Chapter IV | Synthesis and Characterization of (Si-Sn)\textsubscript{x}Sb\textsubscript{y} and (Si-Sn)\textsubscript{x}Sb\textsubscript{y}-CNT (X=2-5, Y=3-6)
4.1 Introduction

Si based composite alloy anodes are much attractive candidate for anode materials in rechargeable Li ion batteries due to their high specific capacity of (Li_{15}Si_4: 3579 mAhg^{-1}, Li_{22}Si_5: 4200 mAhg^{-1}). Many efforts, therefore, have been devoted to improve the cycling performance of Si-based systems [1-3], which include decreasing particle size of active material to nano-scale and the use of intermetallics or composite host material instead of pure metal [4–6]. Moreover, a wide literature survey within the cited survey of Scopus, only few literatures are available for Si-SnSb samples and very few literature is available for CNT incorporated Si-SnSb samples. In this chapter, a novel process is proposed to synthesize (Si-Sn)_xSb_y and (Si-Sn)_xSb_y-CNT at different compositions and deals with the structural, morphological, optical, thermal and electrical characterization of (Si-Sn)_xSb_y and (Si-Sn)_xSb_y-CNT (x=2-5, y=3-6) alloy.

4.2 Structural Characterization

4.2.1 XRD Analysis

Fig. 4.1 (a-b) shows the XRD patterns of (Si-Sn)_xSb_y and (Si-Sn)_xSb_y-CNT (x=2-5, y=3-6) alloy composites. The presence of very minor parent traces of Sn and Sb are observed and also pure Si is present at 47°, which have reported by Guo et al. [7] and Kang et al. [8]. There was no evidence of any kind of Sn-related peaks in Fig. 4.1 (b). No oxide peaks are found in (Si-Sn)_xSb_y and (Si-Sn)_xSb_y-CNT with different concentrations of Si and Sn as mentioned above. In all the X-ray diffractograms, intense peaks are assigned (shown in Table 4.1) to hexagonal structure similar to Sn_xSb_y and Sn_xSb_y-CNT at different Sn and Sb concentrations.
The peak at 48° corresponding to the plane <101> is assigned to CNT as shown in Fig. 4.1 (b). On comparing Sn$_x$Sb$_y$-CNT with different concentrations, the CNT peak at 27° is diminished, which indicates that the CNT is less functionalized with Si added samples. Crystallite size of (Si- Sn)$_x$Sb$_y$ and (Si-Sn)$_x$Sb$_y$-CNT (x=2-5, y=3-6) samples are calculated by Debye Scherrer equation and is tabulated in Table 4.2. The broadening of peaks in XRD is observed through Full Width Half Maximum (FWHM), listed in the Table 4.2, indicating a
Table 4.1 Assignment of different $<hkl>$ planes to the XRD peaks obtained

(Si-Sn)$_x$Sb$_y$ ($x=2, y=3$) (Hexagonal); lattice constants, $a=4.325$ Å and $c=5.346$ Å, ($\alpha=120^\circ$, $\beta=\gamma=90^\circ$)

<table>
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<tr>
<th>No. peaks</th>
<th>20 (deg)</th>
<th>h</th>
<th>k</th>
<th>L</th>
<th>1/d$^2$ obs</th>
<th>1/d$^2$ cal</th>
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<td>0.2112</td>
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<td>1</td>
<td>0</td>
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<td>0.3201</td>
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<tr>
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<td>2</td>
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<td>1</td>
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<td>0.5339</td>
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<td>2</td>
<td>0.6559</td>
<td>0.6389</td>
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Table 4.2 Crystallite size for (Si-Sn)$_x$Sb$_y$ and (Si-Sn)$_x$Sb$_y$-CNT ($x=2-5$, $y=3-6$)

<table>
<thead>
<tr>
<th>No. Samples</th>
<th>Sample Name</th>
<th>20 (deg)</th>
<th>FWHM (deg)</th>
<th>Crystalline Size (nm)</th>
<th>Size</th>
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</thead>
<tbody>
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<td>1</td>
<td>(Si-Sn)$_x$Sb$_y$ ($x=2$, $y=3$)</td>
<td>28.83</td>
<td>0.7037</td>
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<tr>
<td>2</td>
<td>(Si-Sn)$_x$Sb$_y$ ($x=3$, $y=4$)</td>
<td>28.76</td>
<td>0.5700</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>(Si-Sn)$_x$Sb$_y$ ($x=4$, $y=5$)</td>
<td>28.77</td>
<td>0.7529</td>
<td>11</td>
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</tr>
<tr>
<td>4</td>
<td>(Si-Sn)$_x$Sb$_y$ ($x=5$, $y=6$)</td>
<td>28.64</td>
<td>0.6441</td>
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<td></td>
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<tr>
<td>5</td>
<td>(Si-Sn)$_x$Sb$_y$-CNT ($x=2$, $y=3$)</td>
<td>28.56</td>
<td>0.5573</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>(Si-Sn)$_x$Sb$_y$-CNT ($x=3$, $y=4$)</td>
<td>28.73</td>
<td>0.5688</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>(Si-Sn)$_x$Sb$_y$-CNT ($x=4$, $y=5$)</td>
<td>28.66</td>
<td>0.7021</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>(Si-Sn)$_x$Sb$_y$-CNT ($x=5$, $y=6$)</td>
<td>28.52</td>
<td>0.7079</td>
<td>11</td>
<td></td>
</tr>
</tbody>
</table>
reduced particle size compared to \( \text{Sn}_x \text{Sb}_y \) \((x=2-5, y=3-6)\) compositions prepared and the one reported in JCPDS data. It is to be noted that addition of Si and CNT, within the trialled composition taken for this study, does not alter the structure of \( \text{Sn}_x \text{Sb}_y \) \((x=2-5, y=3-6)\) at all. Inferred from the XRD results, compared to \( \text{Sn}_x \text{Sb}_y \)-CNT at different compositions, \((\text{Si-Sn})_x \text{Sb}_y\) and \((\text{Si-Sn})_x \text{Sb}_y\)-CNT \((x=2-5, y=3-6)\) samples shows the availability of formation of single phase is very high and the crystallite size of the samples is very low.

