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Synthesis and characterization of germanium monosulphide (GeS) single crystals grown using different transporting agents

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Abstract. This paper reports the growth of germanium monosulphide (GeS) single crystals by vapour phase technique using different transporting agents. The single crystallinity and composition of the grown crystals have been verified by transmission electron microscopy (TEM) and energy dispersive analysis of X-rays (EDAX) respectively. Resistivity measurements have been carried out in different temperature ranges. Transport parameters, e.g. resistivity, Hall coefficient, carrier concentration and mobility have been measured at varying magnetic fields. All the experimental results have been explained.

Keywords. Crystal growth; transmission electron microscopy; X-ray diffractogram; energy dispersive analysis of X-rays; Hall effect; microstructure.

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1. Introduction

In recent years, the orthorhombic IV–VI semiconducting electronic materials have attracted considerable interest. These materials have layer-type structure, which give rise to a number of interesting properties. GeS is particularly interesting because it is the least anisotropic member of the group and so represents an intermediate state between a true layer structure and a three-dimensional crystal. Increasing interest in these materials is due to their photoelectric properties, as it has been suggested that the material could be used successfully as photosensitive film in TV camera tubes [1,2]. Normally, single crystals of GeS required for investigating the physical properties are prepared by cleaving from the bulk or thicker single crystals. The process of cleaving the as-grown samples for obtaining thin specimens causes bending of the lattice planes and mosaic structure imperfections. The introduction of bending and imperfections [3] severely influences the results obtained from these samples. The single crystals required for characterization have

Table 1. Growth conditions for GeS single crystals using different transporting agents.

Crystal	Temp. range (T_1–T_2) (K)	Rate at which the temperature was increased from room temperature to the temperature range (T_1–T_2) (K/h)	Growth period (days)	Size of the crystals (cm × cm)	Thickness of the crystals (μm)
GeS (PVT)	888–843	50	5	0.9×0.4	30
GeS (I_2)	863–788	50	4	0.4×0.5	40
GeS (NH_4Cl)	863–788	50	3	0.4×0.5	50

therefore been grown by a growth procedure which yields crystals in the form of thin platelets which can be used as-grown for the measurement of various physical properties.

The nature and quantity of the transporting agent [4] alter the dimension and morphology of the obtained single crystals. Therefore, along with physical vapour transport (PVT) technique, chemical vapour transport (CVT) technique in which iodine and NH_4Cl are used as transporting agents is also adopted to grow single crystals of GeS of maximum possible size. The grown crystals are characterized by EDAX, X-ray diffraction, electron diffraction, electrical property measurements and microstructural analysis.

2. Experimental

GeS was prepared from the constituent elements (Ge: 99.99% and S: 99.99%) by reaction at 723 K for 2 days in evacuated quartz ampoules (25 mm OD, 22 mm ID, 22 cm length). 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 in the case of PVT method and the charge plus 4 mg/cc of the transporting agent (I_2/NH_4Cl) in the case of CVT method was kept in the furnace under appropriate conditions (table 1) to obtain single crystals of GeS. After the required period of growth (table 1) the furnace was cooled at the rate of 30 K/h to room temperature. The ampoule containing the crystals was broken and crystals having maximum size as reported in table 1 were carefully removed. Typical crystals of GeS grown by PVT and CVT methods are shown in figure 1.

Thin sections suitable for taking the electron diffraction pattern were prepared by cleaving GeS crystals by cellotape and washing in analar grade chloroform several times to remove all impurities caused by the cellotape. For X-ray diffraction, the samples were ground at room temperature (298 K) and were passed through a 106 micron mesh sieve. The X-ray diffractograms (XRD) of these compounds were recorded on Philips PW 1710 diffractometer using CuKα radiation. The scan rate used to obtain X-ray pattern for the determination of unit cell constant was

