Growth and anisotropic behavior of $GeS_{0.5}Ge_{0.5}$ single crystals grown using direct vapour transport technique

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Abstract

This paper report the growth of single crystals of ternary mixed compounds of group IV–VI in the form of $GeS_{0.5}Se_{0.5}$ using direct vapour transport technique. The grown crystals were characterized by the X-ray diffraction analysis for their structural parameter determination. All the grown crystals were found to be orthorhombic structure. The microstructure analysis of the grown crystals reveals their layered type growth mechanism and are therefore highly anisotropic. The d.c. electrical resistivity measurements perpendicular to c-axis (i.e. along the basal plane) and parallel to c-axis (i.e perpendicular to basal plane) in the temperature range 303–723 K were carried out for grown crystals using four-probe method. The electrical resistivity measurements showed an anisotropic behavior of electrical resistivity for the grown crystals. The anisotropic behavior $GeS_{0.5}Ge_{0.5}$ is presented systematically.

Keywords. Crystal growth; layered structure; resistivity; anisotropy;

Introduction

Natural crystals of many materials are available in nature but they cannot be used directly for device applications. Instead they should give some sort of treatment because of the main problem of purity and perfection. The crystal growth study in the last 10 years [1-5] led to the conclusion that the artificial crystals of most of the materials can be grown in the laboratories.

Sulphides and selenides of the fourth group and metals like germanium and tin (GeS, GeSe, SnS and SnSe) form an interesting family of layered compounds. These compounds are considered intermediate between the three dimensional and the two dimensional materials. The bonding between the layers is weak being of Van der Waal's type and therefore they can be easily cleaved in the (001) plane [6]. From this fact one might expect them to exhibit the typical anisotropy of

electrical properties i.e. conductivity or mobility of a layered structure. Mechanically, single crystals of these layered materials behave extremely two-dimensional. Although layered materials are indeed anisotropic, there is a great variation in the anisotropy ratio among them. In some cases anisotropy factor up to 10^6 have been reported [7]. Since most of the semiconductor applications are governed by the electrical properties of the materials, the electrical properties of the IV–VI compounds (GeS, GeSe, SnS and SnSe) have been carried out by different investigators [8-11]. Most of these studies are nearly confined to investigations of electrical properties along the basal plane and very few of them report the interesting question of electrical transport along the c-axis. These lamellar compounds have attracted considerable attention because of their important properties in the field of optoelectronics, lubricants, photovoltaic/photocatalytic, solar energy converters, liquid junction solar cell, holographic recording systems, electronic switching and infrared production and detection. These compounds have been grown in a crystalline form using various techniques. The vapor transport technique has been proved as a very good technique to grow good quality single crystal and to avoid the contamination of transporting agent; it is preferable to grow crystals by DVT technique. They all exhibit an orthorhombic structure belonging to space group h D2 16 (Pcmn). This paper reports the growth of $GeS_{0.5}Ge_{0.5}$ crystals and a systematic study on the anisotropic behavior of $GeS_{0.5}Ge_{0.5}$.

Material and Methods

The author has grown $GeS_{0.5}Ge_{0.5}$ crystals using direct vapour transport technique. By setting a precise temperature gradients between two zones to enhance the transport of material in vapour form. The mixture was slowly heated to the required temperature. The slow heating was necessary to avoid any explosion due to the strong exothermic reaction between the elements. A total charge of nearly 10 g was kept in the furnace. Energy Dispersive Analysis of X-rays (EDAX) has been carried out for determination of the chemical composition of grown crystals. The X-ray diffractrograms (XRD) of these compounds were recorded on Philips PW 1710 diffractometer using CuK_α radiation. For the study of variation in resistivity with temperature of the grown crystals a high temperature measurement set has been designed and developed in University Shophesticsted Instrumentation Centre (USIC), Sardar Patel University. Using this experimental set up, resistance of sample has been measured from room temperature to 723K temperature in the step of 10K and

for each step the corresponding resistivity can been calculated. To avoid excessive heating of the sample chamber, it is cooled by circulating cold water around it with the help of tubes.

The crystal is mounted in the sample holder which is then in inserted in the sample chamber and closed at the top. Introducing this assembly in vertical tabular furnace. The temperature of the sample is raised using variac. The temperature of the sample is measured with the help of Cr-Al thermocouple kept in vicinity of the sample which is connected to the digital temperature controller which can control and display the acquired temperature. Starting from room temperature (303 K), the temperature of the sample is increased slowly from room temperature to 723 K, in steps of 10 K and at each step the corresponding value of the resistivity of the sample is calculated. Electrical resistivity parallel c-axis and perpendicular to c-axis has been measured and anisotropy ratio has been calculated for all the samples.

