

## Optical properties of GaS crystals: Combined study of temperature-dependent band gap energy and oscillator parameters

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Optical parameters of gallium sulfide (GaS) layered single crystals have been found through temperature-dependent transmission and room temperature reflection experiments in the wavelength range of 400-1100 nm. Experimental data demonstrates the coexistence of both optical indirect and direct transitions and the shift of the absorption edges toward lower energies by increasing temperature in the range of 10-300 K. Band gap at zero temperature, average phonon energy and electron phonon coupling parameter for indirect and direct band gap energies have been obtained from the analyses of temperature dependences of band gap energies. At high temperatures  $kT \gg \langle E_{ph} \rangle$ , rates of band gap energy change have been found as 0.56 and 0.67 meV/K for  $E_{gi}$  and  $E_{gd}$ , respectively. Furthermore, the dispersion of refractive index has been discussed in terms of the Wemple–DiDomenico single effective oscillator model. The refractive index dispersion parameters, namely oscillator and dispersion energies, oscillator strength and zero-frequency refractive index, have been found to be 4.48 eV, 24.8 eV,  $6.99 \times 10^{13} \text{ m}^{-2}$  and 2.56, respectively. The results of the present work will provide an important contribution to the research areas related to the characterization and optoelectronic device fabrication using GaS layered crystals.

**Keywords:** GaS, Single crystals, Optical properties, Oscillator parameters

### 1 Introduction

Layered structured group III–VI semiconductors, generally referred to as layered gallium chalcogenides, have raised increasing scientific and engineering interest due to their fascinating physical and chemical properties<sup>1</sup>. These types of chalcogenides can easily be formed to obtain desired materials, also they have two-dimensional (2D) peculiarity associated with high anisotropy of the interlayer and intralayer bonds<sup>2,3</sup>. Similar to graphite, these 2D layered materials formed by strong in-plane covalent bond and weak out-of-plane van der Waals forces, which enables the micromechanical cleavage into 2D nanosheets<sup>4,5</sup>. Recently, researchers have started paying more attention to other graphene-like 2D materials such as transition metal dichalcogenides (e.g., MoS<sub>2</sub>, WSe<sub>2</sub>) and layered 2D monochalcogenides (e.g., GaS, GaSe, InSe) with sizable band gaps as substitutes for, or complements to, graphene<sup>3</sup>. Besides interesting fundamental physical and chemical properties, the structural

similarity to the graphite have attracted considerable attention to layered gallium chalcogenides and show promise in a wide range of fields such as field-effect transistors, photovoltaic, optoelectronic, thermoelectric, energy conversion and storage, topological insulators, and photodetectors<sup>6-12</sup>.

The crystal structure of the gallium sulfide (GaS) monochalcogenides consists of covalently bonded stacks of four atomic layers. The stacking sequence of S–Ga–Ga–S is held together by weak van der Waals interactions<sup>2</sup>. Depending on how the quadruple layers stack on top of each other, there are typically three different crystal structures ( $\beta$ ,  $\epsilon$ , and  $\gamma$ ). The polytypes can be identified using Raman or infrared spectroscopy. The bulk GaS crystallizes in the  $\beta$  phase with space group<sup>11</sup> no. 194,  $D_{6h}^4(P6_3/mmc)$ . It crystallizes in the hexagonal structure with lattice parameters<sup>13</sup> of (JCPDS card, No. 30-0576):  $a = 0.359$  and  $c = 1.549$  nm. The bond distances of the hexagonal layered GaS structure for the Ga–Ga and Ga–S are 0.248 and 0.237 nm, respectively. Accordingly, the thickness of one formula unit<sup>13</sup> is approximately 0.76 nm.

