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Indian J.Sci.Res. 16 (1): 101-110, 2025 **Original Research Article**

SYNTHESIS OF (Ag_2HgI_4:0.xRbI) NOVEL FAST IONIC COMPOUND AND STUDIED BY SEM, EDX AND FTIR SPECTRAL ANALYSIS

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ABSTRACT

We report the synthesis and structure of the novel ternary halide based compound have been taken to the development of new Rb^+ ion conducting composite fast ionic systems, (Ag_2HgI_4:0.xRbI) (where x = 0.1, 0.2 and 0.3 mol. wt. %), were prepared, using (Ag_2HgI_4) mixed composite system as the host. (Ag_2HgI_4) compound belongs to the fast ion conductors of A_2BX_4 (A = Ag, Cu, B = Hg, Cd, Zn, Pb and others). The compound (Ag_2HgI_4) becomes superionic near 388K as the crystal lattice changes from a tetragonal to a hexagonal structure. Near 445K, (Ag_2HgI_4) is replaced by an equilibrium mixture of α-AgI and HgI_2. At each of these phase transition, ionic conductivity increases by an order of magnitude or more. The substitution of Hg^{++} from Ag^+ in (Ag_2HgI_4) is accompanied by a slight increase in the room temperature conductivity, as a result of either increased crystalline defects or an increased Rb^+ substitution also characterized. FTIR, FAR-IR, SEM and EDAX analyses were performed to confirm the formation of fast ion conductors (Ag_2HgI_4:0.xRbI) (where x = 0.1, 0.2 and 0.3 mol. wt. %).

KEYWORDS: Ftir, Far-Ir, Sem, Edax, Doping, Fast Ion Conductors

Research in solid-state chemistry is essentially concerned with investigations of structures and properties of solids. The primary motivation being understanding and predicting the properties of solids in terms of their crystal structure, chemical composition and electronic structure (Rao and Gopalkrishnan, 1989). A crucial input in this enterprise is the synthesis of the required material. From the early days, chemists have made significant contribution to the development of solid state sciences by synthesizing novel solids that possess unusual structures and properties (Noorussaba and Afaq, 2016). Synthesis of unknown compounds in a structurally related family, in order to extend and extrapolate structure property relations and preparation of known compounds to investigate a specific property, are the challenging and rewarding areas of solid-state chemistry. Preparative effect in solid-state chemistry becomes most rewarding when it is coupled with characterization and property evaluation (Honig and Rao, 1981). This aspect of solid state is being increasingly recognized as evidenced by several articles. (Carbett, 1987) appearing in recent years. Solid fast ion conductors are characterized by very high ionic conductivity, either anionic or cationic relative to the ionic conductivity of most crystalline solids (Khalid and Rafiuddin, 2011). The fast ion conductor (Ag_2HgI_4) exhibits a number of solid state phase transition upon heating. Room temperature covalent phase γ-Ag_2HgI_4 crystallized in a well defined tetragonal structure. (Ag_2HgI_4) is a material with a well known face centered cubic (f.c.c.) anion structure existing in tetragonal (β) phase at room temperature and cubic (α) phase at higher temperature. (Ag_2HgI_4) has an order-disorder transition at about 52°C. The structure of α-Ag_2HgI_4 is similar to that of the β- phase, except that the iodine sublattice is now an ideal ffc arrangement and diffraction studies show the cation to be disordered over half of the tetrahedrally coordinated positions. Crystallographic ally, α-Ag_2HgI_4 is described in the cubic space group $F\bar{4}3m$ with each cation site having an average occupancy of ½ Ag and ¼ Hg^{-2}. The primitive wiegner cell shows S_4 symmetry and the lattice parameters as a = 6.3Å and c = 12.6Å at room temperature. Chemical substitution has been used extensively in recent years to modify either the magnitude of ionic conductivity or the transition temperature separating super ionic and covalent phases in various solid electrolytes. Anion substitution in the fast ion conductors AgI, Ag_3SI and Ag_3SBr, for example, have been found to either raise or lower ionic conductivities and to either raise or lower ionic conductivities and to either raise or lower phase transition temperature, depending upon the specific substitute anion. By contrast, cation substitute have typically been found to modify ionic conductivities while leaving the phase transition temperatures unchanged (Noorussaba and Afaq, 2017).

This paper is a part of our investigation on the synthesis, and characterization of Rb^+ cation substituted (Ag_2HgI_4). In, the present investigation, Although the initial purpose of this work is to see cations (i.e. Rb^+)

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effect by introducing in A_2BX_4 systems, we find that it is quit difficult to see this and instead we find the structure of pure A_2BX_4 systems is different from iodide fast ionic system leading to the phase separation structure (Noorussaba and Afaq, 2011).

MATERIALS AND METHODS

Series of Samples

e.g. 1) **(**Ag_2HgI_4:xRbI) -

a) (Ag_2HgI_4)

b) (Ag_2HgI_4:1RbI)

c) **(**Ag_2HgI_4:2RbI)

d) **(**Ag_2HgI_4:3RbI)

In the (A_2BX_4) where (A = Ag, B = Hg and X = I) systems (A_2BX_4) are pure materials, In (A_2BX_4:xRbI) composite system (where x = 0.1, 0.2, 0.3 mol. wt. %, A = Ag, B = Hg, and X = I), (A_2BX_4) considered as host doped with (xRbI) (where x = 0.1, 0.2, 0.3 mol. wt. %) as the dopant. The composition of the host (A_2BX_4) was kept constant in all the composite samples of (A_2BX_4:xRbI). It has been observed that a much better solid electrolyte composite system can be prepared with the host (A_2BX_4) (A = Ag, Cu, Cd, B = Cd, Hg and X = I) systems) (Noorussaba and Afaq, 2017).

EXPERIMENTAL PROCEDURE

Material

The following materials were used as received; silver iodide and cadmium (II) iodide were of CDH anal grade, each of which had a purity of 99%, 99% respectively.

