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ScienceDirect
Optical Materials 29 (2007) 1763–1767
OPTICAL Materials
www.elsevier.com/locate/optmat

Optical properties of Tl_2InGaS_4 layered single crystal

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Received 21 February 2006; accepted 30 September 2006
Available online 15 November 2006

Abstract

The temperature dependence of the optical band gap of Tl_2InGaS_4 single crystal in the temperature region of 300–500 K and the room temperature refractive index, $n(\lambda)$, have been investigated. The absorption coefficient, which was calculated from the transmittance and reflectance spectra in the incident photon energy range of 2.28–2.48 eV, increased with increasing temperature. Consistently, the absorption edge shifts to lower energy values as temperature increases. The fundamental absorption edge corresponds to an indirect allowed transitions energy gap (2.35 eV) that exhibits a temperature coefficient of -4.03×10^{-4} eV/K. The room temperature $n(\lambda)$, calculated from the reflectance and transmittance data, allowed the identification of the oscillator strength and energy, static and lattice dielectric constants, and static refractive index as 16.78 eV and 3.38 eV, 5.96 and 11.77, and 2.43, respectively.

PACS: 71.23.Cq; 78.20.Ci; 78.66.Jg

Keywords: Semiconductors; Optical properties; Band gap; Refractive index; Lattice parameters

1. Introduction

Layered semiconductors are of research interest due to their structural properties and potential optoelectronic applications. Their quasi two dimensionality, structural anisotropy, optical and photoconductive properties, and other features attract investigators in an effort to acquire a better insight in the physics of these compounds. Tl_2InGaS_4 is formed from the $TlGaS_2$–$TlInS_2$ system of layered crystals, which belong to the monoclinic system, and their space group is known as C_2/c at room temperature. The lattice structure is composed of two dimensional alternating layers arranged parallel to the (0 0 1) plane; each layer is followed by another layer rotated by 90° with respect to the preceding one [1].

Previously, we have studied the temperature-dependent photoluminescence spectra of the Tl_2InGaS_4 crystal in the temperature region of 10–150 K and wide laser excitation intensity range 0.01–110.34 W cm^{-2} [2]. The study allowed the determination of three emission band energies of 1.754, 2.041 and 2.286 eV. Recently, the thermally stimulated current measurements on this layered crystal have been carried out. Two shallow trapping centers with activation energies of 4 and 10 meV have been detected at low temperatures [3].

The purpose of this work is to study the band gap energy of Tl_2InGaS_4 crystal as a function of temperature in the high temperature region (300–500 K) to obtain the rate of change of the band gap with temperature. In addition, the room temperature reflectance and transmittance data of this crystal will be analyzed to identify the refractive index, oscillator strength and energy, static and lattice dielectric constants, and static refractive index. The determination of these optical constants is expected to widespread the related available physical information.

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doi:10.1016/j.optmat.2006.09.008

2. Experimental

Tl_2InGaS_4 polycrystals were synthesized from the high-purity elements (at least 99.999% pure) prepared in stoichiometric proportions. Single crystal of Tl_2InGaS_4 was grown by Bridgman method. X-ray powder diffractometer Philips PW1740 (Cu Kα radiation) was used for structural characterization. Fig. 1 shows the X-ray pattern of Tl_2InGaS_4 crystal. The lattice parameters of the monoclinic unit cell, calculated by a least squares computer program "Treor 90", were found to be $a = 1.0639(4)$, $b = 1.0441(4)$, $c = 1.5334(6)$ nm, and $\beta = 100.12°$. The obtained parameters are close to the corresponding values reported for $TlInS_2$ ($a = 1.0942$, $b = 1.0484$ and $c = 1.5606$ nm, and $\beta = 100.70°$ [4]) and $TlGaS_2$ ($a = 1.031$, $b = 1.043$ and $c = 1.507$ nm, and $\beta = 99.60°$ [5]) as expected. The reported data in Ref. [4] does not match other literature values (ICDD card numbers 74-0030 and 85-0636). At the same time the structure of the two compounds $TlGaS_2$ and Tl_2InGaS_4 are not solved yet, except ours, in the literature available to us. Hence, the structure of such compounds needs further study, which can be one of our future interests. The diffraction data: Miller indices (hkl), interplanar spacings (d) and relative intensities (I/I_0) of the diffraction lines are listed in Table 1.