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Due to a broad range of potential applications, it is very important to determine the structural, electrical and optical properties of GaS layered crystals. Regarding the band gap characteristic of GaS, there are few research works on the GaS compound<sup>14-17</sup>. Optical absorption measurements on GaS crystals at room temperature revealed the presence of indirect transitions with 2.59 eV energy and direct transitions at approximately 0.45 eV higher in energy<sup>14</sup>. Ho and Lin<sup>17</sup> reported the temperature-dependent optical properties of the interband transitions in GaS layered solid using optical absorption and piezoreflectance measurements in the temperature range between 15-300 K. Previously, we have performed temperature-dependent photoluminescence<sup>18</sup> and room temperature ellipsometry<sup>19</sup> measurements on GaS crystal to investigate its optical properties. In this study, we continue to further explore the optical characteristics of the GaS layered crystals by means of temperature-dependent transmission measurements carried out at 10–300 K in the wavelength range of 400-1100 nm. In the following sections, we report the results of temperature-dependent band gap energies, band gap at zero temperature, average phonon energy, electron phonon coupling parameter, and the rate of band gap change with temperature. Moreover, refractive index, oscillator energy and strength, dispersion energy, zero frequency dielectric constant and refractive index were found from the analysis of room temperature reflection experimental data. The results of the present work will provide an important contribution to related research areas and expand the studies on optical characteristics of GaS layered crystals.

## 2 Experimental Details

Gallium sulfide polycrystals were synthesized using high-purity elements (at least 99.999%) taken in stoichiometric proportions. GaS 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  $0.5 \text{ mm h}^{-1}$  was subjected to temperature difference varying between 1000 and 650 °C through a thermal gradient of  $30 \text{ °C cm}^{-1}$ . The samples were obtained by easy cleavage of an ingot parallel to the crystal layer.

Transmission and reflection measurements were performed in 400-1100 nm spectral range using Shimadzu UV 1201 model spectrophotometer with resolution of 5 nm. 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. Transmission spectra were obtained under normal incidence of light with a polarization direction along the (001) plane. This plane is perpendicular to the *c*-axis of the crystal. The reflection experiments were carried out using a specular reflectance measurement attachment with a  $5^\circ$  incident angle. Transmission measurements were performed in the 10-300 K range using a closed-cycle helium cryostat (advanced research systems, model CSW 202). The temperature of the sample was adjusted using a computer interfaced temperature controller (Lakeshore model 331).

## 3 Results and Discussion

The temperature-dependent transmission (*T*) spectra of GaS single crystals in the wavelength ( $\lambda$ ) range of 400-1100 nm and temperature range of 10-300 K with 30 K intervals are presented in Fig. 1. By increasing temperature we can observe a clear red shift in the absorption edge as evidence to the decreasing of band gap. Reflection spectrum (inset of Fig. 1) was only obtained at room temperature since our experimental set-up for reflection measurements cannot be adapted to the cooling system. Therefore, when the absorption coefficient ( $\alpha$ ) was calculated at different temperatures, the spectral dependence of room temperature reflectivity was uniformly shifted taking into account the shift of transmittance spectra.

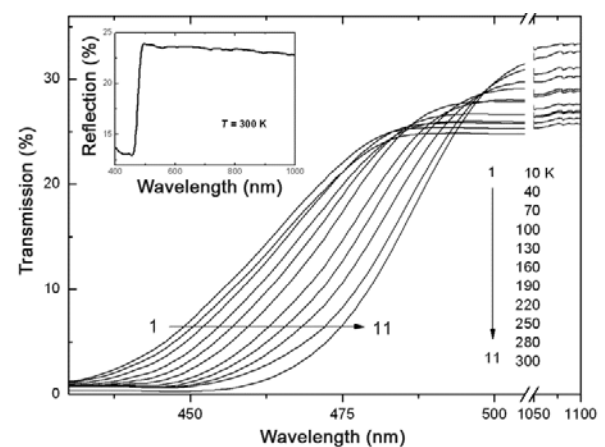


Fig. 1 – Transmission spectra of the GaS layered crystals at different temperatures. Inset shows the reflectance spectrum at room temperature.

