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Determination of trapping parameters of thermoluminescent glow peaks of semiconducting $Tl_2Ga_2S_3Se$ crystals

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ABSTRACT

Thermoluminescence (TL) properties of $Tl_2Ga_2S_3Se$ layered single crystals were researched in the temperature range of 290–770 K. TL glow curve exhibited two peaks with maximum temperatures of ~373 and 478 K. Curve fitting, initial rise and peak shape methods were used to determine the activation energies of the trapping centers associated with these peaks. Applied methods were in good agreement with the energies of 780 and 950 meV. Capture cross sections and attempt-to-escape frequencies of the trapping centers were reported. An energy level diagram showing transitions in the band gap of the crystal was plotted under the light of the results of the present work and previously reported papers on photoluminescence, thermoluminescence and thermally stimulated current measurements carried out below room temperature.

1. Introduction

Thallium dichalcogenides $TlBX_2$ (where B=In or Ga, X=S, Se or Te) compounds have become attractive materials in the optoelectronic applications due to their structural, optical and electrical properties [1,2]. Members of this family have both layered ($TlGaSe_2$, $TlGaS_2$, $TlInS_2$) and chain ($TlInSe_2$, $TlInTe_2$, $TlGaTe_2$) structures. $TlGaS_2$ and $TlGaSe_2$ layered crystals are useful in the optoelectronic applications since they have high photosensitivity in the visible spectral range and wide transparency range of 0.5–14 μm [3]. The optical and electrical properties of these crystals were reported in Refs. [4–7]. The quaternary $Tl_2Ga_2S_3Se$ compound belonging to layered semiconductor group is a structural analog of $TlGaS_2$ in which one quarter of sulfur atoms are replaced by selenium atoms. The bonding between Tl and S(Se) atoms in the crystal is an interlayer type whereas the bonding between Ga and S(Se) is an intralayer type. The indirect and direct band gap energies of the crystals have been found experimentally as 2.38 and 2.62 eV, respectively [8].

The performance of semiconductor crystals in the technological applications is affected due to the presence of defects/impurities in the crystal. The defects may lower the internal quantum efficiency and/or prevent the light generation in optoelectronic devices such as LEDs and laser, by introducing non-radiative recombination centers. Therefore, characterization of trapping centers created due to the presence of defects and/or impurities plays an important role in the related areas. Our research group focuses on getting information about the energetic parameters of trapping centers in semiconducting crystals using thermoluminescence (TL), photoluminescence (PL) and thermally stimulated current (TSC) measurements. Previously, $Tl_2Ga_2S_3Se$ single crystals have been studied by means of these experimental techniques. Low temperature (10–300 K) TL measurements on the crystal resulted in the presence of one trapping center at 16 meV energy level [9]. In the PL spectra, one broad band centered at 550 nm (2.25 eV) was observed at 10 K [10]. Analysis of the temperature and excitation laser intensity dependencies of the band showed that observed PL band is due to the radiative transitions from shallow donor level (E_d=10 meV) to the deep acceptor levels (E_a=160 meV). Analysis of the TSC measurements carried out in the temperature range of 10–300 K revealed the presence of an electron trap at 11 meV [11] and a hole trap at 498 meV [12].

In this paper, we expand our studies on the defect/impurity characterization of $Tl_2Ga_2S_3Se$ single crystals by performing thermoluminescence measurements in the high temperature range of 290–770 K. Thermal activation energies, capture cross sections and attempt-to-escape frequencies of the revealed centers were calculated using basic techniques used for analysis of TL data. Moreover, an energy band structure was plotted under the light of results obtained employing above mentioned experimental

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techniques in this and previously reported papers.

2. Experimental details

$Tl_2Ga_2S_3Se$ polycrystals were synthesized from high-purity elements (at least 99.999%) prepared in stoichiometric proportions. Single crystals were grown by the Bridgman method in evacuated (10^{-5} Torr) silica tubes with a tip at the bottom. The ampoule was moved in a vertical furnace through a thermal gradient of 30 °C cm^{-1}, between the temperatures 880 and 530 °C at a rate of 1.0 mm h^{-1}. The resulting ingot appeared yellow-green in color and the freshly cleaved surfaces were mirror-like. Chemical composition of the growth crystals was obtained from energy dispersive spectroscopy (EDS) measurements performed by JSM-6400 scanning electron microscope. The crystal structure properties were identified using X-ray diffraction (XRD) experiments. Measurements were performed using "Rigaku miniflex" diffractometer with CuKα radiation (λ=0.154049 nm). The scanning speed of the diffractometer was 0.02°/s. Experiments were accomplished in the diffraction angle (2θ) range of 10–80°.

