Chapter - 6

Growth and Characterization of Bi$_2$Se$_3$
Single Crystals by Vapour Phase Technique
6.1 Introduction

In materials that conduct both electricity and heat, the thermal and electrical currents are coupled. This thermoelectric coupling can be used to construct devices that act as temperature sensors, heat pumps, refrigerators, or power generators. A temperature difference $\Delta T$ across any electrical conductor will generate a corresponding voltage difference $\Delta V$. The ratio $\Delta V/\Delta T$ is defined as the Seebeck coefficient $S$ after Thomas Seebeck who first discovered the effect in 1823.

Probably the most familiar use of this effect is the thermocouple in which union of two dissimilar metals generates a voltage in response to an imposed temperature difference. Interestingly an electrical current $I$ passing through the junction of two dissimilar conductors results in the absorption or release of heat in the vicinity of the junction depending on the direction of current. The ability to heat or cool in this manner was first discovered by Peltier and explained by Lord Kelvin. The latter showed that the amount of heat produced (or absorbed) near the junction is given by $\Pi I = STI$ where $\Pi$ is called the Peltier coefficient and $T$ is the temperature. It is primarily this effect that makes thermoelectric (Peltier) refrigeration possible. Thermoelectric refrigerators and power generators are attractive for many applications as they have no moving parts (except electrons and holes), use no liquid refrigerant, and last indefinitely [1].

For both refrigeration and power generation applications, materials with larger values of figure of merit ($ZT$) result in devices that will operate at a higher efficiency.

$$ZT = \frac{S^2\sigma}{K} \quad \ldots \quad (6.1)$$

$\sigma$ is the electrical conductivity, and $k$ is the thermal conductivity of the material at temperature $T$(K) and $S$ is Seebeck co-efficient.

Doped semiconductors are best suited to meet these requirements. Most metals have small values of $S$ and hence very small values of $ZT$. The major problem with these devices is poor efficiency. Current state of the art Peltier refrigerators
use semiconducting Bi$_2$Te$_3$-Sb$_2$Te$_3$ alloys (ZT ≤ 1) that produce only moderate amounts of cooling and are inefficient compared to the compressor based refrigerators.

The major goal of thermoelectric materials research for nearly half century has been to design materials that will improve the efficiency of these solid state devices—that is achieve higher ZT values. Materials with values of ZT of 3 at room temperature would make thermoelectric refrigerators competitive with compressor technology. Recent developments in the field of thermoelectric materials have been examined in several new articles [2-6].

With this thing in mind author selected to work on narrow band gap layered material $A'_2B'_3^{\nu_1}$ (where A=Bi and B=Se) of tetradyomite structure. This compound is a material applied in thermoelectric devices as solid state coolers or generators.

Therefore, studies on various properties of Bi$_2$Se$_3$ are interesting both for basic and applied research. The literature states that mostly the researchers have grown Bi$_2$Se$_3$ crystals by Bridgman technique. However no such investigation has been done on Bi$_2$Se$_3$ single crystal grown by vapour phase technique. Henceforth, in the present research work we have carried out growth of Bi$_2$Se$_3$ single crystal by vapour phase technique and studied its structural and transport properties [7].

