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Defect characterization in neodymium doped thallium indium disulfide crystals by thermoluminescence measurements

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ABSTRACT

Characteristics of defect centers in neodymium doped $TlInS_2$ single crystals have been investigated in virtue of thermoluminescence measurements carried out at low temperatures (10–300 K) with various heating rates between 0.4 and 1.2 K s^{-1}. One glow peak was detected with peak maximum temperature of 26 K at a rate of 0.4 K s^{-1}. The observed glow peak was analyzed using three points and heating rate methods. The analysis results revealed the presence of one trap level with activation energy of 14 meV. Three points method showed that mixed order of kinetic dominates the trapping level. Shift of peak maximum temperature to higher values and decrease in TL intensity were observed as the heating rate was increased progressively. Distribution of traps was demonstrated using an experimental method based on illumination temperature varying between 10 and 14 K.

1. Introduction

Ternary compounds of semiconductor materials have strong potential and offer remarkable opportunities for the applications in optoelectronic technology thanks to structural, optical and electronic properties [1–4]. $TlInS_2$ is one of the ternary semiconductor compounds with layered structure. Many researchers have investigated the structural, optical and electrical properties of $TlInS_2$ crystals to explore the suitability of the material to the requirements of devices produced in micro- and optoelectronic technology [1,2,5–9]. Recently, thermally stimulated current (TSC) studies on $TlInS_2$ crystals have been reported [10,11]. Existence of shallow and deep trap levels with activation energies of 12, 14 meV [10] and 400, 570, 650 meV [11] were revealed, respectively. Moreover, photoluminescence (PL) investigation of undoped $TlInS_2$ crystal was accomplished in the Ref. [12]. Analysis of observed PL spectra affirmed one deep donor energy level centered at 250 meV and one shallow acceptor level with an energy of 20 meV. Optical and electrical properties of $TlInS_2$ single crystals were also explored by virtue of photoconductivity, dark electrical resistivity, and Hall measurements in temperature regions of 110–350 K, 100–400 K, and 170–400 K, respectively [13]. Lately, we have carried out thermoluminescence (TL) measurements in the temperature range of 10–300 K for the purpose of appointing the trapping levels in $TlInS_2$ crystals [14]. Five peaks were revealed with activation energies 14, 19, 350, 420, and 520 meV in the undoped crystal.

In addition to studies on undoped $TlInS_2$ crystals, researchers have also paid great attention to doped $TlInS_2$ crystals in order for observation of the effects of the doped elements on the optical and electrical properties of the crystal [15,16]. Odrinskii et al. [16] reported the activation energies of deep trap levels in undoped and lanthanum-doped $TlInS_2$ crystal by utilizing the photo-induced current transient spectroscopy (PICTS) technique. PICTS spectra measured at low temperatures depicted successive peaks in the temperature ranges of 93–110 K, 115–135 K, 191–240 K and 240–300 K related to trap levels in undoped crystals with activation energies of 160, 180, 300 and 430 meV, respectively. The same technique revealed the presence of five trap levels in lanthanum-doped $TlInS_2$ crystals corresponding to the peaks observed in the temperature ranges of 98–115 K, 115–135 K, 145–181 K, 190–229 K and 270–320 K with activation energies of 200, 250, 300, 290 and 570 meV [16]. As compared PICTS spectra of undoped and La doped $TlInS_2$ crystals, it was clearly seen that the peak observed in the range of 145–181 K in $TlInS_2$:La crystal were not detected in the undoped crystal. Therefore, the authors attributed this peak to the existence of defect level originating from La dopant. The remaining four trap levels obtained in $TlInS_2$:La crystal were thought as arising from native defects which were already determined in undoped crystal. Moreover, doping with La atom caused to decrease in the intensity of PICTS spectra prominently so that the

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peaks observed in 98–115 K and 115–135 K were nearly absent in the PICTS spectra of $TlInS_2$:La crystal [16].

TL is typically used experimental technique to investigate the characteristics of the energy states occurring in the band gap of the semiconductors and insulators owing to the presence of defects. In the present paper, analysis results of TL measurements performed for $TlInS_2$:Nd single crystal in the temperature range of 10–300 K were reported. Trapping center parameters were revealed using a few methods known from TL theory in the literature.

