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Thermoluminescence in gallium sesquisulfide single crystals: usual and unusual heating rate dependencies

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ABSTRACT

Thermoluminescence (TL) experiments were conducted for Ga_2S_3 crystals to obtain information about trapping parameters. TL measurements were performed from 10 to 300 K with varying heating rates in the range of 0.2–0.8 K/s. Two TL glow peaks centered at 44 K (peak A) and 91 K (peak B) were observed at heating rate of $\beta = 0.5$ K/s. For peak A, TL intensity decreased whereas that for peak B increased with elevating the heating rates that means anomalous heating rate occurred for peak B. TL glow curves were analyzed using initial rise method to find activation energies of traps. Distribution of trap centers was investigated using $T_{max} - T_{stop}$ method. Quasi-continuous distributions with increasing activation energies from 40 to 135 meV and 193 to 460 meV were attributed to trap centers A and B, respectively.

1. Introduction

Ga_2S_3 crystals belong to the group III-VI compounds which are promising materials for the applications in optoelectronic devices. The characterization of Ga_2S_3 material were previously performed to search its potential and effectiveness in heterojunction [1,2] and thin film devices [3], solar energy [4], UV photodetection and oxygen sensing [5] applications. Ga_2S_3 crystals have direct band gap energy of 3.44 eV at 10 K temperature [6]. Ga_2S_3 crystals belong to the monoclinic structure with the lattice parameters of $a = 1.114$, $b = 0.641$ and $c = 0.703$ nm, and $\beta = 121.22°$. It was found that Ga_2S_3 crystal cells contained four molecules and sulfur atoms must be nearly hexagonally close-packed in layers perpendicular to the c axis [7].

The structural, optical and electrical characterization of Ga_2S_3 crystals was carried out using thermoreflectance, Raman, photoluminescence, optical-absorption, and photo voltage-current measurements [5]. Photo voltage–current measurements of the Ga_2S_3 sample under different illumination conditions of dark, halogen light, and 405 nm lasers showed that the crystal is a highly-sensitive photoconductive material available for blue to ultraviolet photodetection [5]. The wide and direct band gap semiconducting Ga_2S_3 is promising material for light emitting device applications. Photoluminescence properties of Ga_2S_3 were investigated to get information on its emission characteristics. In the PL spectra of undoped crystals at 96 K, green emission peak at 520 nm and a broad red band ranging from about 590 to 826 nm with slight peaks at 629 and

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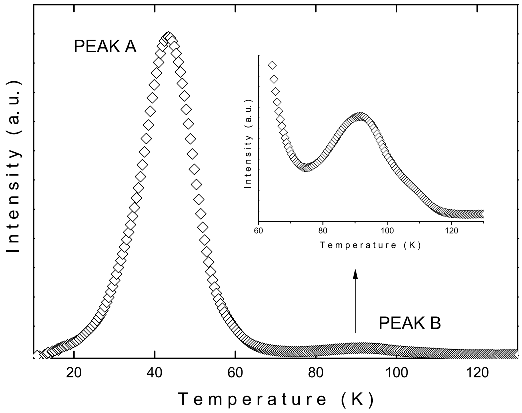

Fig. 1. TL glow curve of Ga_2S_3 crystal at heating rate of β = 0.5 K/s.

725 nm were observed [8]. PL spectra of Ag, Cu and Ge doped Ga_2S_3 crystals presented emission peaks at 496, 514 and 590 nm, respectively, at 94 K [9]. In another paper, PL properties of Ga_2S_3 and Ga_2S_3:Fe single crystals were studied [6]. The measurements performed at 10 K resulted in PL spectra exhibiting blue and red emissions at 424 and 643 nm, respectively, for Ga_2S_3 and the violent and yellow emissions at 424 and 643 nm, respectively, for $Ga_2S_3:Fe^{2+}$ single crystals. Authors proposed energy level schemes showing donor, acceptor levels and possible transitions for both crystals.

Defects are important phenomena in order to study the electrical and optical behavior of semiconductor and insulator materials. Their influence can be critical for the performance of the devices produced in the semiconductor industrial areas like optoelectronics. For example, in lasers, defects may display behaviors as though they are tunneling and non-radiative recombination channels lowering the internal quantum efficiency, depending on defect density. In the case of electronic devices, defects introduce scattering centers lowering carrier mobility. Therefore, it is useful to get information on parameters of trapping centers in semiconductors in order to obtain high-quality devices. Thermally stimulated luminescence (TL) is one of the nondestructive techniques among the several experimental methods to get information about the properties of trapping centers [10]. In the present study, we focused on trapping centers and their distribution in Ga_2S_3 crystal using TL experiments in the temperature range of 10–300 K and in the different heating rates range of 0.2–0.8 K/s. The results of present paper would provide valuable knowledge especially for researchers studying on device characterization and emission properties of Ga_2S_3.

