Growth and characterizations of Sn\textsubscript{0.5}Se\textsubscript{2.5} Single crystal

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Abstract

The Sn\textsubscript{0.5}Se\textsubscript{2.5} is a member of transition metal dichalcogenides. The TMDC materials are very important for their layered structure. The single crystals of Sn\textsubscript{0.5}Se\textsubscript{2.5} were grown by chemical vapour transport technique using iodine as transporting agent. The stoichiometry of as grown crystals was confirmed using Energy Dispersive Analysis by X-Ray (EDAX). The structural properties of as grown crystals were studied by X-ray diffraction analysis (XRD). The lattice parameters, unit cell volume and X-ray density of as grown crystals were computed. The particle size for number of reflections has been calculated using Scherrer’s formula. The growth fault probabilities ‘α’ and deformation fault probability ‘β’ were observed for as grown crystals. This crystal is found to possess hexagonal, layered structure. The grown crystals have been examined using optical microscope to study the growth patterns on their shining surfaces. The results are discussed in detail.

Keywords: Chemical Vapour Transport technique, Sn\textsubscript{0.43}Se\textsubscript{2.57} single crystal, EDAX, XRD

Introduction

The transition metal dichalcogenides (including disulfide and diselenide) showed a wide variety of interesting physical properties, such as semiconducting, metallic, superconducting and magnetic behaviour (Boscher et al., 2006, Boscher et al., 2006, Tsuneta et al., 2003, Salman et al., 2007, Soto et al., 2007, Hu S Y, et al., 2006 and Patel C A et al., 2012). The structural properties of NbSe\textsubscript{2}, WSe\textsubscript{2}, NbS\textsubscript{2}, VSe\textsubscript{2} etc. single crystals were studied (Dave M S et al., 2012, 2015, Patel P R et al., 2012 and Patel Kaushik 2013). The crystal structure of these crystals is hexagonal. The lattice parameters, unit cell volume, X-ray density and grain size of these crystals were
obtained. The tin diselenide single crystals were grown using chemical vapour transport technique, Bridgman stockbarger technique and direct vapour transport by various researchers (Bhatt V. P. et al., 1989, Agrawal M K et al., 1991 and Julien C et al., 1992). The electrical and optical properties of SnSe$_2$ single crystals were studied by Manou as well as Julien (Manou P et al., 1996 and Julien C et al., 1992). The energy band structure, direct and indirect band gap of SnSe$_2$ single crystals has been measured (Sobolev V V and Donetskich V I, 1970). There have no such work done on Sn$_{0.5}$Se$_{2.5}$ single crystals so authors carried out growth and structural properties of this crystals.

**Experimental**

The single crystals of Sn$_{0.5}$Se$_{2.5}$ were grown by chemical vapour transport technique. A highly pure compound of tin powder (purity: 99.99%) and selenide (99.98%) were taken with stoichiometric proportion in the quartz ampoule for charge preparation. It was evacuated to a pressure of $10^{-5}$ torr and then sealed. This sealed ampoule was introduced into a two-zone furnace at a constant reaction temperature to obtain the charge. During the synthesis the temperature was slowly increased upto 1073 K with the rate of 20 K/hr. The ampoule was kept at 1073 K temperature for 3 days. Then the furnace was slowly cooled (50ºC/hr) and brought to room temperature. The resulting brown and/or reddish charge was obtained in the ampoule. This charge was crushed and transferred to another quartz ampoule. Also add iodine (2 mg/cc) filled thin capillaries in the ampoule. After filling the charge and iodine, evacuated it with $10^{-5}$ torr pressure and sealed. This ampoule was kept in a dual zone horizontal furnace for 10 days with appropriate temperature gradient. After then furnace was cooled up to room temperature with the rate of 20 K/hr. The entire material got converted into the form of crystals at the cooler end of the ampoule. The grown crystals were collected after breaking the ampoule. The optimum growth condition and physical parameters of as grown crystals are given in Table 1.

