2.1 Introduction:

Ion conducting composites – the heterogeneous systems made up of ionic salts and insulating chemically inert components that may be regarded as new classes of solid electrolyte interfaces play a major role in influencing the properties of materials especially at low and moderate temperatures. The conductivity enhancement of composites can be explained by the presence of a great number of surfaces and interfaces which act as an additional source of point defects [1]. Heterogenous systems of the ionic salt–oxides have enhanced ionic conductivity. Remarkable properties of such systems can be explained by the presence of disordered or defect enriched region localized near the interfaces [2]. In case of non metallic phases, the surface and grain boundary between the two materials are the areas of point defect where space–charge region often exist [3]. The elaboration of composite material offers new degree of freedom in the search for advanced functional materials; because specific properties can be tailored to a certain degree by mixing appropriate phases. Composite solid electrolytes (superionic conductors) consist of a new class of ion conducting materials suitable for practical applications as their electrical and mechanical properties can easily be altered by a variation of concentration of the dispersed component which is mostly non–conducting such as V$_2$O$_5$ or Al$_2$O$_3$ and insoluble in the host material under the fabrication conditions [4]. Since the discovery of enhancement in the ionic conductivity of LiI due to dispersion of alumina [5], several other researchers have observed the enhancements in various other composites such as polymers electrolytes [2] and dispersed solid electrolyte systems of Ag, Li, and Ca halides [6]. The conductivity of composites depends on many factors: conductivity of individual phases, concentration and the morphology of composites i.e. shape, size, and space distribution of single-phase areas over the composite.
Almost all models proposed to account for the enhancement in conductivity assume the formation of highly conducting space-charge layer along the matrix–particle interface. The space–charge model introduced by Jow and Wagner [3] and further developed by Maier [7-9] has been used frequently to explain the interface defects. According to this model, charge carriers move from the ionic conductors to the interface of the second phase insulator because of the presence of preferential sites at the interface. This charge layer is then compensated by the formation of a layer of charged point defects, which leads to high ionic conductivity. Composite solid ionic conductors may not only offer enhanced ionic conductivity but also superior mechanical properties and low cost [5, 10]. The addition of a dopant in the host material creates defects, which allows smooth flow of electrons leading to enhancement of the ionic conductivity and other properties of the host. Bunde and colleagues [11-12] first used the concept of percolation in a cube lattice to describe the conductivity of ionic conductors with dispersed insulator particles.

Wagner first used the space–charge layer concept to explain conductivity effects in semi conducting two-phase materials [13]. The importance of the space–charge layer for the ionic conduction was first revealed by Liang [5]. After these initial studies, the conductivity enhancement in multiphase materials was confirmed for numerous ceramic composites, including dispersion of fine insulator particles in the ionic conductor matrix and mixture of two different ionic conductors, with a major contribution by J. B. Wagner [14].

In particular, the added oxides led to desirable mechanical properties and enhancement of ionic conductivity at room temperature [15-18]. The theoretical treatment of ionic conduction near the interface was largely developed by Mair [19].
He gave a quantitative description of the conductivity enhancement based on the concept of space–charge layer near the phase boundaries.

Thallium iodide (TII) exists in two polymorphs; yellow β-TII, a double layered orthorhombic structure related to NaCl [20] which transforms to red α-TII (CsI–type cubic structure) at 172 °C. This phase transition is accompanied by about two orders of jump in conductivity. Studies have been carried out to stabilize the high temperature phase to utilize its good transport properties by doping it homogenously with other iodides such as RbI [21], CsI and KI [22], AgI, TIBr and TICl [23]. The results were satisfactory; particularly the RbI–TII and RbI–TII systems show that α-TII was stabilized at room temperature.

