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peparation, crystal structure, thermal properties and vibrational modes of

[$0.75Tl_2HgI_4$:0.25AgI] composite fast ion conductor

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ABSTRACT

The novel compound [$0.75Tl_2HgI_4$:0.25AgI] has been prepared and characterized by IR spectroscopy, powder X-ray diffraction, thermal analysis, far ir spectroscopy. The compounds [$0.75Tl_2HgI_4$:0.25AgI] for which phase diagrams are available in the literature, were characterized by IR spectroscopy and their identities were confirmed by far ir spectroscopy and X-ray powder diffraction. [$0.75Tl_2HgI_4$:0.25AgI], undergoes a sharp order-disorder phase transition at elevated temperatures that can be detected by the measurement of IR spectra as a function of temperature. This work suggests that thallium (I) ionic conductors may exist, analogous to some well-known double salt conductors based on simple silver (I) and copper (I) halides. In addition, the present study demonstrates the usefulness of IR spectroscopy in the characterization of heavy metal ionic conductors. The mobility of Tl^+ in halide compounds has been investigated to develop an understanding of the factors which are important in fast ion conduction. These compounds are characterized by transitions at elevated temperatures to disordered phases in which the M ion is highly mobile. Trends in the transition temperatures, conductivities, and activation energies for ion transport demonstrate that Tl^+ are less mobile than Cut and Ag^+. The crystal structure of the low-temperature phase of [$0.75Tl_2HgI_4$:0.25AgI] has been determined at 160°C. The material crystallizes with two formula units in space group C^2_2-$P2_1$ of the monoclinic system in a cell of dimensions a = 7.661 Å, b = 7.971 Å, c = 10.074 Å, β = 118.39°. The Hg^+ ions are tetrahedrally coordinated by I^- ions. The TI^+ ions are found to reside in seven-coordinate sites approximating C_{2v}, capped trigonal prisms. There is no clear-cut migration path for the Tl^+ ions, but some plausible conduction mechanisms are discussed.

KEYWORDS: **A**. Ftir; **B**. Far-Ir; **C**. Sem; **D**. Edax; **E**. Doping; **F**. Fast ion conductors.

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1. INTRODUCTION

A large number of papers appeared on isomorphous series constituting A_2BX_4 composition. This series could be devided into two groups: one group of materials is expressed by A_2HgX_4 (A = Tl, K, Cs, Rb, NH_4, X = Cl, Br, I) and the another group is A_2MX_4 (A = Tl, K, Cs, Rb, NH_4, X = Cl, Br, I). These salts are known to undergo a successive phase transformation characterized by IC-C features described in [1].

Fast ion conductors, where a single ionic species diffuses in an otherwise static matrix, have been intensively researched since the middle of the last century. These materials are of practical interest since they hold the promise of enabling all solid state electrochemical devices such as high energy density rechargeable batteries [2–4] and solid state electrochemical conductors. A_2MX_4 compounds (where A = Tl, Ag, Cu, M = Cd, Hg, Zn, etc.), belong to a class of fast-ionic solids which are promising materials for use in solid state batteries and fuel cells due to extraordinarily high ionic conductivity at supercritical temperatures [5]. In such ternary fast-ionic conductors mobile ions of different type contribute to the total electric conductivity and thus result in different vibration frequencies. In their turn, the vibration frequencies reflect the interaction between the lattice and charge carriers. Although the lattice dynamics of A_2MX_4 family representatives was extensively studied [6,7]. Results obtained for Tl_2HgI_4, Tl_2CdI_4 are extremely scarce in the literature. Therefore Tl_2HgI_4 and Tl_2CdI_4 remains the only compound in the A_2MX_4 family for which complete information describing the material properties. Motivated by this situation, in our study we make use the mentioned above Tl_2HgI_4, Tl_2CdI_4 as a ternary derivative of the "classic" solid electrolyte, Tl, is an interesting model material to study by combining theoretical and experimental techniques from methodological considerations as well. Thallium batteries or microbatteries can be attractive as power sources for some classes of portable electronic devices operating near room temperature, which may serve as electrolytes in such batteries. Thallium ion conducting composites are interesting materials specially to develop solid-state electrochemical devices such as batteries, fuel cells, sensors, supercapacitors, electrochromic display devices, etc. Therefore, in the present study, the investigations are focused on the following alternative novel composite thallium fast ion conductors. In the [Tl_2MI_4] (where M = Hg) systems, [Tl_2HgI_4] are pure materials, In [$0.75Tl_2HgI_4$:0.25AgI] composite system [Tl_2HgI_4] considered as host doped with [0.25AgI] as the dopant. The composition of the host and dopant was kept constant in all the composite samples of [$0.75Tl_2HgI_4$:0.25AgI] mixed composite solid. It has been observed that a much better solid electrolyte composite system can be prepared with the host [Tl_2HgI_4] [8].