Result and Discussion

The appropriate growth conditions for $GeS_{0.5}$ $Ge_{0.5}$ crystals is shown in table 1. The ampoule containing the crystals was broken and crystals having maximum size shown in Table 1.

Table 1.Growth parameters of $GeS_{0.5}Se_{0.5}$ single crystal.

Crystal	Temperature distribution		Growth Period [Days)	Dimension of the grown crystals (cm^2)
	Reaction Zone (K)	Growth Zone (K)		
$GeS_{0.5}Se_{0.5}$	923	873	7	0.75 X 0.65

The results of the EDAX report shown in table 2, confirms that the stoichiometry of the elements has been maintained in the grown crystals.

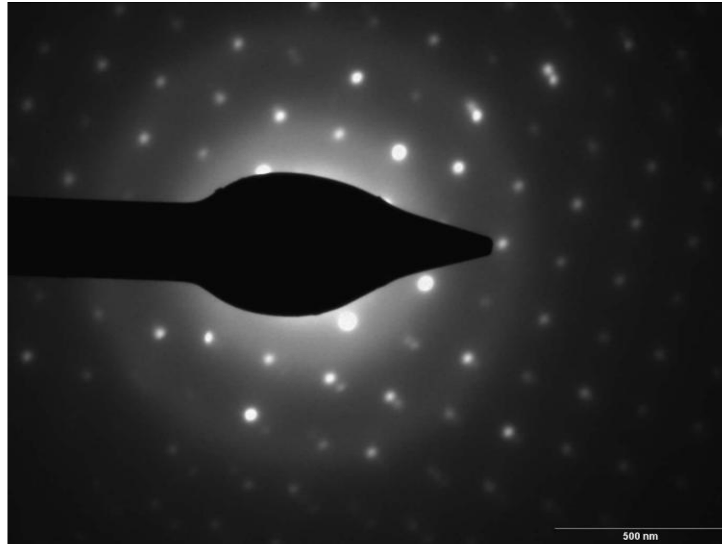

Figure 1.Electron diffraction pattern of $GeS_{0.5}Se_{0.5}$ crystal

Table 2 Chemical composition (wt. %) of as grown $GeS_{0.5}$Se0.5 single crystal obtained 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 values of lattice parameters obtained for $GeS_{0.5}$ $Se_{0.5}$ single crystals are compared and found in agreement with those reported earlier by different investigators. The values of lattice parameter for the crystal shown in table 3 confirms the orthorhombic structure of grown crystals.

Table 3. Lattice parameters, unit cell volume and X-ray density of $GeS_{0.5}Se_{0.5}$

Crystal	A in Å	b in Å	c in Å	Unit Cell Volume (Å)^3	X-ray Density g cm^{-3}
$GeS_{0.5}Se_{0.5}$	4.395	3.712	10.695	174.48	4.875

The variation of log of electrical resistivity parallel to c-axis and perpendicular to c-axis in the temperature range 303–723 K are shown in figures 2 & 3 , respectively. The decrease in electrical resistivity with increase in temperature suggests the semiconducting nature of the grown crystals. Using the resistivity values, anisotropy ratio was calculated using the relation

$$\gamma = \frac{\rho_{\Pi}}{\rho_{\perp}}$$

where ρ|| is the resistivity parallel to c-axis and ρ⊥ the resistivity perpendicular to c-axis.

Table 4. The values of activation energies perpendicular to c-axis and parallel to c-axis for $GeS_{0.5}Se_{0.5}$ single crystal

Sample	Activation energy (eV)			
	Temp. Range	Along a-b axis	Temp. Range	Along c-axis
$GeS_{0.5}Se_{0.5}$	304-428	0.161	308 – 368	0.189
	433-533	0.120	373 – 543	0.491
	538-723	0.407	553 -723	1.743