In this work, titania, alumina and vanadia were selected to be mixed heterogeneously with TII to improve its transport properties. Here, we have achieved enhancement in the ionic conductivity of β-TII and tried to stabilize the high conducting α-phase at lower temperatures.
Structure of Thallium Iodide
2.2 Experimental:

Thallium iodide was prepared by precipitation from thallium acetate solution using potassium iodide. Titania, alumina and vanadia were taken from BDH LABORATORY each with stated purity of 99.9%. Appropriate amounts of these materials were first ground with acetone for two hours followed by drying at 100 °C for three hours. The material was then ground again for an hour and sieved with 200 mesh. The required amounts of TiO$_2$, Al$_2$O$_3$ and V$_2$O$_5$ were mixed thoroughly with thallium iodide using an agate motor and pestle to produce the series:

I. \((1-x)\ TlI–x\ TiO_2\), \(x = 0–0.7\)

II. \((1-x)\ TlI–xAl_2O_3\), \(x = 0–0.7\)

III. \((1-x)\ TlI–xV_2O_5\), \(x = 0–0.7\)

The mixtures were then heated in an electrical furnace at 200 K for three hours with intermittent grinding. The final mixtures were crushed to fine powders, which were of pale yellow colour. These materials were then kept in perfectly closed glass tubes during the annealing process and until the time of analysis. X-ray diffractograms for the materials were recorded using “BRUKER ADVANCED D8” Diffractometer with Cu$k_a$ radiations. DSC traces were taken by heating in the temperature range 25-450 °C using PERKIN–ELMER instrument with Alumina powder as a reference. The heating rate was kept at 10$^0$C/minute. The electrical conductivity (was measured in the temperature range RT-523K) and impedance measurement were performed (in the frequency range 42 Hz–5MHz) using a highmeter HIOKI-353250 LCR METER for circular pellets of above material pressed under 4 tonnes/cm$^2$ pressures. The two opposite surfaces of the pellet were coated with carbon paint and annealed between the electrodes for two hours at 120 K to increase the electrical connectivity between
the samples and the electrodes. SEM micrographs were taken for the pelletized samples using the STEREOSCAN 360 MICROSCOPE.

2.3 Results and discussion:

Figure 2.1(a, b and c) illustrates the behaviour of conductivity with the composition of the system at different temperatures. The conductivity increases with the titania, alumina and vanadia contents in the materials and pass through a threshold value, after which it starts to decrease with a further increase in the mole fraction of the dopant. The threshold value is estimated from Fig. 2.1 (a and c) below to be \( x = 0.5 \) for TlI\(_x\)TiO\(_2\) and TlI\(_x\)V\(_2\)O\(_5\) systems. A continuous increase in the contribution of the grain boundary to the total resistivity of the samples is observed with increasing content of titania and vanadia in the system. This is due to the increase in the phase boundary as can been seen in SEM micrographs (figure 2.6). Figure 2.1(b) shows the behavior of conductivity when the pure thallium iodide is dispersed with different mole percentage of the dispersoid of Al\(_2\)O\(_3\), conductivity seems to be increasing as the amount of alumina increases and reaches the maximum at \( x=0.4 \) mole fraction of alumina, after which it decreases. The maximum increase in conductivity (for \( x=0.4 \)) is about three orders of magnitude at the lowest temperature and this trend continues till the transition temperature (200°C). However, when the concentration of dispersoid exceeds the threshold value, the conductivity drops due to the blocking of conduction pathways by the dopant particles. In figures 2.2 (a and c), similar trends of conductivity were observed with a small difference of threshold value which is found to be \( x=0.5 \). The enhancement of ionic conductivity is observed for two reasons. First, the interface region itself is a disordered one where defect formation and migration enthalpies are notably reduced leading to the enhancement of ionic conductivity within the interface core (grain boundary diffusion). However, the core effect is
generally small, given the reduced interface area in TII doped with TiO$_2$, Al$_2$O$_3$, and V$_2$O$_5$. Secondly, the disordered region induces concentration profiles of point defects in the region adjacent to the interface in the ionic material (space–charge layers) [24]. If we go to higher temperatures, enhancement continues and it is almost two-folds compared to the conductivity of the pure system. The fundamental mechanism is that ions can be trapped at the interface core (this process is equivalent to a segregation phenomenon). The counter species, in general, a trapped ion vacancy, is then accumulated in the adjacent space–charge regions. The impetus behind this phenomenon is the chemical affinity of a second phase towards the trapped ion.
Figure 2.1(a) Electrical conductivity as a function of the composition of (1-x) TlI–x TiO$_2$ samples at different temperatures.

