

# Temperature-dependent absorption edge in AgGaS<sub>2</sub> compound semiconductor

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## Abstract

We have grown high-quality AgGaS<sub>2</sub> single crystals with a chalcopyrite structure. Using an optical absorption measurement, the energy band gap was determined by means of the Elliott-Toyozawa model. The anomalous variation of energy band gap at  $T < 100$  K is discussed in conjunction with AgGaSe<sub>2</sub> compound displaying the same behavior. The exponentially increasing absorption tail was explained in terms of a Urbach tail in the temperature range of 100–300 K. Characteristic Urbach parameters, including the steepness parameter and Urbach energy as a function of temperature, as well as effective phonon energy  $\hbar\omega$ , were obtained. The steepness of the absorption spectra is dominated by the effect of the thermal disorder rather than the structural disorder and/or the deviation from the stoichiometry.

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## 1. Introduction

I-III-VI<sub>2</sub> compound semiconductors crystallized with a chalcopyrite structure have been extensively studied during the last three decades. These semiconductors have a wide range of direct band gap over the infrared to ultraviolet spectral region, and thus have attracted much interest because of their potential applications in opto-electronic devices such as solar cells, optical parametric oscillator, light emission diodes (LEDs), laser diodes (LDs), and detectors [1–4].

I-III-VI<sub>2</sub> compound semiconductors can be divided into Ag-III-VI<sub>2</sub> and Cu-III-VI<sub>2</sub>. Among the Cu-III-VI<sub>2</sub> compounds, quaternary alloys CuIn<sub>x</sub>Ga<sub>1-x</sub>Se<sub>2</sub>, in which CuInSe<sub>2</sub> and CuGaSe<sub>2</sub> are alloyed, have a suitable band gap for solar energy conversion, and devices based on these materials have achieved an efficiency of 18%. AgGaS<sub>2</sub>, an Ag compound, has been of particular interest due to its highly non-linear

optical susceptibility and large birefringence [5]. As such, research on the basic properties of this material has focused on optical characterizations such as photoluminescence [6], photoreflectance [7], and optical absorption spectra [8]. In particular, anomalous band gap variation at low temperature ( $T < 100$  K) remains a matter of debate. Although a large number of studies have been made on the band structure and optical characteristics, little is known about the Urbach tail in AgGaS<sub>2</sub>.

CuAlS<sub>2</sub>, a Cu compound, has a wide band gap of 3.5 eV, which is close to that of GaN, and therefore, it is a promising material as a blue emitting device [9]. For these reasons, several research groups have reported the optical and electrical characteristics of I-III-VI<sub>2</sub>. Additionally, among the II-IV-V<sub>2</sub> compounds with the same structure, it was found that the insertion of manganese into a host CdGeP<sub>2</sub> single crystal results in a new ferromagnetic material, (Cd,Mn)GeP<sub>2</sub>, with a chalcopyrite structure, a promising material for next generation spintronics and information technology [10,11]. In order to realize these applications, defect-free and suitable size crystals are required. However, it is difficult to

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grow high-quality single crystals because I-III-VI<sub>2</sub> compound semiconductors have two-phase transition points below the melting temperature, and compressive strain ( $c/2a < 1$ ) as well as tensile strain ( $c/2a > 1$ ). In addition, as more constitutive elements are included, more native defects can be expected in relation to the II-VI and III-V compound semiconductors. While the growth of single crystals of sufficient size and optical quality for non-linear optical devices has been challenging, recent developments related to crystal growing techniques have enabled the growth of large defect-free single crystals. Furthermore, many attempts have been made to grow single epilayers using various methods, including molecular organic chemical deposition [12], pulsed laser deposition [13], and molecular beam epitaxy [14].

In the present paper, we discuss the anomalous temperature-dependence of the energy band gap and the origin of the variation in the shape of absorption band at different temperatures on AgGaS<sub>2</sub> single crystals.

