13.1 Introduction

During the past decade, single crystals of tin-iodides (SnI$_2$ and SnI$_4$) have been subject of optical and electrical investigations. These studies have advanced the quantitative understanding of photodissociation$^{1,2}$, photolysis$^3$ and luminescence$^4,5$ of these materials. The optical absorption edge measures the gap between the conduction and valence bands, in the absence of excitation states and strong impurity absorptions. Applied research has recently put forward SnI$_4$ as a humidity proof transparent antistatic films coating$^6$. The carrier transport in SnI$_4$ has been
investigated by Whall and Juzova, using the technique of transient photo-conduction.

Raman scattering of light in SnI$_2$ revealed a considerable anharmonicity of vibrations and the inter layer interaction in this crystal has put it in the series of layer compounds like, CdI$_2$, PbI$_2$, HgI$_2$, etc. In spite of the fact that the electrical conductivity of SnI$_2$, SnCl$_2$ and SnBr$_2$ is presently well known, little is known about the transport mechanism governing the conductivity of SnI$_2$.

Unlike metals where the electron is the charge carrier while in insulators, contributing factors are the crystal defects such as isolated anion or cation (Schottky defect), cation substitutional impurities, cation vacancy-cation impurity complexes, vacancy pairs, cationic interstitials (Frenkel defect), colour centres, etc. At room temperature the lattice is electrically neutral due to pairing of various defect sites, which accounts for the very low conductivity of ionic materials. Supplying heat energy to the sample serves to thermally generate the charge carriers because of breaking of temporary bonds, thus enhancing conduction.

The study of electrical conductivity in
association with thermal behaviour has been used in this chapter to understand the mechanism of electrical conduction in SnI₂ and SnI₄ materials in the form of pellets and single crystals.

13.2 Experimental

13.2.1 Specimen preparation

Single crystals of SnI₂ and SnI₄ used in the present investigation were grown by gel technique as described in chapter 5. The octahedral SnI₄ crystals, upto 5 mm in size were selected. For pellet samples, of SnI₂ and SnI₄, the laboratory grown crystals were finely ground and the resulting powders were compressed in a die of diameter 1 cm, under a pressure of 200 kg cm⁻². The average particle size for both materials was 150 µm and the packing fractions for SnI₄ and SnI₂ were 0.764 and 0.637 respectively.

13.2.2 Electrical conductivity measurements

The crystal or pellet, as the case may be, was mounted between the flat platinum electrodes in an ordinary conductivity cell, schematically shown in fig. 13.1. It was then enclosed in a resistance heated furnace and the temperature of the sample increased
slowly by regulating the power from the 250 V, 50 c/s mains through a dimmerstat. The rate of heating was reasonably maintained linear throughout the experiment and the temperature of sample was monitored using a chromel-alumel thermocouple (± 2°C). The thermocouple wires also served as electrical connecting leads.

The electrical resistance measurements of SnI₄ crystal and pellet were made in temperature range from 30°-110°C, using a BPL (India) Million megohmeter Model RM 160 MK. The accuracy of measurements of resistance in the range 10⁶ - 10¹⁰ was about 5%. The experimental set up for the electrical measurements is shown in fig. 13.2.

The resistance of the pellet of SnI₂ in the temperature range 60°-300°C is measured by connecting the electrode assembly in series with a sensitive milliammeter and suitable (constant) d.c. supply. A sensitive voltmeter is connected across it. This arrangement is schematically illustrated in fig. 13.3.

13.3 Results and Discussion

SnI₄

The d.c. conductivity, \( \sigma \text{ ohm}^{-1} \text{ cm}^{-1} \) at
different temperatures was determined for pellets as well as for single crystal sample and are summarized in table 13.1. The variation of $\ln \sigma$ with the reciprocal of absolute temperature of pellet and crystal are illustrated in fig. 13.4. It is clearly seen in the figure that the values of $\ln \sigma$ for crystal are always higher than that for pellets for a given temperature over the temperature range investigated. This may be explained as due to the fact that when an electric field is applied on the two opposite surfaces of the crystal, the charge carriers move freely in the crystal and reach the other electrode, while in case of polycrystalline pellet samples, some will be trapped at the grain boundaries and give rise to interfacial polarization.

