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Experimental investigation on spectral properties of Tl_2HgI_4 fast ion conductors

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ABSTRACT

The new compound Tl_2HgI_4 has been prepared and characterized by IR spectroscopy, powder X-ray diffraction, thermal analysis, far ir spectroscopy. The compounds Tl_2HgI_4 for which phase diagrams are available in the literature were characterized by IR spectroscopy and their identities were confirmed by far-ir spectroscopy, X-ray powder diffraction and thermal analysis. Tl_2HgI_4, 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 Cu^+ and Ag^+. The crystal structure of the low-temperature phase of Tl_2HgI_4 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**. Fast Ion Conductor; **B**. FAR- IR; **C**. Fourier transmission infrared spectra (FTIR); **D**. X-Ray powder diffraction;**E**.Thermalanalysis.

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1. INTRODUCTION

A_2BX_4 compounds (where A = Tl, Ag, Cu, B = Cd, Hg, Zn, X = Cl, Br, I 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 [1]. A_2BX_4-family compounds containing isolated tetrahedral BX_4^{2-} ions form orthorhombic β -K_2SO_4 (Pnma, Z = 4) or monoclinic Sr2GeS4 (*P*21/*m*, *Z* = 2) structures. Many compounds with the β -K2SO4 (*Pnma*, *Z* = 4) structure undergo phase transitions to incommensurate (IC) phases at low temperatures [2].

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_2BX_4 family representatives was extensively studied [3,4]. Results obtained for Tl_2CdI_4 [5], Tl_2ZnCl_4 [2], Cs2CdBr4, Cs2HgBr4 [6], Cs2CdI4 [7] and Cs2HgCl4 [8] are extremely scarce in the literature. Therefore 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, 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_2MI_4] are pure materials, It has been observed that a much better solid electrolyte composite system can be prepared as [Tl_2HgI_4] [9].

2. RESEARCH METHODOLOGY

2.1. Materials

The following materials were used as received; TlI and HgI_2 obtained from HIMEDIA and CDH (India), with stated purity 99.99% of 99% respectively.

2.2. Preparation of composite fast ion conductors [Tl_2HgI_4]

Thallium tetra iodo cadmiate [Tl_2HgI_4] was prepared from TlI and HgI_2 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 silica crucible with intermittent grinding. The rate of heating was initially kept at 50°C per hours for 12 hours. After cooling, 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 [10].

2.3. Characterization of composite fast ion conductors [Tl_2HgI_4]

The novel fast ion conductors [Tl_2HgI_4], were prepared and investigated by X-ray powder diffraction, Fourier Transmission (far-ir and mid-ir region) spectral analysis, 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 systems [Tl_2HgI_4], 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 [Tl_2HgI_4] correspond to standard values of [Tl_2HgI_4] from the literature confirms the formation of compounds.

2.3.2. Far-IR spectral analysis

The Far-IR spectrum was recorder for fast ionic conductor [Tl_2HgI_4]] in the far-infrared range 30-700 cm^{-1} at room temperature using a Perkin Elmer/FTIR Spectrometer measured in KBr. The far-infrared spectral region is the range of wavenumbers where one finds many of the large-amplitude anharmonic vibrations. These include both the symmetric and asymmetric internal torsional modes of many small organic and organometallic molecules.

2.3.3. FTIR measurements

The FTIR spectrum was recorder for the fast ionic conductor [Tl_2HgI_4] 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.

2.3.4. Thermal analysis

Differential thermal analysis (DTA), Differential scanning calorimetry (DSC) and Thermo-gravimetric analysis (TGA) was carried out on [Tl_2HgI_4] 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.

3. RESULTS AND DISCUSSION

3.1. FTIR analysis

3.1.1. FAR-IR discussion in [Tl_2HgI_4]

The IR spectrum of the vapour over solid Tl_2HgI_4 was studied in the 30-700 cm^{-1} region at room temperature are shown in figure 1. The infrared spectrum of Tl_2HgI_4 solid at room temp showed two distinct absorption bands. The absorption around 135.70 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 97.35 cm^{-1} can be attributed to the $(TlI)_2$ dimeric molecule [11]. IR- measurements shows that a significant 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 97.35 cm^{-1} is due to the stretching motion and the peak at ca 60.41 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].

