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Study on thermoluminescence of $TlInS_2$ layered crystals doped with Pr

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ABSTRACT

Praseodymium (Pr) doped $TlInS_2$ crystals were studied by means of thermoluminescence (TL) measurements performed below room temperature with various heating rates. Detected TL signal exhibited glow curve consisting in overlapping two TL peaks at temperatures of 35 K (peak A) and 48 K (peak B) for 0.6 K/s heating rate. TL curve was analyzed with curve fitting and initial rise methods. Both of the applied methods resulted in consistent activation energies of 19 and 45 meV. The revealed trap levels were found to be dominated by mixed order of kinetics. Various heating rate dependencies of TL glow curves were also investigated and it was found that while peak A shows usual behavior, peak B exhibits anomalous heating rate behavior. Distribution of trap levels was explored using an experimental method called as $T_{max} - T_{stop}$ method. Quasi-continuous distributions with increasing activation energies from 19 to 29 meV (peak A) and from 45 to 53 meV (peak B) were ascribed to trap levels. Effect of Pr doping on the TL response of undoped $TlInS_2$ crystals was discussed in the paper.

1. Introduction

Ternary layered $TlInS_2$ single crystals pertain to semiconductor group symbolized with chemical formula of $TlBX_2$ in which B = In or Ga and X = S or Se [1]. This material carries an important potential to be used for different device applications in related fields of technology thanks to its structural, optical and electrical properties [2–4]. In literature, there are studies reported to investigate predisposition of these physical properties of the material to the micro- and optoelectronic device applications [5–7]. $TlInS_2$ is a convenient material for optoelectronic applications since it is high photosensitive in visible region and has high birefringence in conjunction with wide transparency range $0.5 - 14$ µm [8]. Electrical and optical efficiency of optoelectronic devices depend on the structural imperfection of the used materials. Existence of the defects in the material is decisive mechanism for performance of devices. Therefore, exploration of defect mechanism in the materials gains significance for the related technology. Thermoluminescence (TL) is a nondestructive experimental method used by researchers to determine the trapping parameters of defect levels. Earlier, TL experiments were applied in an attempt to reveal the trapping parameters of undoped $TlInS_2$ crystals [9]. Five trap levels with activation energies between 14 and 520 meV were reported from the analyses of observed TL spectra. Defect states in undoped $TlInS_2$ crystals were also investigated by means of thermally stimulated current studies [10,11]. Existence of shallow (12 and 14 meV) and deep (400, 570 and 650 meV) trap levels were established.

Doping of different elements to a host material can end up with different events in the band gap. The doped elements can enhance the concentration of intrinsic defect states, generate new defect levels or recover some trapping centers. The effect of doping of different elements on defect states in $TlInS_2$ was previously investigated by researchers [12,13]. Odrinskii et al. [13] investigated the presence of trap levels in undoped and lanthanum-doped $TlInS_2$ crystals using photo-induced current transient spectroscopy (PICTS) method. PICTS spectra measured at low temperatures displaced four peaks related to trap levels in undoped crystals. Five trapping centers between 200 and 570 meV were revealed in lanthanum-doped $TlInS_2$ crystals. Authors attributed the level with activation energy of 300 meV to the existence of defect level arising from La dopant. The other four trap levels were believed originating from native defects that were already observed in undoped crystal. Moreover, doping with La atom led to lower PICTS intensity [13]. Recently our research group reported the results of TL study on $TlInS_2$:Nd crystals carried out at low temperatures [14]. The results of analyses revealed the presence of one trap level with activation energy of 14 meV.

In the present study, TL investigations of $TlInS_2$:Pr crystals have been achieved below room temperature with various heating rates between 0.4 and 1.2 K/s. Activation energies of revealed trap levels were

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found from curve fitting and initial rise methods. Heating rate dependency and traps distribution were also studied in detail. Effect of praseodymium doping to defect states in undoped $TlInS_2$ was discussed by comparing the TL spectra of doped and undoped crystals.

