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EFFECT OF N DOPING ON $TL_2GA_2S_3SE$ SINGLE CRYSTALS: THERMOLUMINESCENCE CHARACTERIZATION OF DEFECT CENTERS

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ABSTRACT

Thermoluminescence study on nitrogen doped $Tl_2Ga_2S_3Se$ single crystals was achieved by performing the experiments with different stopping temperatures of 10−24 K and various heating rates between 0.4 and 1.2 K/s below room temperature. Thermoluminescence peak with peak maximum temperature of 54 K was detected from the emitted luminescence. Two trap levels were obtained from the observed spectra. Curve fitting and initial rise methods were applied to compute the activation energies and the values of 34 ± 2 and 70 ± 4 meV were found. Thermal cleaning process was applied to separate the overlapping peaks and so true energy region of trapping levels was corroborated. Moreover, variations of shape and position of TL curve were studied by investigating the heating rate behavior of trap levels. The best known behavior which the peak maximum temperature increases while the thermoluminescence intensity decreases with raising heating rate was observed. The effect of the N doping on the existed defects was discussed.

Keywords: Thermoluminescence, Defects, N doping

1. INTRODUCTION

Thallium based ternary and quaternary chalcogenides have been paid considerable attention since they are applicable to devices used in semiconductor technology. Their structural, electrical and optical properties have recently been studied many times as reported in Refs. [1-8]. In the visible range of the spectrum they show high photosensitivity and have wide transparency range between 0.5−14.0 μm which makes them useful for device applications [7]. Some of the implementation areas of these materials are memory switching elements, nonlinear optical transducers, emission modulators and optoelectronics [9, 10]. The quaternary $Tl_2Ga_2S_3Se$ exhibits the properties of semiconductor groups and possesses layered structure. It can be easily obtained from the ternary $TlGaS_2$ by replacing a quarter of sulfur with a same quantity of selenium [11, 12]. The inter- and intra-layer bonds occur between the Tl and S (Se), and between Ga and S (Se) elements, respectively.

Optical and electrical properties of $Tl_2Ga_2S_3Se$ single crystals were previously investigated by different experimental techniques. Transmission and reflection measurements of $Tl_2Ga_2S_3Se$ crystals performed in the photon energy range of 1.1−3.1 eV at room temperature resulted with the existence of indirect and direct band gap transitions with energies of 2.38 and 2.62 eV, respectively [13]. Photoluminescence (PL) studies were accomplished under room temperature (10−60 K) [14]. One PL band having maximum at 550 nm (2.25 eV) was obtained when the measurement was carried out at 10 K. Analysis of the PL band revealed the existences of one shallow donor level with energy E_d = 10 meV and one deep acceptor level with energy E_a = 160 meV. Thermally stimulated current (TSC) investigations were also achieved in the temperature ranges of 10−320 K [15,16]. Two trap levels with activation energies of 11 and 498 meV were established from the analysis of TSC spectra. Lately, thermoluminescence (TL) measurements of undoped $Tl_2Ga_2S_3Se$ crystals was carried out in the temperatures ranging from 10 to 300 K [17]. TL study on undoped $Tl_2Ga_2S_3Se$ found out the presence of quasi-continuous trap centers with activation energies ranging from 16 to 58 meV.

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Defects and/or impurities are significant phenomena for semiconductor materials due to their detrimental effects on the optical and electrical efficiencies. Existences of them in the materials can give rise to decrease of the performance of the devices. For instance, they can behave as recombination center which reduces the internal quantum efficiency. Moreover, they may become scattering center in the materials. Thus, carrier mobility can diminish so that high frequency operation can be impossible. Therefore, exploration of such formations is very important to get knowledge about the materials.

In the present study, we have carried out for the first time the TL experiments for nitrogen doped $Tl_2Ga_2S_3Se$ in the temperature range of 10−300 K with various heating rate (β) between 0.4 and 1.2 K/s. The obtained TL peaks have been analyzed utilizing different TL analysis methods and activation energies (E_t) of associated trap levels have been reported. Heating rate dependency of the TL curve has been elucidated. Effect of N doping on the defects has been investigated.

