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AYTUNÇ ATEŞ

BEKİR GÜRBULAK

MUHAMMET YILDIRIM

SEYDİ DOĞAN

SONGÜL DUMAN

See next page for additional authors

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Urbach's Rule and Optical Properties for TIGaS_{2}

Authors

AYTUNÇ ATEŞ, BEKİR GÜRBULAK, MUHAMMET YILDIRIM, SEYDİ DOĞAN, SONGÜL DUMAN, TACETTİN YILDIRIM, and SEBAHATTİN TÜZEMEN

Urbach's Rule and Optical Properties for TlGaS₂

Aytunç ATEŞ, Bekir GÜRBULAK, Muhammet YILDIRIM,
Seydi DOĞAN, Songül DUMAN, Tacettin YILDIRIM and Sebahattin TÜZEMEN
*Atatürk Üniversitesi, Fen-Edebiyat Fakültesi, Fizik Bölümü,
25240 Erzurum-TÜRKİYE
e-mail: aytnga@rocketmail.com*

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Abstract

Absorption measurements were carried out on TlGaS₂ sample in the temperature range between 10 and 320 K in 10 K steps. There is an abrupt change in the Urbach energy at 180 K and 280 K and steepness parameter at 120 K and 220 K. Obtained from the changing of the Urbach energy, these may be phase transition temperatures. The phonon energies calculated for TlGaS₂ is 19.7±5 meV.

1. Introduction

The ternary semiconducting chalcogenides with the formula ABX₂ (A, B represent metal atoms, X represents a chalcogen atom) have been intensively studied in recent years [1,2] for their structural properties and potential applications in optoelectronics. The long-wavelength tail of the optical absorption in TlGaSe₂ at $\alpha=30\text{-}150\text{ cm}^{-1}$ is shown to obey the Urbach rule in the temperature range 4.2 K to 293 K [3]. Aside from the known phase transitions at 10 K and 120 K [3,4], the anomalous behaviour of the parameters of this rule at 10 K and 246 K suggests the presence of two phase transitions in TlGaSe₂[3,4]. The observed maximum (2.601 eV) in the absorption spectrum is due to formation of Wannier excitons by direct transition, in good agreement with the published data [5] obtained at 6 and 4.2 K. The phase transitions were observed in the temperature dependence of specific heat of TlGaS₂ at temperatures: 73.5, 91, 101, 114, 133.5, 187 K [6]. The anomalies observed in the temperature dependence of low and high frequency phonon modes at 250 K and 180 K, respectively, are explained as due to phase transitions [7]. The room temperature direct and indirect band gap is found at 2.644 eV and 2.41 eV, respectively [8].

2. Basic Equations

The fundamental absorption edge in most semiconductors follows the exponential law. Above the exponential tail, the absorption coefficient of semiconductor has been observed to obey relation [9].

$$\alpha\hbar\omega = B(\hbar\omega - E_g)^n, \quad (1)$$

where $\alpha\hbar\omega$ is the absorption coefficient of an angular frequency of $\omega = 2\pi\nu$, B is a constant and n is an index ($n = 1, 2, 3 \dots$).

An exponentially increasing absorption edge in a number of insulators including ionic crystals, semiconductors, and organic crystals follows the empirical expression [10]

$$\alpha = \alpha_o \exp(\sigma(E - E_o)/kT), \quad (2)$$

where α_o and E_o are characteristic parameters of the material, σ is the steepness parameter, k is the Boltzmann constant and T is the temperature.

The steepness parameter σ , which characterizes the steepness or width of the straight line near the absorption edge, is expressed empirically as a function of temperature [11]:

$$\sigma = \sigma_o (2kT / \frac{h}{2\pi} w_p) \tanh(\frac{h}{2\pi} w_p / 2kT). \quad (3)$$

σ_o is a temperature-independent but material-dependent parameter being inversely proportional to the strength of the coupling between excitons and phonons. Some researchers have stated that hw_p corresponds to the energy of phonons associated with the Urbach tail. The parameter σ/kT for the interaction between exciton and longitudinal-optical (LO) phonons coincides with Eq. (3) by a constant factor [11]. The following empirical expression is often used to describe the temperature dependence of the energy gap [12]:

$$E_{gd}(T) = E_{gd}(0) - \delta \frac{T^2}{T + \beta}, \quad (4)$$

where $E_g(T)$ is the energy gap, $E_g(0)$ is the energy gap at 0 K and δ and β are constants depending on the material. The constant β usually is an estimate of the Debye temperature θ_D .

3. Experimental Procedure

For reasons of purity, basic elements rather than binary compounds were used to compose polycrystalline $A^{III}B^{III}C_2^{VI}$. The materials were weighed in stoichiometric ratios accurate to 0.1 mg. The total mass for any single run was standardized to minimize loss, such as in the case of breakage. The amount of TlGaS₂ was 50 g. The stoichiometric ratio necessary was calculated using the following relationships:

$$M_{Ga} = (M_{Tl} / A_{Tl}) A_{Ga} \quad M_{S_2} = 2 (M_{Tl} / A_{Tl}) A_S$$

with total mass,

$$M(Tl) + M(Ga) + M(S_2) = 50 \text{ g}$$

where M and A are total and atomic masses, respectively. The thallium component was weighed as the first element because of the hardness of the material and the difficulty in with which to cut it to desired accuracy limits.