The optical constants; absorption coefficient ( $\alpha$ ) and refractive index ( $n$ ) were calculated using the transmission ( $T$ ) and reflection ( $R$ ) coefficients in following expressions<sup>20</sup>:

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

$$n = \frac{1+R}{1-R} + \left[ \frac{4R}{(1-R)^2} - \left( \frac{\alpha\lambda}{4\pi} \right)^2 \right]^{1/2} \quad \dots (2)$$

where  $d$  symbolize the thickness of the sample measured as 180  $\mu\text{m}$ . Information concerning the optical band gap of materials is important for practical considerations especially in the optoelectronic device fabrication. The optical absorption spectra play vital role in studying the energy band structure and type of optical transitions. The dependence of the absorption coefficient on photon energy ( $h\nu$ ) was analyzed in high absorption region to reveal the band gap energy ( $E_g$ ). The absorption coefficient is related to photon energy according to the following equation<sup>20</sup>:

$$(\alpha h\nu) = A(h\nu - E_g)^p \quad \dots (3)$$

where constant  $A$  depends on transition probability, and  $p$  is an index used to determine transition type. For indirect and direct transitions,  $p$  is equal to 2 and 1/2, respectively. In order to ascertain the direct or indirect optical band gap, we rearrange Eq. (3) by taking natural logarithm and derivative as follows<sup>21</sup>:

$$\frac{d \ln(\alpha h\nu)}{d(h\nu)} = \frac{p}{h\nu - E_g} \quad \dots (4)$$

The temperature-dependent  $d(\ln(\alpha h\nu))/d(h\nu)$  versus  $h\nu$  plots are shown in Fig. 2. Two maximum points

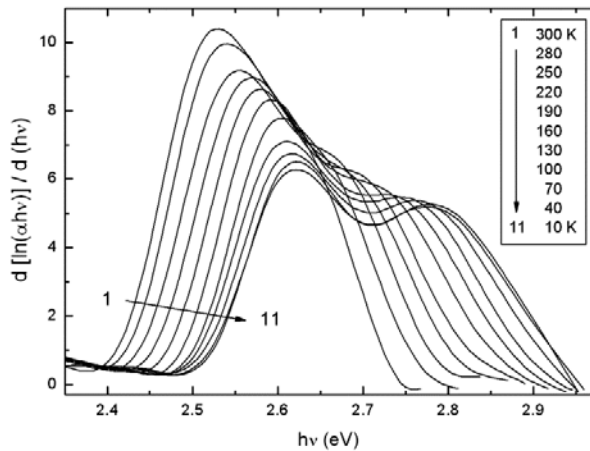


Fig. 2 – Temperature dependent plots of  $d(\ln(\alpha h\nu))/d(h\nu)$  versus  $h\nu$  of the GaS layered crystals.

are observable in each spectrum (especially in low temperatures), which can be interpreted as coexistence of indirect and direct transitions. Peak positions represent approximately the optical band gap energies and help determining the value of  $p$  and hence type of the transition<sup>22,23</sup>. The curves of  $\ln(\alpha h\nu)$  versus  $\ln(h\nu - E_g)$  are plotted to determine  $p$  values using obtained  $E_g$  values. Analysis of the experimental data recorded at 10 K with two maximum points located around 2.60 eV and 2.80 eV (Fig. 3) revealed that the slopes of  $\ln(\alpha h\nu)$  versus  $\ln(h\nu - E_g)$  curves give  $p = 2.08$  and  $p = 0.44$  values in coherence with  $p = 2$  and  $p = 1/2$  corresponding to indirect and direct band gap transitions, respectively. By applying the same procedure for other experimental data in the range of 10-300 K with corresponding  $E_g$  values (demonstrated in Fig. 4)

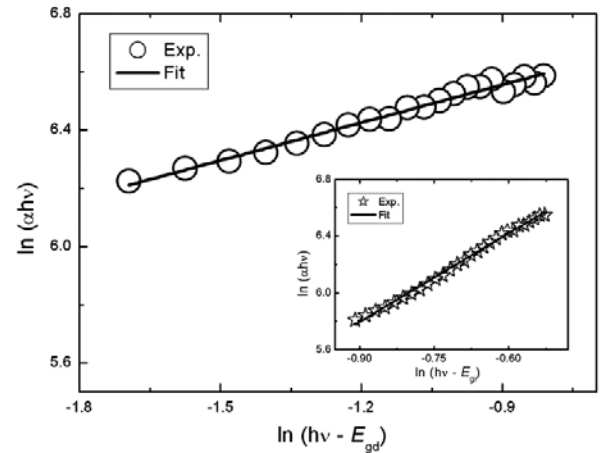


Fig. 3 – Plots of  $\ln(\alpha h\nu)$  versus  $\ln(h\nu - E_g)$  for peak arising at higher energy. Inset shows the same plot for peak at lower energy.

