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Synthesis and IR-vibrational modes of $[(1-x)\{0.75Tl_2CdI_4:0.25AgI\}:xCdI_2]$ nano composite fast ion conductor (where x = 0.2, 0.4, 0.6, 0.8 mol. wt. %)

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Abstract: The novel composite fast ion conducting system $[(1\text{-}x)\{0.75Tl_2CdI_4:0.25AgI\}:xCdI_2]$ (where x = 0.2, 0.4, 0.6, 0.8 mol. wt. %) were prepared and characterized by IR spectroscopy. The IR spectra of $[(1\text{-}x)\{0.75Tl_2CdI_4:0.25AgI\}:xCdI_2]$ (where x = 0.2, 0.4, 0.6, 0.8 mol. wt. %) have been measured in different scattering orientations covering the successive phase transitions down to 473K. $[(1\text{-}x)\{0.75Tl_2CdI_4:0.25AgI\}:xCdI_2]$ (where x = 0.2, 0.4, 0.6, 0.8 mol. wt. %). 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 $[(1\text{-}x)\{0.75Tl_2CdI_4:0.25AgI\}:xCdI_2]$ (where x = 0.2, 0.4, 0.6, 0.8 mol. wt. %)has been determined at 200°C. The Cd^+ 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: Synthesis, Fourier transmission infrared spectra (FTIR), phase transition, Doping, Fast ion conductor.

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1. Introduction

In the past few years the tetrahedrally coordinated A_2BX_4 halides gained much interest because of their sequential phase transition [1].

A_2BX_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 [2]. Among these substances, the tetrahedrally unit cell of Tl_2CdII_4 is known to be isomorphous with the structure of $\beta\text{-}K_2SO_4$ at room temperature [3]. Noorussaba at al. [4] from IR measurements on Tl_2CdII_4 has reported these successive vibrational transition between ---cm-1 and ---cm-1.The structural details of the lower phases are not known but I-nuclear quadrupole resonance [3] reveals that the crystal at 77K has higher symmetry than that of the $\beta\text{-}K_2SO_4$ structure. IR scattering does not provide direct information on the incommensurability but it is well known that near IR there is an activation of extra modes due to change in the optical selection rules [5]. In order to study the dynamics of the mobile ions directly, we have measured the IR spectra of CdI_2 doped $[0.75Tl_2MI_4:0.25AgI]$. Both of these materials are cation conductors with the Cd ions situated in iodine tetrahedral [6].

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, super capacitors, 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 $[(1\text{-}x)\{0.75Tl_2\ MI_4:0.25AgI\}:xCdI_2]$ (where M = Cd, x = 0.2, 0.4, 0.6, 0.8 mol. wt. %) systems, $[Tl_2MI_4]$ are pure materials, In $[(1\text{-}x)\{0.75Tl_2MI_4:0.25AgI\}:xCdI_2]$ composite system $[0.75Tl_2MI_4:0.25AgI]$ considered as host doped with $[xCdI_2]$ (where x = 0.2, 0.4, 0.6, 0.8 mol. wt. %) as the dopant. The composition of the host was kept constant in all the composite samples of $[(1\text{-}x)\{0.75Tl_2MI_4:0.25AgI\}:xCdI_2]$ (where x = 0.2, 0.4, 0.6, 0.8 mol. wt. %) mixed composite solid. It has been observed that a much better solid electrolyte composite system can be prepared with the host $[0.75Tl_2MI_4:0.25AgI]$ [7].

2. Experimental

2.1. Materials

The following materials were used as received; AgI, TlI and CdI_2 obtained from CDH, HIMEDIA and LOBA CHEMIE (India), with stated purity 99%, 99.99% of 99% respectively.

