Appendix B

Growth and Certain Study of Molybdenum Antimony Chalcogenide Single Crystals

Apart from these major studies, we have also grown the single crystals of molybdenum antimony chalcogenides. We have measured the pressure as well as temperature dependent electrical resistivity and surface microtopography of these grown crystals. The electrical resistivity and thermoelectric power measurement studies show the metallic nature of the as grown crystals. The detailed study is discussed in this appendix.
INTRODUCTION

A number of antimonides and antimonide-tellurides and antimonide-selenides are currently being investigated for their potential use as thermoelectric materials [1–4]. These include the filled skutterudites \( \text{LnM}_4\text{Sb}_{12} \) (\( \text{Ln} = \) lanthanide, \( M = \) transition metal atom) [5–7], \( \beta\)-\( \text{Zn}_4\text{Sb}_3 \) [8,9], \( \text{Yb}_{14}\text{MnSb}_{11} \) [10,11] and \( \text{Ni}_y\text{Mo}_3\text{Sb}_{7-x}\text{Te}_x \) [12]. All these materials are bestowed with different, in part non-classical, \( \text{Sb–Sb} \) interactions, which are vital for their thermoelectric properties [13]. The \( \text{Sb} \) motifs include planar \( \text{Sb}_4^{4+} \) rectangles in case of \( \text{LnM}_4\text{Sb}_{12} \), infinite linear chains in \( \beta\)-\( \text{Zn}_4\text{Sb}_3 \) with alternating short and long \( \text{Sb–Sb} \) distances, linear hypervalent \( \text{Sb}_3^{7-} \) in \( \text{Yb}_{14}\text{MnSb}_{11} \), and \( \text{Sb}_8 \) cubes interconnected via short \( \text{Sb–Sb} \) bonds to a three-dimensional network in \( \text{Ni}_y\text{Mo}_3\text{Sb}_{7-x}\text{Te}_x \). Extended \( \text{Sb–Sb} \) interactions were also found in the antimonides of the group 4 elements, when the group 4 content is below 50 at-%. Representatives include the Chimney ladder phases \( \text{Ti}_5\text{Sb}_8 \) [14] and \( \text{Zr}_{11}\text{Sb}_{18} \) [15] with a multitude of intermediate \( \text{Sb–Sb} \) bonds between 3.1 Å and 3.4 Å, \( \text{TiSb}_2 \) with \( \text{Sb}_2^{4-} \) dumbbells [16], \( \text{ZrSb}_2 \) and \( \text{HfSb}_2 \) with antimony ribbons and pairs, [17,18] and \( \text{Hf}_5\text{Sb}_9 \) with a planar \( \text{T}\)-shaped net of antimony atoms [19,20]. Different structures were obtained when replacing part of the antimony atoms with tellurium and with \( E = \) \( \text{Si} \), \( \text{Ge} \), \( \text{Sn} \), namely \( \text{ZrSbTe} \) and \( \text{HfSbTe} \) [21] with planar rectangular antimony layers (\( \text{NbPS} \) type), \( \text{ZrE}_x\text{Sb}_{2-x} \) and \( \text{HfE}_x\text{Sb}_{2-x} \) [22] (\( \text{Co}_2\text{Si} \) type), and \( \text{ZrSi}_{0.7}\text{Sb}_{1.3} \), \( \text{ZrGeSb} \) [23] and \( \text{HfGeSb} \) [24] (with square planar layers formed by the \( \text{Si/Ge} \) atoms with some antimony content (\( \text{ZrSiS} \) type). Square nets of > 80% antimony atoms were observed in the structure of \( \text{Hf}_3\text{Cu}_2\text{Ge}_{3.58}\text{Sb}_{1.42} \) [25]. The replacement of every other \( \text{Se/Te} \) atom in layered \( \text{MoX}_2 \) (\( \text{X} = \text{Se} \) and \( \text{Te} \)) by one \( \text{Sb} \) atom led to the formation of \( \text{MoSbX} \); within its lattice, \( \text{Sb} \) atoms interconnect the \( \text{MoSbSe/Te} \) sheets to form a truly three-dimensional structure, thereby enlarging the octahedral cavities.
The growth parameters for MoSbX (X=Se and Te) single crystals are shown in Table B1. To grow both these materials using chemical vapor transport technique, iodine was used as a transporting agent. The rate of increment and decrement of temperature to grow these materials was 50K/hour. For both materials, growth temperatures were maintained for 120 hours. This complete process results in single crystals of related materials.