![XRD Pattern](image)

**Fig. 4.1 (b) XRD Pattern for \((\text{Si-Sn})_x \text{Sb}_y\)-CNT \((x=2-5, y=3-6)\)**
4.2.2 Morphological Analysis

The SEM images of (Si-Sn)$_x$Sb$_y$ and (Si-Sn)$_x$Sb$_y$-CNT ($x=2-5$, $y=3-6$) alloy powders are shown in Fig. 4.2 (a) and (b). Particles that are directly deposited on the outside surface of CNTs are much smaller, with diameters typically in the range 10–30 nm.

Fig. 4.2 (a) shows that, the particle size of (Si-Sn)$_x$Sb$_y$ ($x=2$, $y=3$), (Si-Sn)$_x$Sb$_y$ ($x=3$, $y=4$), (Si-Sn)$_x$Sb$_y$ ($x=4$, $y=5$) and (Si-Sn)$_x$Sb$_y$ ($x=5$, $y=6$) falls in the range of 40-60 nm, 30-40 nm, 30-80 nm and 40-50 nm respectively, resulting due to the agglomeration of crystallites of the size observed in XRD. Compared to the available literature of Guo et al. [7] and Zhao et al. [9] who have reported very high particle size of 5-10 µm and >20 µm of Si-SnSb particles and presently it is brought forward that this method of preparation has achieved a very low particle size of 30 nm. Obviously, such a granular structure is in favour for increasing the interfacial affinity of Si with the Sn$_x$Sb$_y$ compositions and leading to an ensured electrical contact [10]. Sample (Si-Sn)$_x$Sb$_y$ ($x=4$, $y=5$) shows, higher concentration of parental Sn atoms, as observed in the XRD peaks at 32° and 45°, those could formulates the nucleation sites for agglomerations resulting in higher particle size. In general, from SEM results the addition of Si to Sn$_x$Sb$_y$ could decrease the particle size than that of CNT incorporated Sn$_x$Sb$_y$ samples.

The particle sizes of (Si-Sn)$_x$Sb$_y$-CNT ($x=2$, $y=3$), (Si-Sn)$_x$Sb$_y$-CNT ($x=3$, $y=4$), (Si-Sn)$_x$Sb$_y$-CNT ($x=4$, $y=5$) and (Si-Sn)$_x$Sb$_y$-CNT ($x=5$, $y=6$) are 20-40 nm, 30-50 nm, 20-40 nm and 20-50 nm respectively and are shown in Fig. 4.2 (b). (Si-Sn)$_x$Sb$_y$ and (Si-Sn)$_x$Sb$_y$-CNT with different compositions exhibit with very low particle size compared to above said literature, which may partially be due to the introduction of Si into the Sn$_x$Sb$_y$ alloy and additionally due to the preparation method [11]. From the SEM images, it can be seen that the (Si-Sn)$_x$Sb$_y$-CNT ($x=2$, $y=3$) particles that are directly deposited on the outside surface of
the CNTs are much smaller than that of the unsupported (Si-Sn)$_x$Sb$_y$ (x=2-5, y=3-6), similar to the samples of Sn$_x$Sb$_y$-CNT (x=2-5, y=3-6) compositions. In a related work, Zhang et al. [12] investigated the deposition of various metals on suspended carbon nanotubes by electron-beam evaporation. They found that the coatings of Ti, Ni and Pd on CNTs were either continuous or quasi-continuous. This was in sharp contrast to the deposition of Au, Al and Fe which could only form isolated particles on the CNT surface.

Fig. 4.2 (a) SEM Images for (A) - (Si-Sn)$_x$Sb$_y$ (x=2, y=3), (B)- (Si-Sn)$_x$Sb$_y$ (x=3, y=4), (C)- (Si-Sn)$_x$Sb$_y$ (x=4, y=5) and (D)- (Si-Sn)$_x$Sb$_y$ (x=5, y=6)
4.2.3 EDX Analysis

The atomic weight percentages of (Si-Sn)$_x$Sb$_y$ and (Si-Sn)$_x$Sb$_y$-CNT ($x=2-5$, $y=3-6$) compositions and its contents are tabulated below. For example, an EDX image of only one picture is given here. Fig. 4.3 shows the EDX images of (Si-Sn)$_x$Sb$_y$ ($x=2$, $y=3$) sample.