2. Experimental details

Synthesizing of $TlInS_2$ polycrystals was achieved by using stoichiometric proportions of high purity elements (at least 99.999%). Pr of 99.999% purity at 1 at% was added to stoichiometric melt of $TlInS_2$. The environment enclosed with a quartz tube possessing a tip at the bottom was kept under 10^{-5} Torr for the raw materials. Single crystals were grown by Bridgman method. Prepared material was moved at a rate of 0.5 mm h^{-1} in a vertical furnace controlled between 1000 and 650 °C varying 30 °C per cm. The resulting ingot has mirror-like surfaces and no cracks was created.

TL experiments were done using closed cycle helium gas cryostat (Advanced Research Systems, Model CSW 202) that can keep the temperature between 10 and 300 K. The $TlInS_2$:Pr sample was immobilized by pasting to sample holder with silver paste. Temperature inside the cryostat was decreased to $T_0 = 10$ K. After reaching to this low temperature, sample was exposed to a blue LED (~470 nm) for 10 min to fill the trapping levels. Following an expectation time of 3 min the sample was heated up to 300 K using a temperature controller (Lakeshore Model 331). For various heating rate measurements, the controller was employed to increase the temperature with rates ranging from 0.4 to 1.2 K/s. Thermally emitted luminescence from the sample was compiled by a lens attached to quartz window of cryostat and then was dispatched to photomultiplier (PM) tube (Hamamatsu R928, spectral response: 185 − 900 nm). The electrical pulses of PM tube due to emitted luminescence were converted into TTL pulses (0 − 5 V) using a fast amplifier/discriminator (Hamamatsu Photon Counting Unit C3866) and counted utilizing the counter of a data acquisition module (National Instruments, NI 6211). The whole measurement system was conducted by a software improved in LabView (National Instruments).

3. Results and discussions

3.1. Determination of activation energies

Emitted luminescence from $TlInS_2$:Pr crystals for heating rate of $\beta = 1.0$ K/s in the temperature range of 10 − 300 K exhibited TL curve with two overlapping peaks in the temperature region of 10 − 80 K. The observed TL peaks (labelled as A and B) with peak maximum temperatures (T_{max}) of 35 and 48 K were presented in Fig. 1. The detected TL signal does not present TL peak beyond 80 K. Therefore, the graphs given throughout this paper were presented in the temperature range in which TL peaks were observed. Experimentally obtained TL curve was analyzed using curve fitting method which was applied to TL curve by taking into account the following theoretical formula giving TL intensity as [15]

$$I_{TL} = n_0 \nu \exp\left(-\frac{E_t}{kT}\right)\left[1 + (b-1)\frac{\nu}{\beta}\int_{T_0}^{T} \exp(-E_t/kT)dT\right]^{-\frac{b}{b-1}}.$$

In this equation, n_o is responsible for the initial concentration of trapped charge carriers, ν is attempt-to-escape frequency, E_t is activation energy, b is order of kinetics and T_0 is the starting temperature of heating process. The equation characterizes the behaviors of liberated charge carriers from trap levels which are dominated by mixed or second order of kinetics. Experimental TL curve was repeatedly fitted until the best fit was established. As a result, indicated fitting curve (solid curve) in Fig. 1 was obtained with the kinetic parameters of $b_A = 1.2$ and $b_B = 1.9$ indicating that mixed order of kinetics are responsible for the trap levels associated with both peaks. Under the light of achieved fitting parameters, deconvoluted TL peaks were also presented in the figure (dashed curves). Curve fit analyses resulted in the presence of two trap levels related to peaks A and B with activation energies of 19 and 45 meV, respectively. Inset of Fig. 1 shows the application of initial rise method which does not depend on the order of kinetics [15]. In the initial rising part of the TL curve, peak intensity arises as proportional to $\exp(-E_t/kT)$. When logarithmic plot of the intensity is plotted as a function of $1/T$, a straight line with slope of $-E_t / k$ is obtained. However, in a TL curve composed of overlapping TL peaks, the found activation energy using this method belongs to the shallowest trap level associated with TL peak arising initially. Activation energy of trap level related to peak A was obtained as 19 meV from the initial rise method analyses.

