

Physical, optical and nonlinear properties of InS single crystal



Pallavi Kushwaha^a, Anuradha Patra^{a,*}, E. Anjali^b, Harshad Surdi^a, Abhishek Singh^a, C. Gurada^c, S. Ramakrishnan^a, S.S. Prabhu^a, Achanta Venu Gopal^a, A. Thamizhavel^a

^aDCMP&MS, Tata Institute of Fundamental Research, Homi Bhabha Road, Mumbai 400 005, India

^bNational Institute of Technology Calicut, Kerala 673 601, India

^cDepartment of Physics, University of Mumbai, Mumbai 400 098, India

ARTICLE INFO

Article history:

Received 23 September 2013

Received in revised form 21 October 2013

Accepted 29 October 2013

Available online 23 November 2013

Keywords:

Indium sulphide

Single crystal

THz

Z-scan

ABSTRACT

Indium Sulphide (InS) single crystals are successfully grown by In flux. Single crystal X-ray diffraction shows orthorhombic structure of *Pnmm* space group. Ellipsometry measurements performed on the (010) oriented crystal exhibit low anisotropy in the 300–1000 nm wavelength range and consequently negligible THz transmission is observed. Optical band gap of 2.09 eV is deduced from linear optical measurements. Nonlinear optical properties are studied by single beam Z-scan measurements at 800 nm, where two-photon absorption is present. Nonlinear refractive index and absorption coefficient are estimated to be $n_2 = 2.3 \times 10^{-11} \text{ cm}^2/\text{W}$ and $\beta = 62.4 \text{ cm/GW}$, respectively for excitation intensity of 0.32 GW/cm^2 . The origin of nonlinearity in InS crystal is accounted to be due to the third-order anharmonic motion of the bound electrons.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Indium sulfide is a semiconducting compound belonging to III–VI family. Some of the prominent members in this family are layered crystals of GaS, GaSe and InSe. Indium sulphide has strong anisotropic features in its crystal structure and crystallizes in three crystallographic modifications, namely, α , β , and γ -In₂S₃. The most stable one is β -In₂S₃ which has a tetragonal structure [1]. Being a wide band gap semiconductor [2], thin films of In₂S₃ have been investigated for optoelectronics and photovoltaic applications [3]. Thin films of In₂S₃ were also investigated as a solar energy absorbing material [4], and may serve as a suitable alternative to Cadmium sulfide based solar cells which include the toxic Cadmium [5]. Consequently, studies on thin films of In₂S₃ were reported [1–6]. However, reports on single crystal InS are scarce partly owing to the difficulty in growing single phase crystals [7–14].

The phase diagram of In–S system clearly indicates that the equiatomic composition of In and S is incongruently melting with a dissociation temperature around 600 °C [15]. From electroreflectance measurements on single crystal InS grown from In melt, the direct transition edges are reported to be 2.45 eV, 2.57 eV and 2.58 eV at temperatures of 290 K, 93 K and 10 K, respectively [7]. Nishino and Hamakawa reported n-type conductivity in InS single crystal synthesized using solution growth method from In melt and have estimated room temperature indirect and direct band

gaps to be 1.9 eV and 2.44 eV, respectively [8]. Polymorphism of InS at high pressure has been reported by Kabalkina et al. [9]. It has been found that at high pressure (7.5 GPa/6 GPa at and 293 K/573) and isothermal conditions, the crystal of InS undergoes transition from orthorhombic to tetragonal structure [9]. High pressure Raman and transport measurement were reported by Faradzhev et al. [10] and Takarabe et al. [11], respectively. Studies on the electrical resistance at pressures up to 150 kbar, using uniaxial split-sphere apparatus, indicate possible insulator–metal transition at high pressure due to change in the band structure. In another interesting work, Takarabe et al. [12] showed that the difference in the crystal structures between InS and other III–VI layered semiconductors counterparts can be explained in terms of effective changes or ionicities [12]. Gasanly and Aydinli [13] have reported low temperature photoluminescence bands centered at 605 nm (A-band), 626 nm (B-band) and 820 nm (C-band). Later, Qasrawi and Gasanly [14] have retrieved information about the localized levels in the forbidden gap of InS crystal from dark electrical conductivity, space-charge limited current and photoconductivity measurements in the temperature range of 10–350 K.