2. Experimental details

Ga_2S_3 crystals were synthesized using high-purity elements (at least 99.999%) taken in stoichiometric proportions. Single crystals of Ga_2S_3 were grown by Bridgman method. The samples were light-yellow in color. For TL measurements, the samples with surface area $1.2 \times 0.6\,cm^2$ and thickness 0.4 cm were used. The crystals show p-type behavior which is determined by hot-probe technique. The samples were cooled from 300 to 10 K using an Advanced Research Systems Model CSW 202 closed-cycle helium cryostat. Temperature was controlled using a Lakeshore Model 331 temperature controller. The sample was illuminated by an Ocean Optics D-2000 UV light source that offers stable, continuous output from 215 to 400 nm. The energy of light source is greater than band gap energy of the samples so the charge carriers can easily be excited by this source. After illumination, light source was turned off and sample was waited for 2 min in dark. Then, crystal was heated with constant heating rate. While temperature is increased, the emitted light was collected by a Hamamatsu Model R928 photomultiplier tube and collecting lenses. The pulses from the photomultiplier tube (working in photon counting regime) were converted to TTL logic pulses (0–5 V) using a fast amplifier/discriminator (Hamamatsu Photon Counting Unit C3866) and recorded using the counter of a data acquisition module (National Instruments, NI 6211). The whole measurement set-up was controlled using a LabView (National Instruments) graphical development program.

3. Results and discussion

Fig. 1 shows TL glow curve in the temperature range of 15–130 K at the heating rate of β = 0.5 K/s. Although TL experiments were accomplished from 10 to 300 K, only spectra in the temperature range of 15–130 K is shown in Fig. 1, since no additional TL peaks were observed above 130 K. Two TL peaks, namely peaks A and B, centered at 44 and 91 K, respectively, were observed in the glow curve. Generally, the trapping centers present two different characteristics of either single energy level or quasi-continuously distributed within the band gap. McKeever investigated the behaviors of TL glow curves for these two characteristics [11]. The experimental method called as $T_{max} - T_{stop}$ was applied to understand either traps are single or quasi-continuously distributed. In this method, the sample is kept at temperature of T_{stop} and illuminated at that temperature. Then, sample is cooled to low temperature (T_0) and without any additional illumination, it is heated up with a

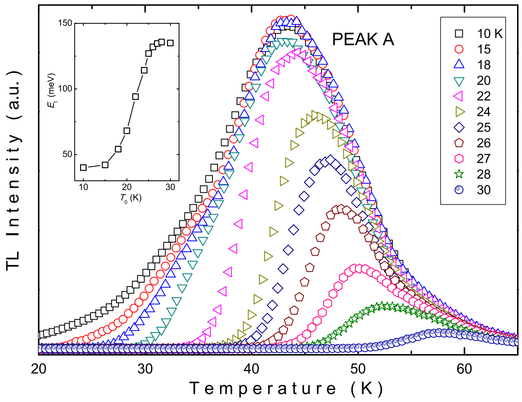

Fig. 2. TL glow curve of Ga_2S_3 crystal (peak A) with various illumination temperatures (T_{stop}). Inset: The variation of activation energy (E_t) values with T_{stop} for peak A.

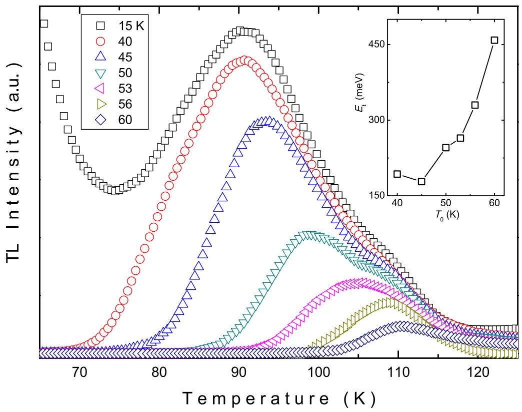

Fig. 3. TL glow curve of Ga_2S_3 crystal (peak B) with various illumination temperatures (T_{stop}). Inset: The variation of activation energy (E_t) values with T_{stop} for peak B.