### 6.2 Structure of Bi$_2$Se$_3$ crystal

As shown in Figure 6.1 the narrow band gap material Bi$_2$Se$_3$ crystallize in hexagonal structure [8]. The crystal structure of Bi$_2$Se$_3$ consist of Bi and Se layers. A Bi layer is made up of Bi atoms arranged to form a plane hexagonal structure, and a Se layer is formed by Se atoms arranged in the same way. As shown in Figure 6.1 in a unit cell, there are two different types of Se layers named Se$^{(1)}$ and Se$^{(2)}$. The unit cell is packed with two Bi layers and three Se layers following the pattern: Se$^{(1)}$-Bi-Se$^{(2)}$-Bi-Se$^{(1)}$. Between two units there is only the vander Waals bond between the neighboring Se$^{(1)}$ planes. Therefore, the crystal cleaves easily between the Se$^{(1)}$ planes.
Bi$_2$Se$_3$ structure consists of periodically repeated five layer lamellae. Se$^{(1)}$-Bi-Se$^{(2)}$-Bi-Se$^{(1)}$ .......Se$^{(1)}$-Bi-Se$^{(2)}$-Bi-Se$^{(1)}$ each Se$^{(2)}$ atom possesses an octahedral coordination of six Bi atoms. Each Bi atom is also coordinated by six Se atoms, there are three Se$^{(1)}$ atoms from one side and three Se$^{(2)}$ atoms from the other side of the Bi atom. Se$^{(1)}$ atoms have also an octahedral coordination of three Bi atoms and three Se$^{(1)}$ atoms from the neighbor lamellae. The chemical bond between Bi and Se in the Bi$_2$Se$_3$ lattice is a $\sigma$ type bond formed from the valence electron from p-orbitals of Bi (6p$^3$) and Se (4p$^4$) [9].

### 6.3 Growth of Bi$_2$Se$_3$ crystals by Chemical Vapour Transport (CVT) technique

Chemical vapour transport reactions are those in which a solid or liquid substance ‘A’ reacts with a gaseous transporting agent ‘B’ at a temperature $T_1$ to from exclusively vapour phase reaction products (AB), which in turn, undergo the reverse reaction at a different place in the system at a temperature $T_2$, resulting in the reformation of crystalline substance ‘A’.
\[ iA (s,l) + jB(g) \rightarrow kAB(g) \quad \ldots (6.2) \]

The process appears to be one of sublimation or distillation. Substance A, however, does not possess an appreciable vapour pressure at the applied temperature. The substance is transported chemically. In addition to a reversible heterogeneous reaction, a concentration gradient must be established. The latter can be the result of temperature gradients, changes in relative pressures, or the difference in the free energy of formation of two substances. The transport of substances by means of heterogeneous reactions has been known for a long time.

### 6.3.1 Fundamentals of chemical vapour transport:

First, the principle of chemical vapour transport reactions in a cylindrical closed tube in a temperature gradient is discussed with the aid of the following equations. (Figure 6.2)

![Figure 6.2 Chemical Vapour transport in a Cylindrical Closed Tube](image)

\[ A(s) + B(g) \rightarrow AB(g) \quad \ldots (6.3) \]

\[ n_{AB} = \frac{(Dq_t / lRT)}{lRT} (P_{AB(1)} - P_{AB(2)}) \quad \ldots (6.4) \]

where \( n_{AB} \) is the number of moles of AB transported, \( D \) is the diffusion coefficient, \( q \) is the tube cross section, \( l \) is the length of the diffusion path, \( t \) is the duration of the experiment, \( R \) is the gas constant, \( T \) is the absolute temperature of the diffusion path and \( P_{AB(1)} \) and \( P_{AB(2)} \) are the partial pressure of AB at temperature \( T_1 \) and \( T_2 \) respectively.

In the expression for \( n_{AB} \), the first term on the right hand side represents gas movement and the apparatus constants and the second term represents heterogeneous reaction.
Furthermore, all transport equations are written so that the solid reactant is on the left hand side of the equation. If the solid material A reacts with a gas B with the formation of a gaseous material AB and if the reaction is reversible, then a chemical vapour transport may take place at the suitable temperatures. If the observed reaction is endothermic, then the solid material A will be consumed at a higher temperature $T_1$, with the formation of gaseous product AB while after the migration of AB to the location with a lower temperature $T_2$, the reverse reaction takes place, and A is deposited from the gas phase with the release of B. For exothermic reaction transport of the solid phase takes place from low temperature to high temperature.

Normally, for the transport reaction the diffusion in the gas phase is rate-determining. This means that the important concentration gradient for the diffusion is determined by the existing heterogeneous equilibrium at the temperatures $T_1$ and $T_2$.