TL glow curves were recorded with RisøTL/OSL DA-20 reader using Schott BG/39, 4 mm of thickness, and Corning7/59, 4 mm of thickness, optical filters. TL glow curves were obtained by heating the sample at a constant rate of 5 K/s up to 770 K. The dose response curves of the sample exposed to ^{90}Sr beta radiation (40 mCi) were obtained in the dose range from 57.2 to 457.6 Gy.

3. Results and discussion

Fig. 1 shows the EDS results used to determine the chemical composition of the crystal. Analysis of the EDS measurements revealed the atomic composition ratio of the constituent elements (Tl:Ga:S:Se) to be 26.0:25.8:35.9:12.3, respectively.

The structural parameters of the crystal were determined from the analysis of the XRD experiments. The crystal system, Miller indices of the diffraction peaks and lattice parameters were evaluated using a least-squares computer program "DICVOL 04". Fig. 2 shows the X-ray diffractogram of $Tl_2Ga_2S_3Se$ crystal. The sharp diffraction peaks are an indication of the well crystallinity of the sample. Miller indices ($h\,k\,l$) are shown on the diffraction peaks. The lattice parameters of the monoclinic unit cell were found to be a=0.46219, b=0.75498 and c=0.78408 nm and β=101.66°.

The observed TL glow curves of $Tl_2Ga_2S_3Se$ crystals irradiated at different doses are shown in Fig. 3. TL curves did not exhibit any peaks beyond 600 K, thus the TL data recorded at higher temperatures will not be shown. Two peaks with maximum temperatures (T_m) of ~373 and 478 K were revealed in the curves.

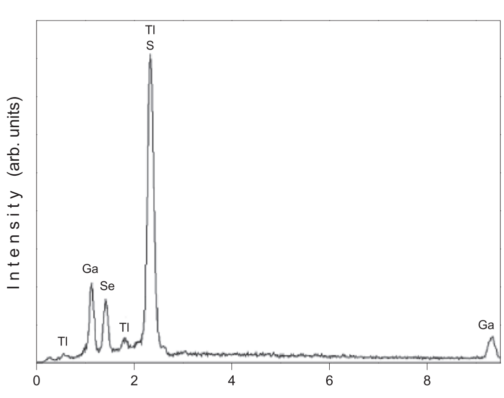

Fig. 1. Energy dispersive spectroscopic analysis of $Tl_2Ga_2S_3Se$ crystal.

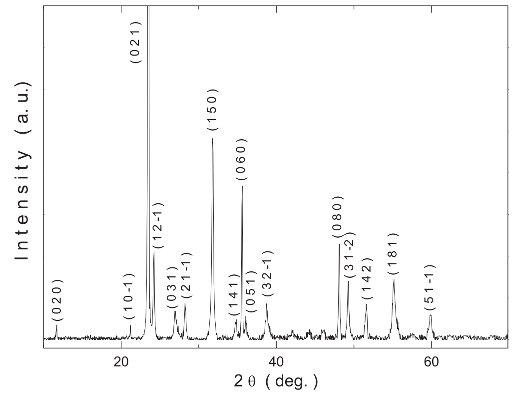

Fig. 2. X-ray powder diffraction patern of $Tl_2Ga_2S_3Se$.

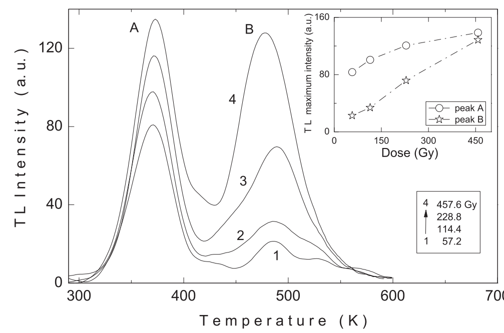

Fig. 3. TL curves of $Tl_2Ga_2S_3Se$ crystals irradiated at different doses. Inset shows the dose dependence of maximum TL intensities of observed peaks.