Preparation and Characterization of Pure and Doped Samples

Preparation of Pure (Ag_2HgI_4) Host Sample

Silver tetramercuroiodate (Ag_2HgI_4) was prepared by the conventional solid state reaction from AgI and HgI_2 (CDH, India), with stated purity of 99.5 respectively. Both reactants i.e. AgI and HgI_2 were mixed thoroughly in a requisite composition in an Agate mortar (each above 300 mesh size). The fine ground stoichiometric mixture of the binary component was sealed in an ampoule and was placed in air oven

$2AgI + HgI_2 \rightarrow Ag_2HgI_4$

(CE 0434 NSW- 144) at about 100°C (373K) for 5 days. After cooling, a dark yellow color compound was formed which is changed to orange yellow. Ag_2HgI_4 is orange yellow below 52°C and dark yellow above 52°C (Noorussaba and Afaq, 2011).

Preparation of doped sample (Ag_2HgI_4:0.xRbI)

RbI were mixing in various x = 0.1, 0.2 and 0.3 mol. wt. % respectively in an Agate motar to form (Ag_2HgI_4:xRbI) composite mixture by solid state reaction. Silver tetra-iodomercurate 02 mol. wt. % (Ag_2HgI_4) were doped by 0.1, 0.2 and 0.3 mol. wt. % (RbI) dopant solid respectively to form (Ag_2HgI_4:xRbI) fast ion conductor, in an Agate mortar at room temperature and heating them at 100°C (373K) for 24 hrs in a silica crucible. After intermittent grinding, all the samples were prepared (Noorussaba and Afaq, 2017).

Characterization of (Ag_2HgI_4:0.xRbI) Composite Fast Ion Conductor

The novel composite fast ion conductors (Ag_2HgI_4:0.xRbI), were prepared and investigated by Scanning Electron Microscopic (SEM), energy dispersive spectral (EDAX), FTIR spectral analysis.

Scanning Electron Microscopic (SEM) and (EDAX) Studies

The scanning electron microscopic (SEM) studies were performed to get information about homogeneity, particle distribution and morphology of all the fast ionic composite systems (Ag_2HgI_4:xRbI) (where x = 0.1, 0.2 and 0.3 mol. wt. % respectively) after the reaction was completed using Jeol JSM 6510LV Scanning Electron Microscope at room temperature and different magnifications (at 3000x and 10,000x).

Energy Dispersive Spectral (EDAX) Studies

Chemical analysis of a (Ag_2HgI_4:0.xRbI) (were 0.1, 0.2 and 0.3 mol. wt. %) processed samples was carried out by EDAX to check if there is any deviation from the initial composition. Fig. 4 shows a typical EDAX result for (Ag_2HgI_4:0.xRbI) sample.

Far-IR Spectral Analysis

The Far-IR spectrum was recorder for all the fast ionic composite systems (Ag_2HgI_4:xRbI) (where x = 0.1, 0.2 and 0.3 mol. wt. % respectively) in the far-infrared range 30-400 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.

FTIR Spectral Analysis

The IR spectrum was recorder for all the fast ionic composite systems (Ag_2HgI_4:xRbI) (where x = 0.1, 0.2 and 0.3 mol. wt. % respectively) 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.

RESULTS

FTIR Analysis

FAR-IR Discussion in (Ag_2HgI_4:0.xRbI)

The IR spectrum of the vapour over solid (Ag_2HgI_4:0.xRbI) (where x = 0.1, 0.2 and 0.3 mol. wt. %) was studied in the 30-700 cm^{-1} region at room temperature are shown in figure 1.

The IR spectrum of (Ag_2HgI_4:0.xRbI) where x = 0.1, 0.2 and 0.3 mol. wt. %) solid at room temperature showed two distinct absorption bands. The absorption around 108.07 cm^{-1}, 108.07 cm^{-1}, 112.20 cm^{-1} in x = 0.1, 0.2 and 0.3 mol. wt. % shows typical PR band structure of a diatomic molecule and is assigned to the fundamental Ag-I stretching frequency of the monomer. For the band origin at 91.55 cm^{-1}, 93.43 and 89.30 cm^{-1} in x = 0.1, 0.2 and 0.3 mol. wt. % can be attributed to the $(AgI)_2$ dimeric molecule respectively (Glushko*et al*, 1982). IR-measurements shows that a sifnificant amount of dimeric molecules is present in the vapour over AgI at the temperature of the present experiments.

Ionic model calculations based on Rittners electrostatic model (10) predicted a square planar structure (D_{2h} symmetry) as the most stable arrangement for $(AgI)_2$. 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 91.55 cm^{-1}, 93.43 and 89.30 cm^{-1} in x = 0.1, 0.2 and 0.3 mol. wt. % is due to the stretching motion and the peak at ca 54.39, 42.01 and 44.26 in x = 0.1, 0.2 and 0.3 mol. wt. % is due to the bending motion of the $(AgI)_2$ molecule. There is however, no clear argument for the assignment of the observed stretching band to the B_{2u} and B_{3v} mode (Noorussaba, 2025).

The spectrum of (Ag_2HgI_4:0.xRbI) where x = 0.1, 0.2 and 0.3 mol. wt. %) solid consisted of two strong absorption bands are listed in Table 1.