2. Experimental details

$TlInS_2$ polycrystals were synthesized from high-purity elements (at least 99.999%) taken in stoichiometric proportions. Stoichiometric melt of $TlInS_2$ was doped with Nd of 99.999% purity at 1 at%. A quartz tube which has a tip at the bottom was employed to enclose and to keep the raw materials under 10^{-5} Torr. Bridgman method was used for growing of the single crystal. Vertical furnace that has temperature variation of 30 °C per cm was adjusted to move the prepared material at a rate of 0.5 mm h^{-1} between the temperatures 1000 and 650 °C. The surface of the resulting ingots was quite smooth and had no cracks. The ingot was cleaved to small pieces convenient for measurements using a razor blade perpendicular to the ***c***-axis of the crystal. p-type electrical conductivity was determined for the studied sample by hot-probe method.

TL measurement was performed at low temperatures using a closed cycle helium gas cryostat (Advanced Research Systems, Model CSW-202). Temperature of the environment was managed with a temperature controller (LakeShore Model 331). Illumination and detection processes were carried out with the help of a compactly constructed light-tight chamber comprising a blue light source (~470 nm), a photomultiplier (PM) tube, and the optic elements (mirror and lenses) by connecting to the optical access port of the cryostat (quartz window). The illumination of the sample was realized at 10 K during 600 sec, which is sufficient for saturation of trap level, by directing the light source to the sample in the cryostat via mirror and lenses which were also controlled to detect the luminescence emitted from the sample by PM tube (Hamamatsu R928; spectral response: 185–900 nm). A fast amplifier/discriminator (Hamamatsu Photon Counting Unit C3866) was employed to convert pulses generated by PM tube into TTL (transistor-transistor logic) pulses. The TTL pulses were counted by the counter of a data acquisition module (National Instruments, NI-USB 6211). Whole measurement system was governed by software written in LabView^{TM} graphical development environment.

3. Results and discussions

Thermoluminescence glow peak recorded for neodymium doped $TlInS_2$ crystals at a heating rate of 0.4 K s^{-1} was shown in the Fig. 1. Due to the lack of TL peak in temperature range detected between 60 and 300 K, merely low side of the TL spectra was represented in the figure. One glow peak correlated to one trapping center in the crystal was observed with peak maximum temperature (T_m) of 26 K. As can be seen from the figure, the shape of the TL peak seems nearly symmetric as the ascending and descending part were compared. This is a powerful indication for the non-first order behavior of the TL peak. In order to calculate the thermal activation energy of the trap and to comprehend the exhibited order of kinetics, three points method improved by Rasheedy [17] was applied to TL peak. This method suggests choosing three arbitrary points on the experimental TL curve to determine the trap parameters. Clearly, assuming the area under the glow curve is proportional to released charge carriers from the trap level, one can obtain the E_t by using the area under the curve remaining between the selected point and final point of the TL peak by utilizing one of the following two equations [17]

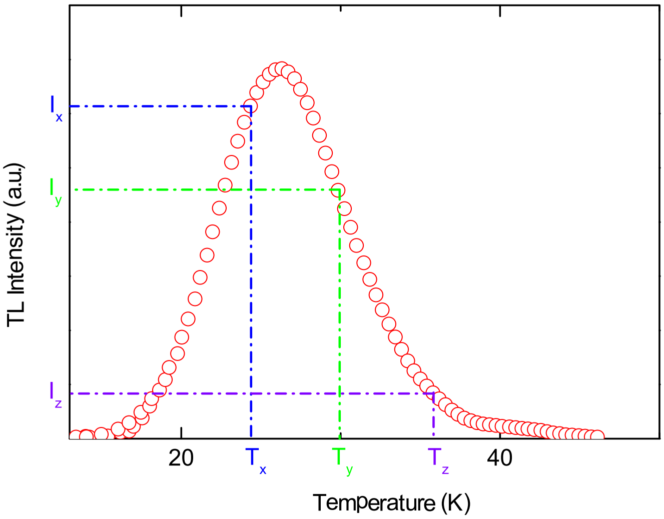

Fig. 1. Experimental TL glow peak observed with heating rate of 0.4 K s^{-1}. The dash-dotted lines are only guides for the eyes.