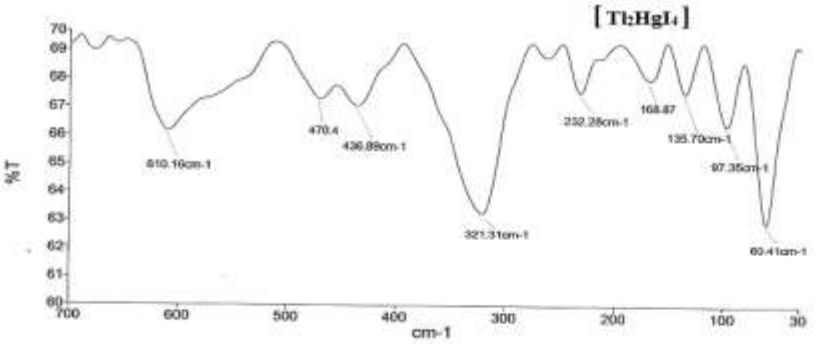

Fig. 1. FAR-IR spectrum for [Tl_2HgI_4] fast ionic conductors.

The spectrum of Tl_2HgI_4 solid consisted of two strong absorption bands are listed in table 1.

Table 1. FAR-IR bands in Tl_2HgI_4 and assignments

[Tl_2HgI_4]			
Compound	**value(cm^{-1})**	**Assignment**	**nature**
TlI	135.70	ω_e	TlI stretch of the monomer
	97.35	B_{2u} and B_{3v}	stretching motion of $(TlI)_2$ dimeric molecule
	60.41	B_{1u}	bending motion of the $(TlI)_2$ molecule
HgI2	232.28	υ_3	symmetric Hg-I stretch
	168.87	υ_2	I- Hg-I blend
Tl_2HgI_4	321.31	___	Dissociation of Tl_2HgI_4 molecule
	436.89	___	TlI - stretch
	470.4	___	$(HgI_2)_2$ -stretch
Tl-Hg-I	610.16	___	Tl-Hg-I species

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 [13-15], 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 ν_3 at 232.28 cm^{-1} and I-Hg-I blending frequency ν_2 at 168.87 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, also shows three distinct absorption bands at 321.31, 436.89 and 470.4 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 [16] 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 H_2O were presents, which were partially removed by spectral subtraction. The present results show that the successive release of HgI_2 and $TlI/(HgI_2)_2$ vapour species occurs during heating, pointing towards dissociation of Tl_2HgI_4 molecules under the conditions of the experiments.

Additional peak 610.16 cm^{-1} that might indicate the presence of Tl-Hg-I species have been observed.

3.1.2. FTIR discussion in Tl_2HgI_4

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 [17-20].

3.1.3. Factor group analysis of Tl_2HgI_4

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

Table 2. [Tl_2HgI_4] fast ionic conductors room temperature peaks and assignments.

Tl_2HgI_4 (cm^{-1})		**Assignments**
2923.88	A	$(HgI_4)^{-2}$ symmetric stretch respectively
1505.06		Tl-I and Hg-I symmetric stretch
1623.81	A	$(HgI_4)^{-2}$ deformation, M-I stretching
1000	?	Deformation
1735.6	B	weak in xx, zz and xz polarization

The unit cell group analysis of Tl_2HgI_4 is also shown in Table 2 [19], 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 [Tl_2HgI_4] fast ionic conductors. In the IR spectra of [$Tl_2HgI_{4\ 4}$] the 2923.88 cm^{-1} peak in Table 2 is strongest in xx, yy and zz direction making it an A. The peak at 1623.81 cm^{-1} and 1735.6 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 1000 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 [Tl_2HgI_4] (Table 2).