### 6.3.2 Experimental Set up

**Dual zone horizontal furnace:**

The furnace is the most important part of present research work to grow the crystals of Bi$_2$Se$_3$. Two-zone horizontal furnace provides an appropriate temperature gradient over the entire ampoule. Normally the temperatures employed are fairly high. The temperature gradient within the furnace is required over a length of about 25 cm. Stability of the temperature plays an important role, therefore, for this purpose electronic temperature controllers are used.

The furnace was constructed in our University Science and Instrumentation Center (USIC) by using a special sillimanite threaded tube (grade KR 80 GA HG) closed at one end, 450 mm in length, 70 mm outer diameter, 56 mm inner diameter with threaded pitch of 3 mm, imported from Koppers Fabriken Feuerfester, Germany. Super Kanthal A1 wire of 17 SWG was wound directly on the muffle tube into two different zones or regions. The tube is enclosed in the hot face insulating brick slabs constructed locally and the brick shell was fully enclosed in thick asbestos sheets, and the entire assembly was supported in a steel framework. This
The power supplied to the furnace windings was regulated by the control circuit. The two regions of windings are provided with independent power supplies and temperature controllers. Transformers with 70, 80 and 100 V taps with 20A current capacity in secondary windings are used to supply sufficient power in order to achieve the required high temperature.

Figure 6.3 The dual zone horizontal furnace with co-axially loaded ampoule.

Microprocessor based temperature programmers purchased from M/s. Indotherm Instruments Pvt. Ltd., Mumbai, are used to control the temperatures in the two zones of the furnace. The fluctuations in the local electrical supply are controlled by AC voltage stabilizer with 180-260 V input and 230 ± 1% output volts of capacity 3 kVA. The output of stabilizer is fed to the primary windings of the transformer, which heated the furnace windings and helped to maintain the stability of growth conditions. With the help of temperature programmers, a required temperature gradient could be established across the length of the working tube in the required temperature range. Thermocouples used are Pt (13%), Rh. Pt. and temperature programmers are calibrated for the above thermocouples. It is found that the thermocouples are stable over the prolonged period of time and are kept within the furnace tube itself showing the furnace tube temperature. The entire length of the furnace is calibrated using Cr-Al thermocouple externally.
Ampoule:

High quality fused quartz tubes of various diameters, having a melting point of about 1500 °C is used for growth experiments. Tubes having internal diameter 22 mm and length 220 mm are found to be more suitable. One end of the ampoule is sealed and the other end was drawn into a neck and joined to another 10 mm inner diameter quartz tube to connect it to the vacuum system for evacuation after introducing the source materials.

Cleaning of ampoule:

This was absolutely necessary to provide growth sites for preferential nucleation. For this purpose, first the ampoule is washed with boiling water along with a suitable detergent, after that it was washed with a hot mixture of concentrated HNO₃ and HF (49 %) taken in equal proportions. Then the washing is carried out by double distilled water. A further washing is done with a mixture of concentrated HNO₃ and H₂SO₄ taken in equal volumes, followed by a final washing for about nine to ten times with double distilled water. The clean ampoule is then transferred into a SICO constant temperature oven at 100 °C and left overnight to make it moisture free.

Charge/Compound preparation:

For charge preparation of elements having the following purities (%) W 99.999%, Se 99.999% & Cu 99.999% are used. This charge (nearly 10 gm) is then introduced into a thoroughly cleaned quartz ampoule in stoichiometric proportions for Bi₂Se₃. The ampoule containing the source material was evacuated to a pressure of 10⁻⁵ torr and sealed and then stirred well to ensure the proper mixing of the powdered elements. The homogeneous mixture is then placed into the two-zone furnace having linear temperature gradient. The temperature of the furnace is increased slowly to avoid any explosion, which might occur due to strongly exothermic reaction between the elements. The ampoule is then maintained at a temperature of 903 K. After heating period of 3 days, the furnace power is switched off and furnace is allowed to cool down to room temperature. At this stage, the compound formed is a polycrystalline mass.
Growth by vapour Transport