2.2. Preparation of [(1-x){$0.75Tl_2CdI_4$:0.25AgI}:xCdI_2] composite fast ion conductor

2.2.1. Preparation of pure sample [Tl_2CdI_4].

Thallium tetra iodo cadmiate [Tl_2CdI_4] was prepared from TlI and CdI_2 obtained from HIMEDIA and LOBA CHEMIE (India), with stated purity 99.99% of 99% respectively by the solid state reactions method. TlI and CdI_2 were mixed in the requisite composition (according to eqn no.1)

$$2TlI + CdI_2 \rightarrow Tl_2CdI_4 \qquad (1)$$

in an Agate mortar and were heated at 115°C (388K) for 5 days (120 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. After cooling, the dark lemony color compound changed to light yellow color. Tl_2CdI_4 is dark lemony color above 115°C. The color transition from light yellow to dark lemony occurred at 115°C and decomposes above 150°C. The resulting material at room temperature was used for further studies [8].

2.2.2. Preparation of host sample [$0.75Tl_2CdI_4$:0.25AgI]

Ag^+-ion doped composite host fast ion conductors were prepared by adding 0.25 mol. wt. % AgI to the pure Tl_2CdI_4 compound. [$0.75Tl_2CdI_4$:0.25AgI] solid solutions was prepared by mixing 0.25 mol. wt. % AgI in pure 0.75 mol. wt. % Tl_2CdI_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 [9, 10].

2.2.2. Preparation of doped host sample [(1-x){$0.75Tl_2CdI_4$:0.25AgI}:xCdI_2]

CdI_2 were mixing in various x mol. wt. % (where x = 0.2, 0.4, 0.6, 0.8 mol. wt.%) to the mixture of [$0.75Tl_2CdI_4$:0.25AgI] in (1-x) ratio to form [(1-x){$0.75Tl_2CdI_4$:0.25AgI}:xCdI_2] by solid state reaction in an Agate mortar and were heated at 100°C (373K) for 2 days (48 hrs) in silica crucible with intermittent grinding. The rate of heating was initially kept at 10°C per hours for 24 hours. After cooling, the dark yellow color compound changed to medium-light yellow color in vatious x (where x = 0.2, 0.4, 0.6, 0.8) mol. wt. % composites. After intermittent grinding, all the samples were prepared and will be used for further studies [9, 11].

2.3. Characterization of [(1-x){$0.75Tl_2CdI_4$:0.25AgI}:xCdI_2] composite fast ion conductor by FTIR measurements

2.3.1. FTIR measurements

The FTIR spectrum was recorder for the fast ionic composite [$0.75Tl_2CdI_4$:0.25AgI] and [(1-x){$0.75Tl_2CdI_4$:0.25AgI}:xCdI_2] 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.

3. Results and discussion

3.1. FTIR analysis

3.1.1. FAR-IR discussion in [$0.75Tl_2CdI_4$: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_2CdI_4 materials.

Tl_2CdI_4: 3A+ 5B+ 5E

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

	Infrared	Raman
Tl_2CdI_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 [12-15].

3.1.2. Factor group analysis of [$0.75Tl_2CdI_4$:0.25AgI]

The irreducible representation for the 10 IR allowed modes are listed in Table 1.

The unit cell group analysis of [$0.75Tl_2CdI_4$:0.25AgI] is also shown in Table 2 [14], 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 1 shows FTIR spectrum for [$0.75Tl_2CdI_4$:0.25AgI] fast ionic conductors. In the IR spectra of [$0.75Tl_2CdI_4$:0.25AgIthe 2926.59 cm^{-1} peak in Table 1 is strongest in xx, yy and zz direction making it an A. The peak at 1611.85 cm^{-1} and 1959.39 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 492.51 cm^{-1} and the 785.57 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_2CdI_4:0.25AgI.

Unassigned and a speculatively assignment for the 785.57 cm^{-1} feature. CdI_2 contamination peaks also found in at 1042.02, cm^{-1} for [0.75Tl_2CdI_4:0.25AgI. Peaks of B and E symmetry are allowed in the IR spectra and should be strong peaks. The occurrence of 492.51 cm^{-1} for [0.75Tl_2CdI_4:0.25AgI in the IR strengthens the E assignment for the peak at 492.51 cm^{-1}. (Table 1).