Table 4.3 shows the atomic weight percentage of Sn, Sb and Si for (Si-Sn)$_x$Sb$_y$ and (Si-Sn)$_x$Sb$_y$-CNT ($x=2-5$, $y=3-6$) composites. Compared to all the compositions, (Si-Sn)$_x$Sb$_y$ ($x=4$, $y=5$) sample only has impurities of Na and Cl, which is in excellent accordance with the X-ray diffraction patterns in Fig. 4.1 (a). Rest of the compositions shows pure, means there is no evidence of Na and Cl impurities. This result reveals that the composition of
**Fig. 4.3** EDX Images of (Si-Sn)$_x$Sb$_y$ (x=2, y=3)

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Atomic wt% - Si</th>
<th>Atomic wt% - Sn</th>
<th>Atomic wt% - Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Si-Sn)$_x$Sb$_y$ (x=2, y=3)</td>
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<td>73.10</td>
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<td>(Si-Sn)$_x$Sb$_y$ (x=3, y=4)</td>
<td>30.65</td>
<td>20.81</td>
<td>48.54</td>
</tr>
<tr>
<td>(Si-Sn)$_x$Sb$_y$ (x=4, y=5)</td>
<td>19.24</td>
<td>19.80</td>
<td>60.97</td>
</tr>
<tr>
<td>(Si-Sn)$_x$Sb$_y$ (x=5, y=6)</td>
<td>22.44</td>
<td>15.80</td>
<td>61.76</td>
</tr>
<tr>
<td>(Si-Sn)$_x$Sb$_y$-CNT (x=2, y=3)</td>
<td>26.17</td>
<td>10.16</td>
<td>63.67</td>
</tr>
<tr>
<td>(Si-Sn)$_x$Sb$_y$-CNT (x=3, y=4)</td>
<td>24.65</td>
<td>17.31</td>
<td>58.04</td>
</tr>
<tr>
<td>(Si-Sn)$_x$Sb$_y$-CNT (x=4, y=5)</td>
<td>21.61</td>
<td>18.92</td>
<td>59.47</td>
</tr>
<tr>
<td>(Si-Sn)$_x$Sb$_y$-CNT (x=5, y=6)</td>
<td>23.44</td>
<td>15.30</td>
<td>61.26</td>
</tr>
</tbody>
</table>
(Si-Sn)_xSb_y nanoparticles in the composites can be assumed to be of (Si-Sn)_2.05Sb_2.95, (Si-Sn)_2.53Sb_4.47, (Si-Sn)_4.33Sb_4.67 and (Si-Sn)_5.12Sb_5.88 phases. In (Si-Sn)_xSb_y-CNT (x=2-5, y=3-6) at different compositions, the carbon was not estimated as explained in section 3.2.3.

4.3 Optical Characterization

To further investigate the crystalline properties of Si and CNT incorporated Sn_xSb_y samples, Raman spectrum is performed. Also it is expected to reflect any of the environmental changes due to the addition of Si and CNT in the lattice through vibrational changes. Hence Raman and Fourier Transform Infrared Spectroscopy would throw light on the lattice changes caused due to substitution. Such changes in the lattice is likely to bring variation in the electronic state due to the change in potential well of atomic lattices. Hence photoluminescence which is powerful in identifying such changes by the process of excitation and emission is employed.

4.3.1 Raman Analysis

Fig. 4.4 (a) and (b) shows the Raman spectrum of (Si-Sn)_xSb_y and (Si-Sn)_xSb_y-CNT (x=2-5, y=3-6) samples with the range from 105 – 135 cm⁻¹ is attributed to Longitudinal Acoustics (LA) modes of crystallinity as observed in Sn_xSb_y and Sn_xSb_y-CNT at different compositions. Due to the addition of Si, the LA mode is not altered in all the compositions. The peak observed at 230 cm⁻¹ and 446 cm⁻¹ does not alter in (Si-Sn)_xSb_y (x=2, y=3), (Si-Sn)_xSb_y (x=4, y=5) and (Si-Sn)_xSb_y (x=5, y=6) compositions but in (Si-Sn)_xSb_y (x=3, y=4) composition, the peak at 230 cm⁻¹ has shifted to 258 cm⁻¹ and the peak at 447 cm⁻¹ has vanished and a new peak has emerged at 635 cm⁻¹. This result indicates that, compared to all the compositions in Fig. 4.4 (a), (Si-Sn)_xSb_y (x=3, y=4) shows drastic variation in Sb (low) and Si (high). This suggests that, this may be due to the effect of Si and it breaks bondage between Sn and Sb and exhibits new bond between Sn-Si or Sb-Si. In addition, the intense
Fig. 4.4 (a) Raman spectrum for (Si-Sn)$_x$Sb$_y$ (x=2-5, y=3-6)

Fig. 4.4 (b) Raman spectrum for (Si-Sn)$_x$Sb$_y$-CNT (x=2-5, y=3-6)
peak observed at 230 cm\(^{-1}\) and 446 cm\(^{-1}\) is higher in (Si-Sn)\(_x\)Sb\(_y\) (x=2, y=3) composition, this indicates that due to the less effect of Si and major effect of Sb than all other compositions. These results are confirmed from EDX.