2. RESEARCH METHODOLOGY

2.1. Materials

The following materials were used as received; AgI, HgI_2 and TlI and obtained from CDH (India), HIMEDIA, with stated purity 99%, 99% and 99% respectively.

2.2. Preparation of [$0.75Tl_2HgI_4$:0.25AgI] composite fast ion conductor

2.2.1. Preparation of pure sample [Tl_2HgI_4].

Thallium tetra mercuro iodate [Tl_2HgI_4] was prepared from TlI and HgI_2 obtained from HIMEDIA and CDH (India), with stated purity 99.99% of 99% respectively by the solid state reactions method. TlI and HgI_2 were mixed in the requisite composition (according to eqn no.1)

$$2TlI + HgI_2 \rightarrow Tl_2HgI_4 \qquad (1)$$

in an Agate mortar and were heated at 116.5°C (388K) for 2.5 days (63 hrs) in an air oven (CE 0434 NSW- 144), in silica crucible with intermittent grinding. The rate of heating was initially kept at 50°C per hours for 12 hours. the light orange color compound changed to dark orange color. Tl_2HgI_4 is dark orange color above 110°C -115°C. The color transition from orange to red occurred at 116.5°C and decomposes above 130°C. The resulting material at room temperature was used for further studies [9].

2.2.2. Preparation of doped sample [$0.75Tl_2HgI_4$:0.25AgI] Ag^+-ion doped composite host fast ion conductors were prepared by adding 0.25 mol. wt. % AgI (from CDH 98%) to the pure Tl_2HgI_4 compound. [0.75 Tl_2HgI_4: 0.25AgI] solid solutions was prepared by mixing 0.25 mol. wt. % AgI in pure 0.75 mol. wt. % Tl_2HgI_4, in an Agate mortar at room temperature with intermittent grinding 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 hours at 100ºC. The resulting material at room temperature was used for further studies [10].

2.3. Characterization of [$0.75Tl_2HgI_4$:0.25AgI] composite fast ion conductor

The novel composite fast ion conductors [$0.75Tl_2HgI_4$: 0.25AgI], were prepared and investigated by X-ray powder diffraction, FTIR spectral analysis. Further studies was carried out on these samples by thermal analysis i.e. Differential thermal analysis (DTA), Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA) to confirmed the formation of all the fast ion conductors.

2.3.1. X-ray powder diffraction studies

X-ray powder diffraction were performed for the doped [$0.75Tl_2HgI_4$:0.25AgI] composite, after the reaction was completed using Rigaku Rad B powder diffractometer and a Bruker AXS D8 Advance diffractometer with a K-beta filter with Cu-Kα (λ=1.54060Å) radiation at room temperature. The angle range for measurement was from 10-70° and the scanning speed was 1° min^{-1}. The x-ray diffractogram values of the samples [$0.75Tl_2HgI_4$:0.25AgI] correspond to standard values of [Tl_2HgI_4] from the literature confirms the formation of compounds.

2.3.2. FTIR measurements

The FTIR spectrum was recorder for the fast ionic composite [$0.75Tl_2HgI_4$:0.25AgI] composite system in the mid-infrared range 400-4000 cm^{-1} (25-25 μm) at room temperature using a INTERSPEC-2020, FTIR spectrophotometer measured in KBr. Mid–infrared spectra used to study the fundamental vibrations and associated rotational-vibrational structures.

2.3.3. Thermal analysis

Differential thermal analysis (DTA), was carried out on [$0.75Tl_2HgI_4$:0.25AgI] mixed composite samples, using DTG-60H thermal analyser in nitrogen atmosphere with flow rate of 30 mL min^{-1} and heating rate 25°C min^{-1} in the temperature range 20-500°C. The reference used was 10 mg alumina powder.