3.1.3. FTIR Comparison in [0.75Tl_2CdI_4:0.25AgI]

From Table 2, the vibrational modes can be assigned by considering [0.75Tl_2CdI_4:0.25AgI] as consisting of the vibrational modes of TlI and $(CdI_4)^{2-}$ species. In fact, as shown in Figure. 1, almost all the bands due to TlI and $(CdI_4)^{2-}$ are seen in the pure Tl_2CdI_4 composites. The band at 1611.85 cm^{-1} can be assigned to the symmetric stretching "A" mode of $(CdI_4)^{2-}$ species and this band is the strongest band at room temperature [12]. This assignment is in good agreement with the other $(CdI_4)^{2-}$ tetrahedral compounds [16]. The 1000-1500 cm^{-1} region consists of bands at the positions 1383.51 cm^{-1} and 1042.02 cm^{-1} at room temperature and at low temperature, these bands are expected to split.

It is known from the IR spectra of [0.75Tl_2CdI_4:0.25AgI-ions conductors that this region consists of mostly of Tl-I [17] stretching modes. Hence, in all [0.75Tl_2CdI_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 492.51 in pure [0.75Tl_2CdI_4:0.25AgI [24], it is known from factor group analysis studies [14] that the bands in this region are due to deformation type metal-iodine vibrations. On comparison with $(CdI_4)^{2-}$ species vibrations, the bands at 492.51 cm^{-1} in pure Tl_2CdI_4, can be assigned to Cd-I deformation type bands. The band at 492.51 cm^{-1} in pure [0.75Tl_2CdI_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 Shriver [15] by referring to the negative pressure dependence and also using theoretical calculations. The value assigned to the attempt frequencies in [0.75Tl_2CdI_4:0.25AgI] is similar to cation transition modes [15, 18]. Another possibility is that motion of very large amplitude (diffusive like) is able to create configurational disorder which allows all IR modes [19].

Inspection of Table 3 and Figure. 2, shows that IR spectra of [0.75Tl_2CdI_4:0.25AgI] conductors exhibit the strongest feature at ca 1611.85 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 $(CdI_4)_2^{2-}/(Tl^+)$ tetrahedral in Tl_2CdI_4 ionic conductors should be excluded at least in concentration detectable by infrared spectroscopy [18].

3.2.1. FTIR discussion in [(1-x){0.75Tl_2CdI_4:0.25AgI}:xCdI_2]

The unit cell group analysis of [(1-x){0.75Tl_2CdI_4:0.25AgI}:xCdI_2] shown in Fig.3, belongs to the D_{2d} point group. The irreducible representation for the 10 IR allowed modes are listed in Table 4 [14], with the D_{2d} - S_4 correlation being A_1 and A_2 to A, B_1 and B_2 to B and E to E. Figure 3 shows FTIR spectrum for [(1-x){0.75Tl_2CdI_4:0.25AgI}:xCdI_2] fast ionic conductors where x = 0.2,0.4, 0.6 and 0.8 mol. wt. %. In the IR spectra of [0.8{0.75Tl_2CdI_4:0.25AgI}:0.2CdI_2 the 2925.95 cm^{-1} peak in Table 4 is strongest in xx, yy and zz direction making it an A. The A peak shifted in x = 0.4, 0.6 and 0.8 at 2925.98, 2926.57, 2926.24 cm^{-1}. The peak at 1609.11 cm^{-1} and 1745.2 cm^{-1} are strongest in the xx and yy polarizations and therefore belongs to A or B classes. This peak shifted in x = 0.4, 0.6 and 0.8 mol. wt. % composites are 1612.48, 1745.2 cm^{-1} for x = 0.4, 1611.42 cm^{-1} for x = 0.6 and 1611.31, 1965.68 cm^{-1} for x = 0.8 mol. wt. %. The only noticeable peaks in xz polarization and E symmetry is at 502.22 cm^{-1} and the 759.50 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 x = 0.2 mol. wt. % . E symmetry peaks are found in x = 0.4, 0.6 and 0.8 are at 504.28 cm^{-1}, 474.09 cm^{-1} and 497.24 cm^{-1}. The shoulder peaks appears in x = 0.4, 0.6 and 0.8 are 790.51, 790.93 and 790.08 cm^{-1} respectively. This leaves three weak peaks at 550.56, 556.88 and 563.31 cm^{-1} in x = 0.2 which shifted in x = 0.4, is at 610.87, in x = 0.6 is at 700.18 and in x = 0.8 are at 531.10 cm^{-1}, 550.64, 600.56 cm^{-1} respectively.

