CdHgI_4 and is associated with a charge transfer process between electron levels of Hg, Cd and I. These observed changes in the phase transition can be explained by assuming an increase in the interaction between I and Cd atoms above the phase transition, and consequently a decrease in the I-----Hg interaction. These changes would be induced by a decrease in the Cd-----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 CdHgI_4 [15].

However, a deviation occurs at the temperature around the $\beta \rightarrow \alpha$ phase transition temperature for $[\text{CdHgI}_4:\text{xAgI}]$ which follows the parent material $[\text{CdHgI}_4]$. In the low temperature region, all the mixed composite systems show an Arrhenius behavior, and at high temperature a small deviation occurs around the $\beta \rightarrow \alpha$ $[\text{CdHgI}_4:\text{xAgI}]$ phase transition [16]. For comparison, an Arrhenius plot of $[\text{CdHgI}_4:\text{xAgI}]$, are shown in Fig. 1 (b). By using Eq. (1), the activation energy, E_a for ionic conductivity for low temperature and higher temperature regions are shown in Table 1.

Table 1. Comparisons of ionic conductivity activation energy values for pure and doped host composite [CdHgI₄:xAgI] system

Compounds	Phase Transition Temp (°C)	Activation Energy (eV) Pre-transition (β) Phase (E_{a1})	Activation Energy (eV) Post-transition (α) Phase (E_{a2})
[CdHgI ₄]	180	0.1152	0.6328
[CdHgI ₄ :0.2 AgI]	170	0.8092	0.9853
[CdHgI ₄ :0.4 AgI]	180	1.6674	2.0255
[CdHgI ₄ :0.6 AgI]	200	1.0712	2.3562

The β -phase of the mixed composite system [CdHgI₄:0.2 AgI] has thermal activation up-to 170 °C as compared to pure compound CdHgI₄ ($T_c=180$ °C, Table 1).

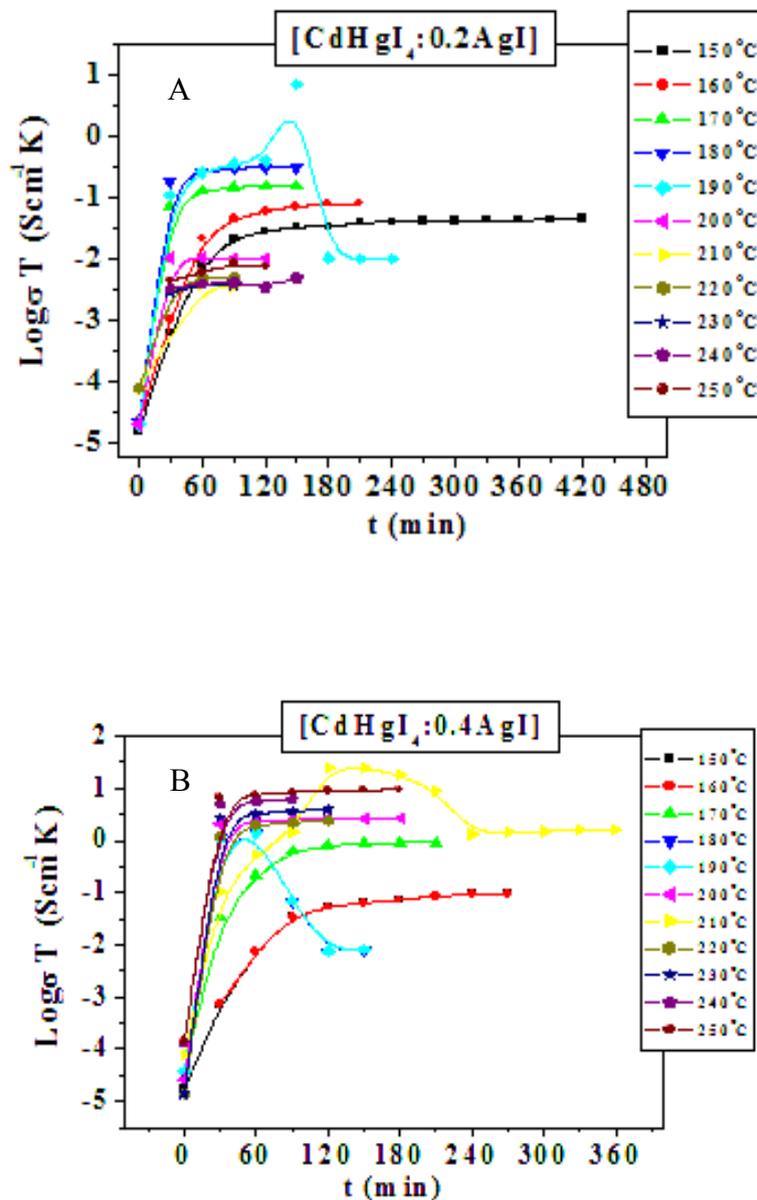
Fig. 1(b) shows that the highly conducting α -phase of this mixed composite system [CdHgI₄:0.2 AgI] (approximately $T_c=170$ °C) is deviate from linear behavior at 170 °C showing conductivity decreases up-to 170 °C and then constant up-to 250 °C. The small jump in the conductivity was due to the β - α transition of the phase in the host. The drop in conductivity was probably due to softening of the materials [17]. The log σT values of the mixed composite host systems are also intermediate between CdHgI₄ and the AgI [18]. Therefore, in the mixed host system [CdHgI₄:0.2 AgI], since Ag⁺ ions has larger ionic radius than the Cd²⁺ ions ($r_{Ag^+}=129$ pm, $r_{Cd^{2+}}=109$ pm) [19], partial replacement of the divalent host ion by the monovalent guest ion gives rise to fill up additional vacancies in the host lattice in accordance with electroneutrality requirement [20], and one may expect that fraction of mobile charge carriers, Ag⁺, decreases leading to a decrease in the Ag----I distance and thus phase transition shifts to lower temperature up-to 170 °C [2]. On further doping of Ag⁺ ions in the host [CdHgI₄], the fraction of mobile charge carriers, Ag⁺, increases proportionately leading to Ag----I distance increase and so phase transition shift to high temperature with increased $x=0.4-0.6$ mol. wt. %, in the host system [CdHgI₄], therefore increased in ionic conductivity and activated up-to T_c .