Although, above reports on the structural, electrical and optical studies on InS are available, to our knowledge, there is no report on the nonlinear optical properties of InS single crystals. In the nonlinear optical regime, the refractive index and absorption coefficient are intensity dependent and leads to wave mixing, harmonic generation, etc. [16]. Z-scan is an established technique to measure the optical nonlinearity in a material [16,17]. Briefly, in Z-scan, the sample is irradiated by high intense laser beam of variable

* Corresponding author. Tel.: +91 02222782932.

E-mail address: anuradha.p@tifr.res.in (A. Patra).

intensity and the transmitted intensity pattern is mapped in sample's transverse plane. The technique, despite being simple, simultaneously measures the magnitude as well as the sign of nonlinear absorption and refraction with high sensitivity. Depending on the sign of nonlinear refraction, the modification in the refractive index results in self focusing or defocusing effects, while that in the absorption coefficient leads to induced transmission or induced absorption effects. In the present work, we synthesized single crystal InS by flux method and present their structural, linear and nonlinear optical properties.

2. Sample preparation and experimental details

The InS single crystals were prepared by flux method in In flux starting with high purity In and S elements. The sample (InS) to flux (In) ratio is taken as 1:19 weight percentage. Required Sulfur powder was repetitively sandwiched and rolled between Indium plates to reduce the Sulfur evaporation. This mixture was kept in alumina crucible and then sealed in a quartz ampule at 10^{-6} Torr. The sealed ampoule was placed in the furnace and heated up to 1050 °C with the rate of 35 °C/h and then kept at this temperature for 24 h in order to achieve proper homogenization. The crystallization was made by cooling the system to 550 °C at a rate of 5 °C/h. Most of the excess Indium was separated by centrifuging. However, a small amount was stuck at the edge of the sample. As grown crystals were in platelet form with clean natural faces that are like cleaved ones and were red color. EDAX measurements showed that the as grown red crystals are having the equiatomic In:S stoichiometry of 1:1. The crystals are of centimeter size and thickness varied from few tens of μm to hundreds of μm (photograph of as grown crystal is shown in the inset of Fig. 1).

3. Result and discussion

3.1. Crystal structure analysis

There is very little literature on In–S system and even the existing ones reported different crystal structure of the equiatomic InS. Thus, it is not clear if InS system is monoclinic or orthorhombic [9,18]. To clear this issue, single crystal X-ray analysis is performed on the grown crystal. The small piece with dimensions of $0.2\text{ mm} \times 0.2\text{ mm} \times 0.05\text{ mm}$ was cut from the big crystal after a thorough investigation under the optical microscope, and the sample was used for single crystal X-ray measurements. X-ray intensity data were collected at 275 K on a Bruker Axs Kappa APEX2 diffractometer equipped with graphite monochromated Mo (K α) radiation ($\lambda = 0.71073\text{ \AA}$). The software programs used for the data

collection, cell refinement and data reduction are APEX2, SAINT-Plus and XPREP respectively [19]. The automatic cell determination routine, with 36 frames at three different orientations of the detector was employed to collect reflections for unit cell determination. The lattice parameters are found to be $a = 4.4506(2)\text{ \AA}$; $b = 10.6503(4)\text{ \AA}$; and $c = 3.9455(2)\text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$. Intensity data were collected for one hemisphere ($h = \pm 5$; $k = \pm 13$; $l = \pm 4$). A total of 4676 reflections with $3.83 \leq \theta \leq 26.36$ were recorded and multi-scan absorption correction (SADABS) was applied. After absorption correction, systematic absences showed the existence of orthorhombic symmetry with $Pnmm$ space group. Two hundred and twenty-two unique data were obtained after merging of equivalent reflections.

