ISSN 0975-3303
MJS, Vol. 8, No. 2, July - December 2009, pp. 1-6
https://doi.org/10.12725/mjs.15.1

GROWTH OF ANTIMONY SELENIDE CRYSTALS BY BRIDGMAN-STOCKBARGER METHOD

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ABSTRACT

Single crystals of antimony selenide were grown from melt by the Bridgman Stockbarger method. X-ray powder diffraction analysis was carried out to determine the lattice parameters of the grown samples. The morphology and chemical analysis of cleavage planes were investigated using SEM and EDAX. The microhardness studies were done by using a Vickers hardness tester. The correlation of energy gap and microhardness has also been investigated.

Key words: Sb_2Se_3, *microindentation, energy gap*
PACS: 81.10.-h, 81.10.Fq, 62.20.-x

1. Introduction

Antimony selenide (Sb_2Se_3) belongs to V-VI group semiconductors, and have potential applications for optical and thermo electronic cooling devices [1-3]. It has also received a great deal of attention due to its switching effects [4, 5]. Hence, the

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growth and characterization of these compounds have been investigated by many researchers [6–12]. Sb_2Se_3 is a direct band gap semiconductor with an energy gap of 1.2 eV [12, 13]. It crystallizes in orthorhombic phase with cell dimensions $a = 11.62 \pm 0.01$ Å, $b = 11.77 \pm 0.01$ Å, and $c = 3.962 \pm 0.007$ Å [14]. The melting point of antimony selenide is 611°C and density is 5810 kg/m^3. Various methods have been employed for the growth of antimony selenide crystals. The growth of crystalline Sb_2Se_3 whiskers has been conducted via a hydrothermal process by Wang et al. [15]. Arivuoli et al. [2] have grown Sb_2Se_3 platelet and needle crystals from vapour in a two-zone furnace. The study of Vickers microhardness on semiconducting single crystals was reported by many authors [16-20]. Although the electrophysical properties of Sb_2Se_3 crystals have been studied to quite a good extent, very little information is available in the literature on the study of mechanical properties of melt grown antimony selenide single crystals. As such, the present authors have grown Sb_2Se_3 single crystals by melt growth method and have studied the load dependence of microhardness on the cleavage planes of these crystals.

2. Experimental

For the growth of antimony selenide crystals by the Bridgman Stockbarger method, appropriate quantities of the constituent elements of 99.99% purity were vacuum sealed in pre-cleaned quartz ampoule of length 10 cm and diameter 10 mm under a pressure of 10^{-5} torr. The sealed ampoule was kept in a constant temperature muffle furnace at 700°C for about 24h, during which the ampoule was periodically rotated for proper mixing and reaction of the constituents. The ingots were then slowly cooled to room temperature. The growth was carried out in a vertical gradient furnace by keeping the ampoule at 650°C for 48h and then lowered at a rate of 0.5 mm per minute. The crystals grown were cleaved at ice temperature to minimize deformation. The morphology of cleaved samples was observed using a scanning electron microscope (Jeol JSM-840 A). X-ray diffraction studies of Sb_2Se_3 crystals were carried out with Ni filtered CuKa radiation (=1.54060 Å) using Philips X'pert diffractometer. The chemical analysis was also done using EDAX to find out the composition of the crystals.

The microhardness measurements were carried out on the cleaved planes at room temperature using a Vickers diamond pyramidal indenter [19]. The indentations were made at different loads from 2.5 to 40g and the time was kept at 15 sec for loading. The hardness H_v was computed using the relation,

$$H_v = 1.8544\ p/d^2 \qquad (1)$$

where p is the load in kg and d is the mean diagonal length in mm. The energy gap of semiconducting compounds is correlated to microhardness H_v using the formula [21].

$$E_g\ (eV) = \frac{H_v\ (kg/mm^2) \times \text{unit cell volume}\ (mm^3)}{1.6 \times 10^{-19} \times 10^2} \tag{2}$$

3. Results and Discussion

Single crystals of antimony selenide having 30 mm long and 10 mm in diameter were obtained as shown in Figure 1. Figure 2 shows the SEM image of a freshly cleaved surface of the antimony selenide crystal. In Figure 3, the powder XRD pattern of Sb_2Se_3 crystals is depicted. The X-ray diffractograms with peak characteristics revealed the crystallinity of the grown samples. The diffraction peaks in the pattern are indexed to the orthorhombic phase.