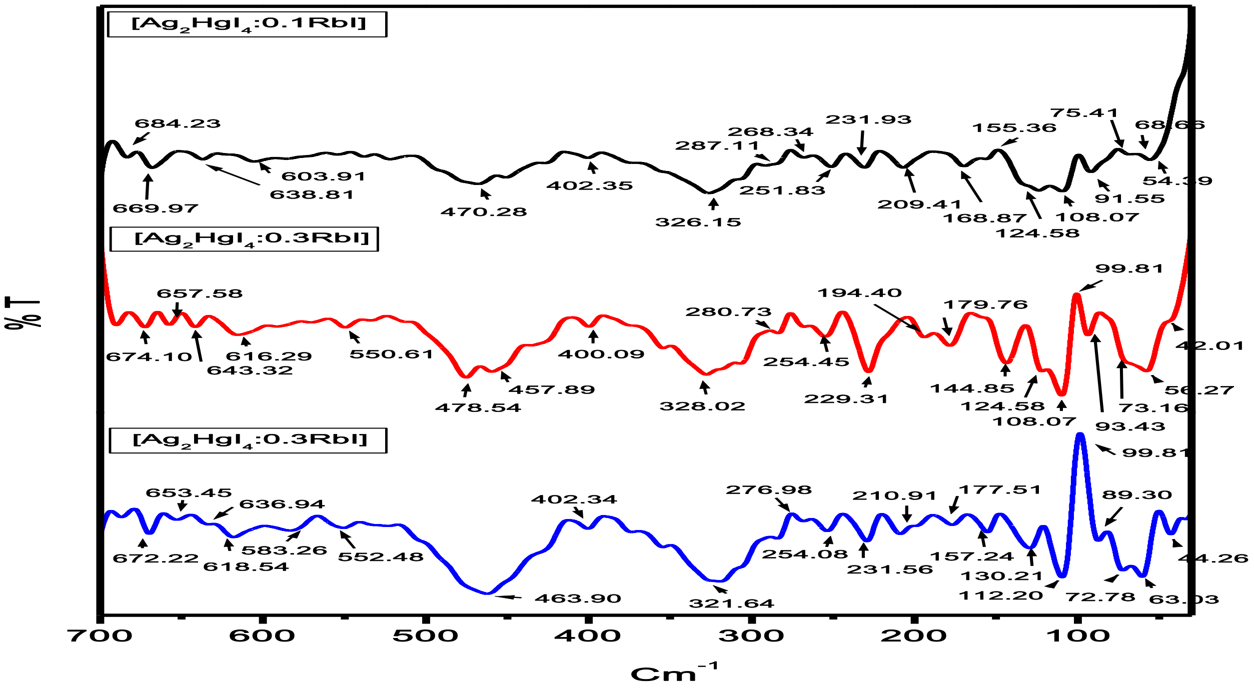


Figure 1: FAR-IR spectrum for (Ag_2HgI_4:0.xRbI) fast ionic conductors

Table 1: FAR-IR bands in (Ag_2HgI_4:0.xRbI) and assignments

Compound	**((Ag_2HgI_4:0.1RbI)**	**((Ag_2HgI_4:0.2RbI)**	**((Ag_2HgI_4:0.3RbI)**	**Assignments**	**Nature**
AgI	108.07	108.07	112.20	ω_e	Ag-I stretch of the monomer
	91.55	93.43	89.30	B_{2u} and B_{3v}	stretching motion of $(AgI)_2$ dimeric molecule
	54.39	42.01	44.26	B_{1u}	bending motion of the $(AgI)_2$ molecule
HgI_2	231.93	229.31	231.56	υ_3	symmetric Hg-I stretch of the dimer
	168.87	144.85	157.24	υ_2	I- Hg-I blend
Ag_2HgI_4	326.15	328.02	321.64	-	Dissociation of the (Ag_2HgI_4) molecule
	470.28	478.54	463.90	-	Ag-I stretch
	638.81	616.29	618.54	-	$(HgI_2)_2$ stretch
RbI	209.41	194.40	210.91	___	RbI-I stretch of the molecule
	251.83	254.45	254.08	___	RbI-I stretch of the molecule
Ag_2HgI_4-RbI	603.91	550.61	552.48	___	formation of the (Ag_2HgI_4:0.xRbI) band
	669.97	643.32	583.26		formation of the (Ag_2HgI_4:0. xRbI) band
	684.23	657.58	636.94	___	formation of the (Ag_2HgI_4:0. xRbI) band
	___	674.10	653.45	___	
	___	___	672.22		

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 (Zandbergen, 1979), 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 231.93, 229.31, 231.56 cm^{-1} in x = 0.1, 0.2 and 0.3 mol. wt. % and I-Hg-I blending frequency υ_2 at 168.87, 144.85, 157.24 cm^{-1} in x = 0.1, 0.2 and 0.3 mol. wt. %. The additional sharp lines in the spectrum are due to the rotational spectrum of H_2O impurities. The IR spectrum of (Ag_2HgI_4:0.xRbI) (where x = 0.1, 0.2 and 0.3 mol. wt. %) solid composite, also shows three distinct absorption bands at 326.15, 470.28 and 638.81 cm$^{-1,}$ in x = 0.1, 328.02, 478.54 and 616.29 cm$^{-1,}$ in x = 0.2, 321.64, 463.90 and 618.54 cm$^{-1,}$ in x = 0.3. On further increasing the wavenumber the position of the absorption bands are in excellent agreement with those of the (Ag_2HgI_4) molecules (Franiv A.V. *et al*, 2013) 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 AgI and indicate the presence of AgI and $(HgI_2)_2$ molecules.

In addition, numerous sharp absorption bands of the rotational spectrum of (Ag_2HgI_4:0.xRbI) where x = 0.1, 0.2 and 0.3 mol. wt. %) were presents, which were at 603.91, 669.97, 684.23 cm$^{-1,}$ in x = 0.1, 550.61, 643.32, 657.58, 674.10 cm^{-1} in x = 0.2, 552.48, 583.26, 636.94, 653.45 and 672.22 cm^{-1} in x = 0.3 mol. wt. %. These absorption bands are in excellent agreement with those of the (Ag_2HgI_4) host composite. Additional peaks that might indicate the presence of Rbl species is at 209.41, 251.83 in x = 0.1, 194.40, 254.45 cm^{-1} in x = 0.2, 210.91, 254.08 cm^{-1} in x = 0.3 mol. wt. % have been observed shows Rb-I stretch of the molecule.

The present results shows that the successive release of HgI_2 and AgI/$(HgI_2)_2$ vapour species occurs during heating, pointing towards dissociation of (Ag_2HgI_4:0.xRbI) where x = 0.1, 0.2 and 0.3 mol. wt. %) molecules under the conditions of the experiments (Table 1). Additional peaks that might indicate the presence of Ag-Hg-I species have been observed.