Differential scanning calorimetry (DSC) and Thermo-gravimetric analysis (TGA) doped [$0.75Tl_2HgI_4$:0.25AgI] composite, was done by Schimadzu SC-TA 60 Thermal analyzer. Approximately weighed 20 mg of the dry powder sample was placed in the alumina cell. The experiments were run in nitrogen atmosphere. The flow rate of N_2 was maintained at 30 mL min^{-1} with a heating rate 10°C min^{-1} in the temperature range 20-500°C. The reference used was 10 mg alumina powder.

3. RESULTS AND DISCUSSION

3.1. FTIR analysis

3.1.1. FAR-IR discussion in [0.75Tl_2HgI_4:0.25AgI]

The IR spectrum of the vapour over solid [0.75Tl_2HgI_4:0.25AgI] was studied in the 30-700 cm^{-1} region at room temperature are shown in figure 1.

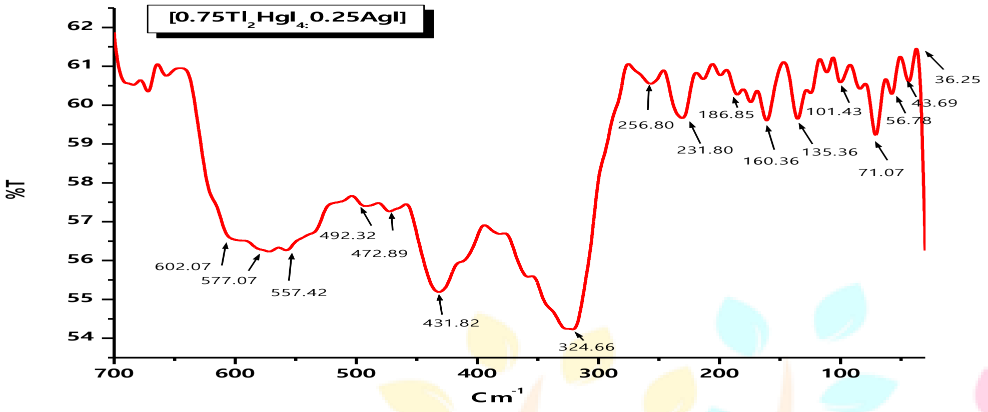

Fig. 1. FAR-IR spectrum for [0.75Tl_2HgI_4:0.25AgI] fast ionic conductors

The IR spectrum of [0.75Tl_2HgI_4:0.25AgI] solid at room temperature showed two distinct absorption bands. The absorption around 101.43 cm^{-1} shows typical PR band structure of a diatomic molecule and is assigned to the fundamental Tl-I stretching frequency of the monomer. For the band origin at 71.07 cm^{-1} can be attributed to the $(TlI)_2$ dimeric molecule [11]. IR- measurements shows that a sifnificant amount of dimeric molecules is present in the vapour over TlI (I) at the temperature of the present experiments.

Ionic model calculations based on Rittners electrostatic model [12] predicted a square planar structure (D_{2h} symmetry) as the most stable arrangement for $(TlI)_2$. This structure allows three of the total six normal modes of vibration to be IR active. The B_{2u} and B_{3v} stretching modes involve high frequency in plane motion and the B_{1u} bending mode lower frequency out of plane motion. On the basis of these consideration the peak at 71.07 cm^{-1} is due to the stretching motion and the peak at ca 43.69 cm^{-1} to the bending motion of the $(TlI)_2$ molecule. There is however, no clear argument for the assignment of the observed stretching band to the B_{2u} and B_{3v} mode [12].

The spectrum of [0.75Tl_2HgI_4:0.25AgI] solid consisted of two strong absorption bands are listed in Table 1.

Table 1. FAR-IR bands in [0.75Tl_2HgI_4:0.25AgI] and assignments

[0.75Tl_2HgI_4:0.25AgI]			
Compound	**Value (cm^{-1})**	**Assignment**	**nature**
TlI	101.43	ω_e	TlI stretch of the monomer
	71.07	B_{2u} and B_{3v}	stretching motion of $(TlI)_2$ dimeric molecule
	43.69	B_{1u}	bending motion of the $(TlI)_2$ molecule
HgI_2	231.80	υ_3	symmetric Hg-I stretch of the dimer
	135.36	υ_2	I- Hg-I blend
Tl_2HgI_4	324.66	___	Dissociation of Tl_2HgI_4 molecule
	431.82	___	TlI - stretch
	602.07	___	$(HgI_2)_2$ -stretch
AgI Tl2HgI4-AgI	36.25 160.36 186.85 256.80	----- ___ ___ ___	Ag-I stretch of the molecule formation of the [0.75Tl_2HgI_4:0.25AgI] band formation of the [0.75Tl_2HgI_4:0.25AgI] band formation of the [0.75Tl_2HgI_4:0.25AgI] band