2. EXPERIMENTAL

$Tl_2Ga_2S_3Se$ polycrystals were synthesized from high-purity elements (at least 99.999%) prepared in stoichiometric proportions. Single crystals of $Tl_2Ga_2S_3Se$ were grown by the Bridgman method in evacuated (10^{-5} Torr) silica tubes (10 mm in diameter and about 25 cm in length) with a tip at the bottom in our crystal growth laboratory. The ampoule was moved in a vertical furnace through a thermal gradient of 30 °C/cm at a rate of 1.0 mm/h. The resulting ingots showed good optical quality. Nitrogen ion beam of 120 keV with dose of 1×10^{16} ions/cm^2 was bombarded to the sample surface which is parallel to the layers. Annealing at 300 °C was achieved in an argon medium for 45 minutes in order for elimination of bombardment damage.

Thermoluminescence experiments were performed with a setup built in the laboratory. The measurement system was assembled around a closed cycle helium cryostat (Advanced Research Systems, Model CSW 202) which have capability of controlling the temperature between 10 and 300 K. Environment of the sample was kept with the intended temperature by employing a temperature controller (Lakeshore Model 331). The device can control the temperature of sample up to 300 K and can ramp the temperature linearly at a maximum rate of 1.2 K/s. In our experiment, the temperature of the sample was decreased to T_0 = 10 K and illumination was accomplished for 600 sec at this temperature. After an expectation time (120 sec) the sample was heated up to 300 K. Thermally emitted luminescence from the sample was compiled by a light tight measurement chamber that has a photomultiplier (PM) tube (Hamamatsu R928, spectral response: 185−900 nm), a blue LED (~470 nm) and some optic elements focusing the luminescence to PM tube. These optics were attached to the optical access port of the cryostat with quartz window. The pulses from the PM tube were converted into transistor-transistor logic pulses (0−5 V) using a fast amplifier/discriminator (Hamamatsu Photon Counting Unit C3866) and counted using the counter of a data acquisition module (National Instruments, NI 6211). All of the measurement setup was managed with a central system by improving a software written in LabView (National Instruments).

3. RESULTS AND DISCUSSIONS

The thermally emitted luminescence from the defect centers in $Tl_2Ga_2S_3Se$:N single crystals were detected by heating the sample with a constant rate of β = 1.0 K/s in the temperatures between 10 and 300 K and one TL peak possessing maximum intensity at 54 K was observed in the temperature range of 10−90 K as illustrated in Figure 1. No peak was recorded beyond 90 K. Thus, the whole spectrum was not shown in the figure. As seen from the experimental TL curve in Figure 1 (circles), there is an indistinct bulge on the descendent part of the TL curve around 59 K. Therefore, it was taken into consideration that there may be more than one individual TL peak in the obtained TL curve. In order to confirm this consideration, we applied the peak shape (PS) method developed by Chen and Kirsh [18]. The PS method is used to determine the geometry factor (μ_g) which may supply important information

about the existence of more than one TL peak. The μ_g value is calculated by employing the following relations, $\delta = T_h - T_{max}$, $w = T_h - T_l$ and $\mu_g = \delta / w$. Here, T_{max} is the peak maximum temperature, T_l and T_h are the low and high temperature sides of the TL peak that are associated with the half of the peak maximum intensity. According to Chen and Kirsh [18], the μ_g value must take values between 0.42 and 0.52 related with first and second order kinetics, respectively. The μ_g value of observed TL curve was found as 0.55 ± 0.01. This is an indication showing that TL curve is composed of more than one individual TL peak. Then, we implemented curve fitting (CF) method to experimentally obtained TL curve by taking account the presence of deconvoluted TL peaks using the following TL equation responsible for the non-first order kinetic.