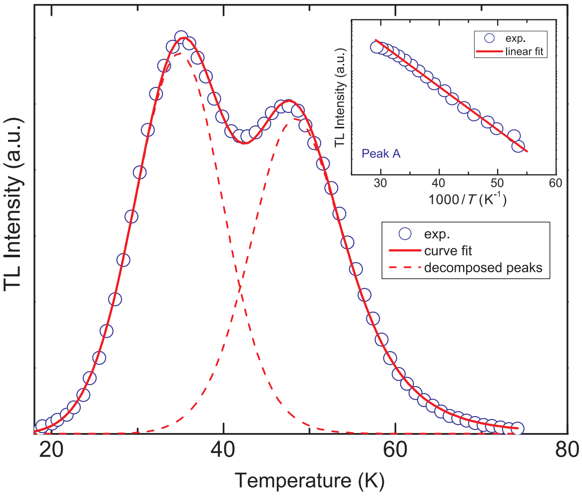

Fig. 1. Experimental TL spectrum (circles) of $TlInS_2$:Pr crystals for $\beta = 1.0$ K/s and decomposition of the curve into separate peaks (dash-dotted curves). Solid curve shows the total fit to the experimental curve. Inset: the plot for initial rise method application for peak A.

Fig. 2 indicates the TL glow curve obtained by thermal cleaning method performed in order to separate and individually analyze the peak. For observation of peak B separately, the temperature of the sample was adjusted to stopping temperature (T_{stop}). Then, the sample was subjected to a light for 10 min. At this T_{stop} value which is bigger than 10 K, some or all of the trapped carriers in shallowest centers would have big probability to escape from these centers. After switching off the light source and decreasing the temperature to T_0, the sample was heated to obtain TL glow curve existing due to remaining trapped charges. Thermally cleaning method was applied to TL curve

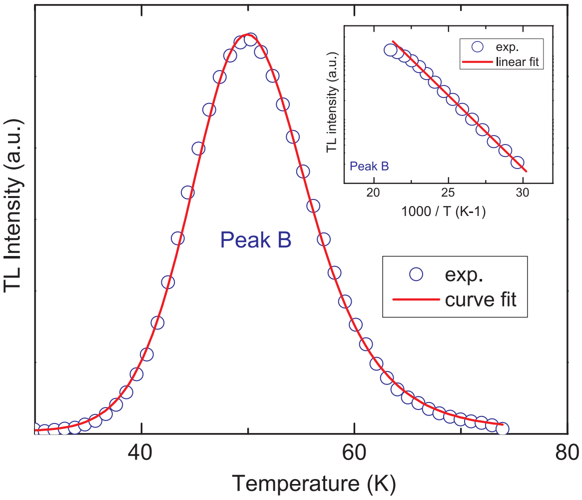

Fig. 2. Experimental (circles) TL curve (peak B) after thermal cleaning for $\beta = 1.0$ K/s. Inset: the plot for initial rise method application for peak B.

for different T_{stop} values. The peak B was completely separated as T_{stop} = 20 K was employed (see Fig. 2). Curve fitting and initial rise method analyses applied to individual TL peak B resulted in activation energy values of 45 and 46 meV, respectively. These obtained values for individual peak B are consistent with those found for overlapped peak.