It is concluded that both peaks are due to HgI_2 molecular species. The linear structure of the HgI_2 molecule ($D_{\infty h}$ symmetry), as established by electron diffraction measurements [13], allow two of the total of three fundamental frequencies to be infrared active and consequently, the assignment is straight forward, the symmetric Hg-I stretching frequency υ_3 at 231.80 cm^{-1} and I-Hg-I blending frequency υ_2 at 135.36 cm^{-1}. The additional sharp lines in the spectrum are due to the rotational spectrum of H_2O impurities. The IR spectrum of [Tl_2HgI_4] solid composite, also shows three distinct absorption bands at 324.66, 431.82 and 602.07 cm^{-1}. On further increasing the wavenumber the position of the absorption bands are in excellent agreement with those of the [Tl_2HgI_4] molecules [14] above 400 cm^{-1}, the intensity of the peaks decreases, owing to condensation of HgI_2 in the colder parts of the optical cell, these bands corresponds to those TlI and indicate the presence of TlI and $(HgI_2)_2$ molecules.

In addition, numerous sharp absorption bands of the rotational spectrum of [$0.75Tl_2HgI_4$:0.25AgI] were presents, which were at 160.36, 186.85 and 256.80 cm^{-1}. These absorption bands are in excellent agreement with those of the [$0.75Tl_2HgI_4$:0.25AgI].

Additional peaks that might indicate the presence of Agl species is at 36.25 cm^{-1} have been observed shows Ag-I stretch of the molecule.

The present results shows that the successive release of HgI_2 and TlI/$(HgI_2)_2$ vapour species occurs during heating, pointing towards dissociation of [$0.75Tl_2HgI_4$:0.25AgI] molecules under the conditions of the experiments.

3.1.2. FTIR discussion in [$0.75Tl_2HgI_4$:0.25AgI]

Assuming the β phase is tetragonal, the number and symmetry of normal modes can be determined. Group theory analysis finds the following number and symmetries for the 10 optical modes in Tl_2HgI_4 materials.

Tl_2HgI_4: 3A+ 5B+ 5E

The Infrared and Raman selection rules give the following allowed mode symmetries.

	Infrared	Raman
Tl_2HgI_4:	5B+ 5E (10 Bands)	3A+ 5B+ 5E (13 Bands)

Using projection operators, we find that the B symmetry mode involve motion of the cation along the tetragonal c axis (z), and the E modes involve motion of the cations, along the a and b axes (x or y), B mode couple to electric fields along the z axis and E modes couple to fields in the xy plane, so that FTIR spectra would determine the mode-symmetry assignments uniquely [14].

Factor group analysis of [$0.75Tl_2HgI_4$:0.25AgI]

The irreducible representation for the 10 IR allowed modes are listed in Table 2.

Table 2. [$0.75Tl_2HgI_4$:0.25AgI] fast ionic conductors room temperature peaks and assignments.

[$0.75Tl_2HgI_4$:0.25AgI] (cm^{-1})	**Symmetry**	**Assignments**
2924.00	A	$(HgI_4)^{-2}$ symmetric stretch respectively
1100.02		Tl-I and Hg-I symmetric stretch
1628.02	A	$(HgI_4)^{-2}$ deformation, M-I stretching
1062.62	?	Deformation
1382.52	B	
490.51	E	weak in xx, zz and xz polarization

The unit cell group analysis of [$0.75Tl_2HgI_4$:0.25AgI is also shown in Table 2, with the D_{2d} - S_4 correlation being A_1 and A_2 to A, B and B_2 to B and E to E. Figure 2 shows FTIR spectrum for [$0.75Tl_2HgI_4$:0.25AgI] fast ionic conductors.