In Fig. 4.4 (b), the radial breathing mode (RBM) of CNT would fall in the same range and no significant alteration of the LA mode is observed as explained in Sn\(_x\)Sb\(_y\) samples. The Raman shift of CNT is given in Fig. 4.4 (b) for comparison. In Fig 4.4 (b), the intensity ratio (I\(_G\)/I\(_D\)) of the CNT at 1587 cm\(^{-1}\) (G band) and 1351 cm\(^{-1}\) (D band) has changed from 15.43 to around 6.21 for (Si-Sn)\(_x\)Sb\(_y\)-CNT at different compositions, which is similar to the D and G line of polycrystalline graphite [13, 14]. The decrease in the ratio indicates that the atomic ordering of crytallinity of the CNT is reduced as similar to the Sn\(_x\)Sb\(_y\)-CNT (x=2-5, y=3-6) compositions. But the observed I\(_G\)/I\(_D\) ratio of (Si-Sn)\(_x\)Sb\(_y\)-CNT at different compositions is very high than Sn\(_x\)Sb\(_y\)-CNT (x=2-5, y=3-6) compositions, and suggests that (Si-Sn)\(_x\)Sb\(_y\) (x=2-5, y=3-6) is less functionalized with CNTs surface than Sn\(_x\)Sb\(_y\) (x=2-5, y=3-6) samples. Also, a Raman red shift of 11.8 cm\(^{-1}\) and 16.8 cm\(^{-1}\) in the G band and 7.1 cm\(^{-1}\) and 8.7 cm\(^{-1}\) of the D band with respect to G and D bands of CNT are observed for (Si-Sn)\(_x\)Sb\(_y\)-CNT at different compositions respectively, which corresponds to the tensile stress experienced by the CNT carbon atom [14]. When comparing Sn\(_x\)Sb\(_y\)-CNT at different compositions, the G and D band shifts of (Si-Sn)\(_x\)Sb\(_y\)-CNT can also represent the grain size variation which is in good agreement with the observed grain size in SEM pictures.

### 4.3.2 FTIR Analysis

Fig. 4.5 (a) and (b) shows that the FTIR spectrum of (Si-Sn)\(_x\)Sb\(_y\) and (Si-Sn)\(_x\)Sb\(_y\)-CNT (x=2-5, y=3-6) samples.

Fig. 4.5 (a) and (b) shows, a broad absorption band situated between 3000-3600 cm\(^{-1}\) and another one around 1600 cm\(^{-1}\) is assigned to O-H stretching and O-H bending vibrations.
respectively. These OH radicals have arisen due to either the strongly acquainted water particle or from the environment similar to the SnₓSbᵧ at different compositions. The peak at 1420 cm⁻¹ and 1360 cm⁻¹ of SnₓSbᵧ (x=2-5, y=3-6) undergo severe changes due to the incorporation of Si and CNT. The disappearance of 1420 cm⁻¹, which is a specific peak representing the bonding between Sn and Sb as seen in Fig. 3.5 (a), is due to the addition of Si in the SnₓSbᵧ (x=2-5, y=3-6) lattice indicating that the Si has introduced in the bondage of Sn to Sb forming Si-Sn and Si-Sb bonding. Lattice strain that was not observed in all other samples except (Si-Sn)ₓSbᵧ (x=3, y=4) can only be due to the insufficiency of Sb for bondage of Si and Sn. Comparing all the compositions of Fig. 4.5 (a), (Si-Sn)ₓSbᵧ (x=3, y=4) shows, the increased peak intensity at 1060 cm⁻¹ which may be correlating with increase in Si effect and in (Si-Sn)ₓSbᵧ (x=2, y=3) composition the peak at 1060 cm⁻¹ is diminished and new peak has emerged, which may be due to the decrease in percentage of Si and this is confirmed by EDX results.

Fig. 4.5 (b) shows minor reappearance of a broad peak at 1420 cm⁻¹ indicating that the binding between Sn and Sb is presented and is disappeared in SnₓSbᵧ when Si was substituted. Hence it is concluded that Si has selectivity with CNT wall. The peak at ~ 600 cm⁻¹ also undergoes changes due to the incorporation of Si whereas it is undisturbed while incorporating CNT alone. This reconfirms the fact observed in Raman with respect to G and D bands regarding the tensile stress experienced by CNT. Addition of Si to SnₓSbᵧ irrespective of the presence of CNT shifts the peak at 615 cm⁻¹ to 488 cm⁻¹ indicating the above-said phenomena.
Fig. 4.5 (a) FTIR spectra of (i)- (Si-Sn)$_x$S$_{3y}$ (x=2, y=3), (ii)- (Si-Sn)$_x$S$_{4y}$ (x=3, y=4), (iii)- (Si-Sn)$_x$S$_{5y}$ (x=4, y=5) and (iv)- (Si-Sn)$_x$S$_{6y}$ (x=5, y=6)

Fig. 4.5 (b) FTIR spectra of (i)- (Si-Sn)$_x$S$_{3y}$-CNT (x=2, y=3), (ii)- (Si-Sn)$_x$S$_{4y}$-CNT (x=3, y=4), (iii)- (Si-Sn)$_x$S$_{5y}$-CNT (x=4, y=5) and (iv)- (Si-Sn)$_x$S$_{6y}$-CNT (x=5, y=6)
4.3.3 Photoluminescence Analysis

In both Raman and FTIR spectrum, various vibrational changes in the lattice due to substitutional strain have been observed. Hence, it is expected to bring changes in electronic states which could be analysed through photoluminescence studies.

Fig. 4.6 (a-d) and 4.7 (a-d) shows the photoluminescence emission (PL) and photoluminescence excitation (PLE) spectrum of (Si-Sn)$_{x}$Sb$_{y}$ and (Si-Sn)$_{x}$Sb$_{y}$-CNT (x=2-5, y=3-6) samples.

Fig. 4.6 (a-d) shows the photoluminescence emission and photoluminescence excitation spectra of (Si-Sn)$_{x}$Sb$_{y}$ (x=2-5, y=3-6) compositions. All the samples are excited at 360 nm to acquire emission spectrum also the photoluminescence (PLE) excitation peaks are obtained fixing the emission at 415-449 nm. Analysis of all the samples resulted in two sets of excitation and emission transitions in the alloy. For all the samples, the emission peaks are fitted using lorentzian fit and found to have two emission peaks at 420 nm and 440 nm.

