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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

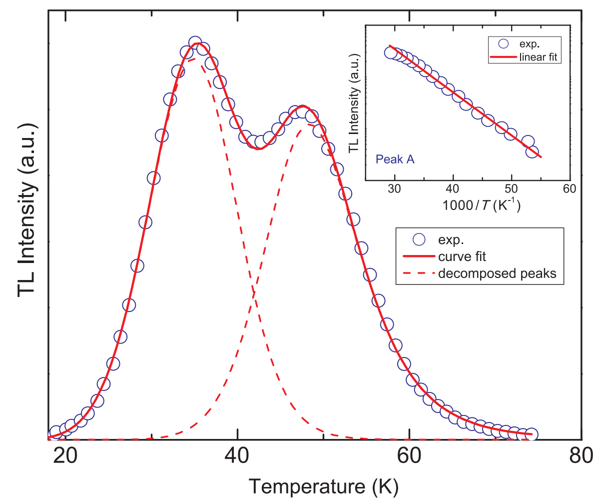

Fig. 1. Experimental TL spectrum (circles) of $TlInS_2$:Pr crystals for $\beta = 1.0$ K/s and decomposition of the curve into separate peaks (dash-dotted curves). Solid curve shows the total fit to the experimental curve. Inset: the plot for initial rise method application for peak A.

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. 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

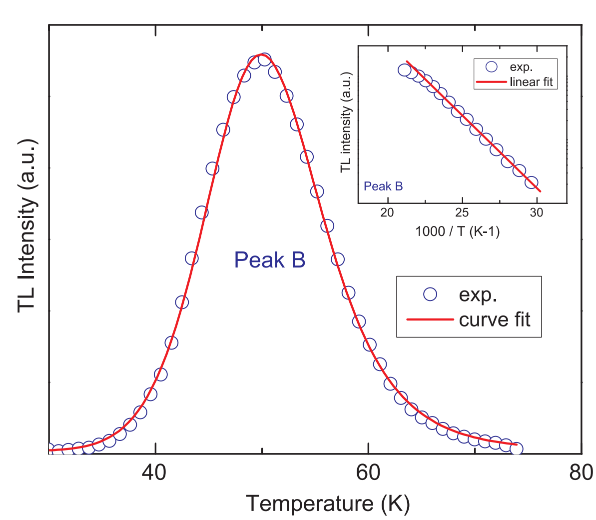

Fig. 2. Experimental (circles) TL curve (peak B) after thermal cleaning for $\beta = 1.0$ K/s. Inset: the plot for initial rise method application for peak B.