TlGaS₂ single crystals were grown by the modified Bridgman-Stockbarger method. A sealed quartz ampoule was annealed at 1000°C for 12 hours in an outgassing furnace. The temperature of the quartz ampoule was decreased to room temperature over 8 hours. The mixture of stoichiometric S-Tl-Ga-S was put into the quartz ampoule which subsequently was sealed under a vacuum of 10⁻⁶ mbar. A quartz crucible (13 mm in diameter and about 250 mm in length) with carbon coating was used. The ampoule was suspended in the middle of a two-zone vertical furnace. The temperature of the furnace was changed to 250°C for 5 hours, then heated at 330°C for 5 hours. Later, the furnace temperature was increased to 930°C for 48 hours. The low temperature zone of the furnace was cooled to 580°C at a rate of 3°C/h. Both zones were cooled to 350°C over 103 hours. The solidified ingot was cooled to room temperature in 52 hours. The prepared TlGaS₂ single crystal ingots were 12 mm in diameter and about 60 mm in length. There were no cracks or voids on the surface. The X-ray Laue back reflection method was used to test the crystallinity of the prepared samples. Absorption spectra were measured on freshly cleaved planes (001) surfaces. The TlGaS₂ surfaces used in this study were of dimensions 1.41x1.3 mm².

4. Results and Discussion

TlGaS₂ single crystals were grown by modified Bridgman method [13]. The optical measurements as a function of temperature were made in a closed-cycle He cryostat. For optical measurements a Perkin Elmer UV/Vis Lambda 2S Spectrometer with 190-1100 nm usable range was employed. The absorption spectra

was measured on a freshly cleaved plane perpendicular to the c axis from the iongots with thicknes $105 \mu\text{m}$. The typical absorption spectra of TlGaS_2 samples versus temperatures at 10 K, 100 K, 200 K and 300 K are shown in Fig. 1. The phonon energies calculated for TlGaS_2 sample is $19.70 \pm 5 \text{ meV}$. The energy gap of the indirect and direct optical absorptions TlGaS_2 is obtained from the upper and lower parts of Fig. 1. The direct and indirect band gaps for TlGaS_2 samples are given in Table 1. These results agree with the investigation of [6]. The indirect and direct band gap for TlGaS_2 sample is presented in Fig. 2. This curve represents the values of $E_g(T)$ found by Eq. (4). The temperature coefficients (δ) of the direct band gap were calculated as: $1.512 \cdot 10^{-4} \text{ eV/K}$ for TlGaS_2 from a satisfactory fitting of the experimental curve using the above Eq. (4). However, for TlGaS_2 sample β was calculated as 138.5 K.

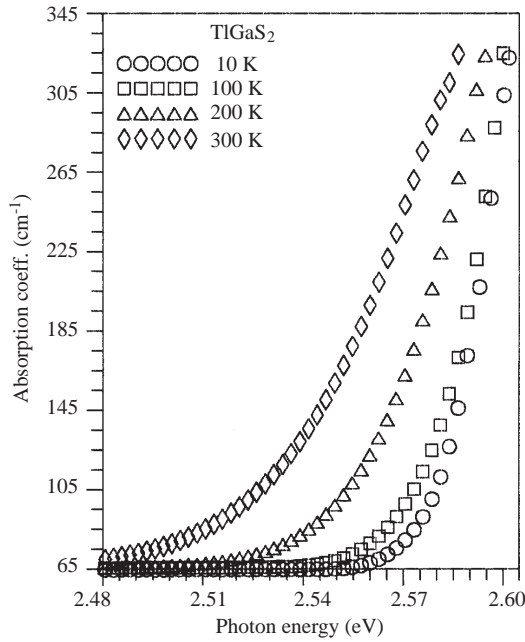


Figure 1. Typical absorption spectra for TlGaS_2 sample.