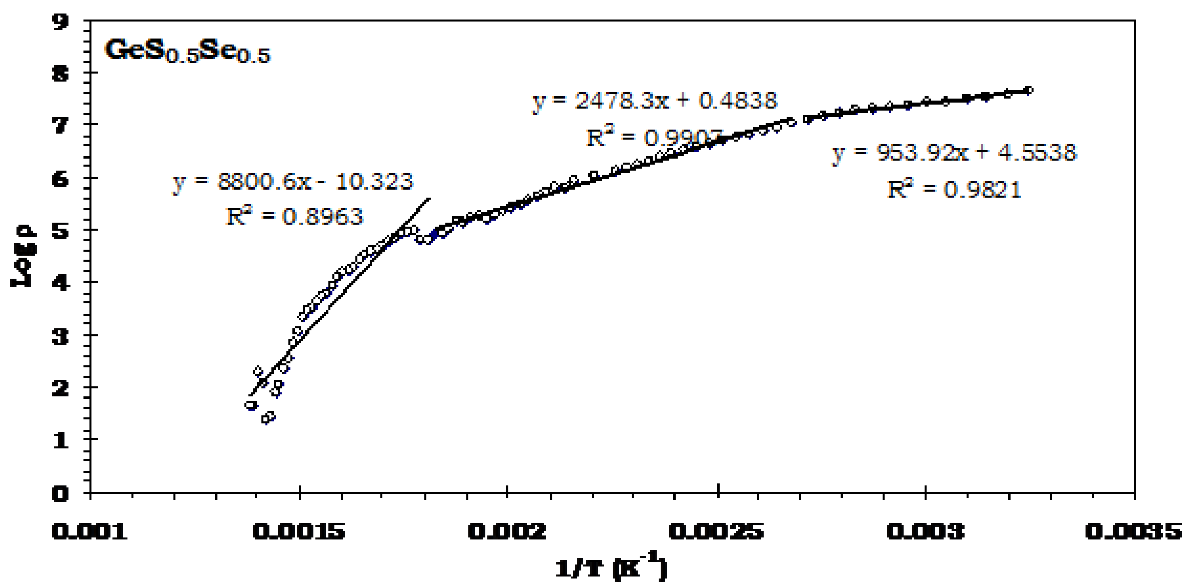

Figure 2. Variation of lnρ vs. inverse of temperature for $GeS_{0.5}Se_{0.5}$ single crystal along the basal plane.

The anisotropy ratio was determined at different temperatures in the range 303– 723 K for grown crystals. Figure 4 shows the variation of log of anisotropy ratio with reciprocal of temperature for grown crystal. The anisotropy ratio increases as the temperature decreases.

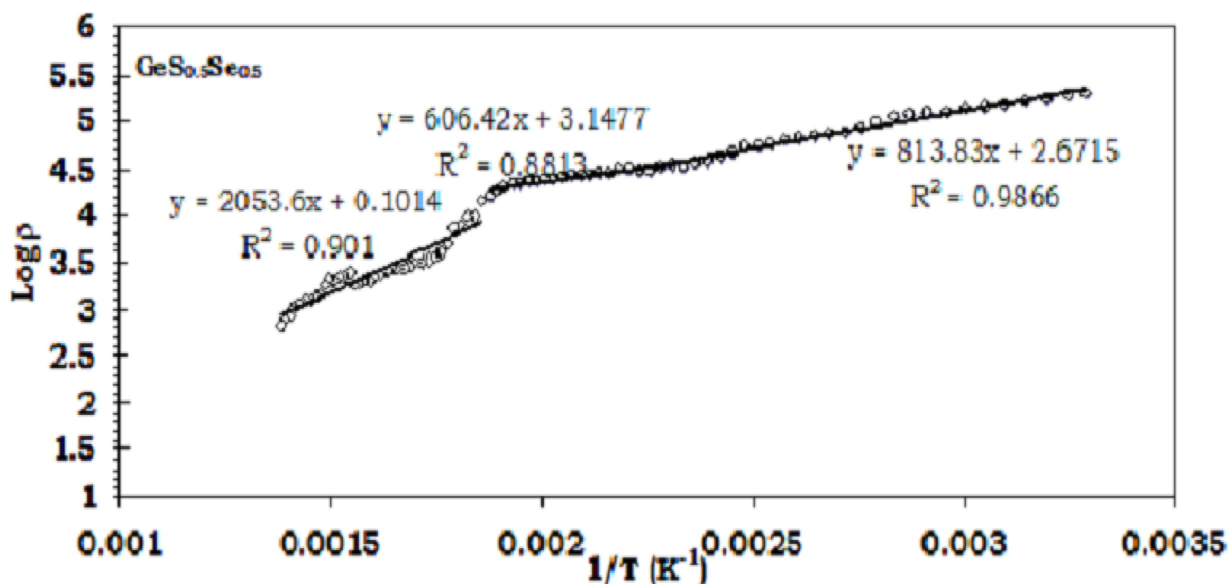

Figure 3. Variation of lnρ vs. inverse of temperature for $GeS_{0.5}Se_{0.5}$ single crystal normal to the basal plane.