Peak B does not appear clearly for small doses. However, as the dose increases, TL height of peak B increases more than that of peak A. Dose dependence of TL intensities shows nearly monotonic behavior in the studied range in which TL intensity grows with the dose (see inset of Fig. 3).

Analysis of the TL glow curves to calculate the trapping center parameters of the revealed centers were accomplished using curve fitting, initial rise and peak shape methods. Curve fitting method is based on the fitting of the observed glow curve to the theoretical expressions [13]

$$I_{TL} = n_0 \nu \exp\left\{ -\frac{E_t}{kT} - \int_{T_0}^{T} \frac{\nu}{\beta} \exp(-E_t/kT)dT \right\} \quad \text{(for first–order kinetics)} \tag{1}$$

$$I_{TL} = n_0 \nu \exp\left(-\frac{E_t}{kT} \right)\left[1 + (b-1)\frac{\nu}{\beta} \int_{T_0}^{T} \exp(-E_t/kT)dT \right]^{-b/(b-1)} \quad \text{(for nonfirst – order kinetics)} \tag{2}$$

where I_{TL} is TL intensity, n_o is the initial concentration of trapped charge carriers, E_t is the thermal activation energy, ν is the attempt-to-escape frequency, T_0 is the starting temperature of heating process and b is the order of kinetics. The details of this method were reported in our previous work [14]. Fitting process has been carried out under the light of Eqs. (1) and (2) for different values of parameter b. The best fitting were achieved for b=1.8 which states the presence of mixed order kinetics. Fig. 4 shows the experimental (open circles), fitted (solid line) and deconvoluted (dash-dotted) curves corresponding to each center with activation energies of 780 and 950 meV (Table 1). Since the studied crystals were not intentionally doped, these trapping centers are thought to originate from anion vacancies caused by nonstoichiometry and/or stacking faults, quite possible to exist in layered $Tl_2Ga_2S_3Se$ due to the weakness of the van der Waals forces between the

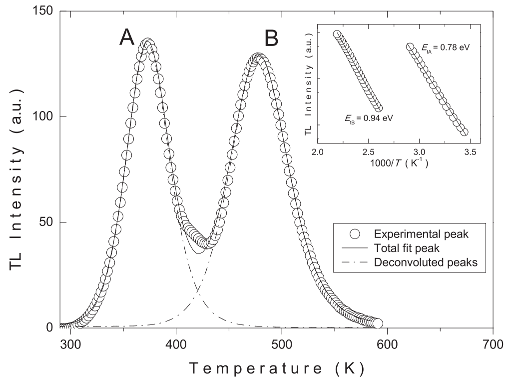

Fig. 4. Experimental TL curve of $Tl_2Ga_2S_3Se$ crystal with heating rate of 5.0 K/s and for 457.6 Gy radiation dose. Open circles are experimental data. Solid curve shows total fit to the experimental data. Dashed curves represent decomposed peaks. Inset: TL intensity vs. $1000/T$. Open circles and lines present the experimental data and theoretical fits, respectively.

Table 1
The trapping center parameters of observed levels of $Tl_2Ga_2S_3Se$ crystal.

Peak	T_m (K)	E_t (meV) Curve fitting method	Initial rise method	Peak shape method	μ_g	S_t (cm^2)	ν (s^{-1})
A	373.0	780	780	800	0.50	1.0×10^{-16}	1.1×10^{10}
B	478.2	950	940	950	0.51	1.3×10^{-17}	2.5×10^{9}

layers [15].

Attempt-to-escape frequencies (ν) and capture cross sections (S_t) of the revealed traps can also be calculated using E_t and T_m values obtained from curve fitting method and expressions [13]

$$\nu = \frac{\beta E_t}{kT_m^2}\exp\left(\frac{E_t}{kT_m}\right) \quad \text{and} \quad S_t = \frac{\nu}{N_c \upsilon_{th}}, \tag{3}$$

where N_c is the effective density of states in the conduction band and υ_{th} is the thermal velocity of a free electron. The calculated ν and S_t values of each trapping centers are given in Table 1.

Initial rise method, one of the powerful techniques with its independency from order of kinetics in TL processes, was also used to calculate the activation energies. TL intensity in the initial portion (~10% of its maximum intensity) of the glow curve is proportional to $\exp(-E_t/kT)$ [16]. This relation gives an opportunity to evaluate the E_t value from the slope of the $\ln(I_{TL})$ vs. $1/T$ graph. Inset of Fig. 4 presents the corresponding plots (open shapes) and their linear fits (solid lines). The activation energies of the centers were obtained as 780 and 940 meV from the slopes.