3.2. Normal and anomalous heating rate behaviors

Heating rate is an important phenomenon for the trapping levels in order to elucidate possible thermal excitation mechanism which can be different for various materials. During the TL investigations, three events; thermal quenching, normal and anomalous heating rate behaviors have been found out in many studied materials. Thermal quenching is known as decrease in TL intensity and area under the TL curves with increase of heating rate [16]. Enhancement in probability of non-radiative transitions with increasing β leads to this phenomenon. Normal heating rate behavior is the most expected event for the luminescence center. In this phenomenon, increasing β results in decrease of TL intensity while area of TL curve remains constant due to constant trap concentration. Lately, an inverse behavior of trap levels due to increasing β, called as anomalous heating rate effect has been reported in some studies [17–21]. Two-stage [22] and semi-localized transition (SLT) [23,24] models were improved to elucidate this behavior. According to two-stage model, there should be a localized excited state in which electrons in the ground state are stimulated before releasing into the conduction band. Radiative transitions only from conduction band to recombination center are taken under consideration. SLT model suggests also non-radiative transitions directly from excited state into recombination center beside radiative recombination of electrons from delocalized band. The increasing heating rate results in elevating the relative rate of radiative transitions while the rate of non-radiative transitions decrease. Therefore, TL intensity enhances with heating rate. Fig. 3 shows TL glow curves observed with various heating rates between 0.4 and 1.2 K/s. As seen from the figure, T_{max} values of TL peaks increase with heating rate. TL intensity of peak A decreases with β as expected whereas the TL intensity of peak B ascends gradually. This means that while the peak A exhibits normal behavior, peak B shows an inverse reaction to increasing heating rate. Even though there are examples revealing the normal and anomalous heating rate behaviors separately, observation of existences of both behaviors in a TL curve are very rare. The same behavior was previously reported in TL study on GaS crystals [20]. Chen et al. [25] developed a model to explain the occurrence of both heating rate behaviors. In the model, there are one electron trap, one recombination center and one reservoir. By assuming the transitions into the recombination center and the reservoir are radiative, they obtained a simulated TL curve having two peaks which TL intensity of one shows decreasing tendency while that of other shows increasing tendency. Fig. 4 depicts the heating rate variations of TL intensities, T_{max} values and area enclosed under the experimental TL curves. T_{max} values of peaks A and B shift from 27 to 37 K and from 38 to 53 K, respectively. TL intensity of peak A diminishes as nearly 27% whereas that of peak B increases as nearly 35%. Moreover, total area increases approximately 60% with increasing β. In order to support the heating rate behavior mentioned above, we also investigated the effect of β to TL peak B individually. Fig. 5 represents the thermally cleaned glow peaks for peak B utilizing various heating rates in the range of 0.4 – 1.2 K/s. As observed in the TL curve, intensity and area of the individual peak B rise with heating rate. This fact supported our previous discussion proposing that peak B exhibits the properties of anomalous heating rate effect. Fig. 6 indicates the heating rate dependencies of TL intensity, T_{max}, full-widths-half-maximum (FWHM) and area of peak B. T_{max} and FWHM values increase from 37 to 52 K and from 14 to 17 K, respectively. Moreover, TL intensity and area increases nearly by 22% and 30% with β, respectively.

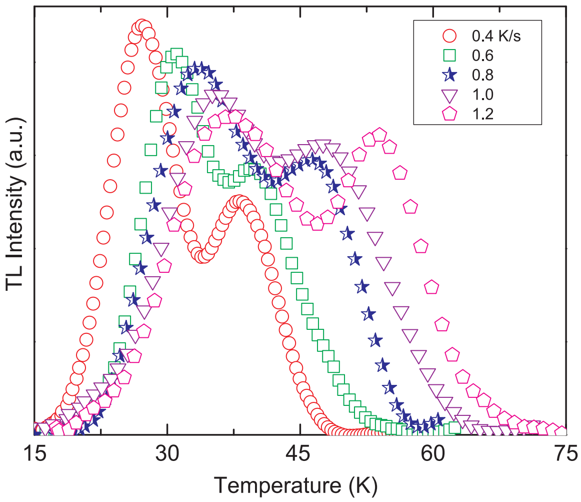

Fig. 3. Experimental TL curves of TlInS$_2$:Pr crystals with various heating rates between 0.4 and 1.2 K/s.

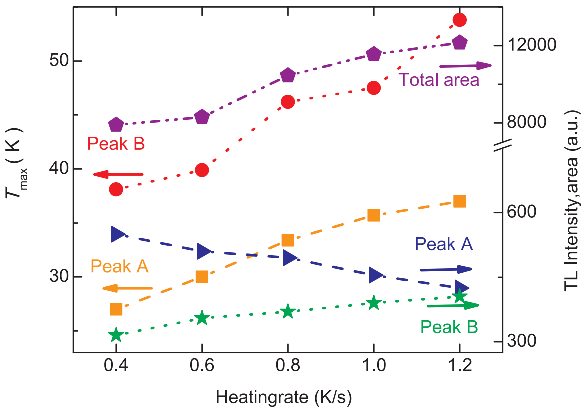

Fig. 4. The heating rates dependencies of the peak maximum temperatures (T_{max}), peak areas and intensities for A and B peaks before thermal cleaning.