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

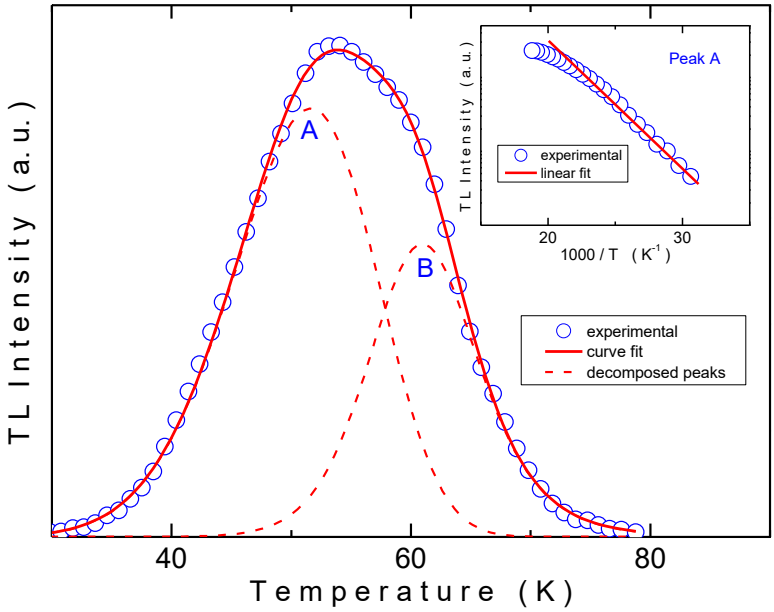

Figure 1. Experimental TL curve of $Tl_2Ga_2S_3Se$:N crystals detected with β = 1.0 K/s. Circles show the experimental data. Solid and dashed lines present the curve fit and deconvoluted peaks, respectively. Inset: Application of initial rise method. Circles and solid line depict the experimental data and linear fit, respectively.

Here n_o is the initial concentration of trapped charge carriers, T_0 is the beginning temperature, k is Boltzmann constant and b is the order of kinetics. The parameter b takes the value between 1.0 and 2.0 which correspond to negligible and non-negligible retrapping, respectively [18]. As seen from Figure 1, experimentally observed TL curve was best fitted (solid curve) as the CF method was applied with kinetic parameters b_A = 1.1 ± 0.1 and b_B = 1.8 ± 0.1. Therefore, existences of two overlapping TL peaks with T_{maxA} = 52 and T_{maxB} = 61 K under the observed TL curve were substantiated. The decomposed overlapping peaks (Peaks A and B) can be easily seen from the figure. The found kinetic parameters showed the mixed order of kinetics was responsible for the trapping process of the charge carriers. Also, implementation of CF method gave the thermal activation energies of trapping levels corresponding to peaks A and B as E_{tA} = 34 ± 2 and E_{tB} = 72 ± 4 meV.

The other analysis technique practical to calculate the activation energy regardless of kinetic order of the trapped charge carriers is known as initial rise (IR) method [19]. As reported by this method, the number of released charge carriers from trap levels inconsiderably changes at the initial part of the

raising tail of the TL peak as the heating process is started. Therefore, initial concentration can be thought as constant and the TL equation giving TL intensity reduces to simple form as $I_{TL}(T) \approx A\exp(-E_t/kT)$. Under this estimation, logarithmic plot of TL intensity as a function of reciprocal of temperature achieves straight line with a slope of $-E_t / k$. A plot for TL peak A of $Tl_2Ga_2S_3Se$:N crystal in accordance with IR method was shown in the inset of Figure 1. Implementation of IR method to observed TL curve established the activation energy of trap level related to peak A as 34 ± 2 meV. This value is consistent with the value found from CF method. Since the initial part of the TL curve is responsible for the peak A, the IR method cannot be applied to peak B.