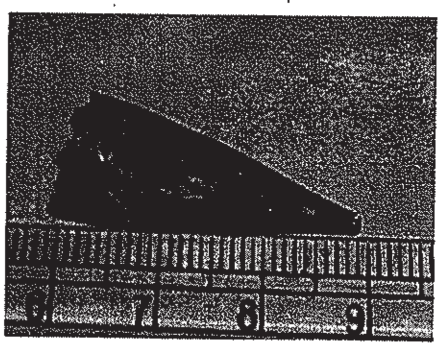

Figure 1. Sb_2Se_3 crystal grown by Bridgman Stockbarger method

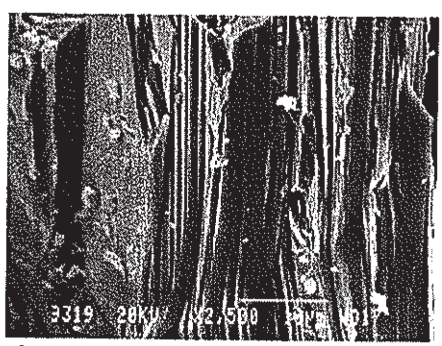

Figure 2. SEM image of a cleaved surface showing parallel steps

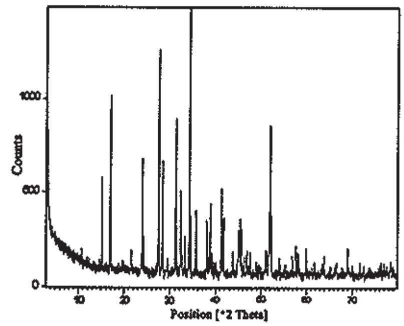

Figure 3. Powder X-ray diffractograms of antimony selenide crystals

Table 1 represents the calculated values of lattice constants and cell volume, from the XRD data, which are fairly in agreement with the values reported by Tideswell et al. [14]. The EDAX analysis (Figure 4) showed the presence of constituent elements in the grown samples.

Table 1. Crystallographic data and energy gap of antimony selenide single crystals

Sample	a (Å)	b (Å)	c (Å)	V(Å³)	E_g (eV)
Sb_2Se_3	11.62	11.76	3.958	540.865	1.219

The most striking feature of layered type crystals is the existence of easy cleavage and since the cleavage planes are easy to glide, some deformation may accompany the cleavage step formation process (Figure 2).

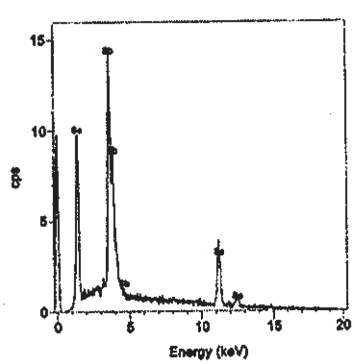

Figure 4. EDAX profiles of Sb_2Se_3

Hardness testing provides useful information concerning the mechanical characteristics of materials such as toughness, brittleness, yield strength, etc. The variation of hardness with load on the cleavage surfaces of pure antimony selenide crystals is shown in Table 2. The decrease in hardness of antimony selenide crystals with increase in load is due to their greater tendency towards crack formation and plastic deformation. The hardness attains a constant value (~35 kg/mm^2), beyond a load of 20g due to decrease in the resistance to the movement of dislocations.

Table 2 Microhardness of antimony selenide crystals

Load p (g)	d^2 (10^{-4} mm^2)	Hardness H_v (kg/mm^2)
2.50	1.2042	38.50
5.00	2.4725	37.50
7.50	3.7896	36.70
10.00	5.1226	36.20
12.50	6.4748	35.80
15.00	7.8354	35.50
17.50	9.1932	35.30
20.00	10.5363	35.20
22.50	11.8871	35.10
25.00	13.2268	35.05

4. Conclusion

X-ray diffraction studies revealed that, the grown crystals by Bridgman Stockbarger method have orthorhombic structure. The lattice parameters agreed well with that reported in the literature. The microhardness was found to decrease with applied load and then become constant for all samples. The EDAX spectra showed the presence of constituent elements. The energy gap of Sb_2Se_3 crystals is found to be 1.219 eV.

Acknowledgements The authors would like to thank the U.G.C., New Delhi for financial support. Thanks are due to Prof. K. L. Sebastian, Chairman, Department of Inorganic and Physical Chemistry, IISc, Bangalore for providing various research facilities.

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