Materials Research Bulletin 70 (2015) 236–240

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

# Transmission, reflection and thermoluminescence studies on $GaS_{0.75}Se_{0.25}$ layered single crystals

S. Delice [a],*, M. Isik [b], N.M. Gasanly [a,c]

[a] Department of Physics, Middle East Technical University, 06800 Ankara, Turkey
[b] Department of Electrical and Electronics Engineering, Atilim University, 06836, Ankara, Turkey
[c] Virtual International Scientific Research Centre of Baku State University, 1148 Baku, Azerbaijan

ARTICLE INFO

*Article history:*
Received 31 December 2014
Received in revised form 5 February 2015
Accepted 19 April 2015
Available online 21 April 2015

*Keywords:*
A. Chalcogenides
B. Optical properties
B. Luminescence
D. Defects

ABSTRACT

Optical and thermoluminescence properties on $GaS_{0.75}Se_{0.25}$ crystals were investigated in the present work. Transmission and reflection measurements were performed at room temperature in the wavelength range of 400–1000 nm. Analysis revealed the presence of indirect and direct transitions with band gap energies of 2.39 and 2.53 eV, respectively. TL spectra obtained at low temperatures (10–300 K) exhibited one peak having maximum temperature of 168 K. Observed peak was analyzed using curve fitting, initial rise and peak shape methods to calculate the activation energy of the associated trap center. All applied methods were consistent with the value of 495 meV. Attempt-to-escape-frequency and capture cross section of the trap center were determined using the results of curve fitting. Heating rate dependence studies of the glow curve in the range of 0.4–0.8 K/s resulted with decrease of TL intensity and shift of the peak maximum temperature to higher values.

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## 1. Introduction

Ternary semiconducting materials having layered structures provide many advantages for researchers. These types of chalcogenides can easily be formed to obtain desired materials, which offer various physical and chemical properties. Due to their tunable compositions with a wide variety of optical and electrical properties, they are used especially in optoelectronic technology. $GaS_xSe_{1-x}$ mixed ternary crystals are formed from GaSe and GaS without restrictions on the concentration of the constituent compounds ($0 \leq x \leq 1$) [1–3]. Band gap energies of the series cover a wide range of the visible spectrum by adjusting the composition of the constituent compounds in the desired way. Optical properties of $GaS_xSe_{1-x}$ mixed crystals ($0 \leq x \leq 0.5$) grown by Bridgman method were studied by transmission and piezoreflectance measurements [1]. The analysis of the obtained spectra showed that band gap energy increases from 1.986 eV (GaSe) to 2.37 eV ($GaS_{0.5}Se_{0.5}$).

Technological applications of $GaS_xSe_{1-x}$ mixed crystals have been studied in recent years. The phase matching properties for second harmonic generation (SHG) in $GaS_xSe_{1-x}$ mixed crystals at room temperature were reported in Ref. [4]. It was reported that SHG efficiency of $GaS_{0.09}Se_{0.91}$ mixed crystal is 2.4 times of GaSe. The possibility of broadband THz pulse generation in mixed crystals has been reported and $GaS_{0.29}Se_{0.71}$ preserving the attractive optical properties of pure GaSe has been thought as efficient converter of laser femtosecond pulses into THz frequency range [5]. Moreover, taking into consideration the applications of constituent compounds, GaSe and GaS, in the near-blue-light emitting device [6], SHG of $CO_2$ laser [7], generation of coherent infrared radiation from mid-IR to THz region [8] and light modulator [9], $GaS_xSe_{1-x}$ mixed crystals can be an important candidate to be used in the relevant areas. Therefore, the characterization of these crystals gives an important opportunity to the researchers to understand the possible usage areas of them. $GaS_{0.75}Se_{0.25}$, one of the members of the $GaS_xSe_{1-x}$ mixed crystals corresponding to the $x = 0.75$, has layered structure so that each layer has four atomic planes with the sequence Se(S)–Ga–Ga–Se(S). Previously, photoluminescence (PL) studies in $GaS_{0.75}Se_{0.25}$ layered crystals have been reported at low temperatures (10–200 K) in the wavelength region of 500–850 nm [10]. PL spectra showed the presence of two PL bands centered at 527 and 658 nm at $T = 10$ K. Analysis of PL data revealed the origin of these bands as radiative transitions from shallow donor levels located at 0.043 and 0.064 eV to the acceptor levels at 0.088 and 0.536 eV, respectively. The frequencies and linewidths of Raman-active modes in $GaS_{0.75}Se_{0.25}$ layered crystal have been measured in the 10–300 K temperature range