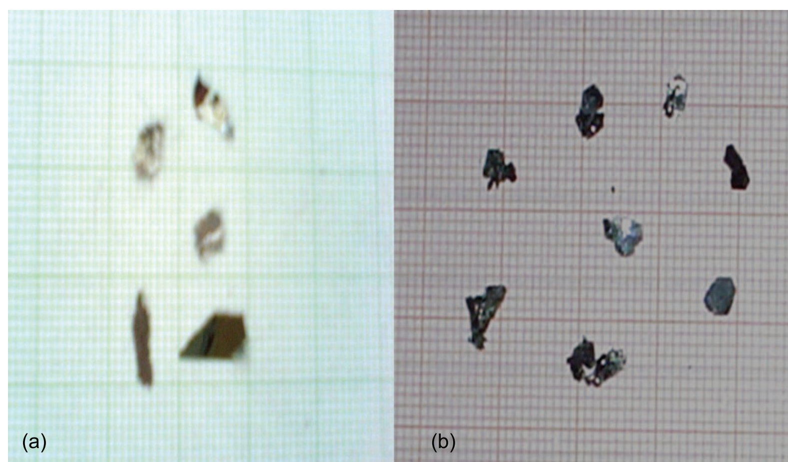

Figure 1. Photograph of typical crystals of GeS grown by (**a**) PVT and (**b**) CVT techniques.

3.01°/min. For determining the chemical composition of grown crystals, energy dispersive analysis of X-rays (EDAX) has been carried out.

In-plane resistivity measurements in the temperature range (363–473 K) were carried out by using the two-probe resistivity set-up developed by Scientific Equipments, Roorkee, India [5]. In-plane resistivity measurements in the temperature range (300–750 K) were performed by the fully automated variable temperature resistivity set-up, VTRM [6], developed by Scientific Solutions, Mumbai. Conventional four-probe measurements in vacuum are possible with this system. To evaluate the type, mobility and carrier concentration, room temperature Hall coefficient measurements were carried out with the help of Hall effect/electron transport system (7504) [6] supplied by Lake Shore Corporation, Inc, USA. Four-probe measurements with van der Pauw configuration are possible with this system. The microstructural examination of crystal surfaces as well as photographic recording of observations was accomplished with the help of Axiotech 100 reflected light microscope, manufactured by Carl Zeiss Jena, Germany.

In the case of resistivity and Hall effect measurements referred above, several experiments were made on each sample. A good reproducibility was obtained and the experimental data were always within the error bar, i.e. ∼5%.

3. Results

The electron diffraction pattern for GeS (PVT) is shown in figure 2.

Figure 3 shows the X-ray diffractograms of GeS (PVT), GeS (NH_4Cl) and GeS (I_2) compounds obtained by powdering the single crystals. It is interesting to note that all diffractograms exhibit good resemblance within themselves suggesting thereby that growth by different transporting agents does not lead to a change in the crystal structure of GeS. It is evident from the diffractograms that for each

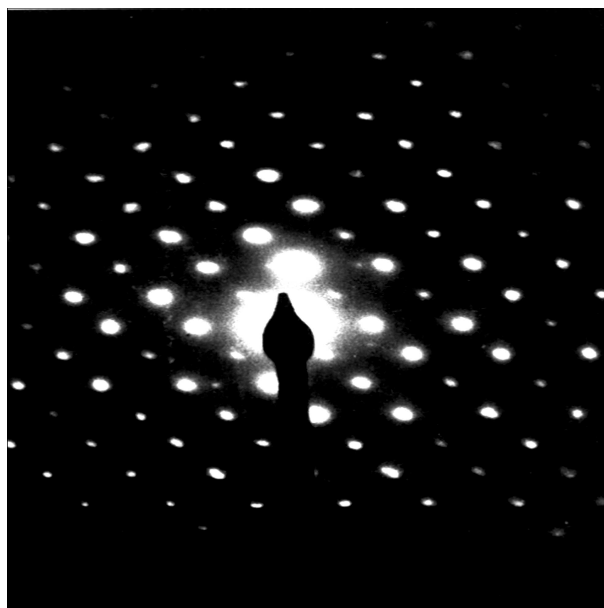

Figure 2. Electron diffraction patterns of GeS (PVT) crystal.