**Table 1:** Optimum condition for the growth NbSe$_2$ single crystals and the physical parameters of as grown crystals.

<table>
<thead>
<tr>
<th>Reaction temperature</th>
<th>Growth temperature</th>
<th>Physical characteristics of the crystals</th>
</tr>
</thead>
<tbody>
<tr>
<td>1123</td>
<td>1073</td>
<td>Growth time hr 240 Plate area mm$^2$ 10 Thickness mm 0.08 Color &amp; appearance Silver shining</td>
</tr>
</tbody>
</table>

The stoichiometry of as grown crystals was confirmed with the help of Energy Dispersive Analysis by X-ray (EDAX). For EDAX analysis the electron microscope (Make: Phillips, Model: XL 30 ESEM) has been used. The EDAX spectrum of as grown crystals is shown in Figure 1.
Growth and characterizations of Sn$_{0.5}$ Se$_{2.5}$ Single crystal

The typical X-ray diffractogram of the as grown crystal of Sn$_{0.5}$Se$_{2.5}$ is shown in Figure 2. It was obtain with the help of Phillips X’pert MPD X-ray diffractometer employing CuK$_\alpha$ radiation. It has verified the phase and crystallinity of the compounds. In order to record the X-ray spectrum of each sample, synthesized product was crushed homogeneously with the help of mortar and pestle. The powdered sample was filled in a specially designed quartz sample holder. The X-ray diffractogram was recorded in the 20 range of 3$^0$ – 100$^0$ employing the wavelength $\lambda$ = 1.5418 Å.

Close examination of the surface composed of layers helps a great deal in understanding the mechanism by which a crystal grows. Therefore, it was thought worthwhile to make surface characterization of these grown crystals by optical microscopy. The surface microstructure of as grown crystals was examined by computer added optical zoom microscope (Make: Carl Zeiss, Model Axiotech 100HD).

**Figure 1:** The EDAX spectrum of as grown crystals.

**Figure 2:** X-ray diffractogram of as grown crystals.
Results and Discussion

The stoichiometric proportion of the constituent elements taken for the growth and data obtained from the EDAX are shown in Table 2, with chemical formula. The EDAX analysis shows that the grown crystals are stoichiometrically perfect without any extra impurities.

Table 2: The stoichiometric proportion and EDAX results of Sn_{0.5}Se_{2.5} single crystals.

<table>
<thead>
<tr>
<th>Stoichiometric Proportion (%)</th>
<th>EDAX result (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>Se</td>
</tr>
<tr>
<td>23.12</td>
<td>76.88</td>
</tr>
<tr>
<td>22.29</td>
<td>77.71</td>
</tr>
</tbody>
</table>

In Figure 2, the pattern consists of well-defined sharp diffraction peaks, indicating good crystallinity of the specimen. The lattice parameters for the hexagonal structure have been computed, using the equation (1), i.e.

$$
\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}
$$

where $d$ is the inter planar spacing obtained from the diffractogram, $h$, $k$, $l$ are the miller indices and $a$ & $c$ are the unit cell dimensions. Substituting the values of inter planar spacing parameter $d$ corresponding to the planes having index \{00l\}, the value of lattice the parameter \(c\) has been determined. Substituting the value o $c$ and $d$ for the rest of the planes, lattice parameters for rest of all the planes have been calculated. Using the values of lattice parameters $a$, $b$, $c$ the unit cell volume ($V$) has been calculated with the help of the equation (3). It is found that there is no significant variation in the values of lattice parameters $a$ and $c$.

Volume, in terms of lattice constants $a$, $b$, $c$ and angles $\alpha$, $\beta$ and $\gamma$ is given as

$$
V^2 = a^2 b^2 c^2 \left( 1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta - \cos \gamma \right)
$$

For hexagonal system, $\alpha = \beta = 90^0$, $\gamma = 120^0$ and $a = b \neq c$,

Substituting above values in equation (2), the unit cell volume is given as,

$$
V = \frac{\sqrt{3}}{2} a^2 c \ (\text{Å})^3 = 0.866 a^2 c \ (\text{Å})^3
$$

The density $\rho$ of the grown crystals was calculated by the formula,

$$
\rho = \frac{\Sigma A}{V N}
$$

Where, $\Sigma A$ is the total weight of the atoms in the unit cell = $MZ$. Here $M$ is the molecular weight and $Z$ is the number of molecules/unit cell, $N$ is the Avogadro number and $V$ is the unit cell volume. The quadratic form of the Bragg equation for a Hexagonal system, of $MX_2$ is given as [Cullity, (1978) and Suryanarayana, (1998)],
The values of lattice parameters $a$, $b$, $c$, X-ray density ($\rho$) and unit cell volume ($V$) have been calculated from the XRD data for as grown crystals of Sn$_{0.5}$Se$_{2.5}$ given in Table 3.