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* Corresponding author. Tel.: +90 312 2105059; fax: +90 312 2105099.
*E-mail addresses:* sdelice@metu.edu.tr, srdrdelice@gmail.com (S. Delice).

http://dx.doi.org/10.1016/j.materresbull.2015.04.037
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and in the 10–380 cm$^{-1}$ frequency region [11]. $GaS_{0.75}Se_{0.25}$ single crystals were also studied by thermally stimulated current (TSC) measurements in the temperature range of 10–150 K [12]. The activation energies of the revealed trap centers were found as 70, 210 and 357 meV.

In the present paper, we intend to expand the studies on $GaS_{0.75}Se_{0.25}$ single crystals. Accordingly, transmission and reflection measurements have been performed in the wavelength region of 400–1000 nm. Energy band gap, one of the most important optical parameter to be known in the optoelectronic device technology, has been obtained from analyses of the observed spectra. Thermoluminescence (TL) properties of the studied crystals have also been investigated below room temperature to characterize the trapping centers arising due to the defects which are one of the principal factors affecting the performance of optoelectronic devices such as LEDs, lasers. In these technological devices, defects may introduce nonradiative recombination centers to lower the internal quantum efficiency or even render light generation impossible, depending on defect density. In the case of electronic devices, defects may act as scattering centers lowering carrier mobility, hence hindering high-frequency operation. Thus, characterization of trap centers existing due to the presence of defects in semiconductors is important in order to get high-quality devices.

## 2. Experimental

$GaS_{0.75}Se_{0.25}$ polycrystals were synthesized from high-purity elements (at least 99.999%) prepared in stoichiometric proportions. $GaS_{0.75}Se_{0.25}$ single crystals were grown by the Bridgman method from the stoichiometric melt of starting materials sealed in an evacuated ($10^{-5}$ Torr) silica tubes (10 mm in diameter and about 25 cm in length) having a tip at the bottom. The ampoule moving vertically in a furnace at a rate of 0.5 mm h$^{-1}$ was subjected to temperature difference varying between 1000 and 650 °C through a thermal gradient of 30 °C cm$^{-1}$. The samples were obtained easily by cleaving the grown ingots along the planes that are perpendicular to the *c*-axis of the crystal. Energy dispersive spectroscopy (EDS) measurements were carried out using JSM-6400 scanning electron microscope to get the knowledge about the chemical composition of the crystals.

"Shimadzu" UV-1201 model spectrophotometer was used to perform the transmission and the reflection measurements in the 400–1000 nm wavelength regions. The spectrophotometer has 20 W halogen lamp creating light focused to monochromator. Holographic grating is employed to disperse the beam and to create the spectrum. The directed beam from monochromator is passed through the sample and a silicon photodiode detector produces the signal by converting the light coming from the sample. The transmission measurements were done under the normal incidence of light with the polarization direction along the (0 0 1) plane, which is perpendicular to the *c*-axis of the crystal. For reflection experiments, the specular reflectance attachment with 5° incident angle was used.

TL measurements were carried out using a closed cycle helium gas cryostat (Advanced Research Systems, Model CSW-202). The temperature of the sample placed in the cryostat was adjusted between 10 and 300 K by Lakeshore Model 331 temperature controller. The sample was exposed to a blue light (~470 nm) for 600 s at low temperature $T_0 = 10$ K. After a waiting time (180 s after the light source was switched off), the sample was heated up to room temperature with a constant rate. The luminescence emitted from the sample was focused to a photomultiplier tube (Hamamatsu R928; spectral response: 185–900 nm) using relevant optical elements. The signal from photomultiplier tube was converted into TTL pulses by Hamamatsu Photon Counting Unit C3866. These TTL pulses were counted by the counter of the data acquisition module (National Instruments, NI-USB 6211). The whole measurement systems were controlled using a software program advanced in LabView$^{TM}$ graphical development environment.

