Chalcogenide Letters Vol. 6, No. 6, June 2009, p. 257 - 263

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-stochiometric single crystals of germanium sulphoselenide $GeS_{0.5}Se_{0.5}$ by direct vapour 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.

(Received May 2, 2009; accepted June 16, 2009)

Keywords:Ge-S-Se; Crystal growth; Vapour transport technique; XRD, EDAX

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 / phtocatalytic, 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 horizontal furnace having required dimensions has been used which is shown in **Figure 1**. The furnace was constructed by University Science and Instrumentation Centre (USIC), Sardar Patel University by using a special sillimanite threaded tube 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. High quality quartz ampoules were used for growth experiment having dimensions of 24 cm length, 2.4 cm outer diameter and 2.2 cm inner diameter. The ampoule was first washed with detergent powder and boiled water after then with hot mixture of concentrated HNO_3 and H_2So_4 taken in equal proportion, followed by washing of ampoule with distilled water. After this ampoule was filled with concentrated HF and heated until whole HF evaporated, so that the inner surface of the ampoule become rough which enhances the nucleation process during the growth. At the end this ampoule was washed at least 8 to 10 times by double distilled water to remove any residue of these chemicals inside ampoule. A cleaned ampoule was kept in a SICO constant temperature furnace at 100^0C for nearly 24 hour to make it moisture free.

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 upto 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 require 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 $GeS_{0.5}Se_{0.5}$ single crystal.

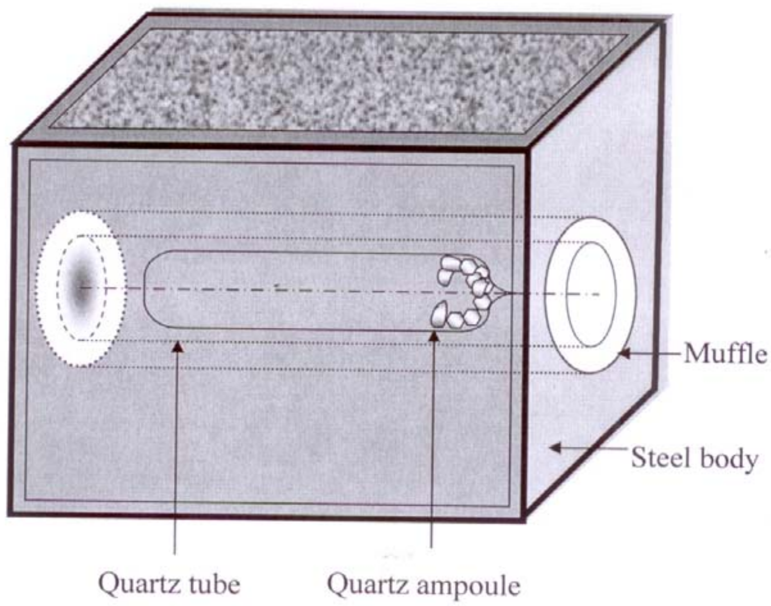

Fig.1. The dual zone horizontal furnace with co-axially loaded ampoule.