### Table 3: Structural parameters for Sn$_{0.5}$Se$_{2.5}$ single crystals

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a = b$ (Å)</td>
<td>3.811</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>6.137</td>
</tr>
<tr>
<td>Volume (Å$^3$)</td>
<td>77.30</td>
</tr>
<tr>
<td>X-ray density (gm/cm$^3$)</td>
<td>3.32</td>
</tr>
</tbody>
</table>

**Particle size determination**

In order to obtain an idea about the particle size distribution in Sn$_{0.5}$Se$_{2.5}$ single crystals, the particle size was calculated using Scherrer’s formula [Al-Hilli and Evans, 1972] given as

$$t = \frac{k \lambda}{\beta_{2\theta} \cos \theta}$$  \hspace{1cm} (5)

Where $t$ is the crystallite thickness as measured perpendicular to the reflecting plane; $k$ is Scherrer’s constant whose value is chosen as unity assuming the particle to be spherical; $\lambda$ is the wavelength of the X-ray radiation, $\beta_{2\theta}$ is the width at half the maximum intensity measured in radians, and $\theta_0$ is the Bragg angle. **Table 4** records the crystallite size for Sn$_{0.5}$Se$_{2.5}$ single crystals. The intense and sharp peaks reveal the excellent crystallinity of the products and confirm their stoichiometric nature. The reflections corresponding to the observed peaks indicate the formation of single-phase material.

### Table 4: The h k l reflections, d-spacing, 2θ Values, Peak Intensity, $\beta_{2\theta}$ value and particle size for Sn$_{0.5}$Se$_{2.5}$ crystals.

<table>
<thead>
<tr>
<th>(h k l)</th>
<th>d-spacing</th>
<th>Angle $2\theta$ (degree)</th>
<th>Peak Intensity (cont/sec)</th>
<th>Tip Width $\beta_{2\theta}$</th>
<th>Grain Size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 0 1</td>
<td>6.0767</td>
<td>29.56</td>
<td>102.6</td>
<td>0.2952</td>
<td>539.08</td>
</tr>
<tr>
<td>0 0 4</td>
<td>2.0446</td>
<td>44.30</td>
<td>180.1</td>
<td>0.2952</td>
<td>563.54</td>
</tr>
<tr>
<td>1 0 4</td>
<td>1.9052</td>
<td>47.73</td>
<td>63.22</td>
<td>0.2952</td>
<td>570.74</td>
</tr>
<tr>
<td>2 1 0</td>
<td>1.7151</td>
<td>53.42</td>
<td>808.3</td>
<td>0.3444</td>
<td>500.83</td>
</tr>
<tr>
<td>1 1 4</td>
<td>1.5336</td>
<td>60.35</td>
<td>352.44</td>
<td>0.3444</td>
<td>517.51</td>
</tr>
<tr>
<td>1 0 5</td>
<td>1.3941</td>
<td>67.14</td>
<td>22.12</td>
<td>0.3444</td>
<td>536.94</td>
</tr>
</tbody>
</table>
The particle size of as grown crystals is found to be in the range of 510 Å – 570 Å as shown in Table 4. The intense and sharp peaks reveal the excellent crystallinity of the products and confirm their stoichiometric nature. The reflections corresponding to the observed peaks indicate the formation of single phase material.

Estimation of growth and deformation fault probabilities

Perfect crystalline structure is an ideal concept since perfect crystals are neither available in nature nor can be grown in the laboratory. Several types of defects are always present in crystal e.g. point defects, stacking fault etc. The study of stacking fault is very important because it plays a fundamental role in the description of defects. The enhanced conduction of the stacking faults along the c-axis is difficult to understand because of the extreme two-dimensional character of the MX\textsubscript{2} layer compounds. The only way to understand this conduction is by supposing the presence of stacking faults in these crystals [Vora A M, 2007]. In the case of hexagonal close packed metals, it is possible to make a realistic estimation of the growth fault probability ‘α’ and the deformation fault probability ‘β’ by measuring the half width of X-ray diffraction lines. Reflections for which h - k = 3n where ‘n’ is an integer, are independent of stacking faults whereas reflections for which h - k = 3n \pm 1 and l \neq 0 depend upon the faults in the crystal structure. An estimation of the deformation and growth fault probability can be obtained from the following formula for (h k l) values with ‘l’ even