The prepared charge was homogenized by grinding with agate mortar and then transferred into another evacuated (10^{-3} Pa) quartz growth ampoule with NH_4Cl as a transporting agent. The sealed growth ampoule was then placed in the dual zone furnace maintaining the source zone at 923 K and growth zone at 873 K temperatures respectively. After 10 days, the furnace was cooled down to room temperature. The ampoule was taken out from the furnace and broken carefully. The resulting crystals of Bi_2Se_3 were grown at the cooler end of the ampoule in the form of thin flakes. The as grown crystals are shown in the Figure 6.4 below.

![Figure 6.4 Maximum size of as grown Bi_2Se_3 Single Crystals.](image)

6.4 Characterization of Bi_2Se_3 Crystal with various techniques:

6.4.1 Energy Dispersive analysis of X-rays (EDAX)

The compositions of all the elements present in the grown crystals are determined by energy dispersive analysis of X-rays (EDAX) using Philips EM 400 electron microscope. The weight percentage of Bismuth and Selenium found in Bi_2Se_3 crystals are given in Table 6.1. This table shows that the crystals possess the nearly desired stoichiometry and are free from any other foreign elements. The EDAX spectra obtained for this sample is shown in Figure 6.5.
Figure 6.5 EDAX spectra of Bi$_2$Se$_3$ single crystal.

Table 6.1 Chemical composition (Wt %) of grown Bi$_2$Se$_3$ single crystal.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Wt% of element from EDAX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$Se$_3$</td>
<td>Bi</td>
</tr>
<tr>
<td></td>
<td>62.14</td>
</tr>
</tbody>
</table>

6.4.2 X-Ray Diffraction (XRD)

The powder X-ray diffractogram of the as grown crystals of Bi$_2$Se$_3$ is shown in Figure 6.6. All the peaks were indexed based on hexagonal crystal structure with space group of $\text{3}m$ and were found to be matching with the reported JCPDF Card No. 33–0214.

The lattice parameters, density, volume, and $c/a$ ratio calculated from the XRD data are tabulated in Table 6.2. All the parameters were in good agreement with the reported data [10]. We determined the fault probability of the grounded powder of Bi$_2$Se$_3$ single crystals from the XRD pattern. Before proceeding with the fault probability calculation, the crystallite size was determined using Scherrer’s formula [11].
Figure 6.6 X-ray diffractogram of Bi$_2$Se$_3$ Crystal.

Table 6.2 Lattice parameters, c/a ratio, unit cell volume and density obtained from X-ray diffractogram for Bi$_2$Se$_3$.

<table>
<thead>
<tr>
<th>Lattice parameter</th>
<th>Bi$_2$Se$_3$ Calculated value</th>
</tr>
</thead>
<tbody>
<tr>
<td>a(Å)</td>
<td>4.14</td>
</tr>
<tr>
<td>c(Å)</td>
<td>28.64</td>
</tr>
<tr>
<td>c/a ratio</td>
<td>6.92</td>
</tr>
<tr>
<td>Volume(Å$^3$)</td>
<td>424.97</td>
</tr>
<tr>
<td>Density(gm/cc)</td>
<td>7.68</td>
</tr>
</tbody>
</table>