Unassigned and a speculatively assignment for the 759.50 cm^{-1} feature. The band seen at 550.50 cm^{-1} arises from CdI_2 contamination. Also the 556.88 cm^{-1} peak may be spurious because it is not observed at low temperature or in room temperature spectra of polycrystalline samples. CdI_2 contamination peaks also seen in x = 0.4, 0.6 and 0.8 mol. wt. % at 610.87, 700.18 and 531.10, 550.64 cm^{-1} respectively. Peaks of B and E symmetry are allowed in the IR spectra and should be strong peaks, the occurrence of 502.22 cm^{-1} (x = 0.2) peak in the IR strengthens the E assignment for the peak at 502.22 cm^{-1}. For the x = 0.4, 0.6 and 0.8 mol. wt. % the peaks are at 504.28, 474.09 and 497.24 cm^{-1} respectively.

3.2.3. FTIR Comparison in $[(1\text{-}x)\{0.75Tl_2CdI_4{:}0.25AgI\}{:}xCdI_2]$

The IR active peaks with symmetry assignments are listed in Table 5. For $[(1\text{-}x)\{0.75Tl_2CdI_4{:}0.25AgI\}{:}xCdI_2]$ in Table 5, 2925.95, 2925.98, 2926.57, 2926.24 cm^{-1} A1 peak is assigned as the CdI_4^{2-} symmetric stretch [14]. Pressure dependence peak at 1609.11, 1612.48, 1611.42 and 1611.31 cm^{-1} resembles that of A symmetry feature respectively [20]. This correlation implies that the 1609.11, peaks in $[(1\text{-}x)\{0.75\ Tl_2CdI_4{:}0.25AgI\}{:}xCdI_2]$ has 1612.48, 1611.42 and 1611.31 cm^{-1} A_1 symmetry. The peak at 550.50, 610.87, 700.18 and 531.10, 550.64 cm^{-1} in x = 0.2, 0.4, 0.6 and 0.8 mol. wt. % of Tl_2CdI_4 can be assigned as B symmetry. Factor group analysis for β-Tl_2CdI_4 shows only two A modes, the CdI_4^{2-} symmetric stretch and a mode which may be described as CdI_4^{2-}symmetric deformation assigned to the (1609.11, 1612.48, 1611.42 and 1611.31 cm^{-1}) in Tl_2CdI_4 composites respectively. This CdI_4^{2-} deformation may be described as a stretch of Cd-I and Ag-I bonds. The broadening of the (1609.11, 1612.48, 1611.42 and 1611.31 cm^{-1}) peaks in β-$Tl_2CdI_{4,}$ as the temperature is increased toward the temperature of the phase transition also suggests that these modes are associated with Cd-I and Ag-I motion respectively.

This behavior contrasts with that of the (2925.95, 2925.98, 2926.57, 2926.24 cm^{-1}) peaks in β-$Tl_2CdI_{4,}$ respectively, which remain sharp up to the order-disorder phase transitions. The pressure dependence also is consistent with an assignment in which (1609.11, 1612.48, 1611.42 and 1611.31 cm^{-1}) peaks involve copper iodide motion [13]. In β- $Tl_2CdI_{4,}$, the Cd-I stretch is contained in a linear modes E (xy_{trans}) – E (xy_{rot}) [21] and possibly one or both of the two weak peaks seen between 3000 and 4000 cm^{-1} at low temperature can be assigned as the Cd-I or Ag-I symmetric stretch (at room temperature). The pressure The low frequency modes in β- Tl_2CdI_4 is expected to have several Cd-I and Ag-I deformation with the Cd-I deformations at higher frequency than those of Tl-I. The low frequency E modes at (502.22, 504.28, 474.09 and 497.24 cm^{-1}) in β-Tl_2CdI_4, are of special interest.