## 2. Experimentals

AgGaS<sub>2</sub> single crystals have been grown by means of a horizontal Bridgman method using 5 N silver, gallium, and sulfur as the starting materials. Since the vapor pressure of S exceeds the rupture strength of a fused silica ampoule at the reaction temperature (1150 °C), a tubular two-zone furnace was used. The boat containing Ag and Ga was maintained at 1200 °C, while the sulfur zone was kept at 400 °C. This method also allows us to grow the crystals under constant sulfur vapor pressure. After maintaining these temperatures for 72 h, the high-temperature zone was cooled at a rate of 2 °C/h to 400 °C. The temperature gradient of the boat was 25 °C/cm. After solidification, the ingot was cooled at a rate of 50 °C to room temperature. The crystal structure was confirmed by powder X-ray diffraction patterns. The sample used in the experiments was lapped down to 300 μm and then polished with alumina powder of 0.1 μm to minimize the loss of transmitted light due to surface scattering. Optical absorption spectra were measured using a spectrophotometer (UV-2401, Shimadzu) in the range of 400–600 nm. The sample temperature was controlled by an APD HS-3 He cryostat, 10–300 K.

## 3. Results and discussion

Fig. 1 shows the variation of the energy band gap according to temperature, which is determined by using the relation  $(\alpha h\nu)^2 \sim (h\nu - E_g)$ . For most compound semiconductors, the temperature-dependence on the energy band gap can be described by Bose-Einstein [15] and Varshni's [16] relations. However, these do not satisfactorily explain AgGaS<sub>2</sub> [17] and AgGaSe<sub>2</sub> [18] compound semiconductors, which display a blue shift at low temperature ( $T < 100$  K). Manoogian and

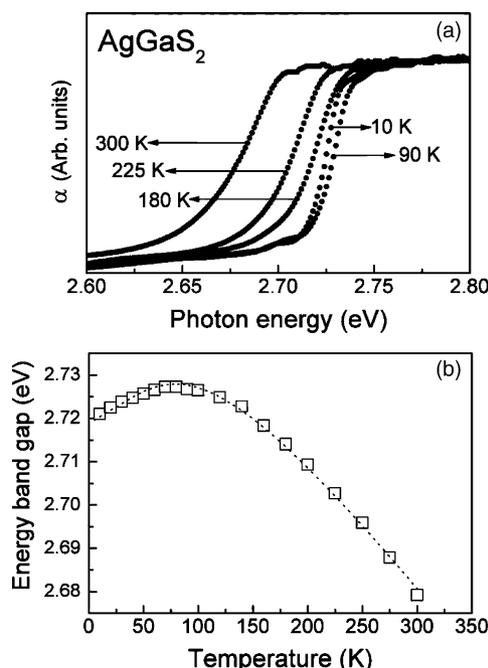


Fig. 1. Temperature-dependence of (a) the band edge and (b) the band gap energy of AgGaS<sub>2</sub> single crystal. The dotted line of (b) is calculated by Eq. (1).

Leclerc suggested a new depleted model as follows [19]

$$E_g(T) = E_g(0) - UT^x - V \frac{E_P}{k_B} \left[ \coth \left( \frac{E_P}{2k_B T} \right) - 1 \right], \quad (1)$$

where the second term in the right side of this equation represents the effect of lattice dilatation, while the third term reflects the effect of the electron–phonon interaction.  $E_P$  is the average energy of a phonon. The result of numerical fitting with Eq. (2) is represented by a dotted line, and the adjustable parameters are listed in Table 1.