Table 6.3 Values of crystallite size for various reflections

<table>
<thead>
<tr>
<th>Reflection planes (h k l)</th>
<th>Crystallite size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0 0 3)</td>
<td>45.42</td>
</tr>
<tr>
<td>(0 0 6)</td>
<td>44.73</td>
</tr>
<tr>
<td>(1 1 6)</td>
<td>48.27</td>
</tr>
<tr>
<td>(1 1 15)</td>
<td>75.53</td>
</tr>
<tr>
<td>(1 0 22)</td>
<td>64.99</td>
</tr>
<tr>
<td>(3 0 8)</td>
<td>58.58</td>
</tr>
<tr>
<td>(3 0 11)</td>
<td>65.77</td>
</tr>
</tbody>
</table>
The determined crystallite size for various reflections is given in Table 6.3. The data shows that the crystallite sizes lies between 45 and 75 Å. The realistic estimation of the deformation fault probability (α) and growth fault probability (β) for the as-grown Bi$_2$Se$_3$ single crystal was done by employing the subsequent hexagonal closed packed structure expression of Warren [12].

For l even,

\[
(3\alpha + 3\beta) = \frac{\beta_2 \pi^2 c^2}{360ld^2 \tan \theta} \quad \ldots\ldots(6.5)
\]

For l odd,

\[
(3\alpha + \beta) = \frac{\beta_2 \pi^2 c^2}{360ld^2 \tan \theta} \quad \ldots\ldots(6.6)
\]

where \(c = 2d_{00l}\), \(\beta_2\) is the full line width expressed in degrees at the half maximum intensity, ‘l’ is Miller indices , ‘d’ is the interplanar spacing for the reflection.

<table>
<thead>
<tr>
<th>Reflection</th>
<th>(\beta_2)</th>
<th>(3\alpha + 3\beta)</th>
<th>(3\alpha + \beta)</th>
<th>(\alpha)</th>
<th>(\beta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3 0 8), (3 0 11)</td>
<td>0.34, 0.49</td>
<td>0.089</td>
<td>0.092</td>
<td>0.030</td>
<td>0.002</td>
</tr>
</tbody>
</table>

The condition for calculation of fault probability from the XRD is that for the breadths of reflections for which h-k =3 n (where n is an integer) are independent of the stacking faults, whereas the breadths of reflections for which h-k = 3n (where n is an integer) and l ≠ 0 depend on the faults within the crystal. In the present XRD of the as-grown Bi$_2$Se$_3$ crystals, only two planes satisfied the condition for determining the fault probabilities. The calculated values are tabulated in Table 6.4. The calculated deformation fault comes out to be 30 per 1,000 atomic layers whereas growth fault are 2 per 1,000 atomic layers for the as-grown Bi$_2$Se$_3$ crystals. The low values of deformation fault and growth fault values clearly states that the grown crystals contain fewer faults despite grounding of the sample.
6.4.3 Atomic Force Microscopy (AFM)

The three-dimensional (3D) AFM image (10 nm×10 nm) of the as-grown Bi$_2$Se$_3$ single crystal is shown in Figure 6.7. The morphology shows homogeneous distribution of small “hill” like structures all over the as-grown scanned surface. They are compact and cover uniformly the entire viewed surface. This uniform surface roughness suggests that the crystal growth is by layer mechanism. The layer growth mechanism is by two dimensional lateral spreading of atoms.

![3D AFM image of Bi$_2$Se$_3$ single crystal.](image)

6.4.4 Seebeck, Hall effect and Resistivity measurement

The variation of Seebeck coefficient of the as-grown Bi$_2$Se$_3$ single crystals in the temperature range 6 K to near ambient temperature (286 K), is shown in Figure 6.8.

In the said temperature range, the Seebeck coefficient variation shows two different regions of behaviour. In the temperature range from 6 K to 115 K the Seebeck coefficient value decreases with the temperature. While in the range of 116 K to 286 K the Seebeck coefficient value increases with temperature. The magnitudes of Seebeck coefficient variations in both the ranges are also different.
The Seebeck coefficient variation in the temperature range from 6K to 115 K is large, whereas between 116 K and 286 K the variation is small. It is seen that as the temperature is lowered below 15.69 K the Seebeck coefficient value changes from negative to positive. The change of sign of Seebeck coefficient as temperature decreases is due to impurity band conduction by low-mobility carriers [13].