## 3. Results and discussion

EDS spectrum of the $GaS_{0.75}Se_{0.25}$ single crystal is shown in Fig. 1. The atomic composition of the constituent elements (Ga:S:Se) was found as 51.0:36.8:12.2, respectively, from the analysis of the EDS spectrum. The structural parameters of the crystal were determined from the analysis of the XRD experiments. In the crystal system, Miller indices of the diffraction peaks and lattice parameters were evaluated using a least-squares computer program "DICVOL 04". Fig. 2 shows the X-ray diffractogram of $GaS_{0.75}Se_{0.25}$ crystal. The sharp diffraction peaks are an indication of the well crystallinity of the sample. Miller indices (*hkl*) are shown on the diffraction peaks. The lattice parameters of the hexagonal unit cell were found to be $a = 0.3625$ and $c = 1.5690$ nm.

Transmission and reflection spectra in the wavelength range of 400–1000 nm are shown in Fig. 3. The obtained transmittance ($T$) and reflectance ($R$) data were used to calculate the absorption coefficient ($\alpha$) through the following relation [13]

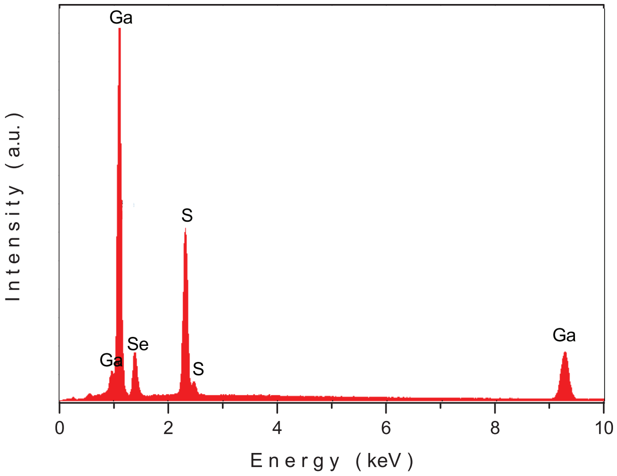

**Fig. 1.** Energy dispersive spectroscopic analysis of $GaS_{0.75}Se_{0.25}$ crystal.

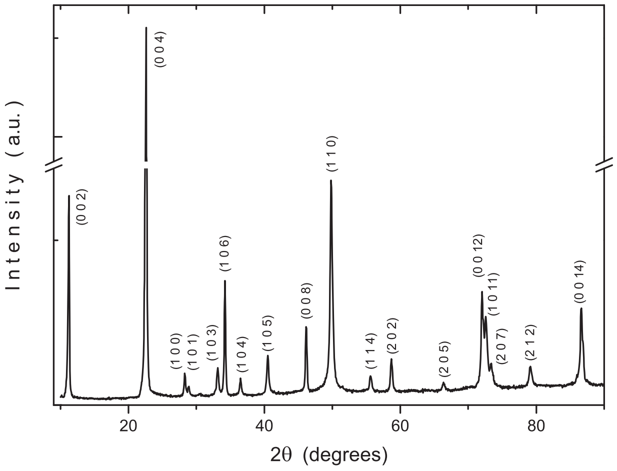

**Fig. 2.** X-ray powder diffraction pattern of $GaS_{0.75}Se_{0.25}$.

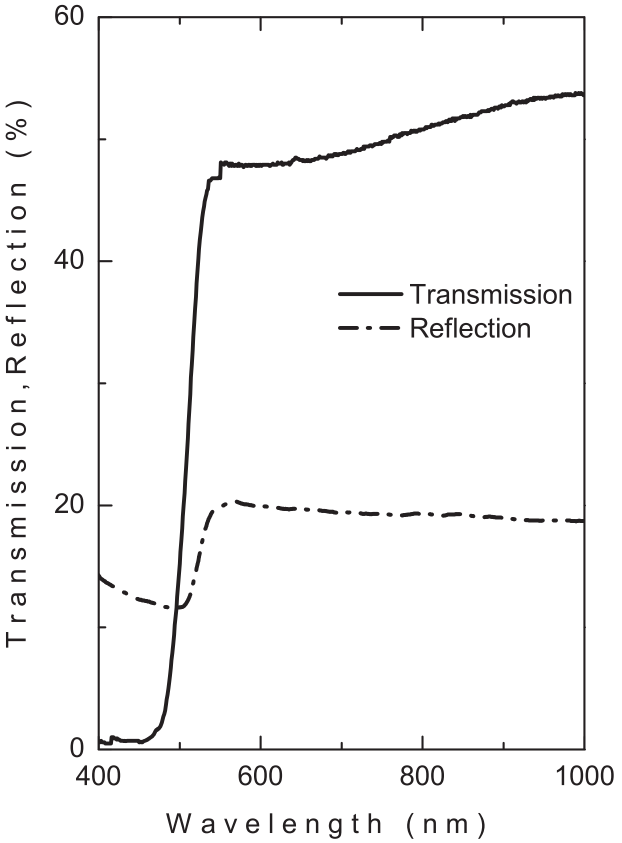

**Fig. 3.** The spectral dependencies of transmission and reflection for $GaS_{0.75}Se_{0.25}$ crystals at $T = 300\,K$.

$$\alpha = \frac{1}{d}\ln\left\{\frac{(1-R)^2}{2T} + \left[\frac{(1-R)^4}{4T^2} + R^2\right]^{1/2}\right\}, \tag{1}$$

where $d$ is the sample thickness.