FTIR Discussion in (Ag_2HgI_4:0.xRbI)

As in Ketelaar description, the α- phase retains the same iodine structure as in the β phase. While the cation and vacancy sites becomes equivalent (Franiv *et al*, 2013). Later studies (Kalyagin, 2008) showed that the low temperature phases are tetragonal and in addition, are not isostructural, differing in the placement of the two monovalent cation (Ag or Cu) and vacancy. Thus based on data from the best single crystals, i.e. tetragonal β-phase was the only stable low-temperature phase and the apparent phase change after cycling could be explained by the formation of domains with the tetragonal c axis randomly oriented along the three spatial axes, thus giving the impression of a cubic lattice. The interpretation of a single low-temperature phase has the broadest base of support of the two views at present (Kalyagin, 2008). 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 18 optical modes in Ag_2HgI_4 materials.

Ag_2HgI_4: 3A+ 5B+ 5E

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

Infrared	Raman
Ag_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 (Hassan and Nawaz, 2008; Wakamura, 2002; Sudharsanan *et al* 1984).

Factor group analysis of (Ag_2HgI_4:0.xRbI)

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

Table 2: **(Ag_2HgI_4:0.xRbI) fast ion conductors, where (x = 0.1, 0.2 and 0.3 mol. wt. %) room temperature peaks and assignments**

(Ag_2HgI_4: 0.1RbI)		**(Ag_2HgI_4: 0.2RbI)**		**(Ag_2HgI_4: 0.3RbI)**	
Peaks (cm^{-1})	Assignments	Peaks (cm^{-1})	Assignments	Peaks (cm^{-1})	Assignments
2762.69	A	2777.89	A	2769.68	A
1619.08	A	1615.38	A	1615.79	A
974.74	?	960.77	?	974.74	?
1225.36	B	1299.85	B	1241.84	B
431.49	B	438.48	B	440.53	B

The unit cell group analysis of Ag_2HgI_4 is also shown in Table 2 (6), 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 (Ag_2HgI_4:0.xRbI) fast ionic conductors where x = 0.1, 0.2 and 0.3 mol. wt. %. In the IR spectra of (Ag_2HgI_4:0.xRbI) the 2827.62 cm^{-1} peak in Table 2 is strongest in xx, yy and zz direction making it an A. The A peak shifted in x = 0.1, 0.2 and 0.3 mol. wt. % at 2762.69, 2777.89, 2769.68 cm^{-1}. The peak at 1246.36 cm^{-1} are strongest in the xx and yy polarizations and therefore belongs to B classes. This peak shifted in x = 0.1, 0.2 and 0.3 mol. wt. % composites are 1225.36 cm^{-1} for x = 0.1, 1299.85 cm^{-1} for x = 0.2 and 1241.84 cm^{-1} for x = 0.3 mol. wt. %.

The only noticeable peaks in xz polarization and E symmetry is at 452.45 cm^{-1} and the 974.74 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 = 0.0 mol. wt. %. E symmetry peaks are found in x = 0.1, 0.2 and 0.3 are at 431.49, 438.48, 440.53cm^{-1} . The shoulder peaks appears in x = 0.1, 0.2 and 0.3 are at 974.74, 960.77 and 974.74 cm^{-1} respectively. The E peaks leaves some weak peaks at (335.96, 532.58 and 675.17cm^{-1}) in x = 0.0 which shifted in x = 0.1, 0.2 and 0.3 are at (355.06, 438.48, 511.62 and 703.12 cm^{-1}), (355.06, 484.09, 532.58 and 619.29 cm^{-1}) and (351.77, 493.95, 558.06 and 622.16 cm^{-1}) respectively (Table 4).

Unassigned and a speculatively assignment for the 974.74 cm^{-1} feature. HgI_2 contamination peaks also found in at 2763.51, 2666.53, 2652.56 and 2620.10 cm^{-1} for x = 0.0, 0.1, 0.2 and 0.3 respectively. Peaks of B and E symmetry are allowed in the IR spectra and should be strong peaks. The occurrence of 452.45 cm^{-1} for (Ag_2HgI_4:0.xRbI) in the IR strengthens the E assignment for the peak at 335.96cm^{-1}. For the x = 0.1, 0.2 and 0.3, the peaks are at 355.06, 355.06 and 351.77 cm^{-1} in (Ag_2HgI_4:0.xRbI) respectively (Table 4).