Fig. 4.6 (a) shows the emission peaks of (Si-Sn)$_{x}$Sb$_{y}$ (x=2, y=3) at 416 nm and 441 nm and have one excitation peak at 364 nm. In Fig. 4.6 (b) shows the peaks of (Si-Sn)$_{x}$Sb$_{y}$ (x=3, y=4), two emission peaks at 417 nm and 443 nm and the two excitation peaks at 265 nm and 362 nm. With the Fig. 4.6 (c) and 4.6 (d) shows (Si-Sn)$_{x}$Sb$_{y}$ (x=4, y=5) and (Si-Sn)$_{x}$Sb$_{y}$ (x=5, y=6) samples with two emission peaks at 417 nm and 443 nm, 416 nm and 443 nm and the excitation for these samples are 360 nm and 368 nm. However increment in Sn to Sb ratio did not bring major change in emission wavelength but the excitation changed by 2-5 nm wavelengths which indicates the increment of non-radiative decay in the increased Sn to Sb ratios, even though there are no major structural changes observed by XRD in all the samples but for the lattice strains observed in FTIR and Raman analysis.
Fig. 4.6 (a) PL and PLE Spectra of (Si-Sn)$_x$Sb$_y$ (x=2, y=3)

Fig. 4.6 (b) PL and PLE Spectra of (Si-Sn)$_x$Sb$_y$ (x=3, y=4)
Fig. 4.6 (c) PL and PLE Spectra of (Si-Sn)$_x$Sb$_y$ (x=4, y=5)

Fig. 4.6 (d) PL and PLE Spectra of (Si-Sn)$_x$Sb$_y$ (x=5, y=6)
Fig. 4.7 (a-d) represents the photoluminescence absorption and emission spectra of (Si-Sn)$_x$Sb$_y$-CNT (x=2, y=3), (Si-Sn)$_x$Sb$_y$-CNT (x=3, y=4), (Si-Sn)$_x$Sb$_y$-CNT (x=4, y=5) and (Si-Sn)$_x$Sb$_y$-CNT (x=5, y=6) respectively. (Si-Sn)$_x$Sb$_y$-CNT (x=2, y=3), (Si-Sn)$_x$Sb$_y$-CNT (x=3, y=4), (Si-Sn)$_x$Sb$_y$-CNT (x=4, y=5) and (Si-Sn)$_x$Sb$_y$-CNT (x=5, y=6) have respective absorption at 361 nm, 362 nm, 363 nm and 367 nm with a major red shift with respect to (Si-Sn)$_x$Sb$_y$-CNT (x=4, y=5) composition. The (Si-Sn)$_x$Sb$_y$-CNT (x=5, y=6) sample has an additional absorption at 267 nm. The change in absorption edge due to the substitutions indicate an increased non-radiative decay as the emissions for all the samples happen at 418 nm, 417 nm, 418 nm and 416 nm respectively for all the four samples along with 444 nm or 445 nm as shown in Figures. However addition of CNT does not alter the structure with ascending ratio of (Si-Sn)$_x$Sb$_y$ concentrations which is confirmed by XRD results.
Fig. 4.7 (b) PL and PLE Spectra of (Si-Sn)$_x$Sb$_y$-CNT (x=3, y=4)

Fig. 4.7 (c) PL and PLE Spectra of (Si-Sn)$_x$Sb$_y$-CNT (x=4, y=5)
When comparing Sn$_x$Sb$_y$ with different concentration samples, due to the incorporation of Si, absorption peaks shift from 365 nm to 364 nm for (Si-Sn)$_x$Sb$_y$ (x=2, y=3), 364 nm to 362 nm for (Si-Sn)$_x$Sb$_y$ (x=3, y=4), 364 nm to 360 nm for (Si-Sn)$_x$Sb$_y$ (x=4, y=5) and 360 nm to 364 nm for (Si-Sn)$_x$Sb$_y$ (x=5, y=6) and no major variation is observed in emission peaks.

When comparing Sn$_x$Sb$_y$-CNT with different concentration samples, due to the incorporation of Si with CNT, absorption peaks shift from 362 nm to 361 nm for (Si-Sn)$_x$Sb$_y$-CNT (x=2, y=3), 360 nm to 362 nm for (Si-Sn)$_x$Sb$_y$-CNT (x=3, y=4), 364 nm to 363 nm for (Si-Sn)$_x$Sb$_y$-CNT (x=4, y=5) and 360 nm to 365 nm for (Si-Sn)$_x$Sb$_y$-CNT (x=5, y=6) and the emission peaks from 420 nm to 418 nm (blue shift) and 449 nm to 444 nm (blue shift) for (Si-Sn)$_x$Sb$_y$-CNT (x=2, y=3) and (Si-Sn)$_x$Sb$_y$-CNT (x=4, y=5) samples but other two compositions shows no major variation.
As the particle sizes of Si and Si-CNT incorporated Sn$_x$Sb$_y$ with different concentration are smaller, only a blue shift is expected and could not be observed except for the emission at 420 nm and 449 nm for (Si-Sn)$_x$Sb$_y$-CNT ($x=2$, $y=3$) and (Si-Sn)$_x$Sb$_y$-CNT ($x=4$, $y=5$) samples. In this case, size effect has not played a role in (Si-Sn)$_x$Sb$_y$ and (Si-Sn)$_x$Sb$_y$-CNT with different concentration samples, while looking into the particle sizes observed by SEM analysis. Therefore lattice strain is not enough to change the electronic states but it is enough to change the thermal and electrical properties. Also the strong PL quenching with Si addition to Sn$_x$Sb$_y$ with and without CNT indicates severe strain caused in the structure that could result in extended defects which usually acts as a non-radiative recombination centres in Si [17]. Hence, though an intensive absorption exists, in Si added samples non-radiative recombination centres trap the carriers and disallow intense visible emission when compared to Sn$_x$Sb$_y$ and Sn$_x$Sb$_y$-CNT at different concentrations. This observation leads to an expectation that this non-radiative decay could decrease the conductivity of the Si substituted samples.

