STRUCTURAL CHARACTERIZATION OF GeS$_{0.5}$Se$_{0.5}$ CRYSTALS GROWN BY VAPOUR TRANSPORT TECHNIQUE

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Crystalline germanium sulphoselenide having a wide band gap has attracted many researchers due to its important properties in solar energy converters. In this paper authors present their investigation on growth of off-stoichiometric single crystals of germanium sulphoselenide GeS$_{0.5}$Se$_{0.5}$ by direct vapor transport technique (DVT) using two zone horizontal furnace. Stoichiometry of the grown crystals is confirmed by Energy Dispersive Analysis of X-rays (EDAX). The structural characterization was accomplished by X-ray diffraction (XRD) studies and it was found to be orthorhombic structure. Lattice parameters, Unit cell volume and X-ray density have been calculated. A study of microstructures on the grown crystals of GeS$_{0.5}$Se$_{0.5}$ has been made.

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1. Introduction

The science and technology enjoy a degree of sophistication today largely due to the availability of high quality materials. Semiconductors form the basic unit of all electronic devices from wrist watches to satellite and many industrial applications [1]. Among topics of current interest in materials science, the layered chalcogenides occupy a prominent place because of the remarkable range of properties they exhibit. In addition to these chalcogenides having interesting electronic and optical properties [2, 3] have also been intensively investigated. The layer like semiconductors have generated enormous interest as a group of anisotropic materials with strong bending within the layers and weak van-der Waals bonds between layers [2], these materials have been used for many years as solid state lubricants [4], photovoltaic / phctocatalytic, solar energy converters [5], Schottky [6] and liquid junction solar cells [7, 8]. These compounds have been investigated in crystalline form grown by various techniques. The vapour transport technique has been proved as a very good technique to grow good quality single crystal though it is associated with some difficulties. In order to avoid the contamination of transporting agent, it is preferable to grow crystals by DVT technique. [9] [10]. In this paper authors reports growth of GeS$_{0.5}$Se$_{0.5}$ crystals by vapour transport technique.

2. Experimental

2.1 Growth

In present investigations, GeS$_{0.5}$Se$_{0.5}$ crystals have been grown by direct vapor transport technique. The main requirement of this technique is precise setting of the temperature gradients between two zones to enhance the transport of material in vapor form. For this purpose, a two zone
For compound preparation the cleaned ampoule was filled with stoichiometric proportion of Ge (99.999%), S (99.99%) and Se (99.99 %) pure of about 10 grams for growth then ampoule was sealed under pressure of 10⁻⁵ Torr. The sealed ampoule was kept in two-zone horizontal furnace. The temperatures of both the zones were slowly but gradually raised up to desired temperature and maintained that temperature for 3 days, after that furnace was cooled off at the room temperature. The ampoule was broken and shaken well with help of agate mortar to prepare fine powder of this compound. For growth of crystals this compound was filled into another chemically cleaned ampoule and repeat procedure mentioned above. Temperature of both zone of furnace raised slowly from room temperature to required temperature at the rate of 40K/hr and temperature of both the zone cooled at the rate of 20K/hr to room temperature. The temperature profile along the furnace showing the position of the ampoule is depicted in Figure 2 for GeS₀.₅Se₀.₅ single crystal.
The ampoule was taken out of the furnace and broken to remove crystals from it. We obtained black opaque shiny crystals in this process. The appropriate growth condition for Ge$_{0.5}$Se$_{0.5}$ sample is reported in Table 1. The maximum size of the crystals grown in this investigation was 1.2 cm × 0.65 cm × 0.033 cm.

**Table 1 Growth condition for Ge$_{0.5}$Se$_{0.5}$ crystal.**

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Temperature</th>
<th>Growth Time</th>
<th>Crystal size</th>
<th>Crystal thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge$<em>{0.5}$Se$</em>{0.5}$</td>
<td>923 K</td>
<td>873 K</td>
<td>96 Hour</td>
<td>1.2 × 0.65 cm</td>
</tr>
</tbody>
</table>

3. Characterization

The crystals grown in present investigations have been characterized for their compositional and structural properties using standard Energy Dispersive Analysis by X-ray (EDAX) and XRD techniques. The results of the EDAX study has been given in Table 2. From these results, it is clear that the crystals grown in present case posses desired stoichiometry i.e. Ge$_{0.5}$Se$_{0.5}$.