3.3. Distribution of trapping levels

As known from previous TL investigations, defect states in the band gap of the luminescent materials can have different trapping characteristics. In order to find out whether the revealed trap levels in

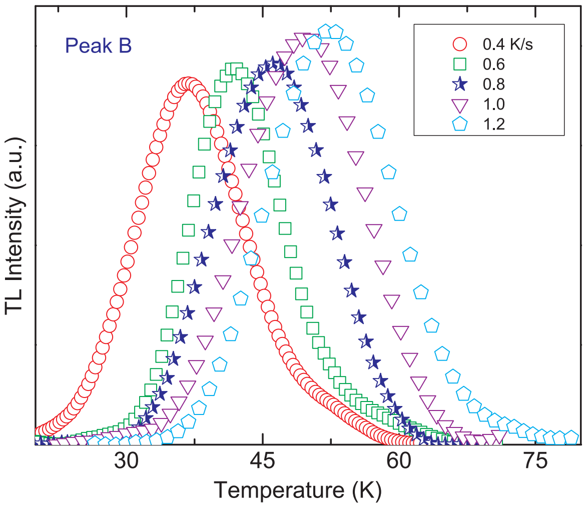

Fig. 5. Experimental TL peaks of TlInS$_2$:Pr crystals with various heating rates between 0.4 and 1.2 K/s after thermal cleaning.

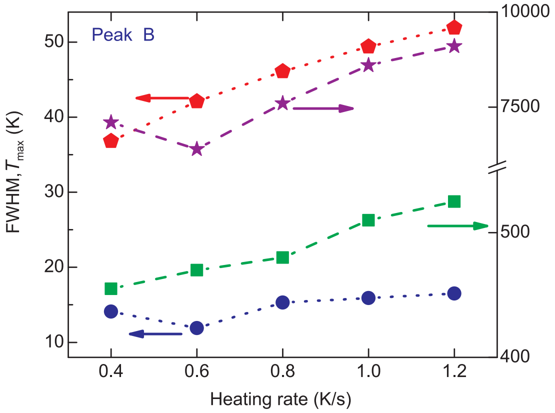

Fig. 6. The heating rates dependencies of the peak maximum temperature (T_{max}), FWHM, peak area and intensity for B peak after thermal cleaning.

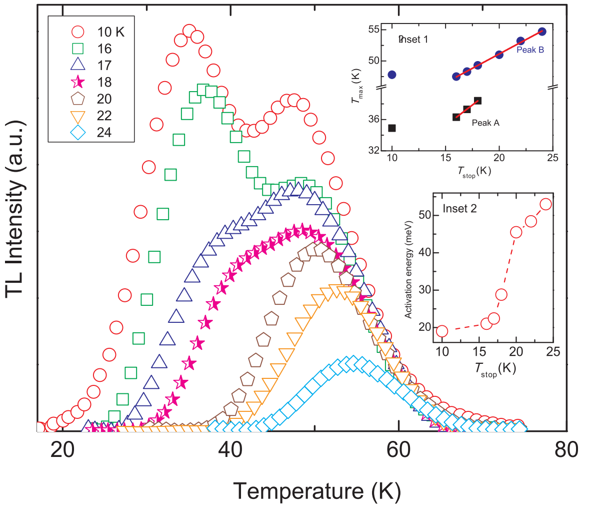

Fig. 7. The glow curves of $TlInS_2$:Pr crystals at different T_{stop} temperatures at heating rate β = 1.0 K/s. Inset 1: $T_{max} - T_{stop}$ plot for peaks A and B. Circles and squares are experimental data. Solid lines are the linear fits. Inset 2: Activation energy plot as a function of various T_{stop}.