4.4 Thermal Characterization

To study the thermal properties of the samples, due to the incorporation of Si and CNT the DSC and TG-DTA analysis is carried out. Fig. 4.8 (a, b) and 4.9 (a, b) shows the DSC and TG -DTA spectrum for (Si-Sn)$_x$Sb$_y$ and (Si-Sn)$_x$Sb$_y$-CNT ($x=2-5$, $y=3-6$) samples. All the compositions heated at the rate of 10° C/min in Nitrogen atmosphere.

DSC and TG-DTA spectrum of (Si-Sn)$_x$Sb$_y$ ($x=2$, $y=3$), (Si-Sn)$_x$Sb$_y$ ($x=3$, $y=4$), (Si-Sn)$_x$Sb$_y$ ($x=4$, $y=5$), (Si-Sn)$_x$Sb$_y$ ($x=5$, $y=6$) compositions are shown in Fig. 4.8 (a) and (b). All the four compositions exhibit one exothermic peak at ~50° C. The (Si-Sn)$_x$Sb$_y$ ($x=2$, $y=3$) and (Si-Sn)$_x$Sb$_y$ ($x=3$, $y=4$) compositions show two endothermic peaks at 510° C, 490° C along with an endothermic at 340° C. (Si-Sn)$_x$Sb$_y$ ($x=4$, $y=5$) shows one endothermic peak at
400° C and (Si-Sn)_xSb_y (x=2, y=3) composition shows three endothermic peak at 340° C, 380° C and 485° C.

The peak at 340° C in (Si-Sn)_xSb_y (x=2, y=3), (Si-Sn)_xSb_y (x=3, y=4) and (Si-Sn)_xSb_y (x=5, y=6) compositions belongs to the melting point of Sn_xSb_y alloy. But in the case of (Si-Sn)_xSb_y (x=4, y=5) has shifted to 340° C to 400° C. In all the cases, the melting point at 420°C [15] has changed and this may be due to the addition of Si. The extra peaks at 510° C, 490° C, 380° C and 485° C is observed in (Si-Sn)_xSb_y (x=2, y=3), (Si-Sn)_xSb_y (x=3, y=4) and (Si-Sn)_xSb_y (x=5, y=6).

Fig. 4.9 (a) and (b) shows DSC and TG-DTA spectrum of (Si-Sn)_xSb_y-CNT (x=2, y=3), (Si-Sn)_xSb_y-CNT (x=3, y=4), (Si-Sn)_xSb_y-CNT (x=4, y=5) and (Si-Sn)_xSb_y-CNT (x=5, y=6) compositions respectively. All the four compositions show one exothermic peak at ~50°C. The (Si-Sn)_xSb_y-CNT (x=2, y=3) and (Si-Sn)_xSb_y-CNT (x=5, y=6) shows two endothermic peak at 340° C, 510° C and 400° C, 475° C. The (Si-Sn)_xSb_y-CNT (x=3, y=4) and (Si-Sn)_xSb_y-CNT (x=4, y=5) shows one endothermic peak at 345° C and 360° C.

In the case of CNT incorporated (Si-Sn)_xSb_y with different composition samples, when increasing the ratio of Si to Sb in (Si-Sn)_xSb_y concentrations, the peak at 340° C has shifted to 345° C for (Si-Sn)_xSb_y-CNT (x=2, y=3), to 360° C for (Si-Sn)_xSb_y-CNT (x=2, y=3) and to 400° C for (Si-Sn)_xSb_y-CNT (x=2, y=3) compositions, which is attributed to the phase transition (melting point) of Sn_xSb_y alloy. This could not be confirmed whether it is a phase transition due to the non availability of literature and high temperature XRD facility. This variation in shift may be due to the addition of Si with CNT. Compared to (Si-Sn)_xSb_y with different concentration samples, the peak at 50° C shows no changes in (Si-Sn)_xSb_y-CNT at different concentrated samples. Also due to the addition of CNT, variation in shift is observed.
Fig. 4.8 (a) DSC for (Si-Sn)$_x$Sb$_y$ (x=2-5, y=3-6) compositions

Fig. 4.8 (b) TG-DTA for (Si-Sn)$_x$Sb$_y$ (x=2-5, y=3-6) compositions
When comparing $\text{Sn}_x\text{Sb}_y$ and $\text{Sn}_x\text{Sb}_y$-CNT with different concentration samples, the recrystallization of Sn peak at 210° C is arrested. This result suggests that, the ratio of loosely bound Sn is very low than $\text{Sn}_x\text{Sb}_y$ and $\text{Sn}_x\text{Sb}_y$-CNT with different concentration samples, i.e.,
the presence of Si could decrease the ratio of Sn in all the compositions. Also due to the addition of Si, the phase transition shift has observed.

4.5 AC Impedance Analysis

Fig. 4.11 - 4.18 shows the impedance spectrum of (Si-Sn)_xSb_y and (Si-Sn)_xSb_y-CNT (x=2-5, y=3-6) compositions. The basic information is explained with Sn_xSb_y (x=2-5, y=3-6) compositions in section 3.5. All the samples are measured from room temperature to 60°C. As, lithium ion battery works only below 70°C, therefore, the conductivity studies are carried out from RT to 60°C.