The crystallographic parameters of Ge$_{0.5}$Se$_{0.5}$ crystal in present case have been evaluated using CuK$_\alpha$ radiation in XRD technique. For X-ray diffraction, the samples were ground at room temperature and were passed through a 106 mesh sieve. The X-ray diffractograms (XRD) of this compound was recorded on Philips PW 1710 Diffractometer using CuK$_\alpha$ radiation. The scan rate used to obtain X-ray pattern for cell constant determination was 3.010°/min. Figure 3 shows the X-ray diffractograms of Ge$_{0.5}$Se$_{0.5}$ compounds obtained by powdering the crystals synthesized.
during their growth. From the X-ray diffraction peaks the lattice parameters, unit cell volume and density have been calculated.

The as grown surfaces of the crystals grown in laboratory or those which occur in nature offer some features which signify how they grow under different conductions. Morphology of grown surfaces of the crystals consists of a variety of structures whose study leads us to derive the mechanism of growth.

The microstructural examination of crystal surface was accomplished with the help of Axiotech 100 reflected light microscope manufactured by Carl Zeiss Jena, Germany. Fig 4 and 5 shows the presence of growth layers on the flat surface of a GeS₀.₅Se₀.₅ crystal.

4. Result and discussion

GeS₀.₅Se₀.₅ single crystals are successfully grown using direct vapour transport technique. Photograph of some grown crystals is show in Figure 3.

![Photograph of grown GeS₀.₅Se₀.₅ single crystals.](image)

The Wt % of elements taken for growth experiment is nearly equal to the Wt (%) of elements from EDAX is shown in Table 2. From EDAX, it has been confirmed that grown GeS₀.₅Se₀.₅ single crystals are nearly stoichiometrically perfect.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Wt (%) of elements from EDAX</th>
<th>Wt % of elements taken for growth experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ge</td>
<td>S</td>
</tr>
<tr>
<td>GeS₀.₅Se₀.₅</td>
<td>55.90</td>
<td>12.10</td>
</tr>
</tbody>
</table>

The X-ray powder diffractrogram obtained for GeS₀.₅Se₀.₅ is shown in the Figure 4.
The sharp peaks indicate the good crystalline structure of the grown compounds. It is evident from the diffractogram that for GeS$_{0.5}$Se$_{0.5}$ single crystal (004) reflections are of maximum intensity, indicating thereby a strong orientation along the c-axis. The intensity of all other reflections is extremely weak as compared to this reflection. Characterizing these crystals using X-rays we have determined the values of lattice parameters, unit cell volume and density is listed in Table 3.

**Table 3. Lattice parameters, Unit cell volumes and X-ray densities for GeS$_{0.5}$Se$_{0.5}$ crystal.**

<table>
<thead>
<tr>
<th>Crystal</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Unit cell volume (Å$^3$)</th>
<th>Density (g cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeS$<em>{0.5}$Se$</em>{0.5}$</td>
<td>4.39</td>
<td>3.71</td>
<td>10.7</td>
<td>174.48</td>
<td>4.875</td>
</tr>
</tbody>
</table>

From these data it is found that the structure of GeS$_{0.5}$Se$_{0.5}$ single crystals is orthorhombic and all the values match with the reported value [11].

From the microstructure study it has been found that crystals have been grown in layers [12].
Fig. 5 (a) Micrograph showing the presence of growth layers on flat surface of GeS$_{0.5}$Se$_{0.5}$ crystal.

Fig. 5 (b) Micrograph showing growth layers in GeS$_{0.5}$Se$_{0.5}$ crystal.

A typical photograph showing the presences of growth layers on homogeneously flat surface of GeS$_{0.5}$Se$_{0.5}$ crystal is shown in Figure 5 (a) and 5 (b).

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References