3.1.4. FTIR Comparison in Tl_2HgI_4

From Table 3, the vibrational modes can be assigned by considering Tl_2HgI_4 as consisting of the vibrational modes of TlI and $(HgI_4)^{2-}$ species.

Table 3. [Tl_2HgI_4] fast ionic conductors room temperature peaks and assignments.

FTIR transmission peaks (cm^{-1})		
[Tl_2CdI_4]	**Symmetry**	**Assignment**
2923.88	A	HgI_4^{2-} Symmetric stretch
1623.81	A	HgI_4^{2-} deformation, M-I stretching
1000	?	deformation
1735.6	B	Tl-I , Ag-I symmetric stretch

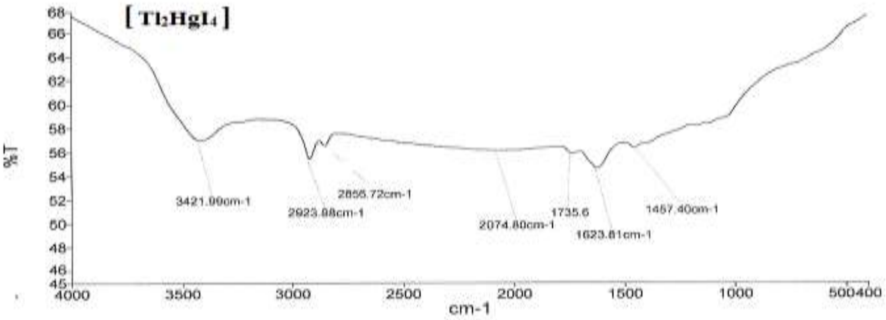

Fig. 2. FTIR spectrum for [Tl_2HgI_4] fast ionic conductors.

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 1623.81 can be assigned to the symmetric stretching "A" mode of $(HgI_4)^{2-}$ species and this band is the strongest band at room temperature [21]. This assignment is in good agreement with the other $(HgI_4)^{2-}$ tetrahedral compounds [22]. The 1000-1500 cm^{-1} region consists of two bands at the positions 1457.40 cm^{-1} and 1623.81 cm^{-1} at room temperature and at low temperature, these bands are expected to split. It is known from the IR spectra of Tl_2HgI_4 -ions conductors that this region consists of mostly of Tl-I [23] stretching modes. Hence, in all [Tl_2HgI_4] composite samples, also the bands in this region can be assigned to symmetric stretching modes of Tl -I.

This assignment is well explained by Shriver [20] by referring to the negative pressure dependence and also using theoretical calculations. The value assigned to the attempt frequencies in Tl_2HgI_4 is similar to cation transition modes [21, 22]. Another possibility is that motion of very large amplitude (diffusive like) is able to create configurational disorder which allows all IR modes [24].

Inspection of Table 3 and Figure. 2, shows that IR spectra of [Tl_2HgI_4] conductors exhibit the strongest feature at ca 1623.81 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 [21].

3.2. X-ray diffraction.

Room temp XRD patterns obtained for [Tl_2HgI_4] sample are shown in figure 3.

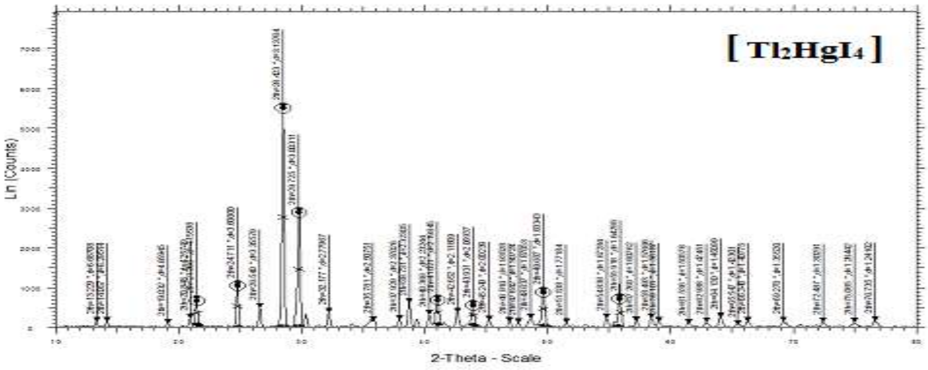

Fig. 3. X-ray diffractogram for [Tl_2HgI_4] fast ionic conductors.