Figure 2.1(b) Electrical conductivity as a function of the composition of (1-x) TlI–x Al$_2$O$_3$ samples at different temperatures.
Figure 2.1(c) Electrical conductivity as a function of the composition of (1-x) TlI-x V$_2$O$_5$ samples at different temperatures.
The temperature dependence of ionic conductivity is given by the Arrhenius expression:

\[ \sigma T = \sigma_0 \exp \left( \frac{E_a}{kT} \right) \]  

(1)

where \( \sigma_0 \) is the pre-exponential factor and \( E_a \) is the activation energy for the ionic motion. The conductivity data were fitted to the above equation to obtain the activation energy for conduction. As shown in figure 2.2 (a, c), two regions are observed in the samples containing titania and vanadia amounts up to \( x \leq 0.4 \), and in figure 2.2 (b) the sample containing alumina amount up to \( x \leq 0.3 \), after which the abrupt change in the conductivity disappears and the curves tend to be straightened along the whole temperature region under study.

This enhancement of conductivity with TiO\(_2\) and V\(_2\)O\(_5\) becomes maximum at \( x=0.5 \). However, in case of alumina, the conductivity increases up to \( x=0.4 \) and finally decreases with a further increase in the alumina content, this can be explained by the stabilizing effect of \( \beta \)-TII at a higher temperature, and the high temperature \( \alpha \)-phase might have been suppressed in these samples within the temperature range studied. Uvarov et al. have also observed this effect in the two systems Li\(_2\)SO\(_4\)–Al\(_2\)O\(_3\) and AgI–Al\(_2\)O\(_3\) [17, 25].

The activation energies were calculated using the Linear Regression method in the temperature range 25–170 °C and tabulated in Table 2.1. These values followed the opposite trend of ionic conductivity with the composition, i.e. with an increase in titania, alumina and vanadia content activation energy decreases and a drop in activation energy always follows with a rise in the conductivity. The activation energy for pure thallium iodide is calculated as 0.639 eV which is in good agreement with the value found in another work [22], however, a slight disagreement is found by Samara [26] who reported it to be \( \approx 0.42 \) eV. This may be due to the different sample shapes used in the different works.
Table 2.1 Activation energies of conduction in the temperature range 25–170 °C of (1-x) TlI–xM samples (M= TiO$_2$, Al$_2$O$_3$ and V$_2$O$_5$)

<table>
<thead>
<tr>
<th>Mole fraction</th>
<th>Activation energy (eV) TiO$_2$</th>
<th>Activation energy (eV) Al$_2$O$_3$</th>
<th>Activation energy (eV) V$_2$O$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.639</td>
<td>0.639</td>
<td>0.639</td>
</tr>
<tr>
<td>0.1</td>
<td>0.707</td>
<td>0.713</td>
<td>0.736</td>
</tr>
<tr>
<td>0.2</td>
<td>0.602</td>
<td>0.600</td>
<td>0.630</td>
</tr>
<tr>
<td>0.4</td>
<td>0.514</td>
<td>0.520</td>
<td>0.521</td>
</tr>
<tr>
<td>0.5</td>
<td>0.322</td>
<td>0.505</td>
<td>0.411</td>
</tr>
<tr>
<td>0.6</td>
<td>0.419</td>
<td>0.525</td>
<td>0.437</td>
</tr>
<tr>
<td>0.7</td>
<td>0.562</td>
<td>0.609</td>
<td>0.443</td>
</tr>
</tbody>
</table>
Figure 2.2 (a) Electrical conductivity as a function of temperature of (1-x) TlI–xTiO₂ samples.