The structure was solved by direct methods (SHELXS-97), and the atoms were refined anisotropically using full matrix least squares on $|F|^2$ with all unique reflections (SHELXL-97). The atom positions are unambiguously identified. Table 1 shows the fractional coordinates, site occupancies, and thermal parameters of the atoms in the asymmetric unit. The structure is refined with a residual factor of 0.0295 and goodness of fit value of 1.284. Fig. 1 shows the In and S atom arrangement in the unit cell generated using the parameters listed in Table 1. The inset in Fig. 1 shows the photograph of as grown crystal, and the Laue diffraction on these surfaces confirmed that this plane corresponds to the (010) plane. Fig. 2 shows the observed and generated powder X-ray diffraction for InS. For clarity, only high intense peaks are indexed. All observed peaks match well with generated pattern except the peaks marked by asterisk and corresponded to elemental In from flux residuals. As shown by the image (a) in inset of Fig. 2, SEM images clearly shows some white patches, which are confirmed to be indium by energy dispersive analysis by X-ray (EDAX). However cross section SEM image shows InS in bulk as shown in image (b). From XRD data, one can notice that the strongest peaks in observed and generated patterns are noticeably different in intensity. It may be due to the contribution of the little extra indium and also due to the fact that the grown InS crystals are malleable in nature, which preserves the crystal from becoming powder. From Laue diffraction, we find that the crystal surface corresponds to (010) plane so in powder pattern peak analogous to (010) like (040) and (080) shows higher intensity compared to other peaks because of preferred orientation.

3.2. Linear and nonlinear optical studies on InS single crystal

The linear transmittance and reflectance spectra of single crystal InS were recorded at room temperature in JASCO V-670 spectrophotometer over the wavelength range of 200–2500 nm and are displayed in Fig. 3a and b, respectively. From the curves shown in Fig. 3a and b, it is clear that the single crystal InS has low transmission and reflection. The complex refractive index of the crystal has been extracted by performing ellipsometry measurements. The data for psi and delta values were acquired in the wavelength range of 245.44–999.61 nm. The angle of incidence was varied from 55–75° in steps of 5°. The obtained ellipsometry data was fitted for uniaxial anisotropy using WVASE32 software, which uses Muller-Matrix method [20,21]. The variation of real and imaginary parts of the complex refractive index computed from the ellipsometry data are shown in Fig. 3c. All the measurements were performed on a 50 μm thick crystal. The absorption coefficient, α was calculated from the relation, $\alpha = 4\pi k/\lambda$, where k is the extinction coefficient, which is the imaginary part of the complex refractive index and λ is the wavelength. Optical band gap of InS crystal was calculated from the $(\alpha h\nu)^2$ vs photon energy ($h\nu$) plot shown in Fig. 3d. From the intercept of the straight line fit to the linear portion of the curve (χ^2 minimization fit shown in Fig. 3d), band gap value was found to be 2.09 eV. There is a considerable deviation

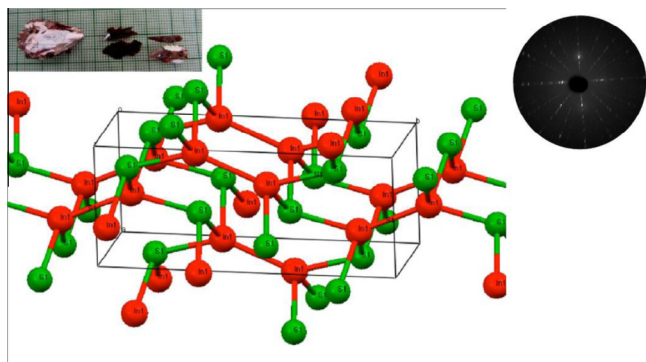


Fig. 1. Atomic arrangement of In and S atom in unit cell generated by using parameter listed in Table 1. The left inset shows the photograph of as grown crystal and the right inset shows the Laue diffraction pattern corresponding to (010) plane.

Download English Version:

<https://daneshyari.com/en/article/1494441>

Download Persian Version:

<https://daneshyari.com/article/1494441>

[Daneshyari.com](https://daneshyari.com)