Secco et al. reported parallel ionic conductivity behavior for Rb⁺-doped Na₂SO₄ based compounds [13].

Ionic conduction is determined by thermally activated defect. The increase of conductivity up-to 210 °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 pre-transition phases have higher activation energy than the post-transition phase, consistent with the conductivity behavior [21].

3.2. Time dependence of conductivity

Fig. 2 (a,b,c) displays the conductivity behavior of all the mixed composite system vs. time at a 30 min interval in the temperature range 150 °C to 250 °C in $[\text{CdHgI}_4:0.x\text{AgI}]$ composite systems for different dopant ratios. The 30 min time interval was selected in order that the structural changes, if any, would homogenize during this interval. 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. 2 (d) displays the conductivity degradation rate constants as well as the apparent activation energies extracted from the curve slopes and a standard Arrhenius analysis [22, 23] reported in Table 2.



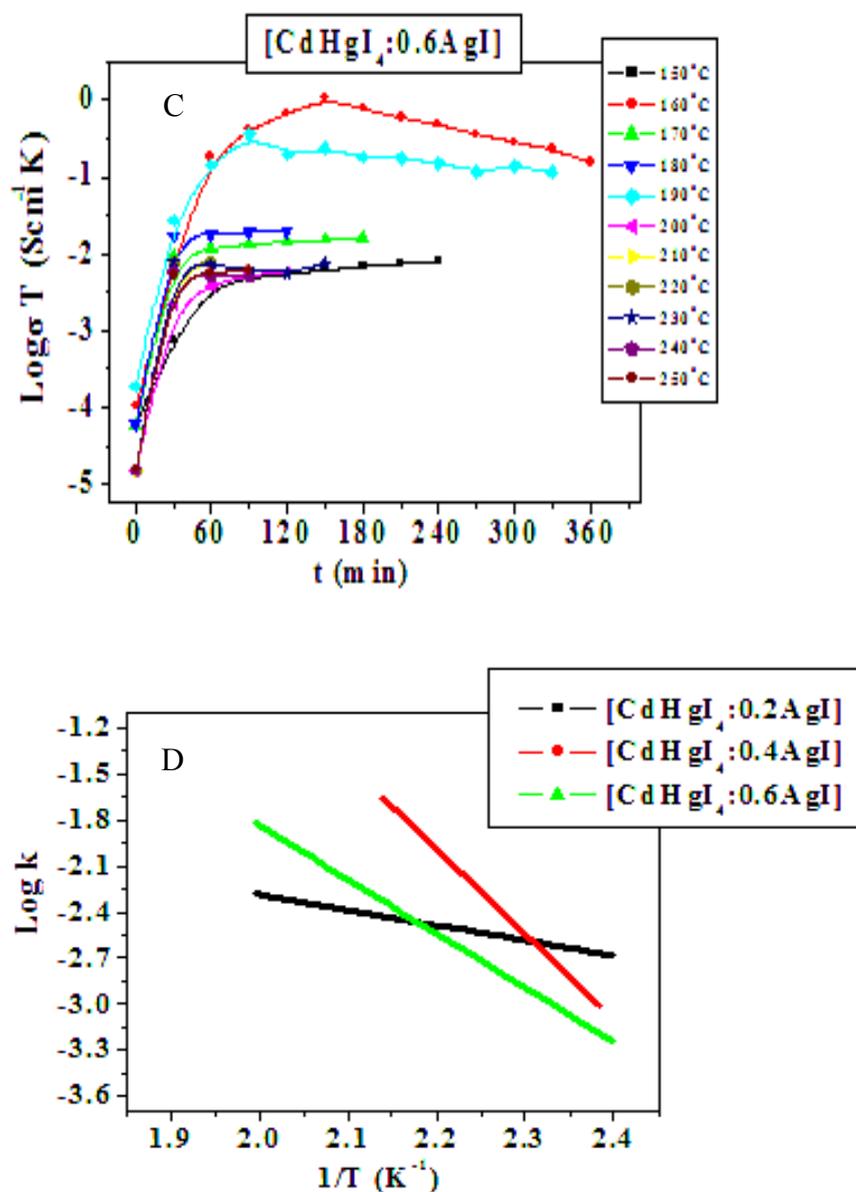


Fig. 2. The time dependence of electrical conductivity of mixed composite systems $[\text{CdHgI}_4:x\text{AgI}]$, (A) $\text{Log } \sigma T$ vs. (t min) plots for mixed composite system, $[\text{CdHgI}_4:0.2\text{AgI}]$ (B), $\text{Log } \sigma T$ vs. (t min) plots for mixed composite system, $[\text{CdHgI}_4:0.4\text{AgI}]$ (C), $\text{Log } \sigma T$ vs. (t min) plots for mixed composite system, $[\text{CdHgI}_4:0.2\text{AgI}]$ (D), Plot of $\text{log } k$ vs. $1000/T$ (K⁻¹) for all mixed composite system $[\text{CdHgI}_4:x\text{AgI}]$

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

Compounds (eV)	average activation energy
[CdHgI ₄ :0.2AgI]	0.1968
[CdHgI ₄ :0.4AgI]	1.0968
[CdHgI ₄ :0.6AgI]	0.7044

3.3. X-ray diffraction