Thermally cleaning procedure is known as the easiest and the most suitable way to find out the TL emission contributions of charge carriers trapped by overlapped individual energy levels. One can separate the overlapping peaks by performing this process and thus can almost characterize the true region of occupied trap centers individually. For this purpose, some consecutive experiments were carried out for different stopping temperatures (T_{stop}). To be clear, the temperature was decreased to T_{stop} value and was kept constant for a while to bring the temperature of the environment at this value. The sample was exposed to blue LED for 600 sec. at T_{stop}. By this way, the shallowest traps, which had capacity to capture the charge carriers as the sample was illuminated at T_0 =10 K, were deactivated and deeper trap levels were allowed to be occupied by charge carriers. Then, the sample cooled down to T_0 and heated up to 300 K without additional excitation so that the TL emission was released due to the deeper levels. Sequential measurements were achieved for different T_{stop} values between 10 and 24 K. Figure 2 depicts the TL curves obtained with a constant heating rate of 1.0 K/s after applying the thermally cleaning process. As seen from the figure, TL intensity and area enclosed under the TL curves decrease, T_{max} and ascendant part of the TL curves shift to higher temperatures and the shape of the TL curve changes with increasing T_{stop} values. These behaviors are result of the emptied shallowest trap levels by using different T_{stop} ranging from 10 to 24 K. Inset of Figure 2 shows the activation energy plot as a function of different T_{stop} values. The activation energies were found by applying the IR method to successively observed TL curves. Employing T_{stop} = 16 K did not affect the TL curve so much that thermal activation energy was nearly same with the value obtained from TL curve at T_0 = 10 K. After T_{stop} = 16 K, the activation energy increased with elevating stopping temperature as seen in the inset of Figure 2. To clarify which curve is responsible for the peak B obtained from CF method (see Figure 1), the geometry factor values of each observed TL curve were calculated. The values were bigger than 0.52 for TL curves at T_{stop} = 16 and 18 K. Therefore, it can be thought for these T_{stop} values that contribution to TL emission comes from both of the trap centers. However, the μ_g values of TL curves at T_{stop} = 20, 22 and 24 K were found nearly as 0.50 ± 0.01 that implies the general order of kinetics is exhibited by trap levels. This is a significant indication of that trap level corresponding to peak A was completely emptied and the charge carriers were trapped by energy level related to peak B. In order to corroborate this point, the TL curve observed at T_{stop} = 20 K was taken into account in detail. CF and IR methods were implemented to the TL peak as shown from the Figure 3. CF achieved the best fit with the kinetic parameter b = 1.9 ± 0.1. The T_{max} of the fitted curve is 60 K. The activation energy was obtained as 70 ± 4 meV by CF method. IR method was applicable for the TL peak B after thermally cleaning procedure. The E_{tB} was found to be 69 ± 4 meV using this method (see inset of Figure 3). Thanks to these close values of E_{tB}, T_{maxB} and b found out before and after thermal cleaning, the TL curve recorded for T_{stop} = 20 K was ascribed to existence of a second trap level associated with peak B.

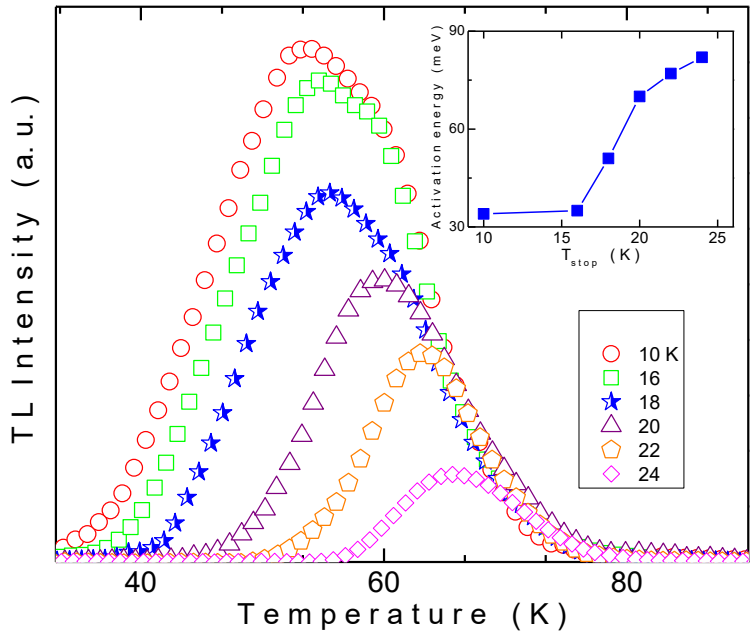

Figure 2. Experimental TL curves of $Tl_2Ga_2S_3Se$:N crystals obtained with β = 1.0 K/s at different T_{stop}. Inset: E_t vs T_{stop} graph. Blue squares show the calculated activation energies. Solid line is the guide for the eye.