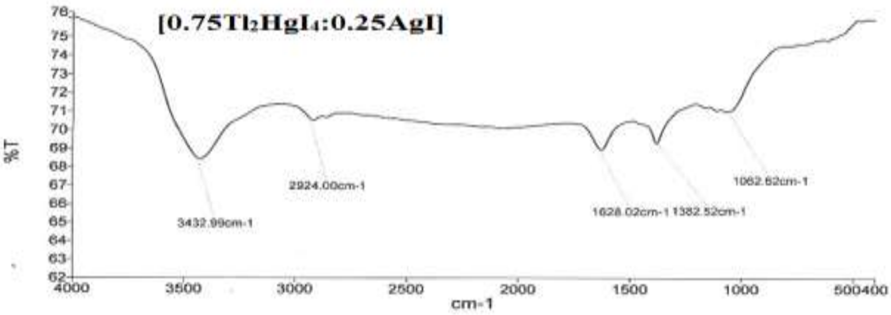

Fig. 1. FTIR spectrum for [$0.75Tl_2HgI_4$:0.25AgI] fast ionic conductors.

In the IR spectra of [0.75Tl_2HgI_4:0.25AgIthe 2924.00 cm^{-1} peak in Table 2 is strongest in xx, yy and zz direction making it an A. The peak at 1628.02 cm^{-1} and 1328.52 cm^{-1} are strongest in the xx and yy polarizations and therefore belongs to A or B classes. The only noticeable peaks in xz polarization and E symmetry is at 490.51 cm^{-1} and the 1062.62 cm^{-1} shoulder appears to be weak in xx, zz and xz polarization making it likely that at least some of the peaks causing this feature would be maximized in the xy polarization and therefore of B symmetry in [0.75Tl_2HgI_4:0.25AgI.

Unassigned and a speculatively assignment for the 1062.62 cm^{-1} feature. HgI_2 contamination peaks also found in at 1102.02, cm^{-1} for [0.75Tl_2HgI_4:0.25AgI. Peaks of B and E symmetry are allowed in the IR spectra and should be strong peaks. The occurrence of 490.51 cm^{-1} for [0.75Tl_2HgI_4:0.25AgI in the IR strengthens the E assignment for the peak at 490.51 cm^{-1}. (Table 2).

3.1.3. FTIR Comparison in [0.75Tl_2HgI_4:0.25AgI]

From Table 3, the vibrational modes can be assigned by considering [0.75Tl_2HgI_4:0.25AgI] as consisting of the vibrational modes of TlI and $(HgI_4)^{2-}$ species. In fact, as shown in Figure. 2, almost all the bands due to TlI and $(HgI_4)^{2-}$ are seen in the pure Tl_2HgI_4 composites. The band at 1628.02 cm^{-1} can be assigned to the symmetric stretching "A" mode of $(HgI_4)^{2-}$ species and this band is the strongest band at room temperature [14]. This assignment is in good agreement with the other $(HgI_4)^{2-}$ tetrahedral compounds [15]. The 1000-1500 cm^{-1} region consists of bands at the positions 1382.52 cm^{-1} and 1062.62 cm^{-1} at room temperature and at low temperature, these bands are expected to split.

Table 3. **[0.75Tl_2HgI_4:0.25AgI] fast ion conductors, room temperature peaks and assignment.**

FTIR transmission peaks (cm^{-1})		
[0.75Tl_2HgI_4:0.25AgI] (cm^{-1})	**Symmetry**	**Assignment**
2924.00	A	HgI_4^{2-} Symmetric stretch
1628.02	A	HgI_4^{2-} deformation, M-I stretching
1062.62	?	deformation
1382.52	B	Tl-I , Ag-I symmetric stretch
490.51	B	Tl^+attempt frequency

It is known from the IR spectra of [0.75Tl_2HgI_4:0.25AgI-ions conductors that this region consists of mostly of Tl-I [16] stretching modes. Hence, in all [0.75Tl_2HgI_4:0.25AgI composite samples, also the bands in this region can be assigned to symmetric stretching modes of Tl -I. Below 700 cm^{-1}, there are five sharp bands at 490.51 in pure [0.75Tl_2HgI_4:0.25AgI], it is known from factor group analysis studies that the bands in this region are due to deformation type metal-iodine vibrations. On comparison with $(HgI_4)^{2-}$ species vibrations, the bands at 490.51 cm^{-1} in pure Tl_2HgI_4, can be assigned to Hg-I deformation type bands. The band at 490.51 cm^{-1} in pure [0.75Tl_2HgI_4:0.25AgI], is attributed to the E symmetry of Tl^+ translational mode and is the characteristic attempt frequency of Tl^+ ion arising from the diffusive behaviour to oscillatory behaviour. This assignment is well explained by Noorussaba [10] by referring to the negative pressure dependence and also using theoretical calculations. The value assigned to the attempt frequencies in [0.75Tl_2HgI_4:0.25AgI] is similar to cation transition modes [10]. Another possibility is that motion of very large amplitude (diffusive like) is able to create configurational disorder which allows all IR modes [17].