Table 2. Lattice parameters, unit cell volumes and X-ray densities for GeS (PVT), GeS (NH_4Cl) and GeS (I_2) crystals.

Crystal	a (Å)	b (Å)	c (Å)	Unit cell volume (Å^3)	Density (g cm^{-3})
GeS (PVT)	4.79±0.01	3.62±0.01	10.48±0.0006	181.721	3.825
GeS (NH_4Cl)	4.33±0.0001	3.63±0.006	10.46±0.009	164.409	4.228
GeS (I_2)	4.30±0.003	3.64±0.003	10.50±0.0005	164.346	4.229

specimen, (0 0 4) reflection is of maximum intensity, indicating thereby a strong orientation along c-axis. The intensities of all other reflections are extremely weak as compared to this reflection.

The lattice parameters determined from these X-ray diffractograms are given in table 2. The unit cell volumes and densities calculated from the data on lattice parameters are also given in table 2.

For getting an idea about the grain size distribution in GeS samples, the particle size of each representative sample was calculated using Scherrer's formula [7].

$$t = \frac{K\lambda}{\beta_{2\theta}\cos\theta_0}, \tag{1}$$

where t is the crystallite thickness measured perpendicular to the reflecting plane, k is the Scherrer's constant the value of which is chosen as 0.9 by assuming the particle to be spherical, λ is the wavelength of X-ray radiation, $\beta_{2\theta}$ is the width at half the maximum intensity measured in radians and θ_0 is the Bragg angle.