$$E_t = \left\{\ln(y) - b\ln(A_x/A_y)\right\}\frac{kT_xT_y}{T_x - T_y}, \tag{1}$$

$$E_t = \left\{\ln(z) - b\ln(A_x/A_z)\right\}\frac{kT_xT_z}{T_x - T_z}, \tag{2}$$

where

$$b = \frac{T_y\left(T_x - T_z\right)\ln(y) - T_z\left(T_x - T_y\right)\ln(z)}{T_y\left(T_x - T_z\right)\ln\left[\frac{A_x}{A_y}\right] - T_z\left(T_x - T_y\right)\ln\left[\frac{A_x}{A_z}\right]}. \tag{3}$$

In the Eqs. (1) and (2), A_x, A_y, and A_z are the areas under the curves which are rest of the TL peak after masking the initial part of the peak up to arbitrarily selected temperature points T_x, T_y, and T_z, respectively. y and z are determined as $y = I_x/I_y$ and $z = I_x/I_z$, where I_x, I_y, and I_z are the TL intensities corresponding to T_x, T_y, and T_z (see Fig. 1). b is the order of kinetics. We chose one point from the ascending tail and two points from the descending tail of the TL peak for implementation of the three points method. Thus, the activation energy and order of kinetics were found as $E_t = 14$ meV and $b = 1.4$. Also, the result indicated that the trap levels were dominated by general-order kinetics.

Influence of various heating rates (β) on TL glow curve(s) is one of the remarkable phenomena for investigation of TL properties of trapping states in luminescent materials. In the present work, linear heating rate response of the trap level existing in $TlInS_2$:Nd crystal was studied. Fig. 2 illustrates the TL glow curves achieved through heating the sample with various rates (0.4–1.2 K s^{-1}) in the temperature range of 15–60 K. Shift of T_m value to higher temperatures and decrease in TL intensity with increasing heating rates can be seen from the Fig. 2. Explicit variation of T_m values with increasing heating rate was explained by Anishia et al. in their TL study [18]. Many authors of published papers interpreted the reason of diminishing TL intensity with raising heating rate by ascribing to thermal quenching [19–21]. In addition, full-widthhalf-maximum of the TL curve obtained with 0.4 K s^{-1} rate increases with rising heating rates to conserve the number of charge carriers released from trap levels at each preheating treatment. Heating rate method was affirmed many times as a practical approach for estimation of activation energy (E_t) of the trap levels. In literature, various calculation methods using particular heating rates were reported by many authors. One of the most chosen ways to evaluate the activation energy of luminescence center depends on the following equation [22]

$$\beta=(sk/E_t)T_m^2\exp(-E_t/kT_m), \tag{4}$$

where s is the frequency factor, and k is the Boltzmann constant. In the Eq. (4), T_m in exponential term contributes to the variation of luminescence process predominantly more than the term T_m^2. Under this consideration, logarithmic plot of β as a function of reciprocal of T_m value presents a straight line which has a theoretical slope of $-E_t/k$. Inset of Fig. 2 demonstrates analogous plot of experimentally obtained TL data (circles) and its linear fit (solid line). Activation energy of revealed trap level was obtained from the slope of the plot as $E_t=13$ meV.

Fig. 3 represents the heating rate dependences of T_m, TL intensity and integral of TL glow curves recorded with heating rates between 0.4 and 1.2 K s^{-1}. The peak maximum temperature and TL intensity exhibit increasing (from 26 to 36 K) and decreasing (from 68 to 48 (a.u.)) tendency with rising heating rates, respectively. The area under the glow curves remains constant since the number of charge carriers populating the trap level is conserved for each preheating treatment repeated under same experimental conditions.