Inspection of Table 3 and Figure. 2, shows that IR spectra of [0.75Tl_2HgI_4:0.25AgI] conductors exhibit the strongest feature at ca 1628.02 cm^{-1}, while the infrared activity below 900 cm^{-1} is weak. On the basis of the above discussion, these results strongly suggest that the existence of $(HgI_4)_2^{2-}/(Tl^+)$ tetrahedral in Tl_2HgI_4 ionic conductors should be excluded at least in concentration detectable by infrared spectroscopy [9].

3.2. X-ray diffraction.

Figure 3 shows the typical XRD diffractogram obtained for [0.75Tl_2HgI_4:0.25AgI] composite sample. In γ-AgI, iodide ions are known to form a mixture of close packed structures, at temperatures well below 420K (140°C) consisting of fcc and hcp structures which are commonly designated as γ-AgI and β-AgI respectively. However, for pedagogical reasons only γ-AgI is considered at room temperature. According, to the xrd data obtained during the present study have been compared with that of γ-AgI. It is clear from table 4 that all the xrd data contain 2θ values different from that of the starting materials. Also it is obvious from table 4, that the above compositions are polycrystalline in nature consisting of a multiphase mixture of AgI phases. These phases have been identifies as follows.

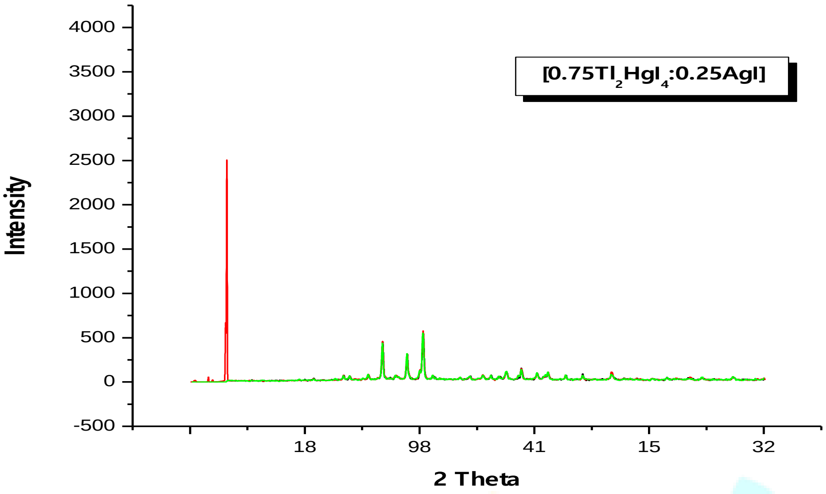

Fig. 2. X-ray diffractogram for [0.75Tl_2HgI_4:0.25AgI] fast ionic conductors.

In case of [0.75Tl_2HgI_4:0.25AgI]-doped composites system, the peaks at 18.84°, 24.03°, 31.81° and 42.19° can be attributed to the presence of γ-AgI, whereas peaks observed at 52.56° and 57.75° have been compared with that of AgITl_2HgI_4. In addition, γ- HgI_2 lines have also been observed at 65.53° and 75.91°. The peaks at 65.53° can be attributed to the presence of Tl-Tl_2HgI_4, whereas peaks observed at 18.39°, 37.00°, 42.19° and 47.37 for Tl_2HgI_4. Effectively the composition of [0.75Tl_2HgI_4:0.25AgI]-doped composites system consists of γ-AgI, AgITl_2HgI_4, γ-HgI_2, Tl-Tl_2HgI_4, and pure Tl_2HgI_4 phases [18].

Table 4. X-ray diffractogram peaks and assignment for [0.75Tl_2HgI_4:0.25AgI] fast ion conductors.