In all the samples of (Si-Sn)_xSb_y and (Si-Sn)_xSb_y-CNT (x=2-5, y=3-6), the dotted line indicates the measured spectrum and the line represents the simulated spectrum. The fitting of the impedance model to the experimental data was performed using Zview 11 software. For all the samples, the lower frequency (1-10 Ω) region has been omitted. For all the Si and CNT incorporated Sn_xSb_y samples, the proposed equivalent circuit is (R_1Q_1)(R_2Q_2), except one for (Si-Sn)_xSb_y-CNT (x=5, y=6) is (R(RQ), as explained in section 3.5. All the samples exhibit grain and grain boundary region. This equivalent circuit is represented in Fig. 4.10.

![Fig. 4.10 Equivalent circuit for the one in the dotted line appears in (Si-Sn)_xSb_y (x=2-5, y=3-6) and (Si-Sn)_xSb_y-CNT (x=2,3,4 y=3,4,5) samples and not in (Si-Sn)_xSb_y-CNT (x=5, y=6) sample](image)

The Nyquist plot of (Si-Sn)_xSb_y (x=2, y=3), (Si-Sn)_xSb_y (x=3, y=4), (Si-Sn)_xSb_y (x=4, y=5) and (Si-Sn)_xSb_y (x=5, y=6) compositions shows grain and grain boundary and are
represented in Fig. 4.11, 4.12, 4.13 and 4.14. The total conductivity of \((\text{Si-Sn})_x\text{Sb}_y (x=2, y=3)\), \((\text{Si-Sn})_x\text{Sb}_y (x=3, y=4)\), \((\text{Si-Sn})_x\text{Sb}_y (x=4, y=5)\) and \((\text{Si-Sn})_x\text{Sb}_y (x=5, y=6)\) at room temperature are \(10.1\times10^{-5}\) S/cm, \(0.273\times10^{-5}\) S/cm, \(2.41\times10^{-5}\) S/cm and \(1.5\times10^{-5}\) S/cm and at 60°C for all the abovesaid compositions are \(31.9\times10^{-5}\) S/cm, \(0.0775\times10^{-5}\) S/cm, \(8.78\times10^{-5}\) S/cm and \(2.97\times10^{-5}\) S/cm respectively. \((\text{Si-Sn})_x\text{Sb}_y (x=3, y=4)\) has very low conductivity than all other samples as expected from Raman studies where severe lattice strain is observed that is not seen in other compositions. \((\text{Si-Sn})_x\text{Sb}_y (x=2, y=3)\) sample shows high total conductivity at room temperature and 60°C, and this may be due to the presence of Sb higher ratio. Very low conductivity obtained in \((\text{Si-Sn})_x\text{Sb}_y (x=3, y=4)\) is due to the electron scattering caused by insufficient Sb concentration resulting in severely strain lattice as observed in Raman studies. Though the same order of conductivity has been observed for \((\text{Si-Sn})_x\text{Sb}_y (x=4, y=5)\) and \((\text{Si-Sn})_x\text{Sb}_y (x=5, y=6)\) compositions, the conductivity of \((\text{Si-Sn})_x\text{Sb}_y (x=5, y=6)\) has no much change at 60°C compared to the increase in \((\text{Si-Sn})_x\text{Sb}_y (x=4, y=5)\). This correlates well with the high entropy observed at 400°C for \((\text{Si-Sn})_x\text{Sb}_y (x=4, y=5)\) than \((\text{Si-Sn})_x\text{Sb}_y (x=5, y=6)\) composition in DSC measurements. In general, compared to Sn, Sb, alone and Sn, Sb, CNT at different compositions, Si added samples have higher conductivity as it provides closer electronic states, as observed through PL studies, for non-radiative charge transfer resulting in higher conduction.

The Nyquist plot of \((\text{Si-Sn})_x\text{Sb}_y\)-CNT \((x=2, y=3)\), \((\text{Si-Sn})_x\text{Sb}_y\)-CNT \((x=3, y=4)\), \((\text{Si-Sn})_x\text{Sb}_y\)-CNT \((x=4, y=5)\) and \((\text{Si-Sn})_x\text{Sb}_y\)-CNT \((x=5, y=6)\) samples showing activated grain and grain boundary regions are represented in Fig. 4.15, 4.16, 4.17 and 4.18. The total conductivity of \((\text{Si-Sn})_x\text{Sb}_y\)-CNT \((x=2, y=3)\), \((\text{Si-Sn})_x\text{Sb}_y\)-CNT \((x=3, y=4)\), \((\text{Si-Sn})_x\text{Sb}_y\)-CNT \((x=4, y=5)\) and \((\text{Si-Sn})_x\text{Sb}_y\)-CNT \((x=5, y=6)\) compositions at room temperature are \(0.20\times10^{-5}\) S/cm, \(3.22\times10^{-5}\) S/cm, \(9.02\times10^{-5}\) S/cm and \(62.7\times10^{-5}\) S/cm and at 60°C for all the
The above-mentioned compositions are $0.49 \times 10^{-5}$ S/cm, $1.44 \times 10^{-5}$ S/cm, $4.6 \times 10^{-7}$ S/cm, and $117 \times 10^{-5}$ S/cm respectively. (Si-Sn)$_x$Sb$_y$-CNT ($x=5$, $y=6$) sample shows high conductivity than all other compositions. The (Si-Sn)$_x$Sb$_y$-CNT ($x=4$, $y=5$) sample shows very low conductivity of the order of $10^{-8}$ than all other compositions. Compared to (Si-Sn)$_x$Sb$_y$ with different

![Nyquist plots](image)

**Fig. 4.11 Nyquist plot of (Si-Sn)$_x$Sb$_y$ ($x=2$, $y=3$) at different temperatures**
Fig. 4.12 Nyquist plot of (Si-Sn)$_x$Sb$_y$ (x=3, y=4) at different temperatures

concentration samples, CNT incorporated samples shows very low conductivity except (Si-
Sn)$_x$Sb$_y$-CNT (x=5, y=6) composition.