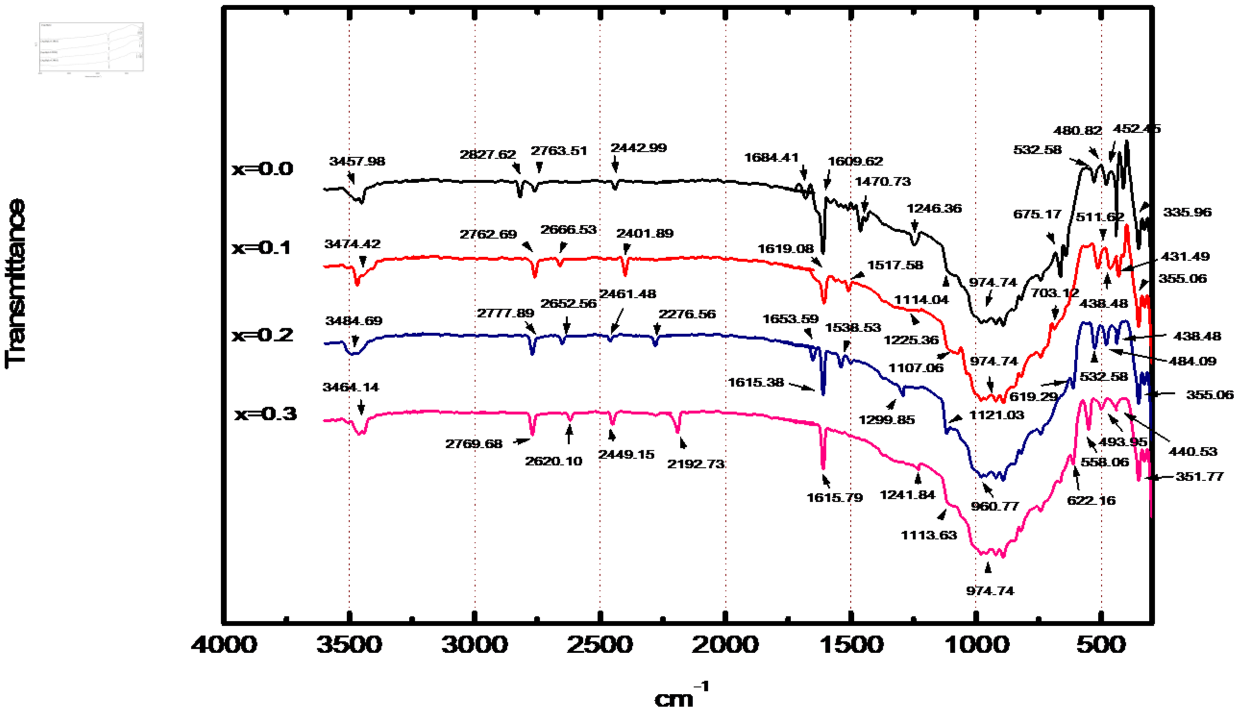


Figure 2: FTIR spectrum for (Ag_2HgI_4:0.xRbI) fast ionic conductors

FTIR Comparison in (Ag_2HgI_4:0.xRbI)

From Table 3, the vibrational modes can be assigned by considering Ag_2HgI_4 as consisting of the vibrational modes of AgI and $(HgI_4)^{2-}$ species. In fact, as shown in Fig. 2, almost all the bands due to AgI and $(HgI_4)^{2-}$ are seen in the pure Ag_2HgI_4 composites. The band at 1609.62 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 (Secco and Sharma, 1995). This assignment is in good agreement with the other $(HgI_4)^{2-}$ tetrahedral compounds (Goodenough, 1997). In the pure (Ag_2HgI_4), all seven bands shifted to 335.96, 452.45, 532.58, 675.17, 1114.04, 1246.36 and 1609.62 cm^{-1}. The 1000 - 1500 cm^{-1} region consists of two bands at the positions 974.74 cm^{-1} and 1246.36 cm^{-1} at room temperature and at low temperature, these bands are expected to split.

Table 3: (Ag_2HgI_4:0.xRbI) fast ion conductors, where (x = 0.1, 0.2 and 0.3 mol. wt. %) room temperature peaks and assignment

FTIR transmission peaks (cm^{-1})				
(Ag_2HgI_4: 0.1RbI)	**(Ag_2HgI_4: 0.2RbI)**	**(Ag_2HgI_4: 0.3RbI)**	**Symmetry**	**Assignment**
1619.08	1615.38	1615.79	A	HgI_4^{2-} deformation, M-I stretching
974.74	960.77	974.74	B	deformation
1225.36	1299.85	1241.84	E	Ag -I , Ag -I symmetric stretch
431.49	438.48	440.53	E	Ag^+ , Rb^+ attempt frequency

It is known from the IR spectra of pure (Ag_2HgI_4)- ions conductors that this region consists of mostly of Ag-I (Beg *et al*. 2008) stretching modes. Hence, in all (Ag_2HgI_4:0.xRbI) composite samples, also the bands in this region can be assigned to symmetric stretching modes of Ag-I. Below 700 cm^{-1}, there are five sharp bands at 355.06, 431.49, 438.48, 511.62, 702.12 cm^{-1} in (Ag_2HgI_4:0.1RbI) (Secco and Sharma, 1995), while species vibrations, the bands at 355.06, 438.48, 484.09, 532.58, 619.29 cm^{-1} and 351.77, 440.53, 493.95, 558.06, 622.16 cm^{-1} in x = 0.2 and 0.3 (Rb^+)-ions conductors respectively, it is known from factor group analysis studies (Goodenough, 1997) 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 511.62 and 702.12 cm^{-1} in (Ag_2HgI_4:0.1RbI) are at 532.58 cm^{-1} and 619.29 cm^{-1} in x = 0.2 and 558.06 cm^{-1} and 622.16 in x = 0.3 (Rb^+)-ions conductors respectively can be assigned to Hg-I deformation type bands. The band at 452 cm^{-1} in pure Ag_2HgI_4, and 431.49, 438.48 and 440.53 cm^{-1} in x = 0.1, 0.2 and 0.3 mol. wt. % (Rb^+)- doped ions conductors respectively, is attributed to the E symmetry of Rb^+ translational mode and is the characteristic attempt frequency of Rb^+ ion arising from the diffusive behavior to oscillatory behavior. This assignment is well explained by Viswanathan and Suthanthiraraj, 1993 by referring to the negative pressure dependence and also using theoretical calculations. The value assigned to the attempt frequencies in Ag_2HgI_4 is similar to cation transition modes in other related (Rb^+)-doped fast ionic conductors (Viswanathan and Suthanthiraraj, 1993). Another possibility is that motion of very large amplitude (diffusive like) is able to create configurationally disorder which allows all IR modes (Kartini *et al.*, 2008).

Inspection of Table 3 and Figure 2, shows that IR spectra of all pure and (Ag_2HgI_4:0.xRbI) and conductors exhibit the strongest feature at ca 1609.62, 1619.08, 1615.38 and 1615.79 cm^{-1} respectively, 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 $(HgI_4)_2^{2-}/(Rb^+)$ tetrahedral in the x = 0.1, 0.2 and 0.3 mol. wt. % (Rb^+)-doped fast ionic conductors should be excluded at least in concentration detectable by infrared spectroscopy.