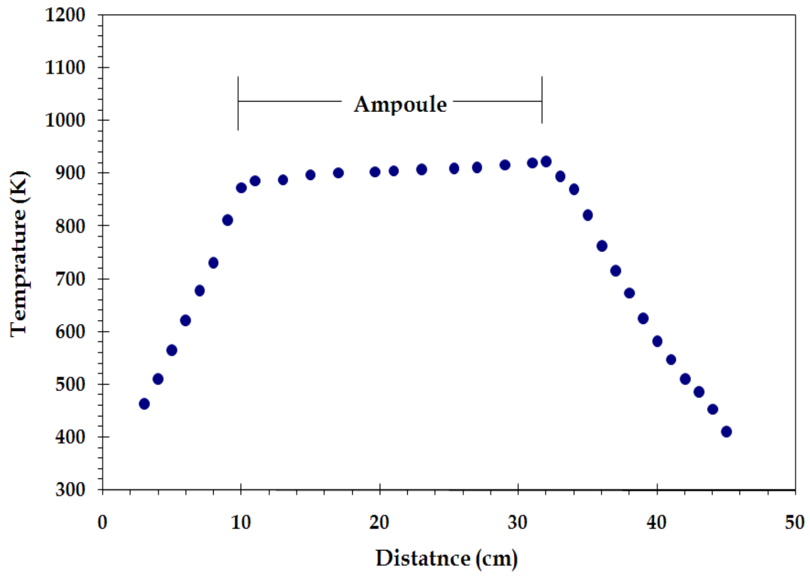

Fig.2. Temperature profile of $GeS_{0.5}Se_{0.5}$ single crystal along with the two zone furnace showing the position of the ampoule.

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 $GeS_{0.5}Se_{0.5}$ 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 $GeS_{0.5}Se_{0.5}$ crystal.

Crystal	Temperature		Growth Time (Hour)	Crystal size (cm x cm)	Crystal thickness (μm)
	Hot Zone (K)	Cold Zone (K)			
$GeS_{0.5}Se_{0.5}$	923	873	96	1.2 × 0.65	33

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. $GeS_{0.5}Se_{0.5}$.

The crystallographic parameters of $GeS_{0.5}Se_{0.5}$ crystal in present case have been evaluated using CuK_{α} 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_{α} radiation. The scan rate used to obtain X-ray pattern for cell constant determination was 3.010 2θ/min. **Figure 3** shows the X-ray diffractograms of $GeS_{0.5}Se_{0.5}$ 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 $GeS_{0.5}Se_{0.5}$ crystal.

4. Result and discussion

$GeS_{0.5}Se_{0.5}$ single crystals are successfully grown using direct vapour transport technique. Photograph of some grown crystals is show in Figure 3.

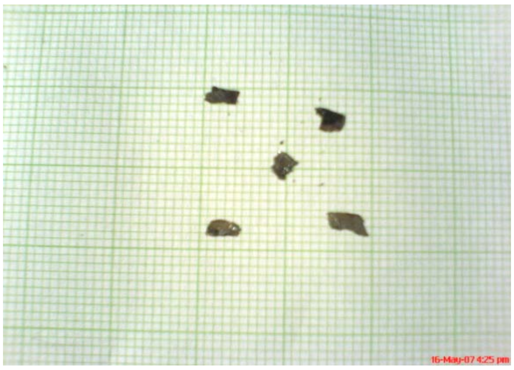

Fig.3. Photograph of grown $GeS_{0.5}Se_{0.5}$ single crystals.

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 $GeS_{0.5}Se_{0.5}$ single crystals are nearly stoichiometrically perfect.

Table 2. Chemical composition (Wt %) of grown $GeS_{0.5}Se_{0.5}$ crystal by EDAX analysis.

Crystal	Wt (%) of elements from EDAX			Wt % of elements taken for growth experiment		
	Ge	S	Se	Ge	S	Se
$GeS_{0.5}Se_{0.5}$	55.90	12.10	32.00	56.66	12.5	30.81

The X-ray powder diffractrogram obtained for $GeS_{0.5}Se_{0.5}$ is shown in the Figure 4.