Another analysis technique used to determine the activation energy of the trapping centers and get information about the order of kinetics was peak shape method in which three parameters $\tau = T_m - T_l$, $\delta = T_h - T_m$ and $w = T_h - T_l$ are utilized for purpose. T_l and T_h correspond to low and high half-intensity temperatures, respectively. E_t value is calculated from the average of energies [16]

$$E_\tau = \left[1.51 + 3.0(\mu_g - 0.42)\right] kT_m^2/\tau - \left[1.58 + 4.2(\mu_g - 0.42)\right] 2kT_m \tag{4}$$

$$E_\delta = \left[0.976 + 7.3(\mu_g - 0.42)\right] kT_m^2/\delta \tag{5}$$

$$E_w = \left[2.52 + 10.2(\mu_g - 0.42)\right] kT_m^2/w - 2kT_m \tag{6}$$

where μ_g is equal to δ/w and was predicted as 0.42 and 0.52 for

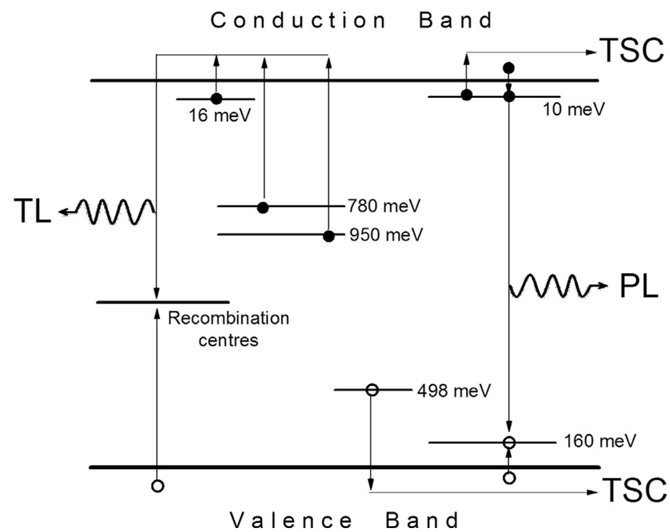

Fig. 5. Energy level diagram showing main transitions in the forbidden band gap under the light of results of photoluminescence [10], thermoluminescence (present work, [9]) and thermally stimulated current [11,12].

first and second order of kinetics, respectively. Peak shape analysis for peaks A and B resulted in activation energies of 800 and 950 meV and μ_g values of 0.50 and 0.51, respectively (Table 1). The values of μ_g support the presence of mixed order of kinetics.

And finally, we would like to take a look on the transitions in the energy band gap of $Tl_2Ga_2S_3Se$ combining the results of present and previously reported works. The energy band diagram and transitions under the light of results of photoluminescence, thermoluminescence and thermally stimulated current measurements are displayed in Fig. 5. Analysis of the PL experiments in the 10–60 K temperature range established the presence of radiative transitions between donor and acceptor states located at 10 and 160 meV, respectively [10]. The results of TSC study in the 10–300 K temperature range showed the existence of electron (11 meV) and hole (498 meV) traps [11,12]. Taking into account the possible errors, the obtained energies of 10 and 11 meV in the PL and TSC studies, respectively, may possibly be attributed to the same level. This level is supposed to be partially compensated permitting for both PL emission and thermally stimulated current. Furthermore, the low (10–300 K) and high (290–770 K) temperature TL experiments resulted in the presence of one (16 meV) [9] and two (780 and 950 meV) trapping centers, respectively.

4. Conclusion

Thermoluminescence properties of $Tl_2Ga_2S_3Se$ crystals in the high temperature range of 290–770 K were reported in the present work. Two TL peaks nearly at ~373 and 478 K were observed in the TL glow curve. Activation energies of the trapping centers associated with these peaks were calculated using various methods which agree on the energy values of 780 and 950 meV. Capture cross sections and attempt-to-escape frequencies of the centers were also established. An energy level diagram showing transitions in the band gap of the crystal was plotted taking into account the results of present work and previously reported papers on photoluminescence, thermoluminescence and thermally stimulated current measurements carried out below room temperature.

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