![Figure 6.8 Plot of thermoelectric power (S) as a function of temperature (T).](image)

Here the Bi deficient as-grown Bi$_2$Se$_3$ sample is n-type, meaning donor atoms greatly outnumber the acceptor atoms, that is, the sample is not highly compensated. Below 15.69 K most of the electrons gets attached to the impurity atoms dominant at low temperature and are interacting to form the impurity band.

The impurity band is practically full and is not overlapping the conduction band, and acts as if it were the valence band of a semiconductor and gives rise to a positive Seebeck effect. This indeed is the qualitative explanation of the reversal of sign seen at low temperature. It has also been observed that the absolute Seebeck coefficient values are very low compared with the values obtained for crystals grown by Bridgman method [14,15]. The Fermi energy ($E_F$) was calculated for the two different temperature regions using the following well-known expression [16].
\[
S = \pm k \left[ \frac{A + \frac{E_F}{kT}}{e} \right]
\]

\[\ldots (6.7)\]

where \(k\) is the Boltzmann constant, \(e\) is the electronic charge, \(A\) is the dimensionless parameter determined by the dominant scattering process, and \(E_F\) is the separation of the Fermi level from the top of the valence band. The calculated values are tabulated in Table 6.5.

**Table 6.5 Values of Fermi energy \((E_F)\) of as-grown Bi\(_2\)Se\(_3\) single crystal**

<table>
<thead>
<tr>
<th>Temperature range</th>
<th>(E_F) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi(_2)Se(_3)</td>
<td></td>
</tr>
<tr>
<td>16–115 K</td>
<td>0.042</td>
</tr>
<tr>
<td>116–286 K</td>
<td>0.146</td>
</tr>
</tbody>
</table>

The obtained \(E_F\) values are very small, indicating that the as-grown Bi\(_2\)Se\(_3\) to be semimetallic in nature. The electrical resistivity measurements were performed on these as-grown Bi\(_2\)Se\(_3\) single crystal between temperature range of 6K–286K (Figure 6.9). The variation of \(\log \rho \) Vs \(1/T\) shows that the resistivity increases linearly with temperature, indicating metallic conductivity. The curve has two regions of resistivity variation, similar to the Seebeck coefficient variation with temperature, one lying between 6K- 115K and the other in the range 116K-286 K.
The values of activation energy $E_a$ for the range 6K-115K is $8.7 \times 10^{-5}$ eV and for the range 115K-286K is $1.72 \times 10^{-3}$ eV. The low values of activation energy confirm the semimetallic behaviour of the sample also seen in the Seebeck coefficient study. Also precisely it tells that electrons from impurity levels are involved in the conduction in this low-temperature range.

The Hall effect measurements were carried out on Bi$_2$Se$_3$ samples at three different low temperatures, 15K, 150K, and 300K. In all the measurements a 5 KG magnetic field was used. Prior to Hall effect measurements, the ohmic behaviour of different contacts (viz. $R_{12,12}$, $R_{23,23}$, $R_{34,34}$, $R_{41,41}$) were confirmed by measuring I-V characteristic (Figure 6.10). The Hall parameters calculated from the measurements are tabulated in Table 6.6.

![I-V characteristic between $R_{12,12}$, $R_{23,23}$, $R_{34,34}$, $R_{41,41}$ contacts.](image)

The Hall coefficient $R_H$ values at all three low temperatures is negative, confirming the as-grown Bi$_2$Se$_3$ single crystals to be n-type in nature. The values of carrier concentrations ($\sim 10^{18}$ cm$^{-3}$) at three different low temperatures confirm the sample to be semimetallic in nature, substantiating the observations obtained
from the Seebeck coefficient and resistivity variation with temperature. The values of zero field resistivity at 15K, 250K, and 300K evidently states that it increases by a factor of $10^{-1} \ \Omega \cdot \text{cm}$. This linear increase of zero-field resistivity with temperature is due to increase in lattice vibrations with temperature.