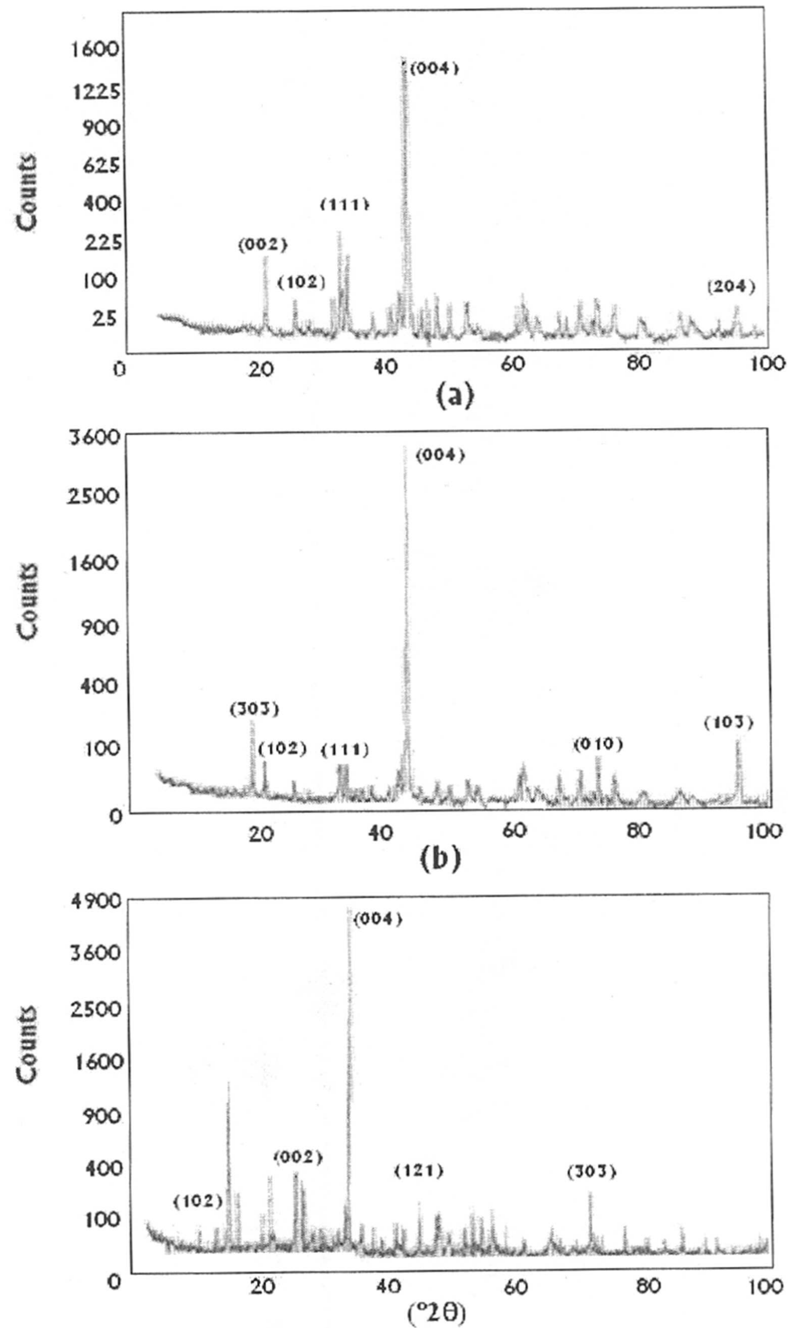

Figure 3. X-ray dffractograms of (**a**) GeS (PVT), (**b**) GeS (I_2) and (**c**) GeS (NH_4Cl).

Table 3. Particle size distributions (Å) in GeS (PVT), GeS (NH_4Cl) and GeS (I_2) single crystals.

$h\ k\ l$	GeS (PVT)	GeS (NH_4Cl)	GeS (I_2)
0 0 2	1004	940	1016
0 0 4	895	832	867
0 0 8	1055	983	1058
1 0 1	853	891	848
1 1 1	887	829	890

Table 3 records the crystallite size for each of the three kinds of samples. As the thickness measured perpendicular to different planes is more or less the same, there exists an isotropy towards the crystallite size.

EDAX spectra are taken from representative samples. The quantitative elemental data obtained from the analysis of these photographs are given in table 4.

A careful study of the data indicates the following:

1. Single crystals of GeS grown using iodine as the transporting agent are perfectly stoichiometric.
2. Single crystals of GeS grown with NH_4Cl as the transporting agent are slightly off-stoichiometric.
3. Off-stoichiometry is increased when the crystals are grown by the PVT technique where no transporting agent is used.

Measured values of the in-plane (perpendicular to c-axis) resistivity ρ (Ω cm) in the temperature range (363–473 K) are plotted as $\log\rho$ vs. $1/T$ in figure 4.

It can be affirmed from the plots that the resistivity in each case decreases with increase in temperature thereby indicating that all the samples show classical semiconducting behaviour.

All the plots of figure 4 give a good fit to the representative equation

$$\rho = \rho_0 \exp\left[\frac{-E_\mathrm{a}}{kT}\right], \tag{2}$$

where ρ_0 is the pre-exponential factor, E_a is the activation energy for DC conductivity and k is the Boltzmann constant.

The values of E_a calculated using the slopes of the curves in figure 4 are given in table 5. Data obtained by previous investigators are also shown in this table for comparison.

Since the resistivity measurements in the temperature range (300–750 K) by VRTM-408 and room temperature Hall effect measurement by (7504) system required perfectly flat surfaces, reproducible and unambiguous results could only be obtained in GeS (I_2) crystals. A graphical variation of the in-plane resistivity $\log\rho$ vs. $1/T$ in the temperature range (300–750 K) is reported in figure 5.

As is evident, the material exhibits the expected semiconductor behaviour in the whole temperature range. By a least square fit of the resistivity data, three activation energies (table 5) were determined.

Table 4. Chemical composition (wt%) of the grown GeS (PVT), GeS (NH_4Cl) and GeS (I_2) single crystals by EDAX analysis.