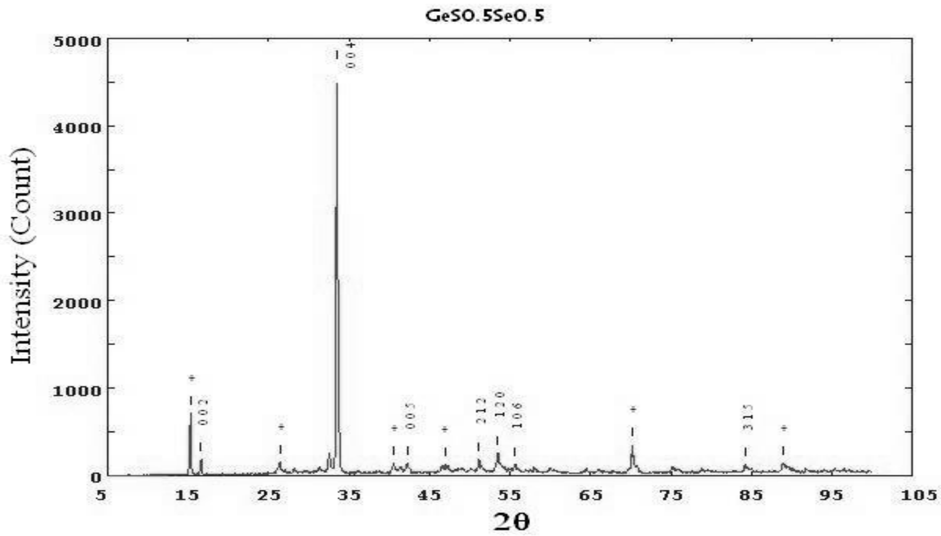

Fig. 4 X-ray diffractrogram $GeS_{0.5}Se_{0.5}$ crystal grown by direct vapour transport technique.

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.

Crystal	a (Å)	b (Å)	c (Å)	Unit cell volume $(Å)^3$	Density (g cm^{-3})
$GeS_{0.5}Se_{0.5}$	4.39	3.71	10.7	174.48	4.875

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].

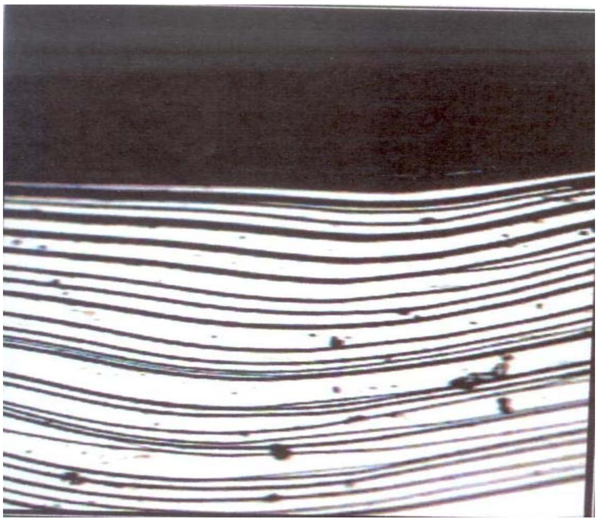

Fig. 5 (a) Micrograph showing the presence of growth layers on flat surface of $GeS_{0.5}Se_{0.5}$ crystal.

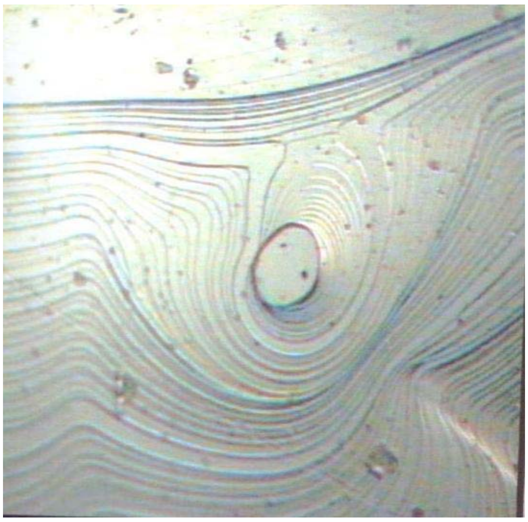

Fig. 5 (b) Micrograph showing growth layers in $GeS_{0.5}Se_{0.5}$ crystal.

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)**.

Acknowledgement

Authors are thankful to UGC, New Delhi, India for the sanction of a research project to G. K. Solanki which provided the necessary financial help for carrying out this work.

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