



Original research article

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

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ABSTRACT

Thermoluminescence (TL) experiments were conducted for Ga₂S₃ 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 $T_{\max} - T_{\text{stop}}$ 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.

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1. Introduction

Ga₂S₃ crystals belong to the group III–VI compounds which are promising materials for the applications in optoelectronic devices. The characterization of Ga₂S₃ 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. Ga₂S₃ crystals have direct band gap energy of 3.44 eV at 10 K temperature [6]. Ga₂S₃ crystals belong to the monoclinic structure with the lattice parameters of $a = 1.114$, $b = 0.641$ and $c = 0.703$ nm, and $\beta = 121.22^\circ$. It was found that Ga₂S₃ 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 Ga₂S₃ crystals was carried out using thermoreflectance, Raman, photoluminescence, optical-absorption, and photo voltage-current measurements [5]. Photo voltage-current measurements of the Ga₂S₃ 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 Ga₂S₃ is promising material for light emitting device applications. Photoluminescence properties of Ga₂S₃ 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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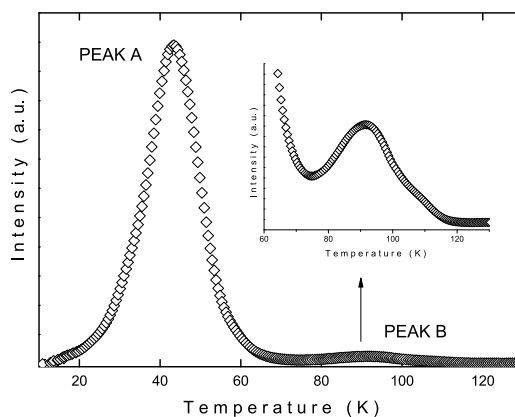


Fig. 1. TL glow curve of Ga_2S_3 crystal at heating rate of $\beta = 0.5 \text{ K/s}$.

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 $\text{Ga}_2\text{S}_3:\text{Fe}$ 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 violet and yellow emissions at 424 and 643 nm, respectively, for $\text{Ga}_2\text{S}_3:\text{Fe}^{2+}$ 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 $1.2 \times 0.6 \text{ cm}^2$ 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 $\beta = 0.5 \text{ K/s}$. 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 $T_{\text{max}} - T_{\text{stop}}$ 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

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