When comparing Sn$_x$Sb$_y$ with different concentration samples, Si incorporated sample shows higher conductivity. Contrasly compared to Sn$_x$Sb$_y$-CNT with different concentration samples, CNT incorporated to (Si-Sn)$_x$Sb$_y$ shows very low conductivity.
Fig. 4.13 Nyquist plot of (Si-Sn)$_{x}$Sb$_{y}$ (x=4, y=5) at different temperatures
Fig. 4.14 Nyquist plot of (Si-Sn)$_x$Sb$_y$ (x=5, y=6) at different temperatures
Fig. 4.15 Nyquist plot of (Si-Sn)$_x$Sb$_y$-CNT (x=2, y=3) at different temperatures
Fig. 4.16 Nyquist plot of (Si-Sn)\textsubscript{x}Sb\textsubscript{y}-CNT (x=3, y=4) at different temperatures
Fig. 4.17 Nyquist plot of (Si-Sn)$_x$Sb$_y$-CNT (x=4, y=5) at different temperatures.
4.5.1 Temperature Dependent Conductivity

Fig. 4.19 (a) and (b) shows the Arrhenius plot for grain and grain boundary of (Si-Sn)$_x$Sb$_y$ (x=2-5, y=3-6) samples. In (Si-Sn)$_x$Sb$_y$ with different concentration samples, two types of conducting phenomena is observed. In (Si-Sn)$_x$Sb$_y$ (x=2, y=3), (Si-Sn)$_x$Sb$_y$ (x=4,
y=5) and (Si-Sn)$_x$Sb$_y$ (x=5, y=6) possess negative temperature co-efficient resistance and (Si-Sn)$_x$Sb$_y$ (x=3, y=4) possess positive temperature co-efficient resistance. Positive temperature coefficient occurs due to elastic scattering and negative temperature coefficient is due to inelastic scattering. Elastic scattering which occurs due to the mean free path is higher than the particle size (very low grain size) appears in particular sample and inelastic scattering which occurs due to the mean free path is lower than the particle size (higher particle size) as explained in section 3.5.1. This result is concurrent with SEM result. Also the positive temperature coefficient of (Si-Sn)$_x$Sb$_y$ (x=3, y=4) sample exhibits with the higher intensity of recrystallization of Sn indicating the smaller particle size and also the very high percentage of Sn ratio. Remaining samples exhibit lower intensity of recrystallization of Sn indicating the higher particle size and lower percentage of Sn ratio.

![Graph](image_url)

**Fig. 4.19 (a) Arrhenius plot for (Si-Sn)$_x$Sb$_y$ (x=2-5, y=3-6)-Grain Conductivity**

Fig. 4.20 (a) and (b) shows the Arrhenius plot for grain and grain boundary of (Si-Sn)$_x$Sb$_y$-CNT (x=2-5, y=3-6) samples. CNT incorporated (Si-Sn)$_x$Sb$_y$ samples also possess
positive and negative temperature coefficient of resistances. Positive temperature coefficient of resistance exhibited in (Si-Sn),Sb\textsubscript{y}-CNT (x=3, y=4) sample which have higher intensity of
recrystallization of Sn. Remaining samples exhibit lower intensity of recrystallization of Sn, larger particle size and lower percentage of Sn ratio. Hence these three factors are considered...
to be responsible for the elastic collision too. The activation energy for all the samples are given in Table 4.4.

4.6 Summary

The XRD results show that, all the samples ((Si-Sn)$_x$Sb$_y$ and (Si-Sn)$_x$Sb$_y$-CNT (x=2-5, y=3-6)) resulted in hexagonal crystallite structure and within the limits of substitution under present study confirmed no major change of crystalline structure occurred due to substitution. The SEM images show that Si and CNT added Sn$_x$Sb$_y$ samples exhibit very low average particle size of 30-40 nm. The content of Si, Sn and Sb are in the expected ratio identified through EDX and hence the results are worth comparing. The Raman and FTIR measurements indicate the lattice strains and environmental changes occurring in the lattice due to substitution of Si and CNT. The result observed converges to the fact that CNT is functionalized by Si added Sn$_x$Sb$_y$ alloy particles. From DSC analysis, in all the samples the recrystallization of Sn peak has not occurred at 210° C. This phenomenon would not favour lithiation and delithiation process. The conductivity happens to exhibit positive temperature co-efficient of resistance (metallic) in Sn$_x$Sb$_y$ but possess negative temperature coefficient of resistance (TCR) when Si and CNT are incorporated. Si added Sn$_x$Sb$_y$ samples shows higher conductivity than Si-CNT added Sn$_x$Sb$_y$ samples. At (Si-Sn)$_x$Sb$_y$-CNT(x=5, y=6) sample, particle size effect is obvious with sudden decrease in resistance that reflects elastic scattering of electrons in the material.

4.7 References