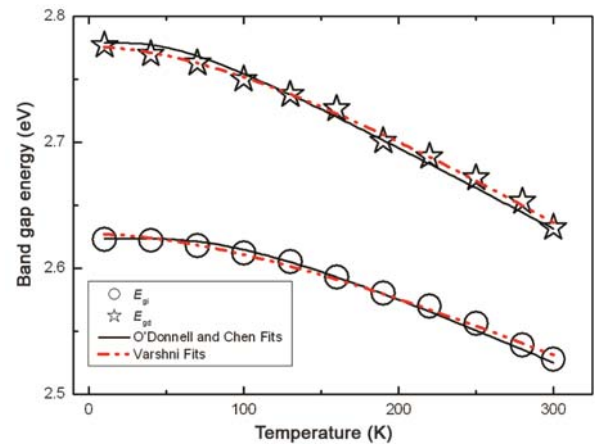


Fig. 4 – The band gap energies (open circles and stars) at different temperatures. Dashed-dotted and solid lines present the fits according to Eq. (5) and Eq. (6), respectively.

similar  $p$  values between 1.83–2.08 and 0.44–0.52 are obtained. Therefore, our results suggest that the fundamental absorption edges in the GaS crystal are formed by indirect and direct allowed transitions which evolve in the range of 2.62–2.53 and 2.78–2.63 eV, respectively, by increasing temperature from 10 to 300 K.

The temperature dependence of the fundamental energy gap is a basic empirical property of semiconductor materials. A detailed knowledge of this  $E_g(T)$  dependence is of great importance, above all, for applications in optoelectronic devices that are intended for operation within a relatively large temperature interval. Figure 4 presents the decrease of the  $E_{gi}$  and  $E_{gd}$  as the temperature increases from 10 to 300 K. The data describing the temperature dependence of the energy gap for GaS have been fitted using the Varshni formula and Bose-Einstein-type empirical expression proposed by O'Donnell and Chen. In the Varshni model, band gap energy is related to absolute zero value of band gap ( $E_g(0)$ ), rate of change of the band gap with temperature ( $\gamma$ ) and Debye temperature ( $\beta$ ) as<sup>20</sup>:

$$E_g(T) = E_g(0) + \frac{\gamma T^2}{T + \beta} \quad \dots (5)$$

The experimental data (open circles and stars) and fit outcome (dashed lines) in Fig. 4 show a good consistency for optical parameters of  $E_{gd}(0) = 2.78$  eV,  $\gamma_d = -8.7 \times 10^{-4}$  eV/K,  $\beta = 260$  K for direct transitions and  $E_{gi}(0) = 2.63$  eV,  $\gamma_i = -6.1 \times 10^{-4}$  eV/K,  $\beta = 275$  K for indirect transitions. Previously, temperature dependent band gap energy was analyzed using Varshni model on gallium (Ga) based binary semiconducting crystals of GaAs, GaP and GaSe. The analyses resulted in  $E_g(0) = 2.86$  eV and  $\beta = 372$  K for GaP<sup>24</sup>,  $E_g(0) = 1.515$  eV,  $\gamma = -5.5 \times 10^{-4}$  eV/K and  $\beta = 255$  K for GaAs<sup>25</sup>,  $E_{gd}(0) = 2.095$  eV,  $\gamma = -6.6 \times 10^{-4}$  eV/K and  $\beta = 181$  K for GaSe<sup>26</sup>.