constant heating rate up to room temperature [12]. This step is repeated with changing just illumination temperature. Since T_{stop} is greater than T_0, trapped charge concentration decreases due to release of some trapped charges. In this work, T_{stop} was changed from 10 to 60 K, sample was illuminated for 5 min and then cooled to initial temperature $T_0 = 10$ K. After that, sample was heated up with a constant heating rate of $\beta = 0.5$ K/s up to room temperature. Observed glow curves for each T_{stop} are responsible for remaining trapped charge carriers in defect centers. Figs. 2 and 3 show the variation of glow curves with different T_{stop} values for peaks A and B, respectively. As seen from the figures, TL intensity decreases and T_m values shifts to higher temperatures with increase of T_{stop}. This behavior is indication of that traps are distributed quasi-continuously within the band gap [11].

For each TL curve for different T_{stop} values, initial rise method was used to find activation energies (E_t) of traps. According to this method, TL intensity is proportional to exp ($-E_t/kT$) when the trapped charge carriers started to excite with the help of increasing temperature. In this way, the activation energies of obtained traps can be evaluated from the logarithmic plot of TL intensity as a function of $1/T$ giving a straight line with a slope of ($-E_t/k$). Using this method, thermal activation energies were calculated. Thermal activation energies increased from 40 to 135 meV by increasing T_{stop} values from 10 to 30 K for peak A as seen in inset of Fig. 2 and from 193 to 460 meV by increasing T_{stop} values from 40 to 60 K for peak B as shown in inset of Fig. 3. The increase of the activation energies with the increase of T_{stop} values is consistent with the gradual emptying of shallowest trapping levels during each preheating treatment [10,12,13].

Activation energies of trapping centers can be used to find the attempt-to-escape frequency (ν) and capture cross section (S_t) using the following equations;

$$\nu = \frac{\beta E_t}{kT_m^2} \exp\left(\frac{E_t}{kT_m}\right) \text{ and } S_t = \frac{\nu}{N_\nu \upsilon_{th}}. \tag{1}$$

where $N_v = 2\,(2\pi\, m_p^*\, kT/h^2)^{3/2}$ is the effective density of states in the valence band and ν_{th} is the thermal velocity of a free hole. The capture cross section (S_t) was calculated using effective mass for holes as $m_p^* = 5.3 \times 10^{-32}$ kg [14]. The ν and S_t were found as $8.41 \times 10^3\ s^{-1}$, $6.78 \times 10^9\ s^{-1}$ and $2.09 \times 10^{-18}\ cm^2$, $4.77 \times 10^{-19}\ cm^2$ for centers A and B, respectively.

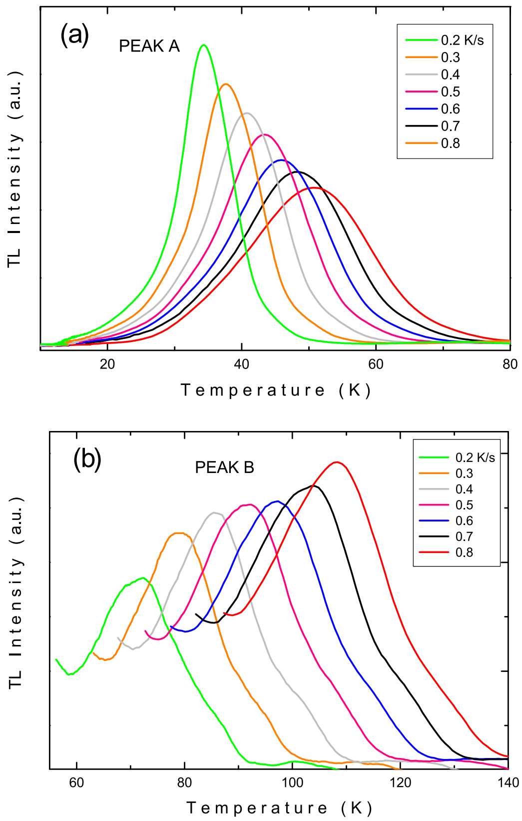

Fig. 4. TL glow curves of Ga_2S_3 crystal with various heating rates for (a) peak A, (b) peak B.