Figure 2.2 (b) Electrical conductivity as a function of temperature of (1-x) TlI–xAl₂O₃ samples.
Figure 2.2 (c) Electrical conductivity as a function of temperature of (1-x) TII-xV_2O_5 samples.
Figure 2.3 (a, b and c) shows the impedance spectra of pure thallium iodide and its mixture with titania, alumina and vanadia. Each spectrum shows clearly two depressed semicircles; the large one in the low frequency range is attributed to the grain boundary contribution and the second one (shown in the inset) is for bulk contribution. The DC conductivity can be estimated from the intersection of the bulk semicircle with the real impedance axis. The data from an impedance measurement can be given in the form: It is known that the complex impedance \((Z^{*}(\omega))\) is defined as the sum of its real \((Z')\) and imaginary part:

\[
(Z^{*}(\omega) = Z' + jZ'' ; j = \sqrt{-1})
\]  

(2)

For our modeled equivalent circuit, \(Z'\) and \(Z''\) are given as follows:

\[
Z' = \frac{R_g}{1 + \omega^2 C_g^2 R_g^2}
\]  

(3)

\[
Z'' = \frac{R_g^2 \omega C_g}{1 + \omega^2 C_g^2 R_g^2}
\]  

(4)

\(\omega = 2\pi f\) and \(f\) is the maximum frequency in Hz

where the resistance of the grain \((R_g)\) and the grain boundary \((R_{gb})\) can directly be obtained from the intercept of the \(Z'\)-axis [27]. The angular frequency of the grain \((\omega_g)\) and the grain boundary \((\omega_{gb})\) is obtained at the maxima of the semicircles. As \(Z' = Z''\) at the maximum point in the semicircle, the capacitances of the grain and the grain boundary \(C_g\) and \(C_{gb}\) can therefore be calculated according to eqs. (5) and (6) respectively.

\[
C_g = \frac{1}{R_g \omega_g}
\]  

(5)

\[
C_{gb} = \frac{1}{R_{gb} \omega_{gb}}
\]  

(6)
The relaxation time \( \tau_g \) and \( \tau_{gb} \), due to these effects, is obtained from the angular frequency at the maxima using eqs. (7) and (8):

\[
\tau_g = \frac{1}{\omega_g} = C_g R_g \quad (7)
\]

\[
\tau_{gb} = \frac{1}{\omega_{gb}} = C_{gb} R_{gb} \quad (8)
\]

In general,

\[
\sigma = \frac{1}{R}
\]

\[
R = \frac{1}{\sigma} \quad (9)
\]

Substituting equation (9) in (8) we get,

\[
\tau = \frac{1}{\sigma} C \quad (10)
\]

Where \( \sigma \) denotes the conductivity. Eqn. 10 implies that relaxation time is inversely proportional to conductivity and in our study we have observed a decrease in the relaxation time in the system of TlI–TiO\(_2\) and TlI–Al\(_2\)O\(_3\). It was also assumed that \( \tau_g \) indicates the mean time between two consecutive jumps of a cationic vacancy.

Alternatively, the diffusion coefficient \( D \) is related to \( \tau_g \) as follows:

\[
D \propto \frac{\gamma \alpha^2}{\alpha \tau_g} \quad (11)
\]

\[
D \propto \frac{1}{\tau_g} \quad (12)
\]

where \( d^2 \) is the mean square jump distance between two adjacent cationic sites in the crystal lattice; \( \gamma \) and \( \alpha \) the correlation and geometric factors, respectively. Thus, the shorter the \( \tau_g \) is, the faster the cationic diffusion which leads to high ionic conductivity. The values(\( \tau, R, C \)) of equivalent circuit parameters of both grain and
grain boundary contributions which are estimated from the impedance plots at room

temperature (25° C) and are calculated by using these equations and tabulated in
table 2.2.