$TlInS_2$:Pr crystals are single or quasi-continuously distributed within the band gap, thermal cleaning procedure for different T_{stop} values was applied. The details about the procedure was explained in previous section. Fig. 7 demonstrates the experimental TL curves detected for various T_{stop} values between 16 and 24 K for β = 1.0 K/s. TL curve at T_0 = 10 K was represented in the figure for comparison. As seen from the figure, as the higher T_{stop} was employed the ascending tails and T_{max} of the TL curves shift towards higher temperatures and TL intensities of both peaks deplete gradually with T_{stop}. These variations are the result of the emptied shallowest trapping levels in the revealed traps. Only deeper trapping levels contribute to the emitted luminescence due to higher T_{stop}. This provides possibility to have information about depth of traps. Up to 18 K, TL peaks A and B are exhibited together in the TL curves. The peak A depletes completely with T_{stop} = 20 K. After 24 K, peak B almost dies out so that further analysis cannot be achieved. Inset 1 of Fig. 7 shows $T_{max} - T_{stop}$ plot for $TlInS_2$:Pr crystals. This method is the most effective to explore the distribution of trap levels. McKeever [26] was previously investigated the various T_{max}—T_{stop} behaviors. According to study, if the T_{max} values of consecutive TL peaks show linearly increasing behavior with a slope of nearly 1.0, related trap levels are quasi-continuously distributed within the band gap. As can be seen from the inset 1, $T_{max} - T_{stop}$ dependencies of TL peaks A and B exhibit a linear enhancement behavior with slopes of 1.05 and 0.92, respectively. Therefore, quasi-continuous distribution characteristics was attributed for the trap levels associated with peaks A and B. Inset 2 of Fig. 7 depicts the activation energies of all sequential TL peaks as a function of increasing T_{stop}. The E_t values were calculated using initial rise method. As seen from the inset, activation energies increase from 19 to 53 meV. As stated above, peak A arises in the TL curves recorded up to T_{stop} = 18 K and completely cleaned for T_{stop} values higher than this value. Therefore, initial portions of the curves used for initial rise method are related with peaks A and B for T_{stop} values of 10-18 K and 20–24 K, respectively. This point implies that activation energies increase from 19 to 29 meV and from 45 to 53 meV for peaks A and B, respectively.

3.4. Effect of praseodymium doping

Doping is generally used to alter optical and electronic properties of host materials. It gives opportunities to reach intended physical properties if process is done carefully. However, doping can also lead to new formations lowering the efficiency of host materials. For defective host materials, doping can either result in formation of new defect centers or recovering of existing levels within the band gap. The former causes the TL spectrum to possess additional TL peaks and latter leads some TL peaks of undoped material to completely disappear or deplete in intensity since vacancies of host is filled by doping. In order to elucidate the influence of praseodymium doping on the existing defect states in $TlInS_2$ crystals, comparison of TL curves of undoped, Nd and Pr doped crystals was established as seen in Fig. 8. Figure displays the TL glow curves below room temperature of undoped and doped (Pr, Nd) crystals detected using same heating parameter (β = 0.6 K/s). TL peaks revealed for undoped crystal are also available in the TL spectrum of $TlInS_2$:Pr crystal in the same heating temperature region. However, intensities of TL peaks observed for undoped and Pr doped crystals exhibit differences. In the undoped crystal, intensity of peak B is higher than that of peak A whereas peak A has higher TL intensity than peak B in the Pr doped crystal. When intensities of TL peaks of $TlInS_2$:Pr are compared with that of undoped crystal, it can be easily understood that doping with Pr lowers the TL intensity of peak B rigorously while does not affect the TL intensity of peak A considerably. The decrease of TL intensity and/or disappearing of a TL peak after doping were also observed in some materials such Yb doped ZnO [27], Nd doped $TlInS_2$ [14]. By taking into account the results of similar studies reported previously, a tentative explanation can be suggested for the experienced behavior of TL peaks. In our previous study, TL responses of Nd doped $TlInS_2$ crystals was investigated [14]. TL intensity of peak A decreased substantially and peak B disappeared as crystal was doped with Nd (see Fig. 8). This result was attributed to recovering of defect centers reckoned as created due to indium vacancies in undoped $TlInS_2$ by inspiring from some reported studies. Thus, it is observed that Pr and Nd doping causes to decrease in TL intensity of the peak B by repairing some of indium vacancies. TL intensity and T_{max} values of peak A are not varied significantly with Pr doping. This states that peak A arises due to the native defects in $TlInS_2$ crystal.