The thickness of the samples was enough such that $\alpha d \gg 1$ and the cleavage plane was suitable for reflection measurements. The same sample was used for transmission measurements. Then, the sample thickness was reduced enough ($13\,\mu m$) to reach higher transmission value as much as possible. The absorption coefficient dependence of the photon energy ($h\nu$) can be utilized to obtain the optical band gap energy. Relation between absorption coefficient and photon energy is given by the following equation [13]

$$(\alpha h\nu) = A(h\nu - E_g)^p. \tag{2}$$

In this equation, $A$ is a constant related with the transition probability and $p$ is an index responsible for optical absorption process. $p$-index is equal to 1/2 and 2 for direct and indirect transitions, respectively. The Eq. (2) can be rewritten as [14]:

$$\frac{d[\ln(\alpha h\nu)]}{d(h\nu)} = \frac{p}{h\nu - E_g}. \tag{3}$$

Therefore, the plot of $d[\ln(\alpha h\boldsymbol{\nu})]/d(h\nu)$ as a function of photon energy ($h\nu$) exhibits a peak having maximum value at optical band gap energies [15]. Fig. 4 shows relevant graph that gives two maximum points establishing the coexistence of indirect and direct transitions with the energy band gaps of $E_{gi} = 2.39\,eV$ and $E_{gd} = 2.53\,eV$, respectively. At this point, it will be worthwhile to compare the band gap energies of the constituent compounds and mixed crystals. Table 1 gives the reported values of direct and indirect band gap energies. As can be seen from Table 1, the increase of sulfur composition in the mixed crystal raises the both type of energies.

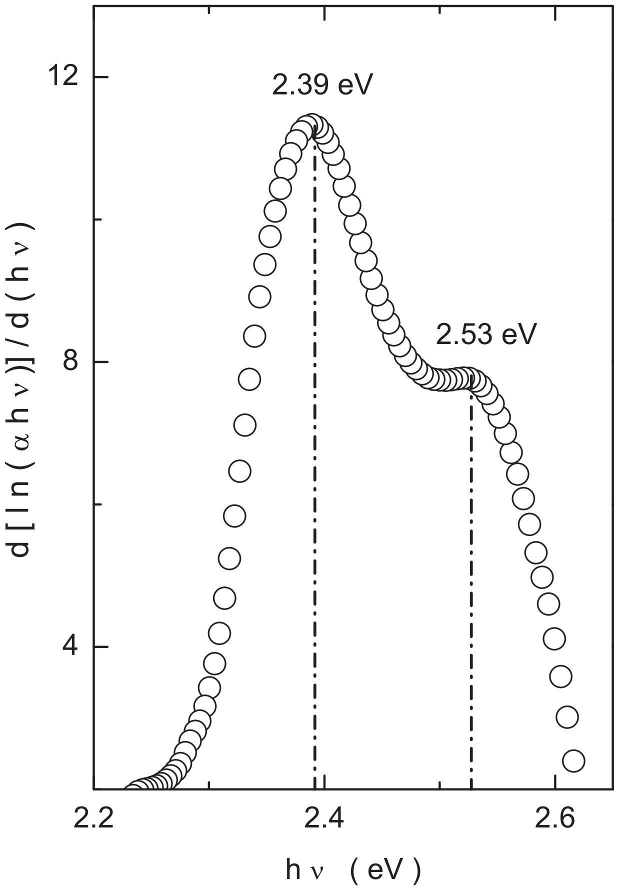

**Fig. 4.** The plot of $d[\ln(\alpha h\nu)]/d(h\nu)$ vs. photon energy ($h\nu$). The dash–dotted lines are only guide for the eye.