[0.75Tl_2HgI_4:0.25AgI]	
2θ	**Peak Assignment**
28.423° 41.02° 49.687°	γ-AgI
21.366° 24.711° 38.731	AgITl_2HgI_4
40.369° 43.931 ° 65.547°	γ-HgI_2
35.781° 37.929 ° 69.278°	Tl-Tl_2HgI_4
29.725° 45.249°	Tl_2HgI_4

3.3. Thermal analysis

3.3.1. Differential scanning calorimetry (DSC)

Figure 4 depicts the DSC thermograms recorded for the sixteen different samples in the mixed fast ionic composite systems [0.75Tl_2HgI_4:0.25AgI].

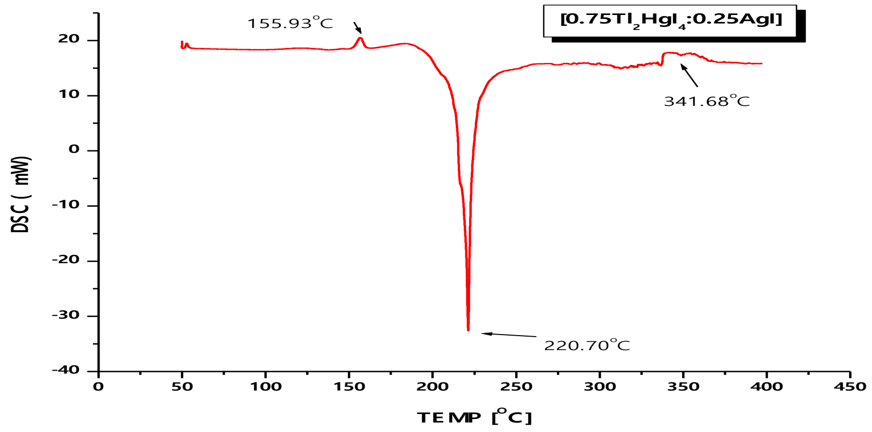

Fig. 3 DSC for [$0.75Tl_2HgI_4$:0.25AgI] fast ionic conductors

It is clear from figure 4 that exothermic peaks are observed for [$0.75Tl_2HgI_4$:0.25AgI] composite, exhibits three peaks at 145.19K, 207.45K and 373.83K, that can be assigned to the partial decomposition of ε-Tl_2HgI_4 in TlI, HgI_2 and β-Tl_2HgI_4 [18], γ-α phase transition of AgI (at 383.46K), tends to notify the presence of AgI [19]. On the other hand the endothermic peak that appears at 213.91K in the case of [$0.75Tl_2HgI_4$:0.25AgI] composition is found to compare well with the observed melting temperature of AgITl_2HgI_4 composite [20].

A careful analysis of the xrd patterns in figure 3 also reveals the formation of various other phases apart from Tl_2HgI_4, AgI. Therefore, the DSC results have indicated the presence of major content phases in [$0.75Tl_2HgI_4$:0.25AgI] composite. On the other hand the exothermic peaks obtained in dsc curves of [$0.75Tl_2HgI_4$:0.25AgI] composites are at clearly, the above mentioned exothermic peaks are comparable to that of β-α phase transition of pure AgI (≈383.46K). The DSC results therefore suggest that the combination of the two starting materials namely (AgI) and Tl_2HgI_4 is complete for a composition around 50 mol. % Tl_2HgI_4 resulting in the formation of new substances which are probably Ag^+ ion conductors having very small traces of AgI [21].

3.3.2. Differantial thermal analysis (DTA)

DTA curves for **[**$0.75Tl_2HgI_4$:0.25AgI] samples is shown in Figure 5. On comparing these curves, we note the following important features.