X-ray diffraction patterns for pure host [CdHgI₄] and all the doped samples of [CdHgI₄:xAgI] system, recorded at room temperature are shown in Fig. 3 at room temperature.

The X-ray diffractogram values of all the composite samples [CdHgI₄:xAgI] correspond to standard values of [CdHgI₄] and careful analysis revealed that in addition to standard peaks of pure host [CdHgI₄], a number of peaks appeared for the Ag⁺-ions in doped composite system .

In [CdHgI₄:xAgI] composite samples (Fig. 3), the appearance of four tiny peaks occurs in host (reflections at 33.08°, 39.72°, 49.01° and 54.54°) shifted to (24.86°, 41.45°, 48.53° and 53.58°), (24.35°, 40.79°, 42.79° and 47.88°) and (24.62°, 40.59°, 47.46° and 53.69°) in the x=0.2, 0.4 and x=0.6 AgI-doped composite systems, respectively, and the corresponding peaks were more intense upon doping .

The findings indicate a significant structural change with only small compositional changes [24] in the host composite system [CdHgI₄] with a gradual increase in AgI content. It is therefore concluded that the phase composition is influenced by the presence of the dopant [21, 25].

3.4. Thermo-gravimetric analysis

Phase transitions of all the composites were studied by thermogravimetric analysis in the temperature range 30-300 °C (Fig. 4). Thermo-gravimetric analysis (TGA) is used to study the kinetics of the reactions [26]. In CdHgI₄-AgI system all the TGA curves are shifted to lower temperature. It may be expected that the reactions are constantly reached up-to a particular temperature and then decreases to a lower temp. In 0.2 Ag⁺ doped sample the reaction reached up-to 181.65 °C temperature, on further doping of AgI it shifts to lower temperature up-to 175.62 °C and 170.65 °C temperatures in 0.4 and 0.6 Ag⁺ doped samples respectively due to the interaction between Ag⁺ ions and host [CdHgI₄] the shift decreases with increasing AgI content.