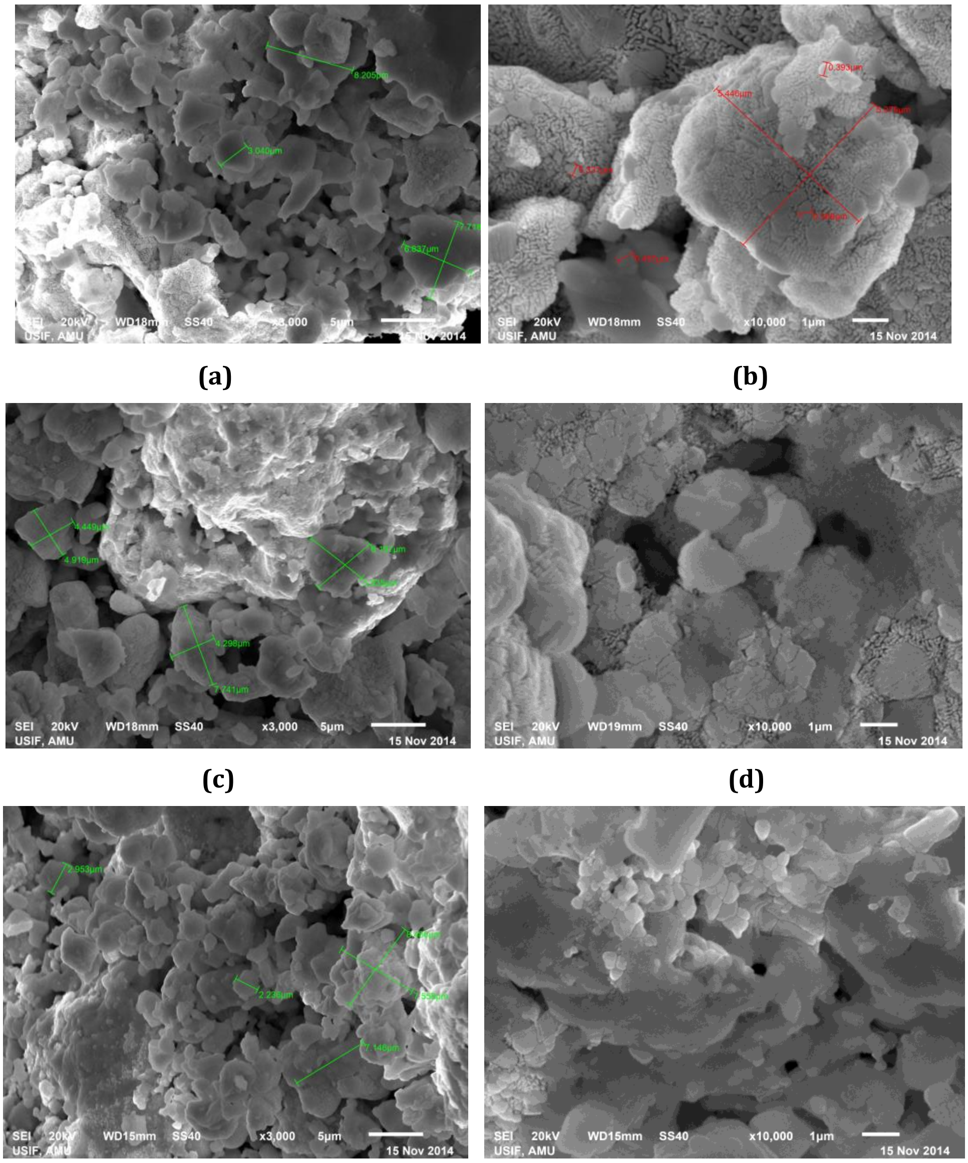
Therefore, it is found that the infrared activity of the x = 0.1, 0.2 and 0.3 mol. wt. % (Rb^+)-fast ionic conductors arises from $(HgI_4)^{2-}$ tetrahedral. Increasing the Rb^+ content induces a decreases to increase of the infrared activity in (Ag_2HgI_4:0.x RbI) (Secco and Sharma, 1995).

Scanning Electron Microscopic (SEM) Studies

The scanning electron microscopic (SEM) studies were performed to get information about homogeneity, particle distribution and morphology of all the fast ionic composite systems (Ag_2HgI_4:xRbI) (where x = 0.1, 0.2 and 0.3 mol. wt. %) after the reaction was completed (sintered) at room temperature. Fig 3. shows typical results at two different magnifications (at 3000x and 10,000x), which clearly indicates the highly agglomerated nature of particles.

Table 4: (Ag_2HgI_4:0.xRbI) fast ion conductors, where (x = 0.1, 0.2 and 0.3 mol. wt. %), room temperature peaks and assignment

FTIR -transmission (cm^{-1})				Assignment
Pure (Ag_2HgI_4)	(Ag_2HgI_4: 0.1RbI)	(Ag_2HgI_4: 0.2RbI)	(Ag_2HgI_4: 0.3RbI)	
335.96 532.58	355.06 438.48	355.06 484.09	351.77 493.95	Ag-I deformation
675.17	511.62 703.12	532.58 619.29	558.06 622.16	Hg-I deformation
2442..99 532.58	2401.89 511.62	2461..48 2276.56 532.58	2449.15 2192.73 558.06	Rb-I symmetric stretch
1609.62	1619.08	1615.38	1615.79	$(HgI_4)^{2-}$- I symmetric stretch



(a) (b)

(c) (d)

(e) (f)

Figure 3: SEM photographs of (a) (Ag_2HgI_4:0.1RbI) at 3000x and (b) at 10,000 x, (c) (Ag_2HgI_4:0.2RbI) at 3000x and (d) at 10,000 x, (e) (Ag_2HgI_4:0.3RbI) at 3000x and (f) at 10,000 x respectively. The particles are seen in a highly agglomerated state. The typical agglomerated particle size is in the range 1.5–1.99 µm

The average size of agglomerated particles is 1.5–1.99 µm in diameter. Here it may be noted that the agglomeration is more obvious at higher magnification (Fig. 4b). Further, there is a distinct possibility of existence of nanosize amorphous particles. The sintering temperature of all the samples cannot be high enough to synthesize the pure phase of monoclinic (Ag_2HgI_4:xRbI) sample as indicated by FTIR. The sem images shown in Fig. 3 suggest that the particles of all the samples sintered at particular temperature are covered with a slice of RbI which are attributed to the residual RbI particles left over from the solid state reaction method (Zhu *et al.*, 2008). The residual RbI particles can favor stabilization of Hg^{2+} and facilitate the diffusion of Ag^+. This is to say, it is the result as a consequence of Ag_2HgI_4 decomposistion during preheating and sintering process and produces a composite powder (Ag_2HgI_4:xRbI) with superior conductivity (Bolesta *et al.*, 1999).

