Preparation and characterization of Bi_2S_3 compound semiconductor

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Abstract. Bi_2S_3 single crystals were grown by the chemical vapour transport technique using ammonium chloride (NH_4Cl) as a transporting agent. The stoichiometry of Bi_2S_3 single crystal was confirmed by energy-dispersive analysis of X-rays (EDAX). The powder X-ray diffraction (XRD) pattern showed that Bi_2S_3 crystals belong to the orthorhombic phase with calculated lattice constant $a = 11.14 \text{ \AA}$, $b = 11.30 \text{ \AA}$ and $c = 3.96 \text{ \AA}$. Scanning electron microscopy (SEM) pictures indicate the presence of layer lines on the surface of crystals thereby proving that these crystals are grown by layer by layer mechanism. We studied the transport properties *viz.* Hall effect, resistivity, thermoelectric power and thermal conductivity on Bi_2S_3 pellets. Raman spectroscopy and thermal gravimetric analysis (TGA) were carried out on Bi_2S_3 single crystal for studying their optical and thermal behaviours.

Keywords. Single crystal; chemical vapour transport technique; semiconductor.

1. Introduction

Over the past few decades, semiconducting chalcogenides compounds (A_2B_3 with $A = \text{Sb, Bi, As}$ and $B = \text{S, Se, Te}$) have been receiving much attention because of their wide range of applications in various field of science and technology. One of the most promising areas is their use in thermoelectric refrigeration. The $\text{V}_2\text{--VI}_3$ binary compounds such as Bi_2S_3 , Bi_2Te_3 , Bi_2Se_3 are narrow band gap semiconductors with homologous layered crystal structure and are interesting and important because of their major contribution in solar cells, photodetectors, opto-electronic, light amplifiers, electro-photography, light-emitting diodes, lasers, photo-electrochemical cells.¹ Bi_2S_3 semiconductor with the direct band gap $\Delta E_g = 1.3 \text{ eV}$ ^{2,3} has been suggested to be useful material for photodiode arrays or photovoltaic applications.^{4–6}

2. Experimental

2.1 Experimental procedure

Single crystals of Bi_2S_3 were prepared from high purity (99.999%) bismuth (Bi) and sulfur (S) powders. Firstly, the powders were weighed and loaded into thoroughly cleaned thick walled quartz ampoule. The ampoule was then evacuated to 10^{-5} torr and sealed and then placed in the horizontal single zone furnace to prepare charge at 630°C for 3 days. The prepared charge was taken in another quartz ampoule with NH_4Cl as a transporting agent and then again sealed at 10^{-5} torr and placed in the dual zone furnace at temperature 650°C of the source zone and growth zone at 600°C . After

8 days, the furnace was cooled to room temperature and then ampoule was taken out from the furnace and broken which resulted in the growth of single crystals of Bi_2S_3 in shape of needles. The length of these grown Bi_2S_3 single crystals varied between 0.1 and 0.3 cm as shown in figure 1.

2.2 Characterization techniques

Grown single crystals of Bi_2S_3 were characterized by energy-dispersive analysis of X-rays (EDAX) (Philips EM 400 electron microscope) for elemental identification and by powder X-ray diffraction (XRD) (Philips Xpert MPD) for structure determination. The surface morphology was studied by using scanning electron microscopy (SEM) (Model-XL 30 ESEM). The electrical resistivity and thermoelectric power were measured over the temperature range $40\text{--}150^\circ\text{C}$ whereas thermal conductivity was measured at 100°C . The Hall effect experiment was carried out at room temperature. Raman scattering experiments were carried out at room temperature under the backscattering geometry using a Jobin–Yvon Horiba labram, HR800 single monochromator coupled with ‘peltier cooled’ charged coupled device (CCD) with 488 nm line Argon (Ar^+) laser source. We also studied thermogravimetric analysis (TGA) on the sample in the range between room temperature and 700°C in N_2 atmosphere to know the thermal stability of the material.

3. Results and discussion

3.1 Elemental and structural characterization

The composition of grown crystals were determined by the spectra obtained from the EDAX which is shown in figure 2.

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Figure 1. Photograph of Bi_2S_3 single crystals grown in different sizes.