As shown in Fig. 1, the energy band gap increases to higher energy up to 100 K, followed by a decrease at higher temperature. This well-known phenomenon is referred to as anomalous band gap variation. The blue shift of the energy band gap at a low temperature range ( $T < 100$  K) has been ascribed to the thermal expansion of the crystal lattice, and the red shift at higher temperature arises from electron–phonon interaction. Generally, the energy band gap variation with temperature is given by [20]

$$\frac{dE_g}{dT} = \left. \frac{\partial E_g}{\partial T} \right|_{vib} + \frac{\partial E_g}{\partial \ln V} \beta \quad (2)$$

Table 1  
The adjustable parameters obtained from the fit with Eq. (1)

$E_g(0)$ (eV)	2.72
$U$ (eV/K)	$-1.5 \times 10^{-4}$
$x$	1
$V$ (eV/K)	$2.5 \times 10^{-4}$
$E_P$ (meV)	26 (295 K)

where  $\beta$  is the thermal expansion coefficient  $d \ln V/dT$ . The first term represents the electron–phonon interaction effect, which is dominant in the high temperature region ( $T > 100$  K) and has a negative value. The second term represents the thermal dilatation of the lattice, which is dominant in the low temperature region ( $T < 100$  K) and has a positive value. For Ag-III-VI2 compounds, the theoretically estimated  $(\partial E_g/\partial \ln V)$  is approximately  $-3 \sim -4$  eV [21]. Therefore, the sign of the temperature coefficient  $dE_g/dT$  in the low temperature region is determined by  $\beta$ .

Sermage et al. suggested that with increasing temperature, interatomic distances increase and the p-d hybridization of the valance band is decreased, which leads to an increase of band gap at low temperature ( $T < 100$  K) [22]. However, the principal thermal expansion coefficients,  $\alpha_a$  and  $\alpha_c$ , were found to be negative for ternary chalcopyrite compounds from low temperature thermal expansion measurements [23], conflicting with the description of Semage et al. Thus, we can assume that the linear thermal expansion coefficient  $\alpha_L$  becomes negative at the low temperature region ( $T < 100$  K). Hence, this should give a positive thermal coefficient of AgGaS<sub>2</sub> below 100 K. The problem that must therefore be considered is a measure of the contribution of the thermal coefficient to this anomalous variation.

It is well known that the thermal coefficient at low temperature is approximately 10% of that for high temperature, and is a measure of 30% of the whole temperature coefficient. For the results obtained in this work, the temperature coefficient of the energy band gap is  $6.56 \times 10^{-4}$  eV/K over a temperature range of 10–100 K and  $-3.0 \times 10^{-4}$  eV/K in the range of 100–300 K. The temperature coefficient in the low temperature region is larger by a factor of 2 than that of the high temperature region. Accordingly, this does not adequately explain the positive thermal coefficient. A recent paper [24] argued against the anomalous blue shift of band gap below 100 K based on observations of a remarkable broadening in soft phonon by adding Cu. The authors suggested that a soft phonon mode may be responsible for this blue shift in AgGaS<sub>2</sub>. However, thus far, there have been no reports of observation of soft phonon in AgGaSe<sub>2</sub> with the same behavior in terms of energy band gap. Therefore, the anomalous blue shift cannot be definitely ascribed to the soft phonon. Moreover, there is no accurate data for the linear thermal expansion coefficient of AgGaS<sub>2</sub> in the low temperature region. Although numerous attempts have been made to explain the anomalous blue shift in AgGaS<sub>2</sub> and AgGaSe<sub>2</sub>, this subject remains controversial.

The logarithms of absorption spectra measured at different temperatures are depicted in Fig. 2. The sample thickness was maintained to be sufficiently thick in order that absorption peaks by excitons were not observed. We then focused on the Urbach tail. As the temperature increases, the absorption coefficient just below the band edge increases exponentially with incident photon energy, which is described by Urbach's