Thus this indicates that these modes involve large components of Tl and Ag motions. Accordingly, these E symmetry features are assigned as external Tl^+ or Ag^+ translational modes in the xy plane. The E and B symmetry coordinates for Tl^+ translation, the former symmetry coordinates corresponds to Tl translation in the xy plane and the latter to Tl translation along the z axis.

A linear combination of the E and B symmetry coordinates may be formed in which cation motion occurs in the direction of the tetrahedral face of four iodide ions. The probable Tl^+ and Ag^+ conduction path involves Tl^+ and Ag^+ motion through this face, into an octahedral site, and through another I_3 triangular face into a tetrahedral site [15]. The values assigned to the attempt frequencies in Tl_2CdI_4 are similar to cation translational modes in related electrolytes [15].

Inspection of Table 5 and Figure 3, shows that IR spectra of all $[(1\text{-}x)\{0.75Tl_2CdI_4{:}0.25AgI\}{:}xCdI_2]$, conductors exhibit the strongest feature at ca 1609.11, 1612.48, 1611.42 and 1611.31 cm^{-1} respectively, while the infrared activity below 1000 cm^{-1} is weak. On the basis of the above discussion, these results strongly suggest that the existence of $(CdI_4)_2^{2-}/(Ag^+{:}Tl^+)$ tetrahedral in the x = 0.2 and 0.8 mol. wt. % $(Ag^+{:}Tl^+)$-doped fast ionic conductors should be excluded at least in concentration detectable by infrared spectroscopy.

Therefore, it is found that the infrared activity of the x = 0.2 and x = 0.8 mol. wt. % ($(CdI_4)_2^{2}$)-fast ionic conductors arises from $(CdI_4)_2^{2-}$ while x = 0.4 mol. wt. % ($(CdI_4)_2^{2}$)-fast ionic conductors show weakest feature at lower frequencies. Increasing the $(CdI_4)_2^{2}$ content induces a decreases to increase of the infrared activity in $[(1\text{-}x)\{0.75Tl_2CdI_4{:}0.25AgI\}{:}xCdI_2]$ [18].

4. Conclusions

Thus, novel composite fast ion conductors $[0.75Tl_2CdI_4{:}0.25AgI]$ and $[(1\text{-}x)\{0.75Tl_2CdI_4{:}0.25AgI\}{:}xCdI_2]$ composite fast ion conductors were prepared and investigated also by FTIR spectral analysis, studies to confirmed the formation of all the fast ion conductors.