Figure 2. EDAX of Bi_2S_3 single crystals.

The weight percentage observed from EDAX spectra of each element in sample is given in table 1. This table reveals that the grown crystals are rich in bismuth content in comparison to sulfur. Whereas small impurities of carbon (C) is seen because of carbon replica used in this analysis.

The XRD pattern of the Bi_2S_3 crystalline powder is shown in figure 3. From this figure it is found that almost all diffraction peaks in the pattern could be indexed based on orthorhombic phase of Bi_2S_3 (JCPDS no. 17-0320) with lattice constant $a = 11.14 \text{ \AA}$, $b = 11.30 \text{ \AA}$, $c = 3.96 \text{ \AA}$. The calculated density, volume and c/a ratio are given in table 2. We used Scherrer's formula⁷ to calculate the crystallite size for various reflections, which shows variation in size from 45 to 75 $\text{\AA}$.

Figure 4 shows the photographs of the surface morphology of Bi_2S_3 single crystal studied by scanning electron microscopy. It is seen that Bi_2S_3 single crystal possesses a flat surface as shown in figure 4a. The magnified images of as seen single-crystal surface shows some layer lines in figure 4d–f which is an indication that these crystals are grown by layer growth mechanism. Figure 4e and f is also

Table 1. Chemical composition (wt%) of grown Bi_2S_3 single crystal.

Element	Obtained wt%	Calculated wt%
Bi	68.26	81.29
S	10.14	18.71
C	21.61	—

reflecting that how one layer is displayed with respect to other layer.

3.2 Transport properties

The electrical resistivity of Bi_2S_3 pellets was studied in the temperature range 306–403 K using dc four-probe method. Figure 5 shows the Arrhenius plot of change in resistivity (ρ) as a function of reciprocal of temperature. It is seen that resistivity decreases with increase in temperature, indicating semiconducting nature of Bi_2S_3 compound. The thermal activation energy is calculated using relation⁸ which comes out to be 0.38 eV.

Figure 6 shows the variation of Seebeck co-efficient (S) as a function of reciprocal of temperature for Bi_2S_3 pellets. It is reflected that as temperature increases thermoelectric power ' S ' decreases. The values of Seebeck coefficient ' S ' is negative suggesting that sample is behaving n -type in nature which may be because of excess of bismuth in sample. From the plot of S vs. $1/T$ shown in figure 6 we calculated the Fermi energy (E_F), constant A and scattering parameter(s) in two regions which are given in table 3 using well-known expression⁹ given as

$$S = \pm \frac{k}{e} \left[A + \frac{E_F}{kT} \right],$$

Figure 3. XRD pattern of Bi_2S_3 crystalline powder.

Table 2. Lattice parameter, c/a ratio, unit cell volume and density obtained from X-ray diffractogram for Bi_2S_3 compound.

Lattice parameter	Bi_2S_3
	Calculated value
a (Å)	11.14
b (Å)	11.30
c (Å)	3.96
Volume (Å) ³	498.49
Density (g cm ⁻³)	6.84

where k is the Boltzmann constant, e the electronic charge, A the dimensionless parameter determined by the dominant scattering process and E_F the separation of the Fermi level from the top of the valence band. These parameters along with their values obtained is displayed in table 3. The value of scattering parameter(s) 2.31 and 2.29 in two different temperature regions clearly suggest that lattice vibrations is dominant scattering mechanism in this sample.

Thermal conductivity of the Bi_2S_3 single crystalline pellet was determined at 100°C and it comes out to be 0.422 W cm⁻¹ deg⁻¹. To be a useful thermoelectric material, it must have large thermoelectric figure of merit defined as $Z = S^2/K\rho$, or its dimensionless equivalent ZT . But in our result calculated figure of merit ZT of Bi_2S_3 crystalline pellets comes out to be very low which suggests that prepared pellets of Bi_2S_3 crystals grown by the chemical vapour transport technique may not be suitable for thermoelectric application in comparison to those grown by the Bridgman technique.¹⁰

From the measurement of Hall effect at room temperature, it is evident that the sign of Hall coefficient of Bi_2S_3 is negative. This indicates that the compound is n -type semiconductor matching with the results of Seebeck coefficient.