Fig. 5 shows the observed TL glow curve of the $GaS_{0.75}Se_{0.25}$ crystals accomplished by heating the sample at a constant rate of $0.4\,K\,s^{-1}$ between the temperatures 140 and 200 K. Since the studied crystals gave luminescence only within these temperature intervals, the rest of the TL spectra were not presented in the figure. As can be seen from the figure, one TL glow peak appearing at maximum temperature $T_m = 168\,K$ was obtained. Analysis of the TL curve was accomplished using curve fitting, initial rise and peak shape methods. Moreover, attempt-to-escape frequency ($\nu$) and capture cross section ($S_t$) values were calculated using the results of curve fitting method.

Curve fitting method is based on the fitting of the following equations, giving the TL intensity ($I_{TL}$) as a function of temperature, to the experimental glow curve

$$I_{TL} = n_0 \nu \exp\left\{-\frac{E_t}{kT} - \int_{T_0}^{T} \frac{\nu}{\beta}\exp\left(-\frac{E_t}{kT}\right)dT\right\} \quad \text{(for first order kinetics)} \tag{4}$$

**Table 1**
Direct ($E_{gd}$) and indirect ($E_{gi}$) band gap energies (eV) of $GaS_xSe_{1-x}$ mixed crystals.

| Composition, $x$ | 0 | 0.25 | 0.50 | 0.75 | 1.0 |
|---|---|---|---|---|---|
| $E_{gi}$ | 1.98[a] | 2.08[b] | 2.28[c] | 2.39[d] | 2.53[e] |
| $E_{gd}$ | 2.03[a] | 2.16[b] | 2.38[c] | 2.53[d] | 2.93[e] |

[a] Ref. [20].
[b] Ref. [21].
[c] Ref. [22].
[d] Present work.
[e] Ref. [23].

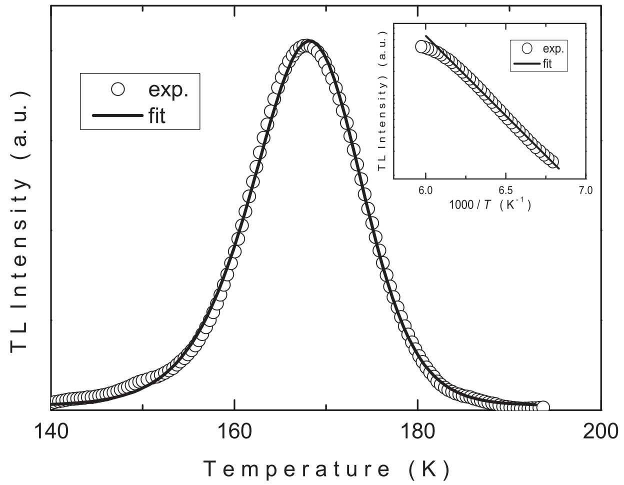

**Fig. 5.** Experimental TL glow curve of $GaS_{0.75}Se_{0.25}$ crystal with heating rate of $0.4\,K\,s^{-1}$. Open circles are experimental data. Solid curve shows the fit to the experimental data. Inset: TL intensity vs. 1000/$T$ for observed TL peak. Open circles are experimental data and solid line is the fitted straight line.

$$I_{TL} = n_0 \nu \exp\left(-\frac{E_t}{kT}\right)\left[1+(b-1)\frac{\nu}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E_t}{kT}\right)dT\right]^{-\frac{b}{b-1}} \quad \text{(for non-first order kinetics)}. \tag{5}$$

In above equations, $n_0$ is the initial concentration of trapped charge carriers, $\nu$ is the attempt-to-escape frequency, $\beta$ is the heating rate, $T_0$ is the starting temperature of heating process and $b$ is the order of kinetics. Application of Eq. (4) to the TL curve was not successful and did not give reliable results. Therefore, we decided to use Eq. (5) to obtain the best fit by varying the parameter $b$ in the fitting program. The most reliable result was obtained with $b = 1.5$ which is responsible for general (mixed) order of kinetics [16]. The activation energy of the trap level was found as $E_t = 495$ meV (see Fig. 5). This value is in satisfactory agreement with activation energy of 465 meV determined from the analysis of temperature-dependent electrical resistivity of $GaS_{0.75}Se_{0.25}$ crystal [17].