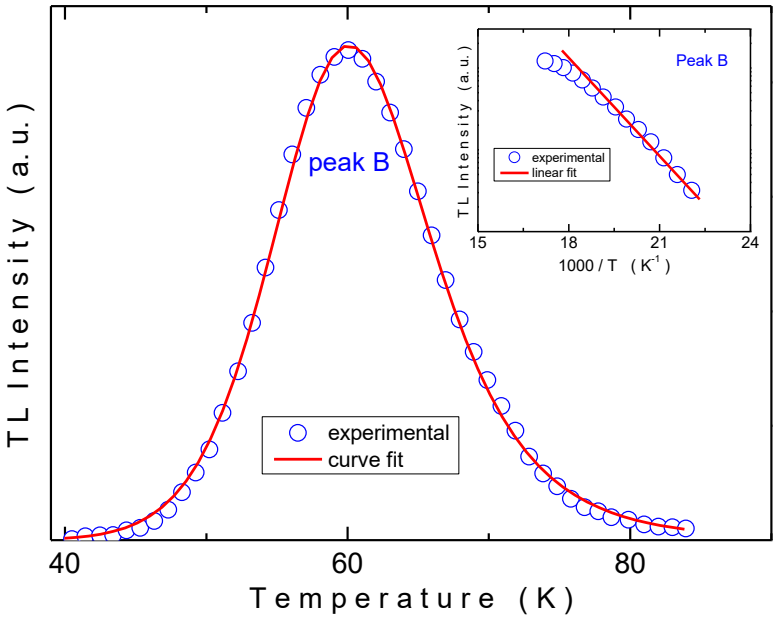

Figure 3. Experimental TL curve of $Tl_2Ga_2S_3Se$:N crystals obtained with β = 1.0 K/s at T_{stop} = 20 K. Circles and solid line represent the experimental data and curve fit, respectively. Inset: Ln(I_{TL}) vs 1000/T graph. Circles and solid line depict the experimental data and linear fit, respectively.

At this point, comparison of revealed energy values of 34 ± 2 and 70 ± 4 meV for N doped $Tl_2Ga_2S_3Se$ crystals with the value reported in our previous TL study for undoped $Tl_2Ga_2S_3Se$ [17] was focused to elucidate the origin of defects. The energy level of 34 ± 2 meV can be considered as in the energy region distributing between 16 and 58 meV which was previously demonstrated for undoped crystal [17]. Therefore, this level may be thought as a native defect existed already in the undoped crystal. The trap

level with activation energy of 70 ± 4 meV obtained in $Tl_2Ga_2S_3Se$:N was not previously observed in the undoped crystal. As a result, this energy level can be thought to arise from the N atom doping.

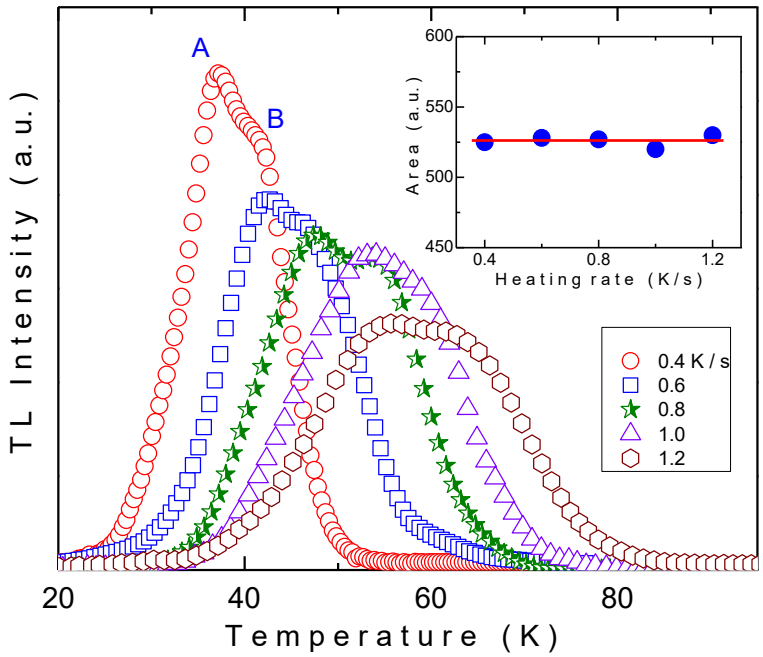

Figure 4. Experimental TL curves of $Tl_2Ga_2S_3Se$:N crystals observed with various β between 0.4 and 1.2 K/s. Inset: Areas under the TL curves as a function of heating rate. Blue circles are experimental data. The solid line is the average variation of area with heating rate.