**Table 2.2** Values of the equivalent circuit parameters estimated from the impedance
spectra for \((1-x)\) TlI–xM samples (M= TiO\(_2\), Al\(_2\)O\(_3\) and V\(_2\)O\(_5\)) at 25°C and different

mole fraction

<table>
<thead>
<tr>
<th>Molefraction (x)</th>
<th>Rg (kΩ)</th>
<th>Cg (F)</th>
<th>(\tau_g) (s)</th>
<th>Rgb (kΩ)</th>
<th>Cgb (F)</th>
<th>(\tau_{gb}) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure TlI</td>
<td>78.52</td>
<td>4.9×10(^{-7})</td>
<td>1.85×10(^{-4})</td>
<td>3012.23</td>
<td>2.6×10(^{-8})</td>
<td>7.8×10(^{-5})</td>
</tr>
<tr>
<td>TlI-TiO(_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TlI(_{0.9})-TiO(<em>2) (</em>{0.1})</td>
<td>309.5</td>
<td>5.3×10(^{-7})</td>
<td>1.6×10(^{-4})</td>
<td>2732.46</td>
<td>2.8×10(^{-8})</td>
<td>7.65×10(^{-5})</td>
</tr>
<tr>
<td>TlI(_{0.7})-TiO(<em>2) (</em>{0.3})</td>
<td>136.58</td>
<td>6.4×10(^{-7})</td>
<td>8.74×10(^{-5})</td>
<td>14502.8</td>
<td>3.4×10(^{-8})</td>
<td>4.9×10(^{-4})</td>
</tr>
<tr>
<td>TlI(_{0.5})-TiO(<em>2) (</em>{0.5})</td>
<td>11</td>
<td>7.2×10(^{-7})</td>
<td>8.0×10(^{-6})</td>
<td>525</td>
<td>6.1×10(^{-8})</td>
<td>3.20×10(^{-5})</td>
</tr>
<tr>
<td>TlI-Al(_2)O(_3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TlI(_{0.7})-Al(_2)O(<em>3) (</em>{0.3})</td>
<td>40</td>
<td>9.8×10(^{-7})</td>
<td>3.92×10(^{-5})</td>
<td>10066.4</td>
<td>1.2×10(^{-9})</td>
<td>1.20×10(^{-5})</td>
</tr>
<tr>
<td>TlI(_{0.5})-Al(_2)O(<em>3) (</em>{0.5})</td>
<td>36</td>
<td>1.05×10(^{-6})</td>
<td>3.78×10(^{-5})</td>
<td>901.8</td>
<td>8.7×10(^{-9})</td>
<td>7.84×10(^{-6})</td>
</tr>
<tr>
<td>TlI(_{0.3})-Al(_2)O(<em>3) (</em>{0.7})</td>
<td>4157</td>
<td>2.3×10(^{-6})</td>
<td>9.561×10(^{-3})</td>
<td>10297.66</td>
<td>9.6×10(^{-9})</td>
<td>9.89×10(^{-5})</td>
</tr>
<tr>
<td>TlI-V(_2)O(_5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TlI(_{0.9})-V(_2)O(<em>5) (</em>{0.1})</td>
<td>70</td>
<td>5.5×10(^{-9})</td>
<td>3.85×10(^{-7})</td>
<td>6298.5</td>
<td>3.3×10(^{-9})</td>
<td>2.1×10(^{-5})</td>
</tr>
<tr>
<td>TlI(_{0.3})-V(_2)O(<em>5) (</em>{0.7})</td>
<td>3.34</td>
<td>5.3×10(^{-8})</td>
<td>1.77×10(^{-7})</td>
<td>10.83</td>
<td>4.8×10(^{-8})</td>
<td>5.2×10(^{-7})</td>
</tr>
<tr>
<td>TlI(_{0.5})-V(_2)O(<em>5) (</em>{0.5})</td>
<td>10.21</td>
<td>1.2×10(^{-8})</td>
<td>1.23×10(^{-7})</td>
<td>317.7</td>
<td>1.5×10(^{-5})</td>
<td>4.7×10(^{-7})</td>
</tr>
</tbody>
</table>
Figure 2.3 (a) Impedance spectra of \((1-x)\)TlI–\(x\)TiO\(_2\) the insets show the behaviour at low frequency range.
Figure 2.3(b) Impedance spectra of (1-x) TlI–xAl₂O₃ the insets show the behaviour at low frequency range.
Figure 2.3 (c) Impedance spectra of the (1-x) TII–xV₂O₅ the insets show the behaviour at low frequency range.
These enhancements of electrical conductivity of TII were then confirmed by the following analyses:

- **XRD** (X-ray diffractograms)
- **DSC** (Differential Scanning Calorimetry)
- **SEM** (Scanning Electron Microscopy)

Room temperature X-ray diffractograms of the pure TII and its mixtures with TiO$_2$, Al$_2$O$_3$ and V$_2$O$_5$ are shown in Figures 2.4 (a, b and c). TII shows the standard pattern [28], which corresponds to β–phase stable at room temperature. The diffractograms of the mixtures show two phase nature of these materials with no effect of the second phase on the peak positions of the first one i.e. TII. In Fig 2.4(a) several additional peaks are observed in the diffractograms which grow with the increasing mole fraction of titania. These are attributed to the anatase phase of titania. This phase has been observed to transfer to the rutile phase if titania is sintered at high temperatures or mixed with other impurities [29]. However, in these composites, no indication of the presence of the rutile phase has been detected. It is worthy to mention that the strong X-ray absorption of TII causes the intensity of titania to drop rapidly upon increasing the amount of TII in the system. When pure TII was doped with Al$_2$O$_3$, two additional peaks were observed in the diffractograms, which grew with increasing mole fraction of aluminum oxide. These are attributed to the α-phase alumina. However, the diffractogram of V$_2$O$_5$, at different mole fractions, shows three additional peaks, which grew with increasing the mole fraction of vanadia. These are attributed to the orthorhombic phase of vanadia. In this case also, initial mixing lead to a decrease in the intensity of all TII peaks but their position remains the same and no new phase detected. It can also be concluded that the strong X-ray absorption of TII causes the intensities of vanadia to drop rapidly upon increasing the amount of TII.
in the system as mentioned above in the case of TiO$_2$. The single phase of TII has been fitted equally well to the orthorhombic polymorph with the face centered lattice according to the PCPDF#060279. However, the labeled peaks in composites diffraction pattern shown in figure 2.4(c) are according to the PCPDF#861410. It is clearly shown that both TII and V$_2$O$_5$ have single phases. This is in perfect agreement with the homogeneity of the orthorhombic domain, which is also reflected by the SEM image (fig 2.6 shown below).
Figure 2.4 (a) Room temperature X-ray diffractograms of the (1-x)TlI–xTiO$_2$ samples.
Figure 2.4(b) Room temperature X-ray diffractograms of (1-x) TlI–xAl₂O₃ samples

Figure 2.4(c) Room temperature X-ray diffractograms of (1-x) TlI–xV₂O₅ samples
Figure 2.5 (a, b and c) shows the heating mode of the DSC curves of the samples in the temperature range 25-450 ⁰C. Pure TII shows the expected behaviour with moderate strength peak appearing at 173(2) ⁰C, which corresponds to β-α phase transition of the compound [22], and an intensive peak at 440(2) ⁰C, which is attributed to the melting point. The mixture samples show no appreciable effect on the temperature of the phase transition. However, the intensity of the peak corresponding to β-α phase transition decreases gradually with the increasing mole fraction of the second phase (i.e. titania) and finally disappears at x ≥ 0.5, as can be seen in Fig. 2.5(a). This behavior can be explained in terms of endothermic arrest corresponding to the β-α phase transition of TII disappearing at high titania content.