O'Donnell and Chen expressed the temperature dependence of band gap energy as<sup>27</sup>:

$$E_g(T) = E_g(0) - S\langle E_{ph} \rangle \left[ \coth\left(\frac{\langle E_{ph} \rangle}{2kT}\right) - 1 \right] \quad \dots (6)$$

where  $E_g(0)$  is the band gap at zero temperature,  $\langle E_{ph} \rangle$  is an average phonon energy, and  $S$  is a dimensionless constant related to the electron-phonon coupling. By fitting Eq. (6) to our data of  $E_{gi}(T)$  and  $E_{gd}(T)$  (solid lines in Fig. 4), the following sets of parameters were

obtained:  $E_{gi}(0) = 2.62$  eV,  $\langle E_{ph} \rangle_i = 26$  meV,  $S_i = 3.28$  and  $E_{gd}(0) = 2.79$  eV,  $\langle E_{ph} \rangle_d = 15$  meV,  $S_d = 3.88$ . Our values of the electron-phonon coupling parameter  $S$  for  $E_{gi}$  and  $E_{gd}$  are similar to those of GaAs<sup>27</sup> ( $S=3.00$ ), GaP<sup>27</sup> ( $S=3.35$ ), and ReS<sub>2</sub> ( $S=4.05$ )<sup>28</sup>. These values lead to the conclusion about strong interactions between band edge states and the phonon system in GaS.

From Eq. (6) at high temperatures,  $kT \gg \langle E_{ph} \rangle$ , the slope of the  $E_g$  versus  $T$  curve approaches the limiting value<sup>27</sup> of:  $(dE_g/dT)_{\max} = -2kS$ . The values of  $(dE_g/dT)_{\max}$  were calculated as 0.56 and 0.67 meV/K for  $E_{gi}$  and  $E_{gd}$ , respectively. The obtained larger value of  $(dE_g/dT)_{\max}$  for direct band gap indicates that direct transitions are more affected by increasing temperature from 10 to 300 K, in accordance with the monitored band gap decreasing shown in Fig. 4.

It is worth noting that earlier researches performing optical absorption measurements on GaS crystals at room temperature revealed the presence of indirect band gap with 2.48–2.59 eV energy and direct band gap at 0.45–0.53 eV higher in energy. Our finding of 2.53 eV for indirect transition is in good agreement with the results of previous studies; however, direct band gap of GaS lays 0.10 eV above the indirect band gap. We suggest the possibility that the observed narrow direct-indirect band gap difference may be related to the developed strain on the outer layers of the sample due to O<sub>2</sub> and/or H<sub>2</sub>O adsorption during ageing, as was expected from previous calculations of other groups<sup>5,10,11,29,30</sup>. Our experimental results are in good agreement with the theoretical prediction of the recently published work by Jung *et al.*<sup>10</sup> on the influence of oxygen chemisorption on the convergence of the direct and indirect band gaps in few layer GaS structures. Their theoretical calculation supported by X-ray photoelectron spectroscopy showed that expansion of the lattice constant  $a$  by biaxial tensile strain due to oxygen adsorption dramatically reduces the band gaps, and causes the direct band gap in GaS to approach the indirect band gap. They attributed the observed phenomenon to the flattening of the VB due to the highly electronegative oxygen atom and brillouin zone folding.

The refractive index spectrum at room temperature was plotted in Fig. 5 using Eq. (2). Refractive index ( $n$ ) of GaS layered crystals in the below band gap energy region gradually decreases from 2.79 to 2.65 with increasing wavelength in the range of 570–1000 nm. The dispersive refractive index data in the region of  $h\nu < E_g$

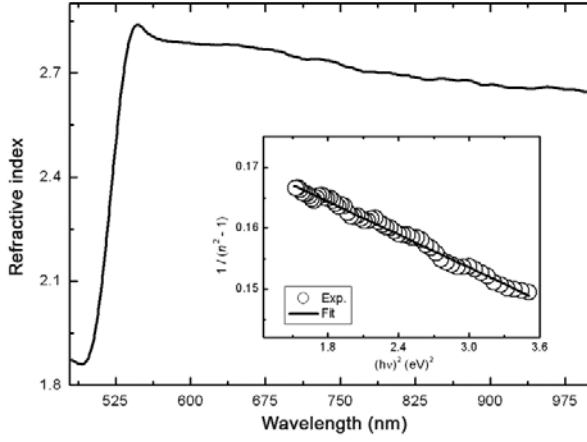


Fig. 5 – Refractive index spectrum at room temperature. Inset shows the plot of experimental  $(n^2 - 1)^{-1}$  versus  $(hv)^2$  (open circles) in the  $hv < E_g$  region and its linear fit (solid line) according to Eq. (6).