	Wt% of elements from EDAX		Theoretical composition	
Crystal	Ge	S	Ge	S
GeS (PVT)	72.49	27.51	69.36	30.64
GeS (NH_4Cl)	68.80	31.20	69.36	30.64
GeS (I_2)	69.67	30.33	69.36	30.64

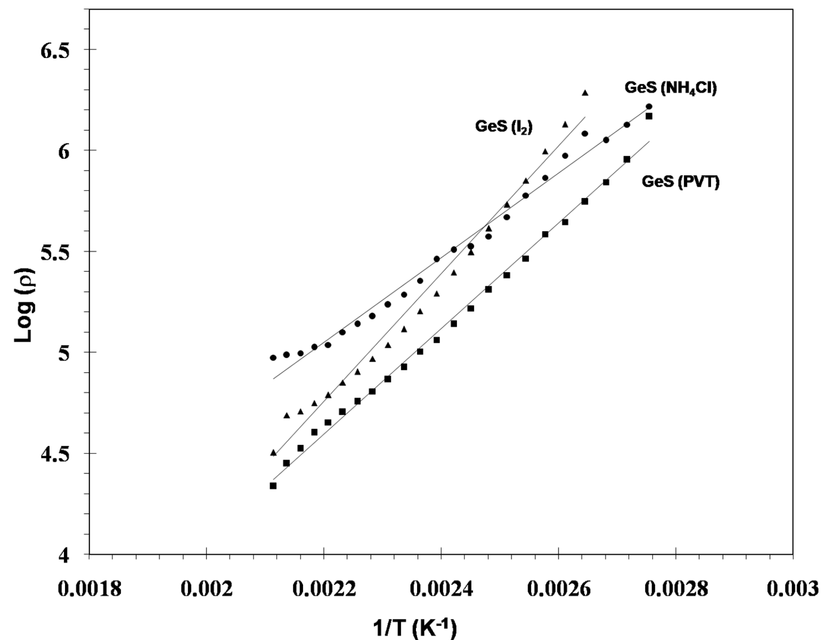

Figure 4. Variation of in-plane resistivity with reciprocal of temperature from 363 to 473 K for GeS single crystals grown using different transporting agents.

All the results obtained from Hall effect measurements are given in table 6. The values of resistivity, carrier concentration, Hall coefficient and Hall mobility at different magnetic fields are also shown in table 6. A variation of all these parameters with magnetic field is shown in figure 6.

It has been observed that GeS (I_2) crystals mainly exhibit flat surfaces. A typical example of a flat surface is shown in figure 7a.

A study of the microstructures on several crystals of this variety showed the complete absence of spirals upon them, whereas examination of a number of GeS

Table 5. Results for activation energies for GeS single crystals grown using different techniques.

Sample	Temperature range (K)	Activation energy (eV)	Source
GeS (PVT)	363–473	0.519	
GeS (I_2)	363–473	0.416	Present work
GeS (NH_4Cl)	378–473	0.658	
GeS single crystal	180–500	0.600	Wiley *et al* [8]
	293–385	0.095	Kyriakos *et al* [9]
	385–450	0.215	
	300–450	0.041	
GeS (I_2)	450–600	0.056	Present work
	600–750	0.122	