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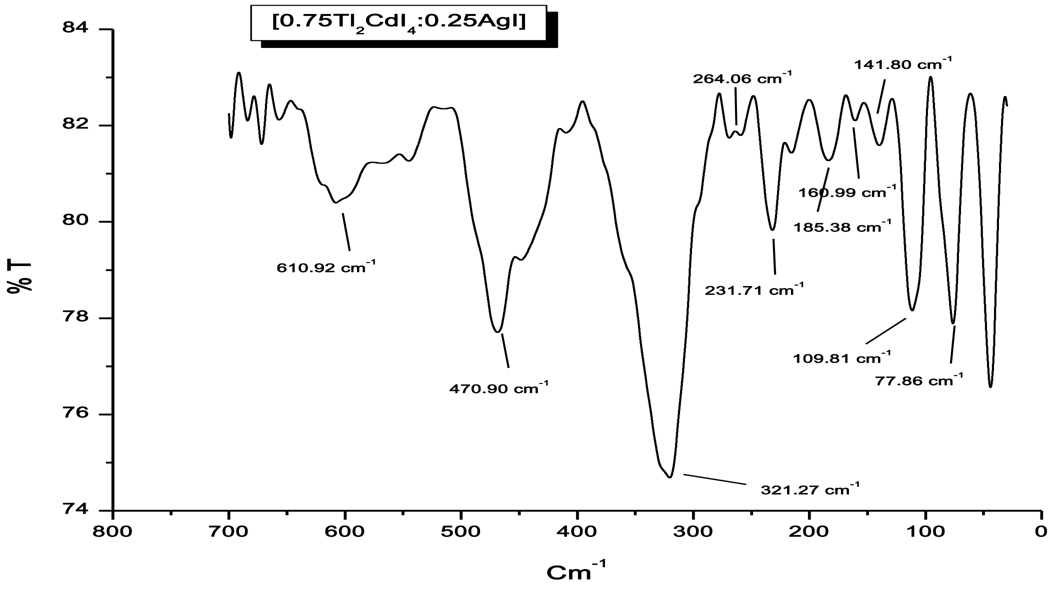

Fig. 1. FAR-IR spectrum for [$0.75Tl_2CdI_4$:0.25AgI] fast ionic conductors.