In order to comprehend the thermal excitation mechanism of trapping levels, the response of these levels to variation of heating rates was investigated. As stated in TL theory, alteration of heating rates brings about the TL curves to change of position and shape. Figure 4 indicates the detected TL curves with various heating rates ranging from 0.4 to 1.2 K/s. As understood from the figure, the T_{max} values shift towards higher temperatures with the increment of heating rates. This behavior was previously explained by Anishia et al. [20]. Stimulation of trapped charge carriers with a lower rate β_1 leads to the carriers to occupy trap levels much more time at temperature T_1. The occupancy of trap levels by charge carriers stimulated with β_2 will take less at this temperature. As a result of this, concentration of charge carriers excited into conduction band with β_2 at T_1 decreases as compared with β_1. Higher temperature T_2 ($T_2 > T_1$) is required for excitation of same amount of charge carriers with β_2. Therefore, the T_{max} of the TL curve shifts to higher values. Another variation with increasing heating rate is in the TL intensity. As seen from the figure, TL intensity of the TL curve decreases with raising β values. Such a decrease in TL intensity is the best known behavior in TL theory [19]. Inset of Figure 4 shows the variation of area (S_0) enclosed under glow curves with rising heating rate. Since each measurement was performed with the same experimental conditions, concentration of trapped charge carriers was kept constant so that the S_0 values were nearly same. Figure 5 illustrates the heating rate dependencies of T_{max} and TL intensity values of successively observed TL peaks. All given TL parameters were obtained after decomposing the TL curves using CF method. As understood from the figure, the T_{maxA} and T_{maxB} increases from 36 to 54 K and from 43 to 64 K, respectively, with increasing heating rate. Also the intensities of TL peaks A and B diminish from 39 to 20 (a. u.) and from 34 to 17 (a.u.), respectively, with elevating heating rate.

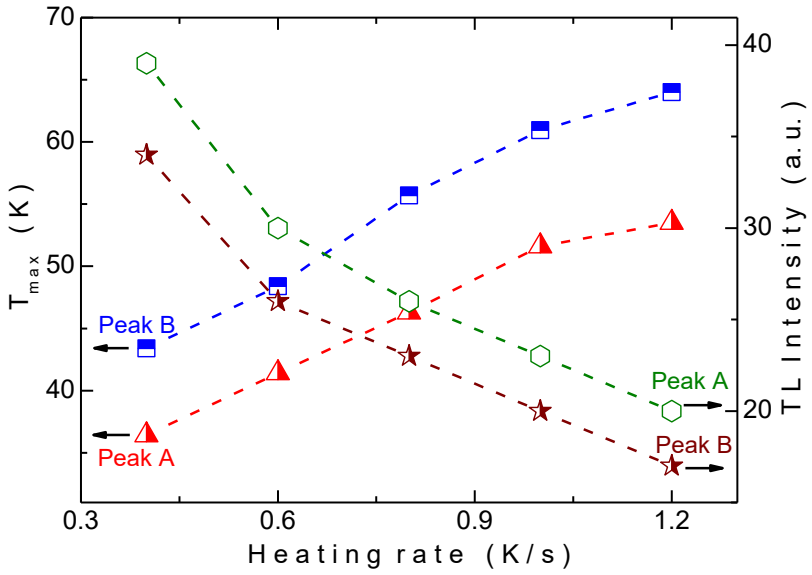

Figure 5. The heating rate dependencies of the peak maximum temperatures and the TL intensities of peaks A and B. The dashed lines are the guides for the eye.

4. CONCLUSIONS

Thermoluminescence characterization of defect levels existed in N doped $Tl_2Ga_2S_3Se$ crystals was accomplished for different stopping temperatures between 10 and 24 K and for various heating rates ranging from 0.4 to 1.2 K/s. Thermally cleaning procedure was successful to separate the overlapping peaks A and B. Activation energies of corresponding trap levels were found to be 34 ± 2 and 70 ± 4 meV using CF and IR methods. The kinetic parameters b_A = 1.1 ± 0.1 and b_B = 1.8 ± 0.1 indicate that the general order of kinetics dominates the trapping process. Heating rate dependency of the traps was also investigated and increase of T_{max} values from 36 to 54 K and from 43 to 64 K, and the decrease of TL intensities from 39 to 20 (a. u.) and from 34 to 17 (a.u.) for peaks A and B, respectively, were obtained with elevating heating rate. The trap level with E_{tA} =34 ± 2 meV was attributed to native defect that has already been observed in undoped $Tl_2Ga_2S_3Se$. However, the energy level of 70 ± 4 meV was asserted to be found due to N doping.

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