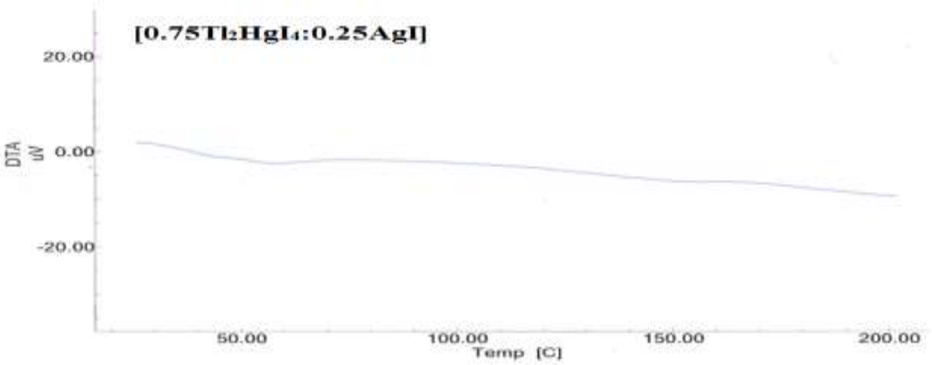

Fig. 5 DTA for [$0.75Tl_2HgI_4$:0.25AgI] fast ionic conductors

A well defined intense peak prepared at ~ 313-353K in all curves. This peak corresponds to a β-α- like transition of the host [Tl_2HgI_4]. The peak strength has increased on further doping of 0.25 mol. wt. % of (AgI). This is indicative of partial and complete stabilization of the high conducting α- like phase of the host [22] in the samples respectively. These observations are exactly correlate our DSC results. A second intense and well defined peak appeared at ~ 433-473K in the DTA curves of **[**$0.75Tl_2HgI_4$:0.25AgI] system. This peak obviously corresponds to the β – α like transition of -AgI solid solutions, while in the DTA curves of Tl_2HgI_4 this peak occurs at around ~ 513-553K. This β – α phase transition peak becomes broad with (AgI) content, this is due to the form of crystalline phase within space charge layer that is expected to form between (AgI) and [Tl_2HgI_4] [23]. It has been observed from the DTA curves of **[**$0.75Tl_2HgI_4$:0.25AgI], that an additional peak is obtained after the β – α phase transition peak with the addition of (AgI) and its intensity increase with the mole fraction of (AgI). This peak attributed to interface interactions between (AgI) and [**[**Tl_2HgI_4]. The above results clearly reveal the partial presence of fast ionic phase in all the samples.

3.3.3. Thermo-gravimetric analysis (TGA)

TGA curves for AgI-doped host samples, it shifts to a lower temperature because of the interaction between dopant AgI and host [Tl_2HgI_4]. In the TGA curves of [$0.75Tl_2HgI_4$:0.25AgI] [figure. 5], from room temperature up to about 400°C.

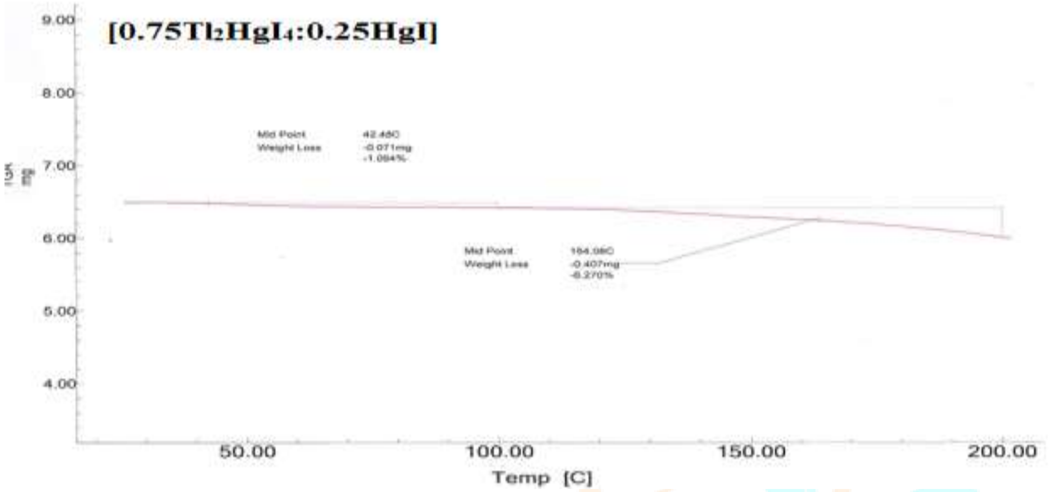

Fig. 6. TGA for [$0.75Tl_2HgI_4$:0.25AgI] fast ionic conductors

One distinct peak of TGA are obtained for the [$0.75Tl_2HgI_4$:0.25AgI], in the temperature range 150–200°C with corresponding mass loss for pure samples, and for AgI-doped host samples [24] are shown. These data corroborate the observations of TGA studies.

4. CONCLUSION

Thus, novel composite fast ion conductors [$0.75Tl_2HgI_4$:0.25AgI], composite fast ion conductors were prepared and investigated also by X-ray powder diffraction, FTIR spectral analysis, Differential thermal analysis (DTA), Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA) studies to confirmed the formation of all the fast ion conductors.

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