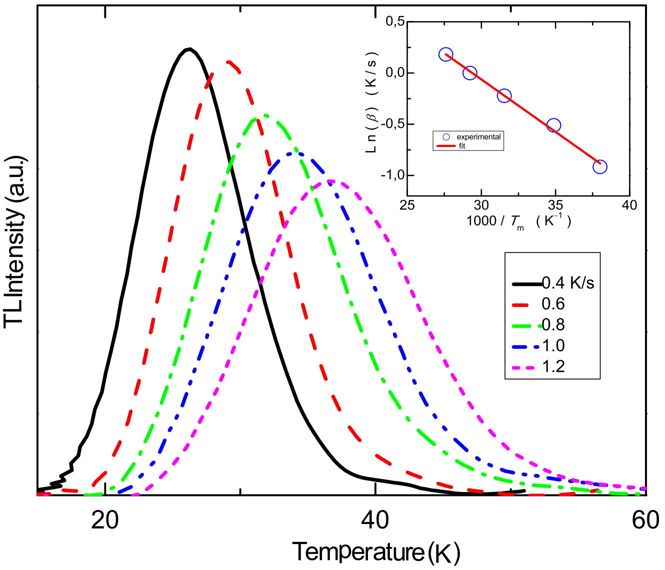

Fig. 2. Experimental TL peaks of TlInS$_2$:Nd crystals with different heating rates between 0.4 and 1.2 K s^{-1}. Inset: Ln (β) plot as a function of 1000/T_m. Open circles are experimental data. Solid line is the fitted straight line.

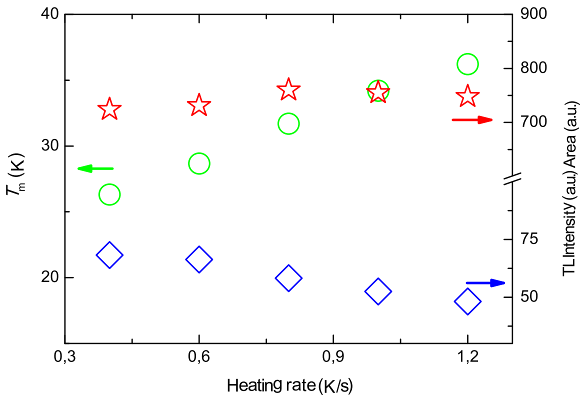

Fig. 3. Heating rate dependencies of TL intensities, peak maximum temperatures and areas under the glow curves.