TL measurements were also expanded by recording TL curves for various heating rates in 0.2–0.8 K/s range. Fig. 4(a) and (b) shows the variation of TL glow curves for peaks A and B, respectively, with various heating rates. As seen from the figures, peak maximum temperatures of both peaks shift to higher values as expected according to theoretical approach. However, TL intensity-heating rate dependencies of peaks differ. TL intensity of peak A decreases whereas that of peak B increases with elevating heating rates. The behavior of peak A is normal according to one trap-one recombination model [12]. However, peak B does not show an expected behavior. This unexpected behavior is called as anomalous heating rate effect in which the intensity of TL glow curve increases with the increase of heating rate. The anomalous heating rate can be explained by semi-localized transition model [15,16]. According to this model, an additional non-radiative transition is considered from the localized excited state to a recombination center [16,17]. TL glow curve can be generated by the localized transitions from the excited state into the recombination center and the delocalized transitions from the conduction band into the center [17]. Possibility of non-radiative transitions at low temperatures is higher and while heating rate increases, possibility of transitions from the localized excited state into the conduction band increases. Since the non-radiative transition does not depend on temperature, the probability of radiative recombination increases as the temperature increases, resulting in a higher TL peak at high heating rates. However, there are also different explanations to the anomalous heating rate effect [18–20]. In two-stage model, it is similar to semi-localized transition model, but it was only paid attention to recombination of electrons going through the conduction band [18]. In Schön – Klasens model, one electron trap and one recombination with one reservoir as two centers define the normal and anomalous heating rate effects [20]. Moreover, we determined the dependencies of the peak maximum temperatures (T_m), full-width-half-maximum (FWHM) values and TL intensities on various heating rates for peaks A and B as seen in Fig. 5. For peaks A and B, FWHM values and T_m values increased with the increase of heating rates, however for peak A intensity decreased. For peak B intensity increased with the increase of the heating rates that means anomalous heating rate occurs for peak B.

4. Conclusion

The Ga_2S_3 crystals were studied by means of TL measurements. Two TL glow peaks centered at 44 K (peak A) and 91 K (peak B) at heating rate of β = 0.5 K/s were observed. TL measurements were conducted from 10 to 300 K with varying heating rates from 0.2 to 0.8 K/s. For peak A, TL intensity decreased whereas that for peak B TL intensity increased with the elevating the heating rates that means anomalous heating rate occurred for this peak. TL measurements were conducted with changing illumination temperature T_{stop} from 10 to 60 K. For both peaks, TL intensity values decrease and T_m values shift to higher

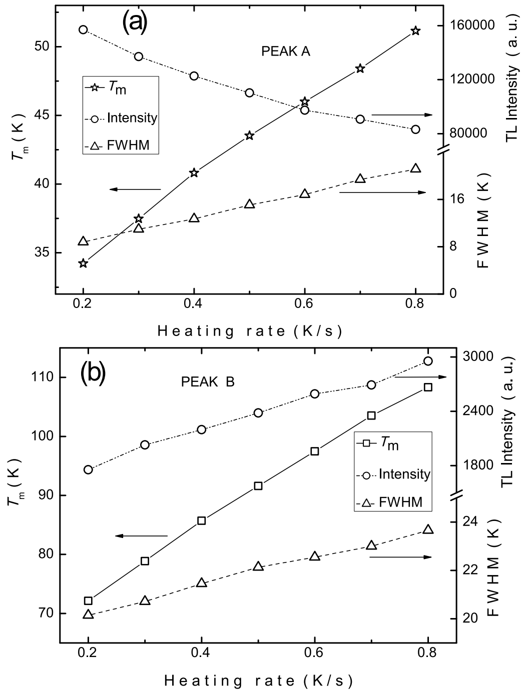

Fig. 5. Heating rate dependencies of peak maximum temperature (T_m), full-width-half-maximum (FWHM) and thermoluminescene (TL) intensity for (a) peak A, (b) peak B.

temperatures with increased of T_{stop}, that means traps were distributed quasi-continuously. For each TL curve for different T_{stop} values, initial rise method was used to find activation energies of traps. Thermal activation energies increased from 40 to 135 meV by increasing T_{stop} values from 10 to 30 K for peak A and those for peak B increased from 193 to 460 meV by elevating T_{stop} values from 40 to 60 K. The increase of the activation energies with the increase of T_{stop} values is consistent with the gradual emptying of shallowest trapping levels during each preheating treatment. Moreover, attempt-to-escape frequencies and capture cross sections for peaks A and B were calculated.