were analyzed by means of the single-effective oscillator model proposed by Wemple and DiDomenico<sup>31</sup>. The refractive index is associated with photon energy ( $E$ ), single oscillator energy ( $E_{so}$ ) and dispersion energy ( $E_d$ ) by the following expression:

$$n^2(E) = 1 + \frac{E_{so}E_d}{E_{so}^2 - E^2} \quad \dots (7)$$

The plot of  $(n^2 - 1)^{-1}$  against  $E^2$  permits the determination of the oscillator parameters by fitting a linear function to the lower-energy data in the region 1.23–1.88 eV (inset of Fig. 5). The slope and the intersection of the fitted straight line with the  $y$ -axis were used to determine the values of parameters  $E_{so} = 4.48$  eV and  $E_d = 24.8$  eV. The zero-frequency dielectric constant  $\epsilon_0 = n_0^2 = 6.54$  and refractive index  $n_0 = 2.56$  were evaluated using Eq. (7), i.e., based on the expression  $n_0^2 = 1 + E_d/E_{so}$ . The oscillator energy  $E_{so}$  is an ‘average’ energy gap, which is approximately two times the lowest indirect<sup>32</sup> band gap  $E_{gd}(E_{so} \approx 2.0E_{gi})$ . The ratio  $E_{so}/E_{gi}$  for the GaS crystal was found to be 1.77.

For GaS crystal, the single oscillator strength ( $S_{so}$ ) can be found through analysis of the refractive index at low energies by a single Sellmeier oscillator model<sup>32</sup>:

$$\frac{(n_0^2 - 1)}{(n^2 - 1)} = 1 - \left(\frac{\lambda_0}{\lambda}\right)^2 \quad \dots (8)$$

where  $\lambda_{so}$  is the single oscillator wavelength. Equation (8) can be rewritten in terms of  $S_{so} = (n_{so}^2 - 1)/\lambda_{so}^2$  as:

$$(n^2 - 1)^{-1} = \frac{1}{S_{so}\lambda_{so}^2} - \frac{1}{S_{so}\lambda^2} \quad \dots (9)$$

The related optical parameters were evaluated from the  $(n^2 - 1)^{-1}$  versus  $\lambda^{-2}$  graph as  $S_{so} = 6.99 \times 10^{13} \text{ m}^{-2}$  and  $\lambda_{so} = 2.81 \times 10^{-7} \text{ m}$ .

#### 4 Conclusions

The optical transmission and reflection spectra of GaS crystals were measured in the range of 400–1100 nm in order to derive the absorption coefficient and refractive index. The analysis of the room temperature absorption data revealed the coexistence of indirect and direct transitions in GaS crystals with energy band gaps of 2.53 and 2.63 eV, respectively. The narrow direct-indirect band gap difference was attributed to the developed strain on the outer layers of the sample due to O<sub>2</sub> and/or H<sub>2</sub>O adsorption during ageing. The absorption edges were observed to shift toward lower energy values as temperature increases from 10 to 300 K. The observed shift value for  $E_{gi}$  and  $E_{gd}$  are 0.09 and 0.15 eV, respectively, i.e., direct transitions are more affected by temperature. The data describing the temperature dependence of the energy gap for GaS, fitted by a Bose-Einstein-type empirical expression proposed by O’Donnell and Chen, gives the electron phonon coupling parameter  $S$  as 3.28 and 3.88 for indirect and direct band gaps, respectively. These values lead to the conclusion about strong interactions between band edge states and the phonon system in GaS. Wemple-DiDomenico single effective oscillator model was applied to refractive index dispersion data. The oscillator energy, dispersion energy, oscillator strength and zero-frequency refractive index values were found from the analysis as  $E_{so} = 4.48$  eV,  $E_d = 24.8$  eV,  $S_{so} = 6.99 \times 10^{13} \text{ m}^{-2}$  and  $n_0 = 2.56$ , respectively.

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