The values of calculated Hall coefficient, Hall mobility and carrier concentration at room temperature are shown in table 4.

3.3 Optical and thermal analysis

Raman spectroscopy was conducted at room temperature using Raman spectrometer and Ar⁺ laser (488 nm) has been used to excite the sample. Bi_2S_3 belongs to the orthorhombic space group $pbnm$ with 20 atoms per primitive cell. For a 20-atom Bi_2S_3 primitive cell, there are 60 zone-center phonon modes that can be classified according to the D_{2h} point-group symmetry: $10A_g + 10B_{1g} + 5B_{2g} + 5B_{3g} + 5A_u + 5B_{1u} + 10B_{2u} + 10B_{3u}$. Out of these, only A_g , B_{1g} , B_{2g} , and B_{3g} modes are Raman active.¹¹

Raman spectrum of Bi_2S_3 single crystal shown in figure 7 shows three Raman active optical phonon peaks at 186, 238 and 264 cm⁻¹, which are matched with the reported values.^{12,13} Here peaks at 186 and 238 cm⁻¹ are corresponding to A_g phonon mode while peak at 264 cm⁻¹ corresponds to B_{1g} phonon mode.¹¹

The thermogravimetric analysis (TGA) curve of Bi_2S_3 single crystal from room temperature to 700°C under N₂ is shown in figure 8. It is observed from the TGA analysis that sample possess stability up to ~500°C and then a very smooth decomposition occurs approximately from 500 to 700°C with weight loss of 10%. This weight loss can be attributed to the loss of sulfur in the form of SO₂ and the remaining product finally turns into residue Bi₂O₃. This observation can be confirmed from DTA/DTG analysis that can give endothermic peak at this temperature which is corresponding to weight loss of SO₂.¹⁴ We have used Broido (BR) relation¹⁵ for calculating the activation energy in the weight loss region which is shown in figure 9. Calculated activation energy from Broido relation is given in table 5.

Figure 4. SEM images of Bi_2S_3 single crystal.

Figure 5. Variation of resistivity as a function of reciprocal of temperature.

Figure 6. Plot of thermoelectric power (S) as a function of reciprocal of temperature.

Table 3. Values of constant (A), scattering parameter (S) and Fermi energy (E_F) of prepared Bi_2S_3 pellets.

Temperature region ($1/T$) $\text{K}^{-1} \times 10^{-4}$	A	$S = (5/2 - A)$	E_F (meV)
31–27	0.18	2.31	4.94
27–24	0.21	2.29	5.75

Table 4. Values of Hall coefficient, Hall mobility and carrier concentration.

Temperature	Room temperature (303 K)
Hall coefficient (R_H)	$-0.375 \text{ cm}^3 \text{ C}^{-1}$
Hall mobility (μ)	$0.473 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
Carrier concentration (n)	$1.66 \times 10^{19} \text{ cm}^{-3}$

Figure 7. Raman spectrum of Bi_2S_3 single crystal. **Figure 8.** TGA of Bi_2S_3 single crystal powder under N_2 . **Figure 9.** Plot of BR model of TGA in a weight loss region.**Table 5.** Value of activation energy (eV) for Broido model.

Name of model	Broido relation
Activation energy	1.53 eV

4. Conclusion

Single crystals of Bi_2S_3 were successfully grown in our laboratory by the chemical vapour transport technique. EDAX confirmed that Bi_2S_3 crystals are rich in Bi content in comparison to S and powder XRD pattern indicated that Bi_2S_3 crystallizes in a pure orthorhombic structure with calculated lattice parameters $a = 11.14 \text{ \AA}$, $b = 11.30 \text{ \AA}$, $c = 3.96 \text{ \AA}$ which are matching with the reported JCPDF file. SEM images have shown that single crystals are grown by layer by layer mechanism. The semiconducting behaviour of Bi_2S_3 single crystals is confirmed by resistivity, Seebeck and Hall coefficient measurements. Apart from this Seebeck and Hall measurements shows that grown Bi_2S_3 single crystals are n -type in nature.

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