However particular temperature (100 ºC) preparation causes the absupt growth of particles with a smooth surface particle of ≈ 1.5–1.99. It has been reported that the morphology and surface area of obtained particles have a notable effect on the electrochemical performance of (Ag_2HgI_4:xRbI) and optimizing particle size or introducing conducting additives can improve the performance (Bolesta *et al.*, 1999). As nanometer size RbI particles can be dispersed uniformely between (Ag_2HgI_4) particles. It has played a beneficial role in obtaining samples with small and uniform particles size and enhancing overall conductivity. Furthermore, solid state reaction method can prevent particles from agglomeration.

Energy Dispersive Spectral (EDAX) Studies

Chemical analysis of a few processed samples was carried out by EDAX to check if there is any deviation from the initial composition. Fig. 4 shows a typical EDAX result for (Ag_2HgI_4:0.xRbI) (were x = 0.1, 0.2 and 0.3 mol. wt. %) sample.

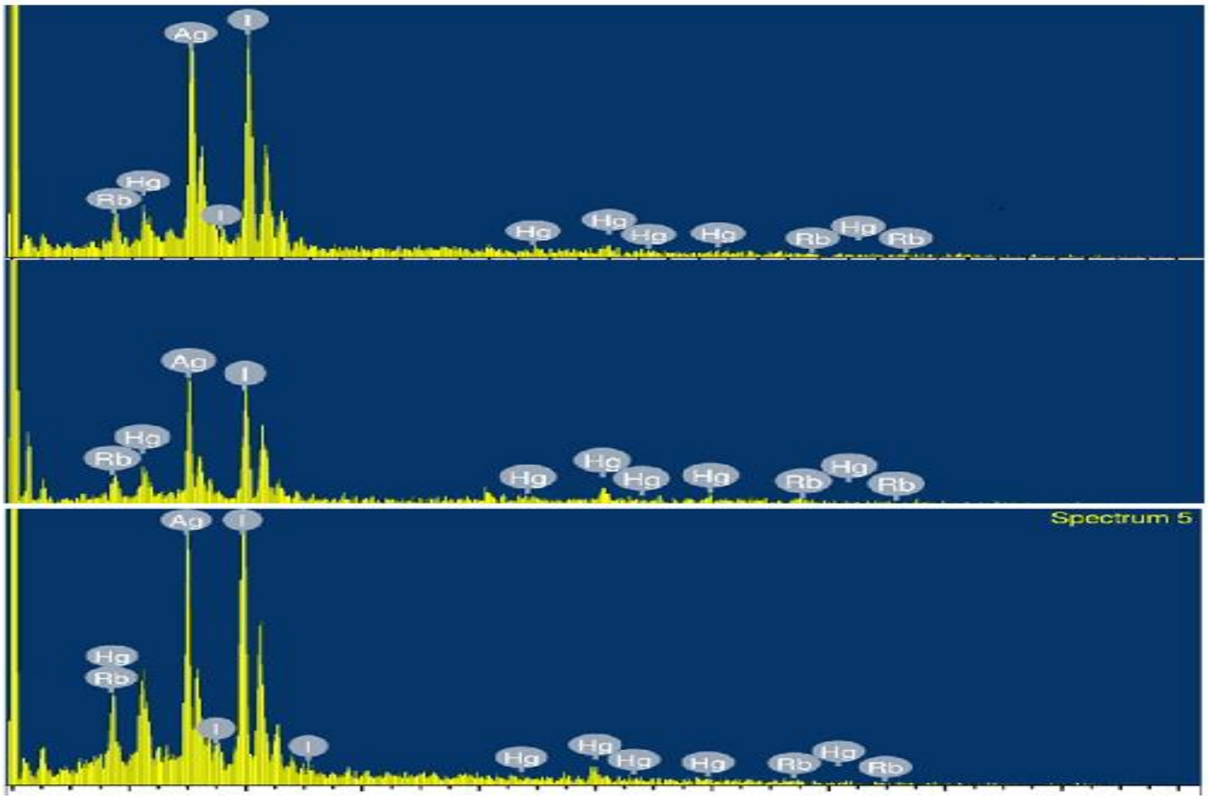


Figure 4: EDAX results for (Ag_2HgI_4:xRbI) sample. Showing the presence of elements (Ag, Cd, Rb, I). The inset shows weight/atomic ratios of the four elements present in the sample are same as that in the unprocessed sample

In a (Ag_2HgI_4:0.xRbI) (were x = 0.1, 0.2 and 0.3 mol. wt. %) samples shows a typical EDAX result, the wt. % of the four elements (Ag = 23.71%, Hg = 17.42%, Rb = 2.21%, I = 56.66%) in a (Ag_2HgI_4:0.1RbI), whereas the wt. % of the four elements (Ag = 22.93%, Hg = 17.25%, Rb = 4.73%, I = 55.09%) and (Ag = 25.99%, Hg = 11.95%, Rb = 5.27%, I = 56.79%) in a x = 0.2 and 0.3 respectively, is nearly same as in the unprocessed (Ag = 25%, Hg = 15%, Rb = 05%, I = 65%) material. It is thus concluded that the formation of all the fast ion conductors by solid state reaction does not alter the composition of the samples (Xianjun *et al.*, 2008).