It is interesting to note from figure 3 that three prominent diffraction peaks, which appears at 2θ = 28.423° 41.02°, and 49.687° respectively, in the case of [Tl_2HgI_4] may be attributed to the presence of TlI. The occurrence of XRD peaks around 2θ = 21.366°, 24.711° and 38.731° reveals the presence of HgI_2 in the samples [25]. Further the appearance of peak around 2θ = 40.369° 43.931 °, and 65.547° indicates the presence of Tl in [Tl_2HgI_4] specimen. The occurrence of XRD peaks at 2θ = 35.781° 37.929 °, and 69.278° indicates the presence of Hg-I in the samples. It is also evident from fig 3 that the occurrence of peaks around 2θ = 29.725° and 45.249° shows the presence of $(HgI_4)_2$ also the appearance of peaks at 2θ = 30.5° and 32.177° reveals the presence of Tl-Hg-I.

A careful analysis of the XRD patterns obtained for [Tl_2HgI_4] has indicated the presence of several phases including TlI, Tl, HgI, $(HgI_4)_2$, Tl-Hg-I in the sample, the formation of two main products $(HgI_4)_2$ and Tl-Hg-I is apparently due to the possible solid state reactions occurring within the sample [25].

Table 4. X-ray diffractogram peaks and assignment for [Tl_2CdI_4] fast ion conductors.

[Tl_2HgI_4]	
2θ	**Peak Assignment**
28.423° 41.02° 49.687°	TlI
21.366° 24.711° 38.731	HgI_2
40.369° 43.931 ° 65.547°	Tl
35.781° 37.929 ° 69.278°	Hg-I
29.725° 45.249°	$(HgI_4)_2$
30.5° 32.177°	Tl-Hg-I

3.3. Thermal analysis

3.3.1. Differential scanning calorimetry (DSC)

Figure 4 depicts the DSC thermograms recorded for [Tl_2HgI_4] sample were found to exhibit certain interesting features.

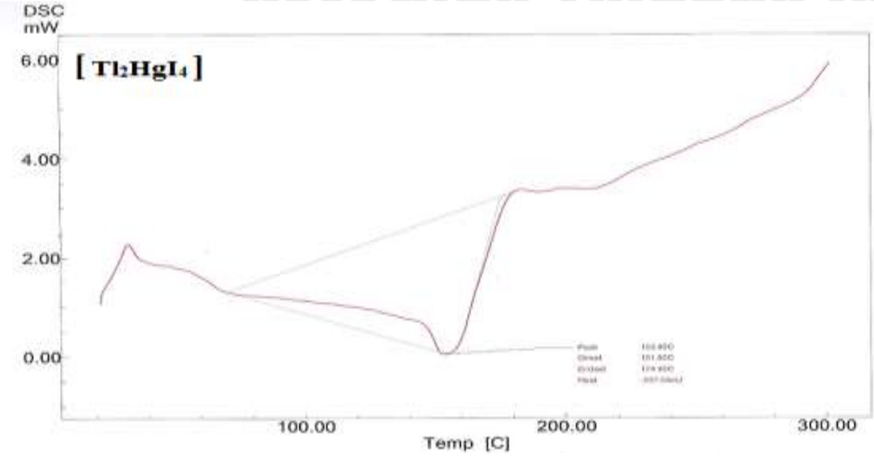

Fig. 4 DSC for [Tl_2HgI_4] fast ionic conductors.