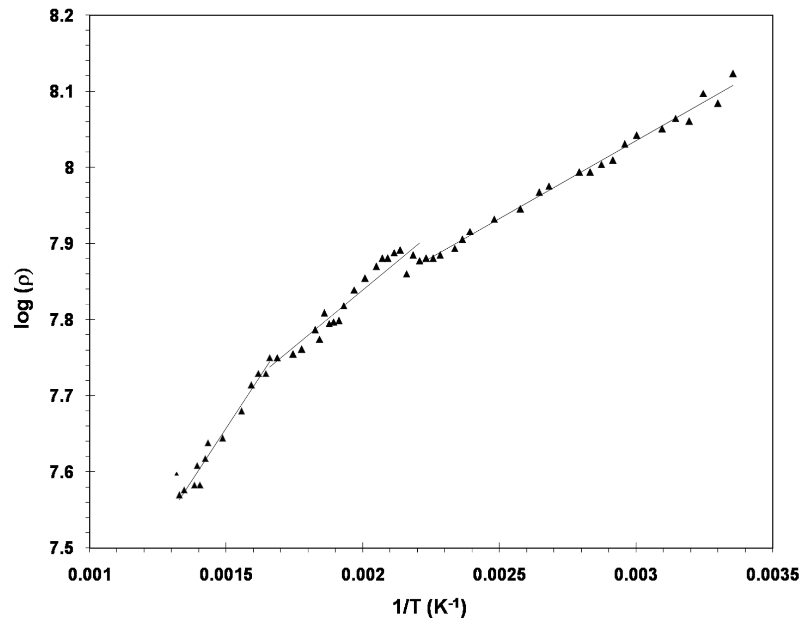

Figure 5. Variation of in-plane resistivity with reciprocal of temperature from 300 to 750 K for GeS (I_2) crystal.

(PVT) and GeS (NH_4Cl) crystals revealed the presence of growth spirals upon them. A typical example of spirals which is a representative of all such observations is depicted in figure 7b. The spiral shown in this figure is a single spiral originating from a single screw dislocation in a rhombohedral shape in accordance with the symmetry of the face.

Table 6. Hall coefficient R_H, carrier concentration (p), resistivity (ρ) and mobility (μ) at room temperature for GeS (I_2) single crystals at different values of the magnetic field (H).

Magnetic field (H) (G)	Hall coefficient (R_H) ($cm^3 C^{-1}$)	Resistivity (ρ) (Ω cm)	Carrier concentration (p) (cm^{-3})	Mobility (μ) ($cm^2 V^{-1} s^{-1}$)
1000	2.83×10^{10}	3.08×10^{7}	2.21×10^{8}	1.22×10^{3}
2000	8.87×10^{10}	5.61×10^{6}	7.04×10^{7}	3.83×10^{3}
3000	3.07×10^{10}	3.82×10^{6}	2.03×10^{8}	1.33×10^{3}
4000	4.20×10^{9}	6.38×10^{6}	1.49×10^{9}	1.82×10^{2}
5000	2.08×10^{9}	1.16×10^{7}	3.01×10^{9}	8.99×10^{1}

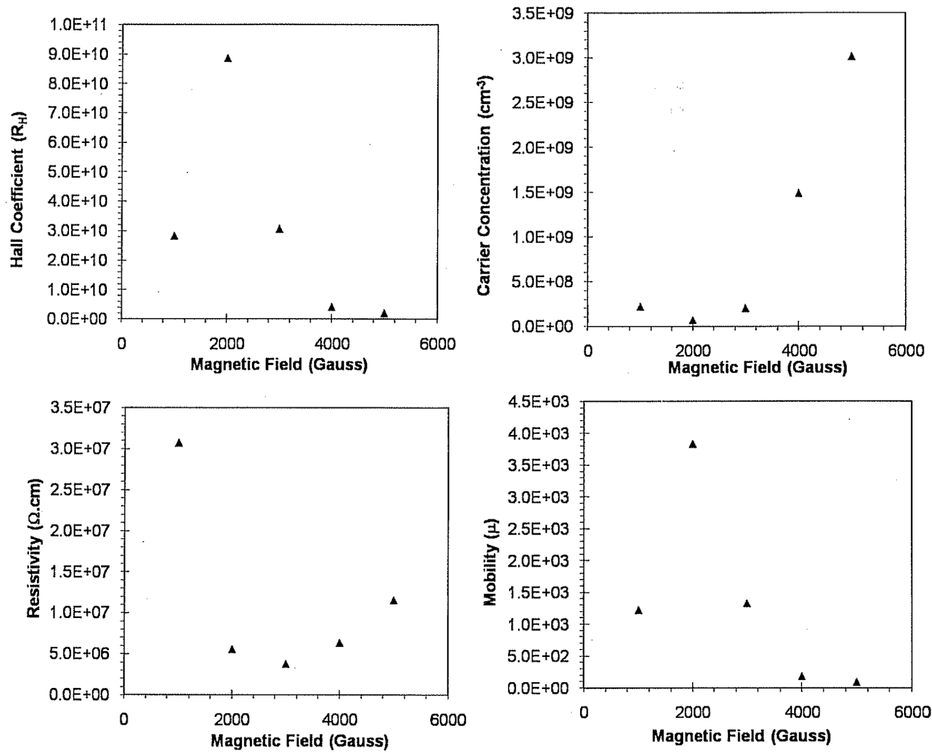

Figure 6. Variation of Hall coefficient, carrier concentration, resistivity and mobility with magnetic field for GeS (I_2) single crystal.