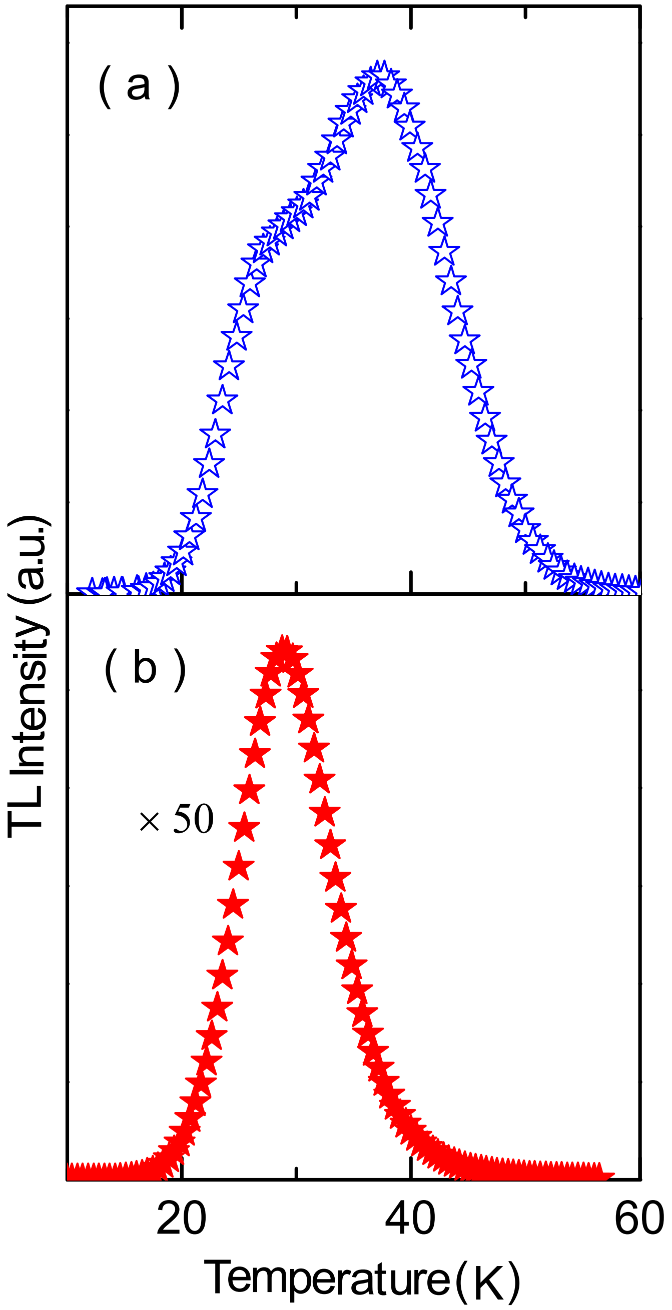

Fig. 4. (a) Experimental TL glow curve of undoped TlInS$_2$ crystals observed with $\beta=0.6$ K s^{-1} (Note: the data was taken from Ref. [14]). (b) Experimental TL curve of TlInS$_2$:Nd crystals observed with $\beta=0.6$ K s^{-1}.

In order to better comprehend the existence and source of defect centers related to trap levels revealed in the Nd doped TlInS$_2$ single crystal, we have donated our attention to comparison of activation energy value found by above mentioned technique with previously reported values for undoped TlInS$_2$ crystal [10,14]. Fig. 4 demonstrates the experimental TL curves of undoped and Nd doped TlInS$_2$ crystals recorded with $\beta=0.6$ K s^{-1}. As compared the intensities of TL curves, one can easily see the remarkable diminishing in the intensity of the TL curve by Nd doping to the

$TlInS_2$ crystal. The intensity of peak appearing at $T_m=29$ K for doped crystal was lower than those of undoped crystals approximately fifty times. Moreover, the peak having maximum temperature of 37 K in Fig. 4a was completely absent in the spectra detected for $TlInS_2$:Nd crystal. Consequently, the trap level related to peak presented for the $TlInS_2$:Nd crystal was also observed in the TL studies on undoped $TlInS_2$ crystal with activation energies of 14 meV [14]. Therefore, it was thought as a native defect in undoped $TlInS_2$ crystal. Seyidov et al. [23] assumed in their study on $TlInS_2$ crystals that the native defects (hole traps) are generally caused by indium vacancies by referring to the study on GaSe crystal indicating that the acceptor level originated from Ga vacancies [24]. Taking into account the same assumption, absence of the trap level corresponding to the peak with $T_m=37$ K in $TlInS_2$:Nd crystal may be explained with the effect of dopant. Indium vacancies occurring in undoped crystal may be compensating by neodymium atoms. Thus, it can be reasonable to suggest the recovering of these defect levels by Nd atoms doping.

TL measurements are very useful to get knowledge about the trap depth and distribution of energy levels of the trap. In order to expand our study on $TlInS_2$:Nd crystals, we applied an experimental method providing opportunity to explore the traps characteristics. Thermally cleaning method basically depends on detecting the luminescence coming from released charge carriers at deeper levels after cleaning the shallowest levels [18,22,25,26]. The TL experiments were performed at different illumination temperatures (T_{ill}) between 10 and 14 K with a constant heating rate of 1 K s^{-1}. Firstly, the sample was cooled down to T_{ill} value and was exposed to light for 600 s at this temperature. Then, temperature was decreased until starting temperature (T_0) and the sample was heated up to $T=300$ K. Employing the higher T_{ill} values caused to empty shallowest levels and TL peaks were recorded by luminescence emitted from charge carriers occupying deeper trap levels. Fig. 5 presents the TL peaks observed with different illumination temperature. Increasing T_{ill} value led to shift of the T_m towards higher temperatures and caused to decrease in TL intensity as expected. Moreover, initial tail of the peaks revealed shifting tendency to higher temperatures while the descending part of the peaks kept their positions. Activation energies of charge carriers liberated from trapping levels were calculated using the successively obtained TL peaks. A shift from 14 to 20 meV was demonstrated with the application of three points method to each peaks in the Fig. 5 (see also Table 1). Quasi-continuous distribution was ascribed for the behavior of the trapping center [27,28].