DSC curves obtained for the [Tl_2HgI_4] exhibited endothermic peaks at 153.88-174.90°C. The above mentioned endothermic peaks are comparable to that of β→α phase transition of pure TlI (≈260°C). The DSC results therefore suggest that the combination of two starting materials namely TlI and HgI_2 is complete, resulting in the formation of new substances [Tl_2HgI_4] which are probably Tl^+ ion conductors having very small traces of TlI. The absence of TlI diffraction peaks in the typical XRD patterns for the [Tl_2HgI_4] may be attributed to the fact that TlI content in this particular compound is very insignificant and that it could not effect any appreciable change in the observed XRD patterns [26].

3.3.2. Differential thermal analysis (DTA)

DTA curves for pure Tl_2HgI_4 sample is shown in Figure 5.

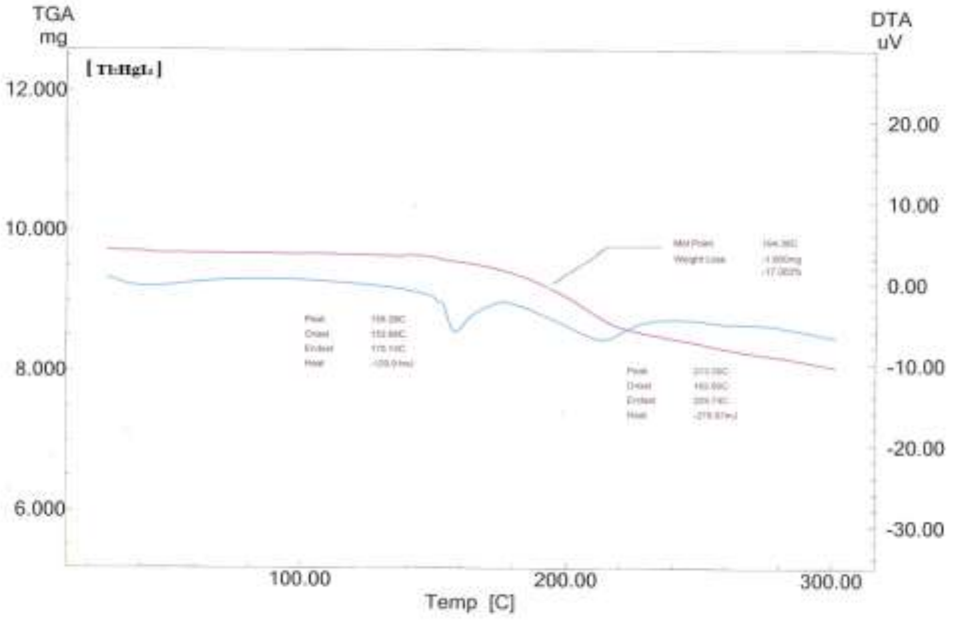

Fig. 5 DTA, TGA for [Tl_2HgI_4] fast ionic conductors

Endothermic peaks observed during the DTA analysis carried out for [Tl_2HgI_4] of the ternary system are shown in table 5. The transition temperature values, which are comparable to that of β→α phase transition temperature (158.28-170.13°C). of pure AgI (≈ 420K), tend to indicate the presence of TlI in these [Tl_2HgI_4] specimen as one of their constituents. This feature is found to be in good agreement with that obtained from the present DSC analysis in view of the fact that the latter confirmed the presence of TlI in [Tl_2HgI_4]. Thus the present structural and thermal features are found to be in conformity with each other [27].

3.3.3. Thermo-gravimetric analysis (TGA)

Figure 5 indicates that [Tl_2HgI_4] is hydrated by the absorption of the atmospheric water. In the TGA analysis of this hydrated sample, the decrease of about 4% in weight with the dehydration was observed at 194.36°C as shown in fig 4. The composition of hydrated compound kept under the ambient atmosphere was determined to be [Tl_2HgI_4].1.5 H_2O [27].

4. CONCLUSION

Thus, novel composite fast ion conductors [Tl_2HgI_4], 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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