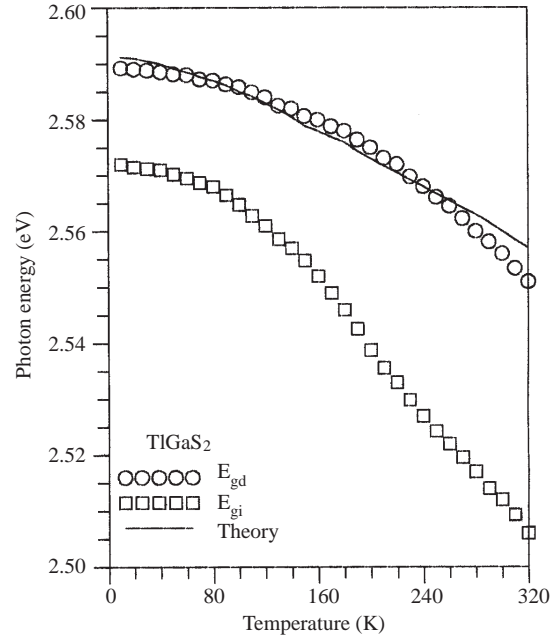


Figure 2. The direct and indirect band gap's energies for TlGaS_2 sample,

The Urbach tail is observed for all samples beetwen 10-320 K. We found that all extrapolations of Urbach tails converge at $(E_0, \alpha_0) = (2.6193 \text{ eV}, 512.89 \text{ cm}^{-1})$. Figure 3 shows the Urbach energy (kT/σ) corresponds to the inverse of a slope of the Urbach tails of the TlGaS_2 sample as a function of temperature. There are abrupt change in the Urbach energy for TlGaS_2 at 180 K, and 280 K. Figure 4 shows the steepness parameter σ value of TlGaS_2 sample as a function of temperature.

Table 1. The direct, indirect band gap, steepness parameter, and Urbach's energy for in TlGaS_2 samples at various temperatures.

Samples	Sample temperatures	E_{gd} (eV)	E_{gi} (eV)	Steepness Parame (σ)	Urbach's Energy (meV)
p- TlGaS_2	10 K	$2.589 \pm 0,008$	$2.572 \pm 0,008$	$0.231 \pm 0,005$	$0.004 \pm 0,005$
	100 K	$2.586 \pm 0,008$	$2.565 \pm 0,008$	$0.335 \pm 0,005$	$0.026 \pm 0,005$
	200 K	$2.575 \pm 0,008$	$2.539 \pm 0,008$	$0.329 \pm 0,005$	$0.052 \pm 0,005$
	300 K	$2.556 \pm 0,008$	$2.512 \pm 0,008$	$0.380 \pm 0,005$	$0.068 \pm 0,005$

The steepness parameter σ value change with increasing temperature. There are abrupt changes in the the steepness parameter and σ_0 values for TlGaS_2 at 120 K and 220 K. The steepness parameter and Urbach energy for TlGaS_2 samples are given in Table 1. Phase transitions were observed in the temperature

dependence of specific heat of TlGaS_2 at the following temperatures: 73.5, 91, 101, 114, 133.5, 187 K [6]. The anomalies observed in the temperature dependence of low and high frequency phonon modes at 250 K and 180 K, respectively, are explained as due to the phase transitions [7]. The values obtained from the steepness parameters σ and change of Urbach energy may indicate a phase transition temperature according to the authors of this paper.

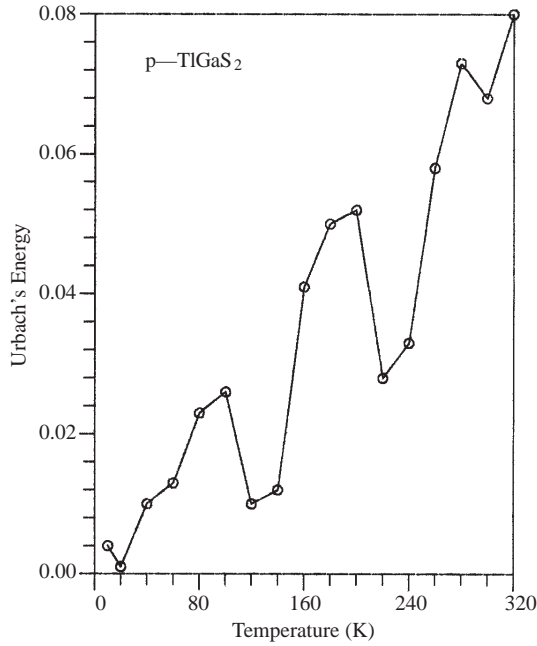


Figure 3. The Urbach energy as a function of temperature. for TlGaS_2 sample.

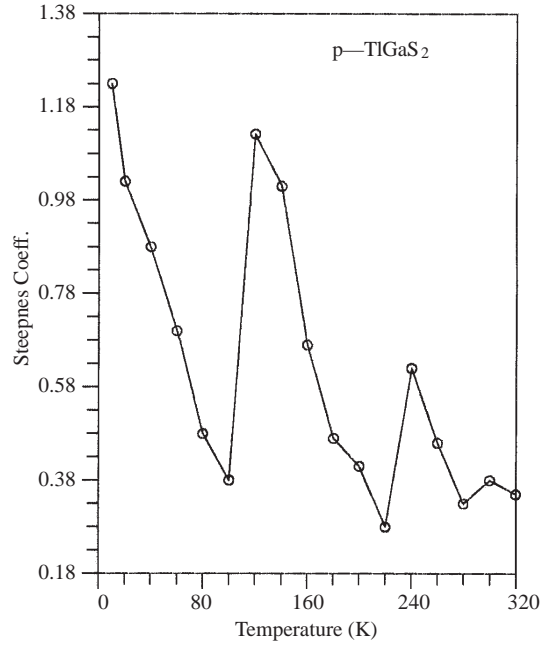


Figure 4. The Steepness parameters (σ) versus the temperature for TlGaS_2 sample.

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