4. Discussion

The growth experiments carried out in this paper clearly indicate that it is possible to grow crystals of fairly large dimensions using the PVT and CVT techniques. The electron diffraction photograph in figure 1 confirms their crystallinity.

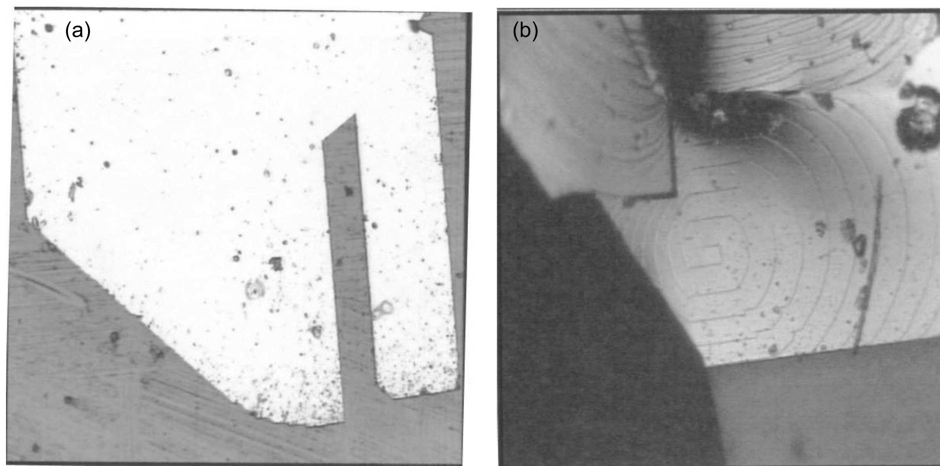

Figure 7. (**a**) Perfectly flat surface with almost no other features on single crystals of GeS (I_2). (**b**) Micrograph showing a spiral having rhombohedral shape originating from a single screw dislocation on a GeS (PVT) single crystal.

The lattice parameters presented in table 2 are nearly in agreement with those obtained by earlier investigators [10,11]. Further, it is seen from the data presented in this table that the density ρ in the case of crystals grown by PVT technique is less than in crystals grown by the CVT technique using NH_4Cl and I_2 as the transporting agents. This decrease in ρ can be attributed to the formation of defects introduced due to off-stoichiometry. That this is indeed true can be seen from the EDAX results obtained on the crystals grown using different transporting agents. Crystals grown by PVT technique are truly off-stoichiometric whereas those grown by iodine as the transporting agent are stoichiometric.

The decrease of density in off-stoichiometric PVT-grown crystals is also supported by the results of Gregora *et al* [12] who observed that density of crystalline GeS was 4.24 g cm^{-3} whereas that obtained for amorphous GeS was 3.49 g cm^{-3}. They have conclusively shown that there is a marked decrease in density when one goes from crystalline GeS which is highly perfect to the disordered phase of amorphous GeS.

The off-stoichiometry in PVT-grown GeS crystals as evidenced in EDAX analysis of the grown crystals can be explained as follows.

It was observed by Vodenicharov *et al* [13] that thin films of GeS deposited at higher temperatures contained larger amount of defects while those prepared at lower temperatures contained only GeS. However, the analytical methods as well as the local analysis by means of an electron probe did not reveal any deviation from stoichiometry in the GeS films formed under both conditions. They attributed the presence of defects in films formed at higher temperatures to the tendency of GeS to thermal dissociation at higher temperatures.