The variation in the electrical conductivity observed in fig. 13.4, yields two straight lines and it is in accordance with the relation:

$$\sigma = n_0 e \mu \exp \left( - \frac{E_g}{kT} \right) \quad (13.1)$$

where $n_0 = \text{number of charge carriers per cm}^3$

$e = \text{electronic charge}$
Table 13.1 Observations of electrical conductivity of different samples

<table>
<thead>
<tr>
<th>Temperature of the sample in °C</th>
<th>Electrical conductivity ($\sigma$) of the samples in ohm$^{-1}$ cm$^{-1}$</th>
<th>Pellet x 10$^{-9}$</th>
<th>Single crystals x 10$^{-9}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>1.767</td>
<td>2.468</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>2.062</td>
<td>4.079</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>2.578</td>
<td>5.279</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>3.256</td>
<td>6.648</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>4.125</td>
<td>7.542</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>4.583</td>
<td>8.749</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>5.380</td>
<td>12.821</td>
<td></td>
</tr>
<tr>
<td>95</td>
<td>6.187</td>
<td>14.958</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>7.279</td>
<td>16.318</td>
<td></td>
</tr>
<tr>
<td>105</td>
<td>9.166</td>
<td>19.944</td>
<td></td>
</tr>
<tr>
<td>110</td>
<td>11.250</td>
<td>22.43</td>
<td></td>
</tr>
</tbody>
</table>
The linear variation of the plot shows a change at the temperature range (95 - 100°C), thereby resulting in two straight lines with different slopes. Equation 13.1 should relate each of the two straight line portions of both curves indicating that at least two conductivity mechanism are acting—probably in parallel or that the sample undergoes a dramatic change in properties at the turning point. It seems much likely that the change in temperature dependence is due to a phase change of SnI₄ molecules, according to the reaction, as explained in previous chapter for dielectric study, at the same temperature range,

\[ \text{SnI}_4 \rightarrow \text{SnI}_2 + I_2 \quad \ldots \quad (13.2) \]

The estimated values of activation energies for pellet and single crystal are given in Table 13.2. It is clearly seen from this that activation energies for crystal is higher than that for pellet samples.

The nature of electrical conduction in SnI₄
### Table 13.2 Activation energy of different samples

<table>
<thead>
<tr>
<th>Particulars of the sample</th>
<th>Activation energy in eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low temperature range</td>
</tr>
<tr>
<td>Pellet</td>
<td>0.776</td>
</tr>
<tr>
<td>Single crystal</td>
<td>0.815</td>
</tr>
</tbody>
</table>
may be understood by considering both band and polaron hopping models of charge transport. Electron-phonon interaction in molecular crystals are treated at length by Friedman\(^{10}\) and Holstein\(^{11}\). Friedman used a band description in which the carriers were scattered by acoustic (lattice) vibrations and found that the mobility depended on temperature according to \(\mu \propto T^{-2}\). In the Holstein model the carriers interact with vibrating molecules and the mobility varies approximately as \(T^{-3/2}\). These models cannot explain the observed temperature dependence of hole mobility in SnI\(_4\), in the experiment of Wall and Juzova\(^{7}\). They have observed the charge mobility variation in SnI\(_4\) approximately as \(T^{-4}\), by considering a non-linear electron-phonon interaction from a modified Holstein model due to Munn and Siebrand\(^{12}\).

Either electrons or holes drifted across the sample, depending on the polarity of the field. The majority carriers contributing to conduction have enough mobility while the minority carriers are severely modified by trapping.

\(\text{SnI}_2\)

The data of the electrical conductivity of pellet samples at various temperatures are given in Table 13.3. The plot of \(\ln \sigma\) against \(1/T\) is illustrated
Table 13.3 Variation of electrical conductivity of SnI₂