**Table B1** Growth parameters of MoSbX (X=Se and Te) single crystals.

<table>
<thead>
<tr>
<th>Growth parameters</th>
<th>MoSbX</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X=Se</td>
</tr>
<tr>
<td>Source zone temperature (K)</td>
<td>1173</td>
</tr>
<tr>
<td>Growth zone temperature (K)</td>
<td>1093</td>
</tr>
<tr>
<td>Ampoule dimensions (length in cm X diameter in cm)</td>
<td>22 X 2.5</td>
</tr>
<tr>
<td>Vacuum level (torr)</td>
<td>$10^{-5}$</td>
</tr>
<tr>
<td>Name and amount of transporting agent</td>
<td>Iodine 1 mg/CC</td>
</tr>
<tr>
<td>Growth period (hour)</td>
<td>120</td>
</tr>
<tr>
<td>Rate of increment of temperature (K/hour)</td>
<td>50</td>
</tr>
<tr>
<td>Rate of decrement of temperature (K/hour)</td>
<td>50</td>
</tr>
<tr>
<td>Crystal dimensions (mm X mm X mm)</td>
<td>13 x 9 x 0.5</td>
</tr>
<tr>
<td>Physical appearance</td>
<td>Shiny Silver</td>
</tr>
</tbody>
</table>
The methods used to measure the electrical transport properties with temperature and pressure for as grown crystals of molybdenum antimony chalcogenides are same as discussed in chapter 5 and 6. Here in this appendix we have discussed the results obtained by the aforesaid measurement in qualitative manner.

**STUDY OF CRYSTAL GROWTH MECHANISM**

**STRUCTURE OF CRYSTAL GROWTH**

The structure of crystal surfaces in equilibrium is important in determining the mechanisms & kinetics of crystal growth from vapor or otherwise. The actual growth form of a crystal is not the equilibrium form, but depends largely on the growth and dissolution rates as a function of a crystallographic orientation and on the kinetics of step motion on these faces.

**Classification of surfaces**

Three types of surfaces which have been known:

1. Singular surfaces
2. Vicinal surfaces
3. Non-singular surfaces or diffuse surfaces

From atomic viewpoint, singular and non-singular interfaces differ in the number of molecular layers parallel to the surface involved in the transition from the crystal to vapor.

For a singular surface the transition occurs in one layer, whereas several layers are involved in a non-singular interface hence, the name “diffuse interface”. But the actual thickness of the transition region is very difficult because the thickness of the molecular layer is larger for the singular case. This differentiation between the two kinds of surfaces is important during growth:

Singular interfaces can only grow by the lateral motion of molecular layers, whereas non-singular interfaces could be able to grow normal to them. For an ideal lattice of fixed molecules, there cannot be any non-singular surfaces.
For a crystal in equilibrium with its vapor, all solids have singular surfaces up to their melting point, this might, however, not be true for crystal in the presence of their melt when the latent heat of fusion is small.

**Dislocation as sources of steps**

Crystal faces should grow by the spread of successive layers created by two dimensional nucleation processes on the faces. The subsequent growth of layer after nucleation would be extremely fast and would not be a limiting factor in controlling the growth rate. Most of the real crystals grow at very low super saturations, leading to the conclusions that source of steps are always present which make the nucleation process unnecessary. The entire kinetic growth is then determined by the motion & interaction of steps on the crystal surface. The problem of the continuous presence of steps on the crystal surface was resolved by Frank’s screw dislocation mechanism of crystal growth. A screw dislocation emergent at a point on the crystal surface provides a step on the surface equal in height to the projection of the burgers vector of the dislocation on the normal to the surface. During growth, these steps form a spiral growth hill, which then advances the face of the crystal with some characteristic growth rate. The dislocation rapidly winds itself up into a spiral, centered on the dislocation, until the curvature at the center reaches the critical value, at which curvature, the rate of advance falls to zero & the whole spiral then rotates steadily with stationary shape.