In the growth of single crystals of GeS by different transporting agents, authors have noticed that temperatures used in the PVT technique are normally higher than those required when the crystals are grown by CVT technique using different transporting agents. The higher temperatures in the PVT technique could lead to thermal dissociation of GeS making them off-stoichiometric as compared to crystals grown by CVT technique using I_2 as the transporting agent. The slight off-stoichiometry in GeS crystals grown with NH_4Cl as the transporting agent could be due to the presence of impurities which the EDAX analysis has failed to detect.

In all the cases of crystals grown using different transporting agents, the high-temperature resistivity experiments by two-probe method accord a linear decrease in the resistivity from 363 to 463 K, thus confirming their semiconducting behaviour. The values of activation energies are nearly of the same order as that obtained by Wiley *et al* [8] using the two-probe resistivity technique. The difference in the activation energies for GeS (I_2), GeS (PVT) and GeS (NH_4Cl) can be attributed to the difference in the stoichiometry of these crystals.

The values of activation energies in different temperature ranges obtained for GeS (I_2) single crystals are of the same order of magnitude as that obtained by Kyriakos *et al* [9] using the four-probe resistivity measurement technique. It is seen that similar to [9], in the present observations also there is an increase in activation energy when the temperature range of resistivity measurement is extended from 300 to 450 K, 450 to 600 K and 600 to 750 K. However, the values of activation energy are quite low as compared to the band gap of GeS (I_2). Looking at the p-type nature of GeS (I_2), such low values of activation energies suggest the presence of defect levels close to the valence band. These levels cannot be associated with the impurities since the crystals of GeS (I_2) are stoichiometrically perfect and EDAX analysis of GeS (I_2) crystals fails to show the presence of any impurities in them. These defect levels could therefore be the result of stacking faults which are very common in crystals with layered structures. The presence of such stacking faults in GeS crystals has been shown by Karakostas [14]. The continuous linear decrease in resistivity from 300 to 750 K does not show the presence of any phase transformation in GeS (I_2). This is probably because the highest temperature (750 K) is lower than the melting point (933 K) [15] and also the phase transformation temperature (853 K) observed by Vodopyanov *et al* [16].

A study of the data presented in table 6 reveals that the values of Hall coefficient are positive which clearly indicates that GeS (I_2) crystals are p-type and majority carriers in them are holes. It is also seen that at higher values of magnetic field, the Hall mobility for GeS (I_2) approaches the same order of magnitude as that obtained by Kyriakos *et al.* The difference in the present results with those obtained by Kyriakos *et al* (*loc cit*) is because the samples used in this work are stoichiometrically perfect and so are more resistive than those used by the latter.

The variation of Hall coefficient with magnetic field in GeS (I_2) can be due to the corresponding variation of the number of carriers and to the variation of mobility as the magnetic field varies. The reason for such a variation can be ascribed to the existence of resonant defect states in the valence bands. Some of these defect states may be induced by the impurities which are responsible for the magnetic properties of GeS. Such states are localized around the defects. The magnetic field

can influence these states by splitting them. In the present case these states could be due to some impurities which have not been detected by EDAX analysis of the samples or due to defects due to stacking faults [14].

The complete absence of spirals in GeS (I_2) single crystals clearly indicates that screw dislocations have no role to play in their formation.

The presence of screw dislocations in GeS (NH_4Cl) and GeS (PVT) crystals is in line with the imperfections introduced due to non-stoichiometry in them.

5. Conclusion

Single crystals of GeS have been grown successfully by using different transporting agents. Growth condition, growth mechanism and lattice parameters of the grown crystals have been determined. EDAX analysis of the crystals reveals that crystals grown by CVT technique using iodine as the transporting agent are stoichiometrically perfect while those grown by PVT technique and with NH_4Cl transporting agent are off-stochiometric. The study of microstructures shows that GeS (I_2) single crystals grow with perfectly flat surfaces and screw dislocations have no role to play in their growth. High-temperature resistivity curves confirm the semiconducting nature of GeS. The positive values of Hall coefficient indicate that GeS (I_2) crystals are p-type in nature and majority carriers in them are holes. The variation of Hall coefficient, mobility, carrier concentration and resistivity with magnetic field in GeS (I_2) single crystals has been explained.

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