The $E_t$ and the $T_m$ values obtained from the curve fitting analysis were used in the following equation to calculate the attempt-to-escape-frequency [18]

$$\nu = \frac{\exp(t_m)t_m^3\beta k}{(2b+t_m)E_t}, \quad \text{where } t_m = \frac{E_t}{kT_m}. \tag{6}$$

Then, capture cross section of the revealed trap center was computed using the expression [18]

$$S_t = \frac{\nu}{N_c \upsilon_{th}}, \tag{7}$$

where $\upsilon_{th}$ is thermal velocity of a free electron and $N_c = 2\left(2\pi m_e^* kT/h^2\right)^{3/2}$ is the effective density of states in the conduction band. The effective mass $m_e^* = 0.41\,m_0$ was taken into account for calculation. The $\nu$ and $S_t$ values of the trap level were obtained as $5.3 \times 10^{13}\,s^{-1}$ and $1.4 \times 10^{-12}\,cm^2$, respectively.

Initial rise method is independent of the order of kinetics and therefore can be applied to the TL curve without considering the retrapping process. As the trapped charge carriers are excited to the non-localized states from trap levels through heating, the initial tail of the TL curve must arise as proportional to $\exp(E_t/kT)$ [18]. Then, the logarithmic plot of the TL intensity as a function of the reciprocal of temperature yields a straight line with slope of $(-E_t/k)$. Inset of Fig. 5 presents this plot giving the activation energy of the revealed trap level as 493 meV. This result is in good agreement with the value found by curve fitting.

Peak shape method is also effective for calculation of the activation energy of the trap level and based on the geometric analysis of the shape of the TL curve. According to this method, low ($T_l$) and high ($T_h$) temperature values of the TL curve, which correspond to the half intensity, are taken into account and $E_t$ value of the trap center is calculated from the average of the following energies [16].

$$E_\tau = \frac{\left[1.51 + 3.0\left(\mu_g - 0.42\right)\right]kT_m^2}{\tau} - \left[1.58 + 4.2\left(\mu_g - 0.42\right)\right]2kT_m \tag{8}$$

$$E_\delta = \frac{\left[0.976 + 7.3\left(\mu_g - 0.42\right)\right]kT_m^2}{\delta} \tag{9}$$

$$E_w = \frac{\left[2.52 + 10.2\left(\mu_g - 0.42\right)\right]kT_m^2}{w} - 2kT_m \tag{10}$$

where $\tau = T_m - T_l$, $\delta = T_h - T_m$, $w = T_h - T_l$ and the geometry factor $\mu_g = \delta/w$. The obtained value of $E_t = 495$ meV was consistent with those of two above mentioned methods. The geometry factor is the crucial parameter for this method since it gives information about the order of kinetics. Chen and Kirch claim this parameter to be approximately equal to 0.42 and 0.52 for the first and second order kinetics, respectively [16]. In our study on $GaS_{0.75}Se_{0.25}$ crystal, $\mu_g$ value was found as 0.48. This value also supported the result found from curve fitting that indicates the trapping level exhibits the properties of general order of kinetics.

Heating rate is an important parameter describing the TL mechanism of the trap level in studied crystals. In compliance with TL theory, variation of the heating rate gives rise to change in the shape and position of the TL curve. Fig. 6 illustrates the heating rate dependency of the TL curve obtained for rates between 0.4 and $0.8\,K\,s^{-1}$ with step of $0.1\,K\,s^{-1}$. As can be seen from the figure, the $T_m$ of the glow curves tends to shift to higher values with increasing heating rate. Anishia et al. [19] explained this behavior in their TL