References

[1] S.E. Al Garni, A.F. Qasrawi, Design and characterization of the Ge/Ga_2S_3 heterojunction, J. Electron. Mater. 46 (2017) 4848–4856.
[2] M.Z. Kovalyuk, V.I. Vitkovskaya, M.V. Tovarnitskii, *p*-GaSe-*n*-Ga_2S_3 heterojunctions, Tech. Phys. Lett. 23 (1997), 385-385.
[3] S.R. Alharbi, A.F. Qasrawi, Effect of ytterbium, gold and aluminum transparent metallic substrates on the performance of the Ga_2S_3 thin film devices, Curr. Appl. Phys. 17 (2017) 835–841.
[4] M. Zervos, A. Othonos, V. Gianneta, A. Travlos, A.G. Nassiopoulou, Sn doped β-Ga_2O_3 and β-Ga_2S_3 nanowires with red amission for solar energy spectral shifting, J. Appl. Phys. 118 (2015) 194302.
[5] C.H. Ho, M.H. Lin, Y.P. Wang, Y.S. Huang, Synthesis of In_2S_3 and Ga_2S_3 for oysgen sensing and UV photodetection, Sens. Actuators A: Phys. 245 (2016) 119–126.
[6] C.S. Yoon, F.D. Medina, L. Martinez, T.Y. Park, M.S. Jin, W.T. Kim, Blue photoluminescence of α-Ga_2S_3 and α-Ga_2S_3:Fe^{2+} single crystals, Appl. Phys. Lett. 83 (2003) 1947–1949.
[7] J. Goodyear, G.A. Steigmann, The crystal structure of α-Ga_2S_3, Acta Cryst. 16 (1963) 946–949.
[8] T. Aono, K. Kase, Green photoemission of α-Ga_2S_3 crystals, Solid State Commun. 81 (1992) 303–305.
[9] T. Aono, K. Kase, Photoemission of Ag, Cu, and Ge-doped α-Ga_2S_3 crystals, Solid State Commun. 83 (1992) 749–752.
[10] R. Chen, S.W.S. McKeever, Theory of Thermoluminescence and Related Phenomena, World Scientific, Singapore, 1997.
[11] S.W.S. McKeever, On the analysis of complex thermoluminescence. Glow-curves: resolution into individual peaks, Phys. Status Solidi A 62 (1980) 331–340.
[12] R. Chen, Y. Kirsh, Analysis of Thermally Stimulated Processes, Pergamon Press, 1981.
[13] R.H. Bube, Photoelectronic Properties of Semiconductors, Cambridge University Press, Cambridge, 1992.
[14] A.T. Nagat, F.S. Bahabri, R.H. Orainy, M. Abou Zied, S.E. Al-Garni, W.S. Al-Ghamdi, Growth and transport properties of some gallium chalcogenides from the group M2 III X3 VI semiconductor compounds, JKAU: Sci. 23 (2011) 31–44.
[15] A. Mandowski, Semi-localized transitions model for thermoluminescence, J. Phys. D: Appl. Phys. 38 (2005) 17–21.
[16] A. Mandowski, A.J.J. Bos, Explanation of anomalous heating rate dependence of thermoluminescence in YPO_4: Ce^{3+}, Sm^{3+} based on the semi-localized transition (SLT) model, Radiat. Meas. 4 (2011) 1376–1379.
[17] R. Chen, J.L. Lawless, V. Pagonis, Two-stage thermal stimulation of thermoluminescence, Radiat. Meas. 47 (2012) 809–813.
[18] G. Kitis, G.S. Polymeris, V. Pagonis, N. Tsirliganis, Thermoluminescence response and apparent anomalous fading factor of Durango fluorapatite as a function of the heating rate, Phys. Status Solidi A 203 (2006) 3816–3823.
[19] A.J.J. Bos, N.R.J. Poolton, J. Wallinga, A. Bessière, P. Dorenbos, Energy levels in YPO_4: Ce^{3+}, Sm^{3+} studied by thermally and optically stimulated luminescence, Radiat. Meas. 45 (2010) 343–346.
[20] R. Chen, V.E. Pagonis, A model explaining the anomalous heating-rate effect in thermoluminescence as an inverse thermal quenching based on simultaneous thermal release of electrons and holes, Radiat. Meas. 106 (2017) 20–25.