\[
(3\alpha + 3\beta) = \frac{\beta_{2\theta} \times \pi^2 \times c^2}{360 \times l \times d^2 \times \tan \theta}
\]

where \(\beta_{2\theta}\) is the full width at half the maximum intensity expressed in degrees, \(c = d_{002}\), l is the Miller index in the (h k l) plane for which the estimation of ‘\(\alpha\)’ and ‘\(\beta\)’ is being made, ‘d’ is the interplaner spacing for (h k l) reflection in question, \(\theta\) is the Bragg angle corresponding to this (h k l) plane.

The formula for (h k l) values with ‘l’ odd is given as

\[
(3\alpha + \beta) = \frac{\beta_{2\theta} \times \pi^2 \times c^2}{360 \times l \times d^2 \times \tan \theta}
\]

From the equations 6 and 7, it is clear that by measuring the half width \(\beta_{2\theta}\) for reflections with both even and odd values of ‘l’ it is possible to calculate the stacking fault probabilities \(\alpha\) & \(\beta\). In calculating the half width of the reflections, instrumental broadening is neglected. The results of estimation of \(\alpha\) & \(\beta\) is presented in Table 5.

**Table 5:** Estimation of stacking fault probability of Sn\textsubscript{0.5}Se\textsubscript{2.5} single crystals.

<table>
<thead>
<tr>
<th>(h k l)</th>
<th>3(\alpha) + 3(\beta)</th>
<th>3(\alpha) + (\beta)</th>
<th>(\alpha)</th>
<th>(\beta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 0 1</td>
<td>-</td>
<td>0.0312</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 0 5</td>
<td>-</td>
<td>0.0550</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 0 4</td>
<td>0.0474</td>
<td>-</td>
<td>0.0122</td>
<td>0.0065</td>
</tr>
<tr>
<td>1 1 4</td>
<td>0.0649</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Growth and characterizations of $\text{Sn}_{0.5} \text{Se}_{2.5}$ Single crystal

From the Table 5, it can be seen that there is a significant variation shown in the deformation fault probability ($\alpha$) and growth fault probability ($\beta$) may be due to small off-stoichiometry as observed by EDAX. The calculations of the stacking faults may be considered as one of the guidelines for further detailed study of defects and various properties of crystals.

**Microstructure of the grown crystals**

The surface microstructure on the face of as grown crystals is shown in Figure 3, which shows layered surface structures.

![Figure 3: Surface microstructure of as grown crystal.](image)

The morphology of the surface of a crystal under near equilibrium condition reflects the symmetry of the latter. As a result, characteristic features on crystal surfaces, the distribution of steps around e.g. a screw dislocation exhibit the symmetry of the surface. The as grown surfaces of the crystal synthesized in the laboratory or those which occur naturally offer some features which signify how they grow under different conditions. Morphology of as grown surfaces of the bulk single crystals consists of a variety of structures whose study leads us to derive the condition and mechanism of crystal growth. A typical micrograph showing the initiation of growth layers from the corner of a crystal periphery is presented in Figure 3. Looking at this micrograph one is inclined to conclude that layer mechanism is operative during crystal growth.

**Conclusion**

Single crystals of $\text{Sn}_{0.5} \text{Se}_{2.5}$ have been grown by the chemical vapour transport technique, they are observed to be larger in size suitable for characterization and transport property measurement studies. The stoichiometry of as grown crystals is nearly preserved. From X-Ray diffraction analysis, crystals possess hexagonal structure. Particle sizes for some (h k l) planes of the as grown crystals are found. Growth and deformation fault probability are found, which shows the layer structure defects of as grown crystals. Optical microscopy shows that a typical spiral, point crack,
microcrystal, mixer of triangular and hexagonal features on the Sn0.5Se2.5 crystal structure and finally cleaved surface with hexagonal growth pattern.

Reference


Growth and characterizations of Sn$_{0.5}$Se$_{2.5}$ Single crystal