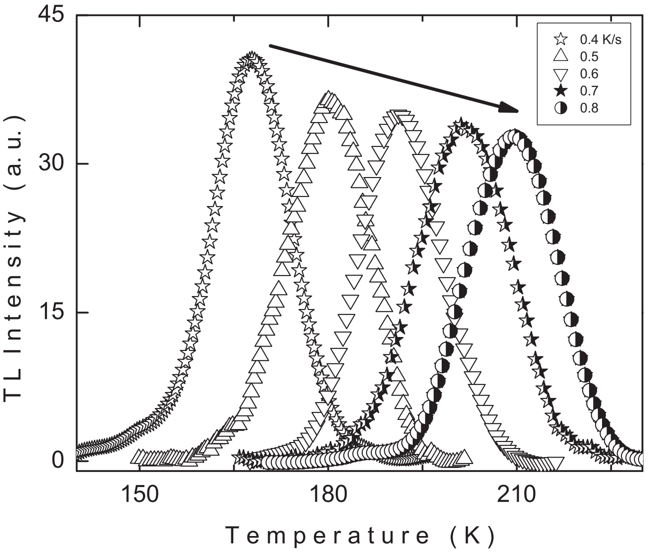

**Fig. 6.** Experimental TL curves of $GaS_{0.75}Se_{0.25}$ crystal with various heating rates between 0.4 and $0.8\,K\,s^{-1}$.

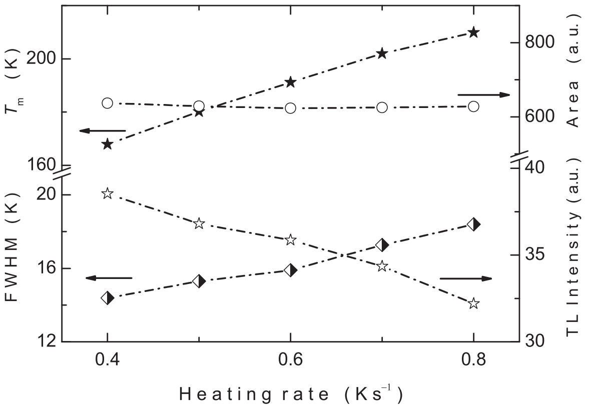

**Fig. 7.** Heating rate dependencies of TL intensity, the area, the peak maximum temperature and FWHM of the TL curves. The dash–dotted lines are only guide for the eye.

study. The trapped charge carriers excited by heating at a lower rate of $\beta_1$ spend much more time at temperature $T_1$ than the charge carriers stimulated with a higher rate of $\beta_2$. For this reason, at the heating rate $\beta_2$, the number of charge carriers released from trapping level at $T_1$ diminishes compared with respect to lower rate of $\beta_1$. To be able to induce same amount of charge carriers with $\beta_2$, we need a temperature $T_2$ ($T_2 > T_1$). As a result, the peak maximum temperature increases with increasing heating rate. In literature, there are many studies explaining the heating rate dependencies of trapping levels in luminescent materials. In a typical TL experiment, one expects that the TL intensity decreases with increasing heating rates. Additionally, the area under the curves remains constant since the number of released trapped charge carriers does not change at each heating process with different rates. The variation of the TL intensities, the peak maximum temperatures, the full-width-half-maximums (FWHM) and the areas enclosed under the obtained curves are represented in Fig. 7. As can be seen from the figure, the $T_m$ and FWHM values raised from 168 to 210 K and from 14.4 to 18.4 K, respectively. Moreover, the TL intensity decreased whereas the area enclosed under the curves did not change with temperature since the experiments were performed for the case of fully filled traps.

## 4. Conclusions

Optical and thermoluminescence properties of $GaS_{0.75}Se_{0.25}$ layered single crystals have been investigated. The absorption edge of the crystal has been studied by means of transmission and reflection measurements at room temperature in the wavelength range of 400–1000 nm. The analysis of the obtained absorption data established the presence of indirect and direct transitions with energy band gaps of 2.39 and 2.53 eV, respectively. TL measurements have been carried out in the temperature range of 10–300 K using various heating rates between 0.4 and 0.8 K s$^{-1}$. The analysis of the obtained TL spectra resulted with the existence of one trap level centered at $E_t = 495$ meV. Attempt-to-escape-frequency and capture cross section of the trap were found as $5.3 \times 10^{13}$ s$^{-1}$ and $1.4 \times 10^{-12}$ cm$^2$, respectively. The results of curve fitting and peak shape methods indicated that revealed trap center exhibited the properties of mixed order kinetics. Heating rate dependence of the trapping level was also investigated. The peak maximum temperature shifted towards higher values and the TL intensity decreased with increasing heating rate.

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