**Kinetics of crystal growth**

In “layer growth” two simultaneously processes are involved:

1. Creation of steps at a source somewhere on the growing surface.
2. Motion of the steps away from the source.
Classification of growth conditions
Under the condition of growth from the vapor some of the faces of the growing crystal are singular or vicinal. Thus, to classify the growth conditions under two headings:
1. The growing surfaces are non-singular (diffuse) and as such do not required a source of steps (we call this Dendritic growth).
2. The growing surfaces are singular (or a combination of vicinal surfaces) which required a source of steps (we call this layer growth).

Dendritic growth
If we have lattice with low symmetry, then growth from vapor can occur easily without the need of source of steps.
For example, the hexagonal metals zinc & cadmium will grow under certain circumstances as very thin plates normal to the c-axis. The growing surfaces, probably prismatic planes in the case of hexagonal metal, appear to behave as non-singular surfaces. From the experimental point of view, dendritic growth appears to be favored by the following conditions:
1. A volume diffusion field operates which favors the non-singular surfaces.
2. High super saturation & high equilibrium concentration producing a high rate of growth in such a way that the growing surface does not wait for the condensing atoms to diffuse to it but goes forward to catch them.

Dendritic growth is limited to low symmetry crystals and cubic crystal also show dendritic growth. Sometimes they show platelet growth, but it is usually because they are twinned crystals. Both surface diffusion and / or impurities are important in favoring the growth of the non-singular surfaces.
Figure B2.1 Surface micro-topographs of MoSbSe single crystals.

Figure B2.1(a) is a micrograph taken with ordinary incident light, and shows the following characteristics: Triangular growth layers cover the whole surface, and a few growth centres, i.e. triangular hillocks, are seen; the triangular growth layers emanate from these centres. When the surface of this crystal is observed with a phase-contrast microscope in reflected light, several striking features can be seen. The features commonly noticed on these photomicrographs are: Triangular growth layers, generated by clusters of screw dislocations; this is shown by the fact that the growth centres, i.e. the triangular hillocks seen in figure B2.1(a), consist of composite spirals (figure B2.1 (b-d)). Along irregular lines, brightness or darkness of the surface changes considerably from place to place.

Straight triangular growth layers show minute shifts where they meet the irregular lines; the shift is greater for thinner layers than for thicker ones. Small triangular spirals, as well as minute triangular
tongue-like terraces, occur along the irregular lines, but they do not extend over a wide area.

**Figure B2.2** Surface micro-topographs of MoSbTe single crystals.

Figure B2.2 shows dendrites of the MoSbTe single crystals. We can see that two main stems from which the tree-like branches grew at an angle of 45°, the main stems are cut exactly perpendicularly by fine cracks. In agreement with this they have an orientation <100> and accordingly the branches have an orientation <110>. In figures B2.2(e-f), the cause of the spirals cannot be existing dislocations, but rather must be the very small crystals or large colloidal particles, which are covered by new layers. Figures B2.2(c-d) show the considerable
differences in the distances between the steps of neighboring spirals. The origin of the spirals is follows as:

At high super saturations, changes in the rates of the growth of the layers are intimately related to the super saturation, all the molecules in the solutions are hydrated although there structures may be different; during crystallizations they become dehydrates. These simultaneous processes reduce the super saturation close to the boundary of the growing layers; the super saturation decreases steadily as the layer approach each other, from lack of influx of material. The super saturation at starved position is maintained only by diffusion and convection, however, replenishment is slow, and so the growth rates vary periodically. The normal relation between supply and consumption allows only insignificant changes in the growth rates of widely separated layers, which rapidly over take more concentrated layers and take part in their structure. This leads to steps grouping, macroscopic steps are produced by accumulation of microscopic steps, and the growth spiral can be expressed in the form of concentric circles.