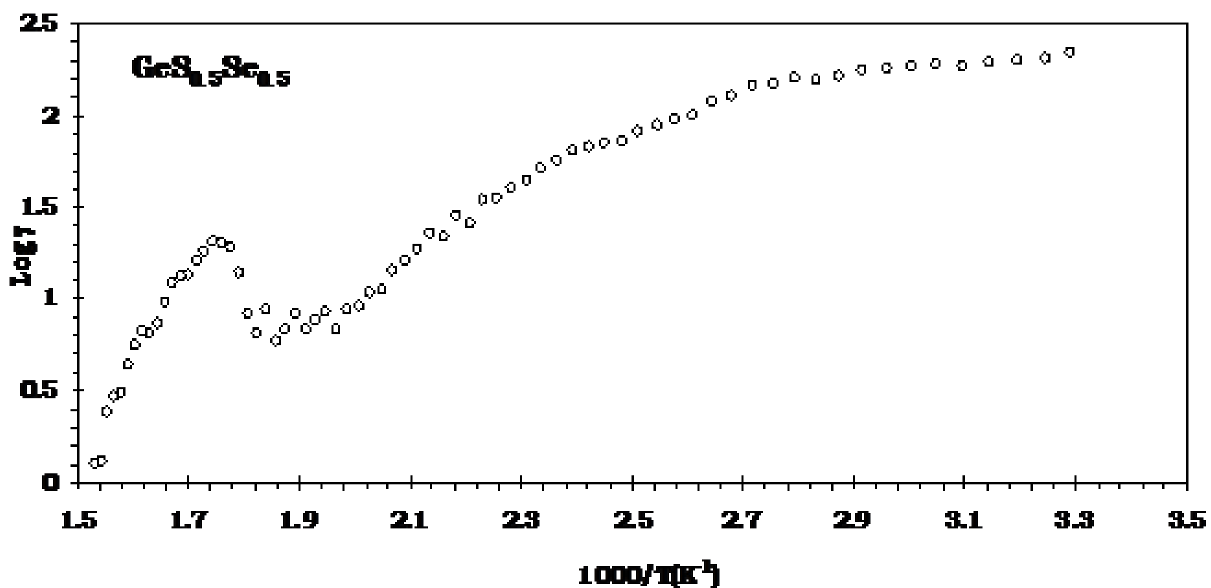

Figure 4. Variation of logγ with temperature for GeS_xSe_{1-x} (x= 0.25, 0.5, 0.75)

For the materials, which are intermediate between two and three dimensions, there is anisotropy of strength of the bonds between atoms. Application of temperature or chemical alloying causes greater changes in the lengths of the weaker bonds than those of stronger ones [12]. This type of anisotropy behavior is an interesting question for the strongly layered materials and it can also be explained as an effect of stacking disorder i.e. effect of a nonperiodic stacking sequence. Since the stacking-fault energy in layered materials is small, real crystals grown at high temperatures usually exhibit a nonperiodic stacking sequence [13]. The disorder produced by the stacking faults is sufficient to localize the electron states normal to the layer. While considering the stacking between the adjacent layers, the whole crystal always remains invariant under the primitive translations parallel to the layers. So the d.c. resistivity parallel to layers is not affected by the presence of stacking disorder. However, the variation of resistivity along the basal plane is attributed to the change in nature. Layered crystals often show predominance of stacking faults [14]. Perpendicular to the layers, however, there is a probability of transport due to the localization of the electron states because of the presence of stacking faults. This will therefore give rise to a fairly large amount of conduction parallel to c-axis. Further the amount of conduction will be more for the crystals where the likelihood of stacking faults is more. However, according to [13] phenomenon of conduction along c-axis is formally a hopping process. It probably occurs in these crystals via a large overlap between states, which extend over many layers.

Conclusion

The growth experiments carried out in this paper clearly indicate that it is possible to grow crystals of fairly large size using direct vaopur transport technique. The electron diffraction photograph in figure 1 confirms their crystalline nature. The lattice parameters shown in table 3 are nearly in agreement with those obtained earlier investigator. From the lattice parameters it has been confirmed that all the crystals having orthorhombic crystal structure. High temperature resistivity curves confirm the semiconducting nature of all the crystals. It is also proved that the crystal having anisotropic nature and having two dimensional as well as three dimensional behaviors. The increase in anisotropy ratio can be attributed to decrease in conduction along c-axis due to decrease in presence of stacking disorder. The increase in anisotropy ratio can be attributed to the change in bond lengths between the anion and cation.in the single crystals.

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