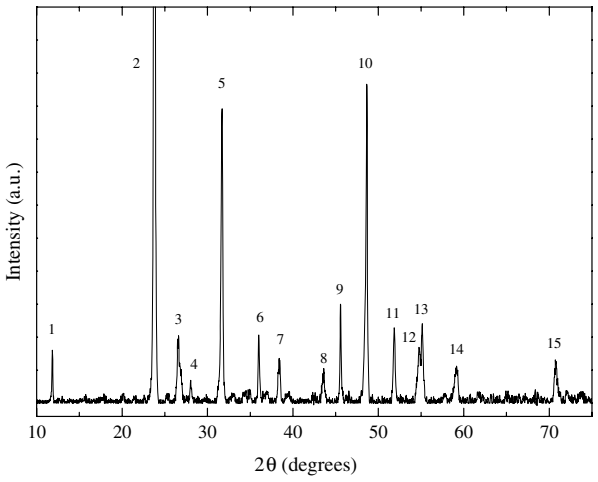

Fig. 1. X-ray diffraction pattern of Tl_2InGaS_4 powder sample.

Table 1
X-ray powder diffraction data for Tl_2GaInS_4 crystal

No.	h	k	l	d (nm)	I/I_0
1	2	0	0	0.7468	3
2	4	0	0	0.3735	100
3	0	3	1	0.3346	4
4	−3	2	2	0.3182	2
5	−4	2	2	0.2820	15
6	−5	2	2	0.2493	4
7	−4	0	4	0.2338	2
8	3	4	2	0.2078	2
9	−5	4	0	0.1989	5
10	−1	4	4	0.1870	16
11	1	5	3	0.1762	4
12	1	6	2	0.1674	3
13	6	0	4	0.1664	4
14	3	6	2	0.1561	2
15	1	3	7	0.1332	2

The samples for optical measurements were prepared by cleaving an ingot parallel to the crystal layer, which is perpendicular to the c-axis, with typical sample dimensions of $5 \times 5 \times 0.35$ mm^3. The transmission and reflection spectra were recorded at various temperatures in the temperature range of 300–500 K using a Hewlet Packard 8453 A UV–VIS spectrophotometer.

3. Results and discussion

The transmittance (T) and reflectance (R) spectra of Tl_2InGaS_4 crystal were recorded at different temperatures varying from 300 to 500 K in the photon energy ($E = h\nu$) range of 1.5–2.6 eV. From these spectral data, the absorption coefficient (α), illustrated in Fig. 2(a), was calculated using the relation [6]

$$T = (1 - R)^2 \exp(-\alpha d), \tag{1}$$

where $d = 350$ μm is the sample thickness. It is clear from the figure that the absorption coefficient of Tl_2InGaS_4 crystal sharply increases with increasing photon energy in the region of 2.35–2.48 eV. It also exhibits higher numerical values and an absorption edge shift with increasing temperature.

To obtain a detailed information about the energy band gap as a function of temperature, the α–E dependencies are analyzed in the sharp absorption region where α can be represented by the relation [6]

$$(\alpha E) = B(E - E_g)^p. \tag{2}$$

In this equation, B is a constant that depends on the transition probability and p is an index that characterizes the optical absorption process and is theoretically equal to 2, 1/2, 3 or 3/2 for indirect allowed, direct allowed, indirect forbidden and direct forbidden transitions, respectively. The best linear plot that covers the widest range of data in accordance with Eq. (2) was obtained for the $(\alpha E)^{1/2}$–E dependence. Some of these plots for different temperatures are presented in Fig. 2(b). The extrapolation of straight lines down to $(\alpha E)^{1/2} = 0$ give the values of indirect band gap energy.

As illustrated in Fig. 2(b), the value of indirect allowed transition energy gap decreases with increasing temperature. Namely, it shifts from 2.35 to 2.28 eV as temperature increases from 300 to 500 K. Moreover, the E_g–T dependence is linear above 420 K. Below which, the E_g–T dependence slightly diverts from linearity. The temperature dependence of the energy band gap can be represented by the relation [6]

$$E_g(T) = E_g(0) + \frac{\gamma T^2}{T + \beta}. \tag{3}$$