**THERMOELECTRIC POWER MEASUREMENT**

Figure B2.3 Variation of thermoelectric power with temperature for MoSbTe single Crystal.
The temperature dependent Seebeck co-efficient measurement is shown in figures B2.3 and B2.4 for MoSbSe and MoSbTe single crystals respectively. The thermoelectric power increases (more or less smoothly) for both materials as the temperature increases. The Seebeck co-efficient $S$ remains between 2 $\mu$V/K to 44 $\mu$V/K and 3 $\mu$V/K to 39 $\mu$V/K for MoSbSe and MoSbTe single crystals respectively over the temperature range 300K to 578K. These values of Seebeck co-efficient are slightly higher than in most other metallic compounds which usually have thermopower values between -20 and +20 $\mu$V/K. Typical Magnitudes of Seebeck co-efficient at 300K (room temperature) range from a few $\mu$V/K for most metals to 10-40 $\mu$V/K for some transition metal elements. The observed thermopower for these two molybdenum antimony chalcogenides is of the same order as most metallic materials.

**Figure B2.4** Variation of thermoelectric power with temperature for MoSbTe single Crystal.
HIGH TEMPERATURE ELECTRICAL RESISTIVITY MEASUREMENT

Figure B2.5 Variation of electrical resistivity with temperature for MoSbSe single crystal.

Figure B2.6 Variation of electrical resistivity with temperature for MoSbTe single crystal.
As shown in figures B2.5 and B2.6, the room temperature resistivity of MoSbSe and MoSbTe crystals ranges from ~0.05 Ω-cm to 0.5 Ω-cm. The resistivity for the whole temperature range increases for both materials which show the metallic trend for these crystals.

PRESSURE DEPENDENT ELECTRICAL RESISTIVITY MEASUREMENT

Figure B2.8 Variation of electrical resistivity with pressure for MoSbSe single crystal.

Figure B2.7 Variation of electrical resistivity with pressure for MoSbTe single crystal.
It is evident from figures B2.7 and B2.8 that at low pressure initially the resistivity remains unstable. In metallic materials the resistance actually originates by the combined influence of the presence of impurity and the departure of atomic lattice from perfect periodicity (such departure influence the amplitude of atomic vibrations). At high pressure, atomic vibrations decrease because of increased stiffness of bonds (or decreased inter-atomic spacing), which reduces the scattering of electrons and hence the resistivity. The increased bond stiffness also decreases the compressibility of material which decreases the rate of change of atomic separation with pressure. Therefore, the rate of decrement of resistance of metal will decrease with pressure. This continues up to the equilibrium inter-atomic separation after which the resistance will start increasing with pressure. In general the pressure dependent resistance will form a convex on the pressure axis. Moreover the pressure coefficient of resistance will be negative and will increase linearly with pressure. This is the general picture of pressure dependent conduction in normal metals, but in the present case, the materials under study are layered type with two different types of bonding along and perpendicular to layers. In such cases the direction of larger inter-atomic separation will have the larger compressibility. In such cases initially the effect of change in the inter-atomic separation in one direction will dominate the overall behavior of material. Gradually it will try to be more isotropic and after some point it will start behaving as depicted for normal metals. This may lead to change the slope of pressure dependent pressure coefficient of resistivity.

CONCLUSIONS

Triangular and dendritic growth was observed on the surfaces of MoSbSe and MoSbTe single crystals respectively. From the preliminary studies of temperature dependent resistivity and thermoelectric power measurements for as grown MoSbSe and MoSbSe single crystals, it is concluded that both these materials show
the metallic nature. Pressure dependent electrical resistivity measurements for both crystals show the decrease in the resistivity as a function of pressure. In metallic materials the resistance actually originates by the combined influence of the presence of impurity and the departure of atomic lattice from perfect periodicity (such departure influence the amplitude of atomic vibrations).
REFERENCES