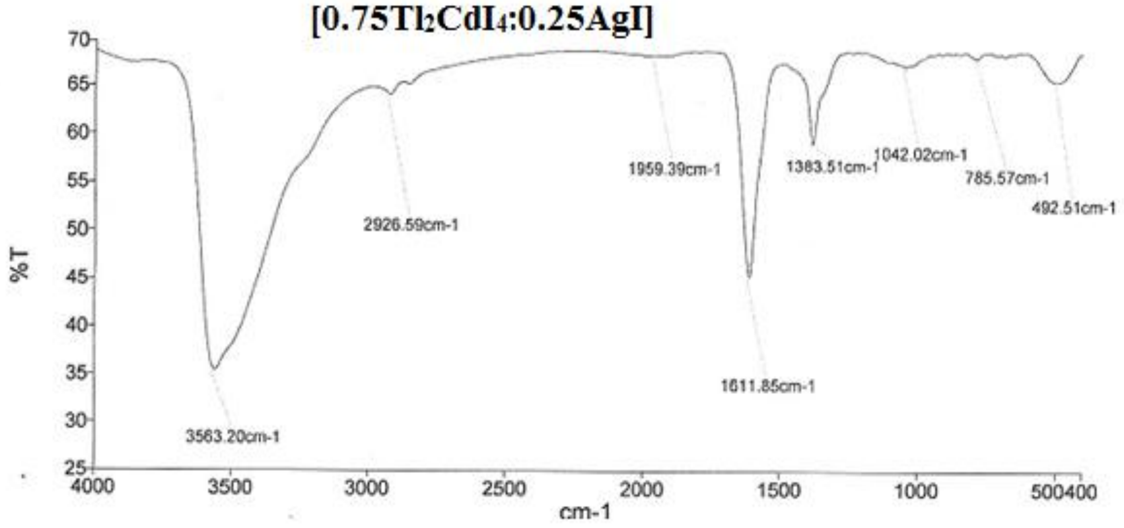

Fig. 2. FTIR spectrum for. [$0.75Tl_2CdI_4$:0.25AgI])] fast ionic conductor

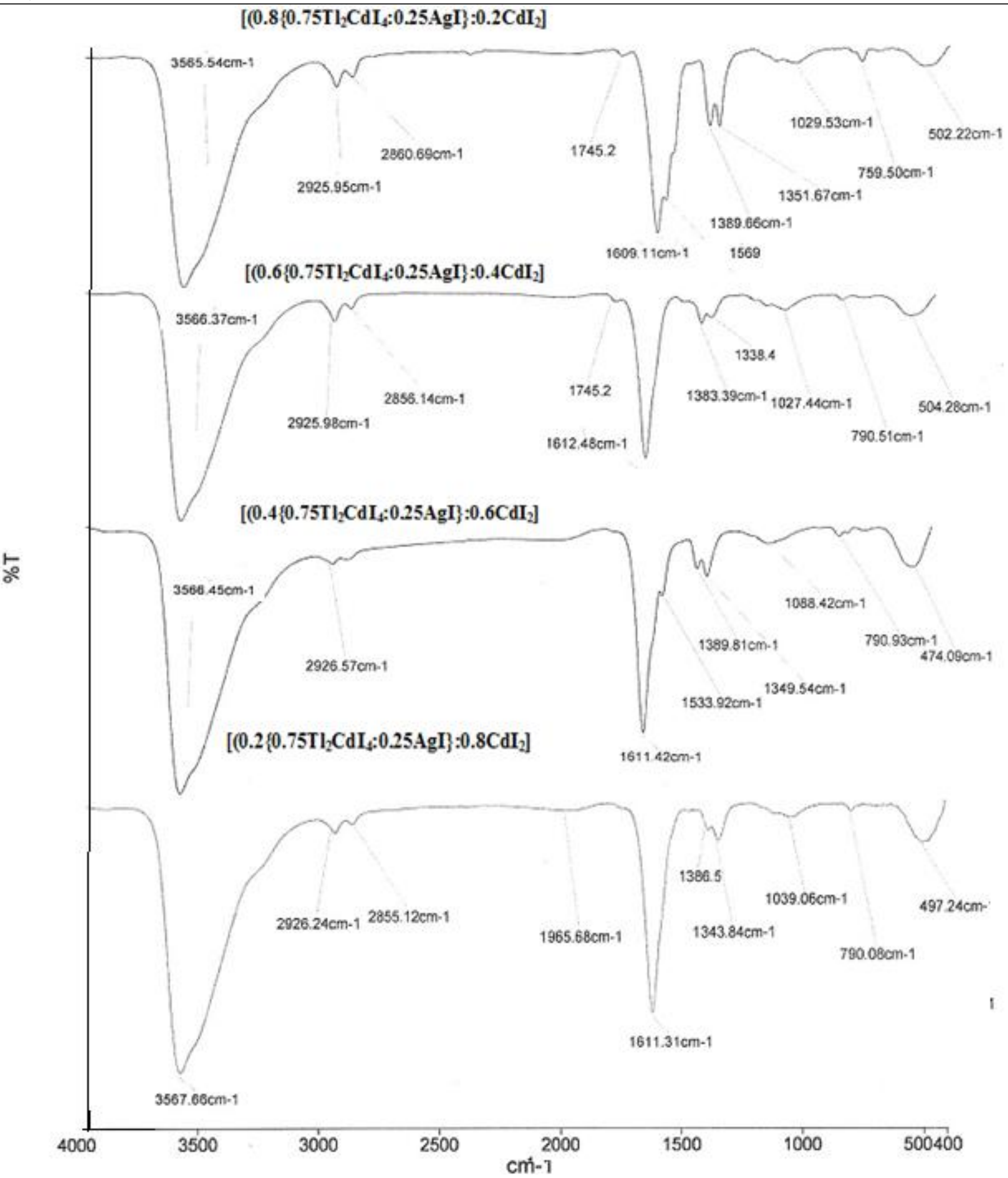

Fig. 3 . FTIR spectrum for.[[(1-x){$0.75Tl_2CdI_4$:0.25AgI}:xCdI_2] fast ionic conductors.