### Table 6.6

Values of Hall coefficient ($R_H$), carrier density ($n$) and Hall mobility ($\mu_H$) and zero field resistivity at three different temperatures for Bi$_2$Se$_3$ Single crystals

<table>
<thead>
<tr>
<th>Temperature T (K)</th>
<th>Hall coefficient $R_H$ (cm$^3$/C)</th>
<th>Carrier density $n$ (cm$^{-3}$)</th>
<th>Hall mobility $\mu_H$ (cm$^3$/V.sec)</th>
<th>Zero field resistivity $\rho_0$ ((\Omega\cdot\text{cm}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>-7.30\times10^{-1}</td>
<td>8.64\times10^{18}</td>
<td>3.41\times10^{2}</td>
<td>2.14 \times10^{-3}</td>
</tr>
<tr>
<td>250</td>
<td>-6.60\times10^{-1}</td>
<td>1.01\times10^{19}</td>
<td>3.79\times10^{2}</td>
<td>1.75 \times10^{-3}</td>
</tr>
<tr>
<td>15</td>
<td>-3.08\times10^{-1}</td>
<td>2.97\times10^{18}</td>
<td>2.11\times10^{3}</td>
<td>2.37 \times10^{-4}</td>
</tr>
</tbody>
</table>

### 6.5 Conclusion

✦ Large-size single crystals of Bi$_2$Se$_3$ have been successfully grown by vapour phase technique in variance to the literature showing its growth usually by Bridgman technique. The as-grown single crystals have been found to possess nearly perfect stoichiometry by EDAX analysis, whereas the XRD showed that the lattice parameters of as-grown single crystals are in good agreement with the standard data.

✦ The study of surface morphology in 3D AFM image of the as-grown Bi$_2$Se$_3$ single crystals shows homogeneous distribution of small hill-like structures. This uniform surface roughness suggests that the crystal growth is by layer mechanism produced by two dimensional lateral spreading of atoms.

✦ The Seebeck coefficient ($S$) variation in the temperature range, 6 K to near ambient temperature (286 K) shows two different regions of behaviour. The two regions are 6K –115 K and 116 K–286 K. In the 6 K–115 K range, the S decreases and in 116 K–286 K the S increases with temperature. As the temperature is lowered below 15.69 K, the S value changes from negative to positive indicating its change of nature from n- to p-type. The change of nature as temperature decreases below 15.69 K is due to impurity band
conduction by low mobility carriers. The values of $E_F$ determined from the $S$ versus $T$ graph for both the regions are very small, indicating that the as-grown $\text{Bi}_2\text{Se}_3$ to be semimetallic.

⇒ The electrical resistivity measurements were performed on these as-grown $\text{Bi}_2\text{Se}_3$ single crystals between temperatures ranging from 6 to 286 K. The resistivity increases linearly with temperature, indicating metallic conductivity in conjecture to the previous observation. The curve also had two different regions of behavior similar to the one seen in the Seebeck coefficient variation with temperature. The two regions are 6 K–115 K and 116 K–286 K. The values of activation energy $E_a$ determined from the logρ Vs 1/T graph for both the regions are very small, indicating that the as-grown $\text{Bi}_2\text{Se}_3$ to be semimetallic.

⇒ The Hall effect measurements were carried out on $\text{Bi}_2\text{Se}_3$ samples at three different temperatures, 15K, 150 K, and 300 K. The Hall coefficient $R_H$ values at all three temperatures is negative, confirming the as grown $\text{Bi}_2\text{Se}_3$ single crystals to be n-type in nature. The values of carrier concentration ($\sim 10^{18} \text{cm}^{-3}$) at three temperatures corroborate the sample to be semimetallic in nature. This Hall effect results supports the conclusion drawn from the Seebeck and resistivity measurements about the sample to be semimetallic in nature.


6.6 References