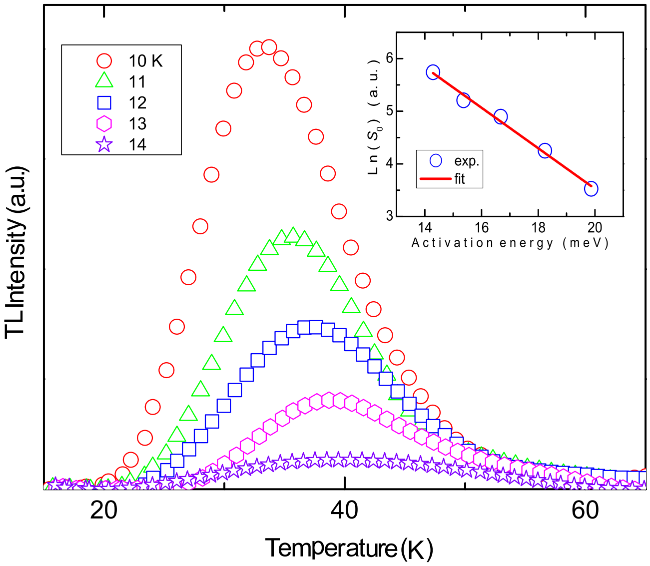

Fig. 5. The glow curves of $TlInS_2$:Nd crystals at different T_{ill} at heating rate of $\beta=1.0$ K s^{-1}. Inset: $\ln(S_0)$ plot as a function of activation energy. Solid line is the fitted straight line.

Table 1
TL parameters for $TlInS_2$:Nd crystal at different illumination temperatures.

Curve	1	2	3	4	5
Illumination Temperature (K)	10	11	12	13	14
Maximum Temperature (K)	34	36	38	39	40
Curve Area (a.u.)	312	183	134	70	34
Activation Energy (meV)	14	15	17	18	20

Conceding that the found activation energies of the trap levels corresponding to each TL peak in Fig. 5 are proportional to density of traps exponentially, one can write an equation for the density as $N_t= A\ \exp(-\ \alpha E_t)$. Since the integrals of the peaks are related to population of the charge carriers in the traps, the equation may be rewritten in the following form for the trap levels occupied at the illumination temperature T_{ill} [27]

$$S_0 \propto A\ exp(-\alpha\ E_t) \tag{5}$$

Here, α is a parameter related to energy distribution of trap and S_0 is the area under the peaks. To find the parameter α using Eq. (5), we showed logarithmic plot of S_0 as a function of activation energy in the inset of Fig. 5. The plot achieved more or less straight line with a slope $\alpha=0.385$ meV^{-1}. This value signifies a variation of one order of magnitude in the traps' density for energy depth of 6 meV.

4. Conclusion

TL mechanism of trapping level observed in $TlInS_2$:Nd single crystal was studied using the TL spectra recorded between 10–300 K. Activation energy of 14 meV was calculated for the revealed trap. Mixed order of kinetics was assigned to the level with the evidence of evaluated kinetic parameter $b=1.4$. Using the closeness of activation energy value of defect level to previously found energy values reported for $TlInS_2$ crystal, this level was attributed to native defect which already exists in the undoped crystal. As being compared with previous TL study on undoped $TlInS_2$ single crystal, it was also shown that the peak correlated to defect level in undoped crystal with energy of 19 meV disappeared in the TL spectra of $TlInS_2$:Nd crystal. This situation was ascribed to recovering of defect levels by doping Nd atoms. Moreover, heating rate behavior of TL curve and distribution of trap level were studied by altering the heating rate between 0.4 and 1.2 K s^{-1} and illumination temperature between 10 and 14 K, respectively. Well-known heating rate dependencies that is increase of T_m of the peaks from 26 to 36 K and decrease of the TL intensity in magnitude from 68 to 48 were demonstrated. A quasi-continuous distribution of the trapping centers was established through increment of activation energy from 14 to 20 meV with rising illumination temperature.

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