Table 1. FAR-IR bands in [$0.75Tl_2CdI_4$:0.25AgI] and assignments

Compound	value (cm-1)	Assignments	nature
Tl-I	109.81	ω_e	Tl-I stretch of the monomer
	73.35	υ_5	Assymmetric Cd-I stretch of the dimer
	41.93	-	
CdI_2	232.71	υ_3	Assymmetric Cd-I stretch of the dimer
	141.80	υ_z	I-**Cd**-I blend
Tl_2CdI_4	321.27	-	Dissociation of the **[**Tl_2CdI_4] molecule
	470.90	-	Tl-I stretch
	610.92	-	$(CdI_2)_2$ stretch
AgI	41.93	-	Ag-I stretch of the molecule
Tl_2CdI_4- AgI	160.99	-	formation of the [$0.75Tl_2CdI_4$:0.25AgI] band
	185.38	-	formation of the [$0.75Tl_2CdI_4$:0.25AgI] band
	264.06	-	formation of the [$0.75Tl_2CdI_4$:0.25AgI] band

Table 2. [0.75Tl_2CdI_4:0.25AgI] fast ionic conductors room temperature peaks and assignments.

Tl_2CdI_4 (cm^{-1})		Assignments
2926.59	A	$(CdI_4)^{-2}$ symmetric stretch respectively
1042.02		Tl-I and Cd-I symmetric stretch
1611.85	A	$(CdI_4)^{-2}$ deformation, M-I stretching
785.57	?	Deformation
1959.39	B	
492.51	E	Tl^+ attempt frequency

Table 3. **[0.75Tl_2CdI_4:0.25AgI] fast ion conductors, room temperature peaks and assignment.**

FTIR transmission peaks (cm^{-1})		
[Tl_2CdI_4]	**Symmetry**	**Assignment**
2926.59	A	CdI_4^{2-} Symmetric stretch
1611.85	A	CdI_4^{2-} deformation, M-I stretching
785.57	?	deformation
1959.39	B	Tl-I , Ag-I symmetric stretch
492.51	B	Tl^+attempt frequency

Table 4. **[(1-x){0.75Tl_2CdI_4:0.25AgI}:xHgI_2] (where x = 0.2, 0.4, 0.6 and 0.8 mol. wt. %.) room temperature peaks and assignments.**

[0.8{0.75Tl_2CdI_4:0.25AgI}:0.2CdI_2]		**[0.6{0.75Tl_2CdI_4:0.25AgI}:0.4CdI_2]**		**[0.4{0.75Tl_2CdI_4:0.25AgI}:0.6CdI_2]**		**[0.2{0.75Tl_2CdI_4:0.25AgI}:0.8CdI_2]**	
Peaks (cm^{-1})	Assignments	Peaks (cm^{-1})	Assignments	Peaks (cm^{-1})	Assignments	Peaks (cm^{-1})	Assignments
2925.95	A	2925.98	A	2926.57	A	2926.24	A
1609.11	A	1612.48	A	1611.42	A	1611.31	A
759.50	?	790.51	?	790.93	?	790.08	?
1745.2	B	1745.2	B	-----	B	1965.68	B
502.22	B	504.28	B	474.09	B	497.24	B

Table 5. $[(1-x)\{0.75Tl_2CdI_4:0.25AgI\}:xCdI_2]$ fast ion conductors, where (x = 0.2, 0.4, 0.6 and 0.8 mol. wt. %), room temperature peaks and assignment.

FTIR transmission peaks (cm^{-1})					**Assignment**
$[0.8\{0.75Tl_2CdI_4:0.25AgI\}:0.2CdI_2]$	**$[0.6\{0.75Tl_2CdI_4:0.25AgI\}:0.4CdI_2]$**	**$[0.4\{0.75Tl_2CdI_4:0.25AgI\}:0.6CdI_2]$**	**$[0.2\{0.75Tl_2CdI_4:0.25AgI\}:0.8CdI_2]$**	**Symmetry**	
2925.95	2925.98, cm	2926.57	2926.24	A	CdI_4^{2-} Symmetric stretch
1609.11	1612.48	1611.42	1611.31	A	CdI_4^{2-} deformation, M-I stretching
759.50	790.51	790.93	790.08	B	deformation
1745.2	1745.2	-----	1965.68	E	Tl-I , Ag-I symmetric stretch
502.22	504.28	474.09	497.24	E	Tl^+ , Ag^+ attempt frequency