Unlike figure 2.5 (a), the melting peak becomes broad with alumina content in the system figure 2.5 (b). This is due to the formation of the amorphous phase within the space-charge layer which is expected to form between TII and Al₂O₃. It has also been observed from the DSC curve fig 2.5(b) that an additional peak is obtained with the addition of Al₂O₃ and its intensity increases with the mole fraction of alumina. This peak is attributed to interface interactions between TII and Al₂O₃. In figure 2.5(c) a similar behavior has been observed and the melting peak becomes broad with vanadia content due to the formation of the orthorhombic phase within the space charge layer that is expected between TII and V₂O₅. It has also been observed from the DSC curve that an additional peak is obtained with the addition of vanadia and its intensity is directly proportional to the mole fraction of the same. However, with the concentration of vanadia above x = 0.5, this additional peak disappears. This is attributed to the interface-interface interactions between TII and V₂O₅. This behaviour has been observed frequently in the ionic salt-oxide composites such as RbNO₃–Al₂O₃ [1], CsCl-Al₂O₃ [17] and Cs₂H₃ (SO₄)₄–SiO₂ [30]. It was noticed that
with increasing titania, alumina and vanadia content, the melting point of the mixture remains unchanged, which is an evidence of the formation of the composite which in turn leads to the enhancement of ionic conductivity as discussed earlier (Fig. 2.2).

Figure 2.6 (a, b and c) shows the SEM micrographs of the samples, the first is of pure titania after the process of its grinding with acetone and then sieving with 200 mesh. The micrograph shows reasonable homogeneity with the average particle size in the range 200–400 nm. The second SEM micrograph is of the mixture having TlI with 0.2 mole fraction of titania. It shows the distribution of titania particles between the particles of thallium iodide which has a higher average grain size. The distribution of titania layers between the grains of ionic salt is favoured from local thermodynamic equilibrium due to the wetting of titania particles by TlI grains during the preparation of the mixture [31]. This type of distribution is very important in creating a great number of surfaces which in turn act as additional source of point defects. This new region between the ionic salt and the added oxide is called the space–charge layer which strongly alters the bulk properties of the ionic salt [32]. It is also clear that low density and a larger number of pores are observed in the mixture sample. This is due to the two phase nature of the sample and the particle size difference between the salt and the added oxide. Similar results were found in micrographs 2.6 (b and c) in which alumina and vanadia were mixed with TlI and a reasonable homogeneity was observed with the average particle size in the range 200–400 nm.
Figure 2.5 (a, band c) DSC curves of (1-x) TlI–xM ((M= TiO$_2$, Al$_2$O$_3$ and V$_2$O$_5$ samples: (1) x=0 (2)x=0.2 (3) x=0.4 and (4) x=0.6
Figure 2.6 (a) SEM micrographs of (1-x)TiI-xTiO$_2$ samples: 1) pure TiO$_2$ and 2) x = 0.2.
Figure 2.6 (b) SEM micrographs of (b) (1-x) TlI–xAl₂O₃ samples: 1) pure Al₂O₃ and 2) x = 0.2.
Figure 2.6 (c) SEM micrographs of (1-x) TiI-xV$_2$O$_5$ samples: 1) pure V$_2$O$_5$ and 2) x=0.2
2.5 Conclusion:

It can be concluded from this study that the ionic conductivity of TII got enhanced on mixing with titania, alumina and vanadia by stabilizing the higher conducting phase of TII at a lower temperature. The activation energy has reduced remarkably in the composite system (1-x) TII–xM (M= TiO₂, Al₂O₃ and V₂O₅). The low temperature phase of TII was stabilized at high temperature when doped with TiO₂, Al₂O₃ and V₂O₅. The highest ionic conductivity was observed in the samples containing at x = 0.5, titania and vanadia each whereas, in the case of alumina the maximum enhancement of ionic conductivity was observed at x=0.4. The impedance spectra showed the prominence of the electrode-electrolyte interface effect due to high level of structural disorder. The X-ray diffractograms, DSC, and SEM analyses and electrical conductivity measurements of the samples also confirmed the formation of composite materials in which the interface layers play an important role in controlling the bulk properties of the material.
References