4. Conclusion

TL characterization of $TlInS_2$:Pr single crystals was established by applying curve fitting and initial rise methods to experimentally observed glow curve presenting two overlapping peaks with T_{max} values of 35 and 48 K. Activation energies of corresponding trap levels were found to be 19 and 45 meV. Implementation of curve fitting indicated that mixed order of kinetics is responsible for trapping levels. Heating rate behaviors of trap levels were explored using different rates between 0.4 and 1.2 K/s. It was observed that peak A exhibits normal behavior in which TL intensity decreases with increasing heating rate. However, peak B presents unusual behavior called as anomalous heating rate effect in which TL intensity increases with heating rate. Moreover, distribution of trap levels was explored by $T_{max} - T_{stop}$

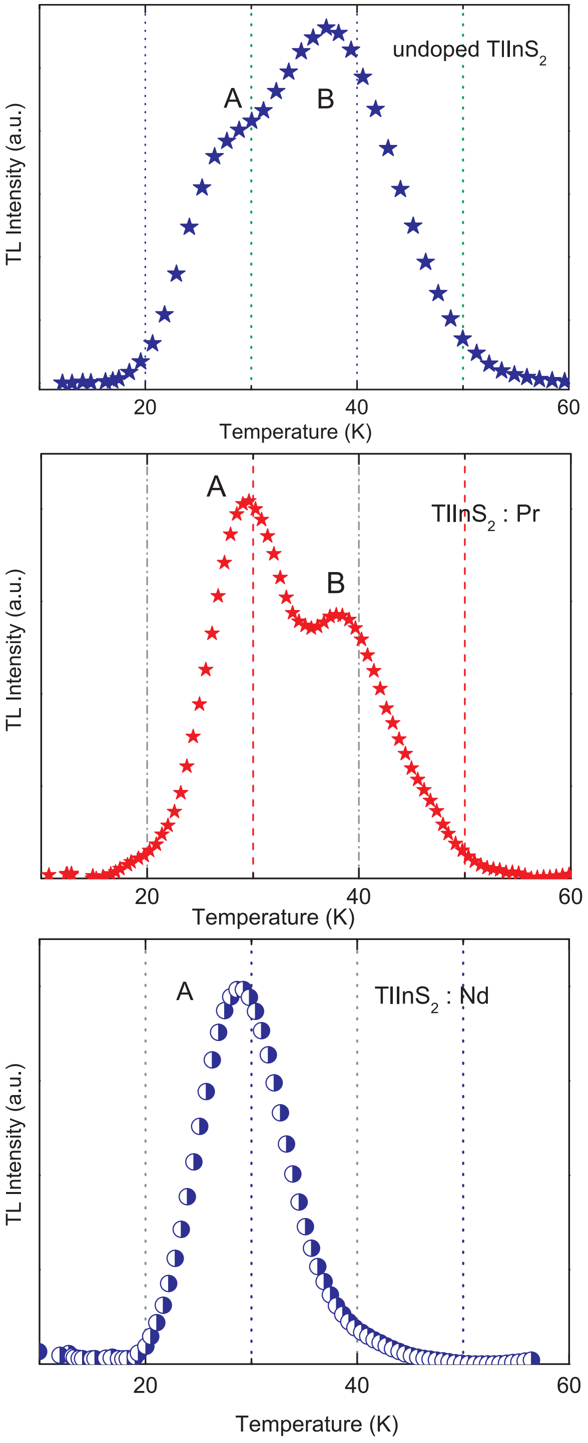

Fig. 8. Experimental TL glow curves of undoped and Pr doped $TlInS_2$ crystals observed with heating rate of $\beta = 0.6$ K/s. Experimental TL curve of $TlInS_2$:Nd crystals registered with heating rate of $\beta = 0.6$ K/s was taken from Ref. [14].

method. The trap levels were found to exhibit the characteristics of quasi-continuous distribution. Activation energies were obtained to be increasing from 19 to 29 meV and from 45 to 53 meV for peaks A and B, respectively. Doping effects on TL properties of $TlInS_2$ were investigated by comparing TL results of undoped and Pr doped $TlInS_2$ crystals. It was observed that doping decreased TL intensity of peak B drastically while did not affect peak A. Peak positions stayed nearly same with doping. This point indicates that doping of Pr does not form new trap levels in $TlInS_2$ crystals. The decrease in TL intensity of peak B was thought to be due to repairing of indium vacancies in the undoped $TlInS_2$.

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