<table>
<thead>
<tr>
<th>Temperature of the pellet sample (°C)</th>
<th>Electrical conductivity (ohm⁻¹ cm⁻¹ x 10⁻⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>9.2528</td>
</tr>
<tr>
<td>70</td>
<td>9.9678</td>
</tr>
<tr>
<td>80</td>
<td>10.7050</td>
</tr>
<tr>
<td>100</td>
<td>11.7450</td>
</tr>
<tr>
<td>110</td>
<td>12.6327</td>
</tr>
<tr>
<td>120</td>
<td>15.0877</td>
</tr>
<tr>
<td>130</td>
<td>17.4324</td>
</tr>
<tr>
<td>140</td>
<td>21.3694</td>
</tr>
<tr>
<td>150</td>
<td>22.0367</td>
</tr>
<tr>
<td>160</td>
<td>23.1120</td>
</tr>
<tr>
<td>180</td>
<td>24.9154</td>
</tr>
<tr>
<td>200</td>
<td>39.1403</td>
</tr>
<tr>
<td>220</td>
<td>67.5982</td>
</tr>
<tr>
<td>250</td>
<td>85.3833</td>
</tr>
<tr>
<td>260</td>
<td>89.0678</td>
</tr>
<tr>
<td>290</td>
<td>113.9070</td>
</tr>
</tbody>
</table>
in fig. 13.5. The variation observed in the figure yielded two straight lines. Thus linear variation of plot is broken at a temperature (T), nearly 150°C, (same as seen in previous chapter for dielectric variation with temperature) thereby resulting two straight lines with different slopes. Our D.T.A. (fig. 13.6) experiment fails to show any phase change in studied temperature range and in particular at temperature (T), so the author believes that there exists two types of conduction in this material, one at low temperature range and other at high temperature range, viz, extrinsic and intrinsic conduction respectively. Therefore, T, may be attributed to transition temperature. The activation energies for low and high temperature ranges are 0.517 and 0.153 eV respectively.

The extrinsic conductivity is attributed to the movement of permanent lattice defects which coexist with impurities in the crystal. SnI₂ is formed by double decomposition of SnCl₂ and KI in silica gels, K⁺, Cl⁻ and Ca⁺⁺ were traced as impurities by electron microprobe analyses, reported in chapter 8. The monovalents ions normally K⁺ may be accommodated in the structure at lattice sites normally occupied by divalent tin ions. They must, however, be associated
with interstitial tin ions or iodine ions vacancies to restore overall charge neutrality. Thus extrinsic conductivity is to be accounted for by the movement of interstitial tin and iodine ions vacancies, or both. The activation energy in the extrinsic range is therefore a measure of energy required to move the permanent defects.

In the intrinsic range, where the conductivity is predominantly due to the movement of defects produced by thermal activation and therefore associated with the pure crystal, X-ray density and pyknometric density, determined in chapter 8, do not differ in this crystal, there may be a small concentration of Frenkel defects in the stoichiometric crystal, seem dominant the electrical conduction in the sample. The activation energy for the intrinsic range is related to the sum of the energy needed to form a defect and the energy required to move it.

A knowledge of the concentration and mobility of point defects in a solid is essential for understanding their interesting properties. Lidiard\textsuperscript{13} has presented a comprehensive review of transport phenomenon in ionic crystals where in many
cases the defects are charged and electronic conduction is negligible. Then, the conductivity is in accordance with the relation,

\[ \sigma = \sigma_0 \exp\left(-\frac{E_g}{kT}\right) \quad (13.3) \]

and

\[ \sigma = N e X_0 (\mu_v + \mu_i) \quad (13.4) \]

where
- \( N \) = Number of Sn\(^{++}\) ions per cm\(^3\)
- \( e \) = electronic charge
- \( X_0 \) = Mole fraction of Frankel defects in pure SnI\(_2\)
- \( \mu_v \) = Mobility of vacancy
- \( \mu_i \) = Mobility of interstitial.

13.4 Conclusions

1. The variation in d.c. conductivity of single crystals of SnI\(_4\) and pellet samples of SnI\(_4\) and SnI\(_2\) have been studied in temperature range 30\(^\circ\) - 100\(^\circ\) C and 60 - 300\(^\circ\) C respectively.

2. The discontinuity in linear rise of ln \( \sigma \) with reciprocal of temperature is attributed to the
dissociation of material in case of SnI$_4$ and by extrinsic and intrinsic conductivities in case of SnI$_2$.

3. The activation energies for the conduction have been estimated for SnI$_4$ pellet and single crystal samples and SnI$_2$ pellet sample.

4. For SnI$_4$ material, the electrical conductivity of crystalline sample is larger than that of pellet samples.
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Captions of the figures

Fig. 13.1 Schematic diagram of conductivity cell.
E - Platunum electrodes.
S - Sample,
T - Thermocouple
M - Metallic body of the cell
L - Connecting Leads.

Fig. 13.2 Experimental set up for electrical measurements using BPL Million Megohmte. Model 2M 160 MK III A.

Fig. 13.3 Schematic arrangement for measurement of conductivity.

Fig. 13.4 Plot of ln $\sigma$ versus reciprocal of temperature for single crystal (▲) and pellet (●) samples of SnI$_4$.

Fig. 13.5 Plot of ln $\sigma$ versus reciprocal of temperature for the pellets of SnI$_2$.

Fig. 13.6 DTA of SnI$_2$. 