CONCLUSION

A novel composite superionic systems (Ag_2HgI_4:0.xRbI) (were x = 0.1, 0.2 and 0.3 mol. wt. %), were investigated. An alternative ternary system (Ag_2HgI_4) was used as host. In the host (Ag_2HgI_4) structure, doping with Ag^+ in the host induces a decrease in the mobile charge carriers, Rb^+ ions that is proportionate with the increased 0.x mol. wt. % (x = 0.1, 0.2 and 0.3 mol. wt. %) in the host mixed system.

FAR-IR, FTIR, SEM and EDAX studies confirmed the formation of a superionic phase in the composite system.

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REFERENCES

Beg S., Al-Areqi N.A.S. and Haneef S., 2008. Study of phase transition and ionic conductivity changes of Cd-substituted $Bi_4V_2O_{11-\delta}$, Sol. Stat. Ionics, **179**: 2260–2264.

Bolesta I.M., Futey O.V. and Syrbu O.G., 1999. Optical Investigations of Superionic phase transitions in

Ag_2CdI_4 thin films. Solid State Ionics, **119**(1-4): 103-107.

Carbett J.D., 1987. Solid State Chemistry Techniques (Calarendon Press, Oxford).

Franiv A.V., Kushnir O.S., Girnyk I.S., Franiv V.A., Kityk I., Piasecki M. and Plucinski K.J., 2013 Growth and optical anisotropy of Tl_4CdI_6 single crystals. Ukr. J. Opt., **14**: 6-13.

Goodenough J.B., 1997. Ceramic solid electrolytes. Solid State Ionics, **94**: 17-25.

Glushko V.P., Gurvich L.V., Bergman G.A., Veits I.V., Medvedev V.A., Khachkuruzov G.A. and Yungman V.S., 1982. Termodinamicheskie Svoista Individual nykh Veshchestv, Vol IV, Nauka, Moskow.

Hassan M., Nawaz M.S. and Rafiuddin, 2008. Ionic conduction and effect of immobile cation substitution in binary system (AgI) 4/5–(PbI2) 1/5, Radiat. Eff. Defect. S., **163**: 885-891.

Honig J.M. and Rao C.N.R., 1981. Preparation and Characterization of Materials (Academic press, New York).

Khalid S. and Rafiuddin, 2011. Effect of cation substitution on the conductivity of Cu_2CdI_4, European Journal of Scientific Research, **50**(2): 187-190.

Kalyagin D.S., Ermolenko Yu. E. and Vlasov Yu. G., 2008. Diffusion of Tl-204 isotope and ionic conductivity in Tl_4HgI_6 membrane material for chemical sensors. Rus. J. Appld. Chem., **81**: 2172-2174.

Kartini E., Sakuma T., Basar K. and Ihsan M., 2008. Mixed cation effect on silver–lithium solid electrolyte $(AgI)_{0.5}(LiPO_3)_{0.5}$, Sol. Stat. Ionics, **179**: 706–711.

Noorussaba and Afaq A., 2016. Preparation, Characterization of a new Fast ionic Conductor (Ag_2CdI_4:0.xRbI) where (x = 0.1, 0.2 and 0.3 mol. wt. %). International Journal of Applied and Pure Science and Agriculture, **2**(12): 209-216.

Noorussaba and Afaq A., 2017 Investigation of nanostructure of a new Fast ionic Conductor (Cu_2CdI_4:0.xRbI) where (x = 0.1, 0.2 and 0.3 mol. wt. %). International Journal of Recent Engineering Research and Development, **2**(1): 31-41.

Noorussaba and Afaq A., 2011. Preparation, electrical conductivity and phase transition in a (Ag_2HgI_4:0.2AgI):xKBr type mixed composite system (x = 0.2, 0.4, 0.6 mol. wt. %). Analytical and Bioanalytical Electrochemistry, **3**(4):406 - 419.

Noorussaba and Afaq A., 2017. Investigation of a rubidium fast ion conductor (Cu_2HgI_4:0.xRbI) (where x = 0.1, 0.2 and 0.3 mol. wt. %). Oriental Journal of Physical Sciences, **2**(2):1-7.

Noorussaba, 2025. Investigation of the Characteristics of a new Fast ionic solid conductor ($CdHgI_4$:0.xRbI) where (x = 0.1, 0.2 and 0.3 mol. wt. %). International Research Journal, **12**(6**):** 433-438.

Rao C.N.R. and GopalKrishnan J., 1989. “New Directions in Solid State Chemistry” (Cambridge University Press)

Sudharsanan R., Srinivasan T.K.K. and Radhakrishna, 1984. Raman and far IR studies on Ag_2CdI_4 and Cu_2CdI_4 superionic compounds. Solid State Ionics, **13**: 277-283 North-Holland, Amsterdam.

Secco E.A. and Sharma A.**,** 1995. Structure stabilization: locking-in fast cation conductivity phase in TlI, J. Phys. Chem. Sol., **2**: 251–254.

Viswanathan A. and Suthanthiraraj S.A., 1993. Impedance and modulus spectroscopic studies on the fast ion conducting system CuI-Ag_2MoO_4,, Solid State Ionics, **62**(1–2): 79-83.

Wakamura K., 2002. Characteristic properties of dielectric and electronic structures in super ionic conductors, Solid state ionics, **149**: 73–80.

Xianjun Z., Yunxia L., Liangmei G., Longbin C., Hanxing L. and Mingle C., 2008 Synthesis and characteristic of Li3V2(Po4) as cathode materials for lithium-ion batteries. Solid State Ionics, **179**: 1679-1682.

Zandbergen H.W., 1979. The crystal structure of α-thallium hexaiodochromate, α-Tl_4CrI_6, Acta Cryst. B., **35**: 2852-2855.

Zhu X.J., Liu Y.X., Geng L.M. and Chen L.B., 2008. Synthesis and performance of lithium vanadium phosphate as cathode materials for lithium ion batteries by a sol-gel method. J. of Power Sources, **184**: 578-582.