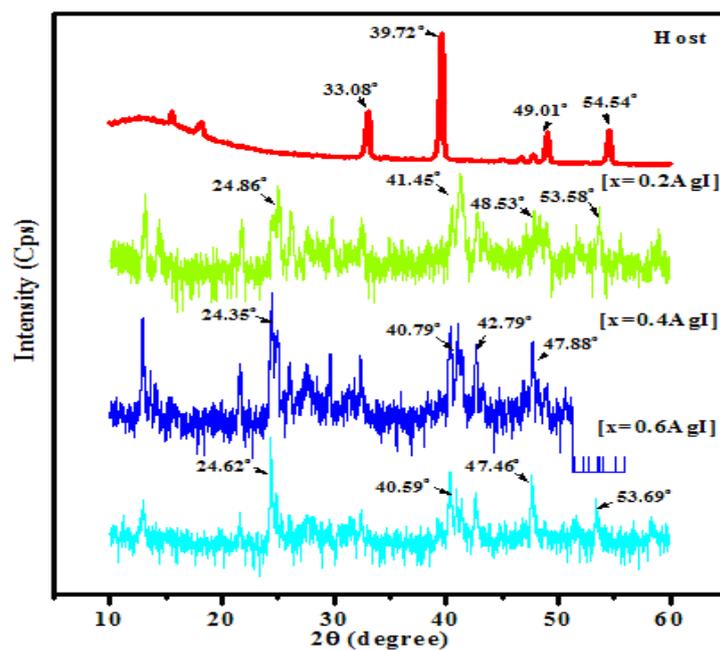


Fig. 3. X-ray diffractograms for all mixed composite system $[\text{CdHgI}_4:\text{xAgI}]$

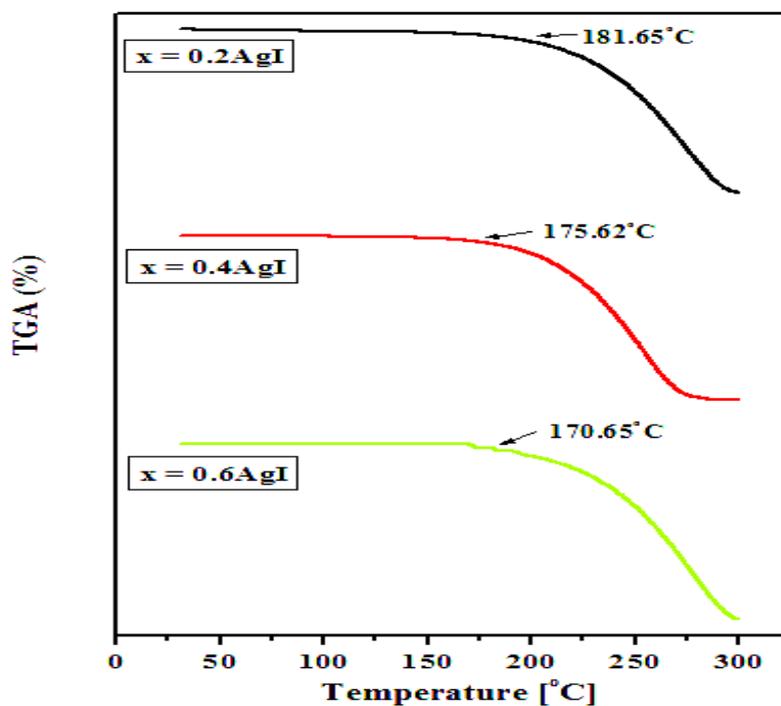


Fig. 4. TGA curves for mixed composite systems $[\text{CdHgI}_4:\text{xAgI}]$

4. CONCLUSION

The [CdHgI₄:xAgI] composite family comprises some important compounds that may be efficient solid electrolytes which can be used technologically in the electrochemical devices. These superionic systems [CdHgI₄:xAgI] was synthesized by solid-state reactions. From the electrical conductivity measurements, it was found that the [CdHgI₄:xAgI] systems undergoes β - α phase transitions, with increasing Ag⁺ concentration, the concentration of vacancies increases and up-to 170-200 °C can be attributed to the extra enhancement of I⁻ orientational disorder. X-ray powder diffraction, 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 phase transition.

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