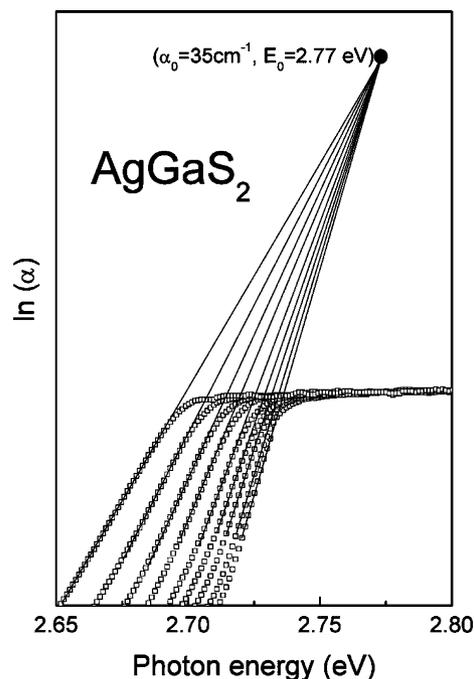


Fig. 2. The logarithmic variation of the absorption coefficient spectra at several temperatures between 120 K and 300 K.

rule [25]

$$\alpha = \alpha_0 \exp\left(\frac{E - E_0}{E_U(T)}\right), \quad (3)$$

where  $E_U$  is Urbach energy. This, in turn, implies that the logarithm of the absorption coefficient just below the band edge can be approximated by a straight line. As is shown in Fig. 2, the logarithm of the absorption coefficient just below the band edge,  $\ln\alpha$ , converges at a coordinate ( $\alpha_0 = 35$  cm,  $E_0 = 2.77$  eV), which indicates that the absorption spectra of AgGaS<sub>2</sub> obeys Urbach's rule.

There are several widely known explanations of the Urbach tail. Sumi-Toyozawa ascribes the exponential shape of the absorption coefficient to the coexistence of free excitons and momentarily localized self-trapped excitons [26], whereas the Dow-Refield model states that the Urbach tail is due to the broadening of the exciton absorption band by the phonon-induced micro electric fields present in the lattice [27].

On the other hand, it was also recently reported that the average phonon energy contributing to Urbach's tail is related to the stoichiometry and molecularity of the materials [28]. Moreover, if the temperature-induced phase transition is included, more than one convergence point may exist [29]. First, we conjectured that the anomalous variation in the low temperature region might be due to the phase transition. No changes, however, were detected in the convergence point of the extrapolated lines. The steepness parameter  $\sigma(T)$ , which characterizes the steepness or width of the straight line near the absorption edge, is expressed empirically as a function of

temperature [30–32]

$$\sigma(T) = \sigma_0 \left( \frac{2k_B T}{\hbar\omega} \right) \tanh \left( \frac{\hbar\omega}{2k_B T} \right), \quad (4)$$

where  $\sigma_0$  is a material-dependent parameter that is inversely proportional to the strength of the electron–phonon interaction and  $\hbar\omega$  is the average phonon energy contributing to the Urbach tail formation. The dashed curve in Fig. 3 represents a fitting curve using Eq. (4).  $\sigma_0$  is a material characteristic parameter as discussed above and is linearly proportional to the ionization of materials [32]. Considering that the ionization of AgGaS<sub>2</sub> is 0.65 and the results of ref. [35], the steepness parameter  $\sigma_0$  is approximately 2.35, which is similar to that of HgS and ZnSe [32]. However, we obtained a  $\sigma_0$  value of 1.03 in this work. The steepness parameter appeared to be influenced by defects such as the introduction of impurities, deviation from the stoichiometry, interstitial atoms, and vacancies generated during the growth process, and therefore the steepness parameter was estimated differently from each sample used in measurements.

From the fitting with Eq. (4), the average phonon energy  $\hbar\omega$  was estimated to be 25 meV, which is very close to the reported optical modes of 26 meV [33]. Hence, it may be concluded that the longitudinal optical (LO) phonon plays an important role in the Urbach tail with temperature. Some researchers have suggested that higher observed phonon energy than the averaged value calculated from the reported optical phonon modes is caused by lower symmetry and structural distortion [32]. However, our results are in good agreement with the LO phonon energy obtained via Raman spectroscopy.

Fig. 3 shows the Urbach energy  $k\theta/\sigma$  with temperature. Using  $\sigma_0$  obtained from Eq. (4) and the Debye temperature reported in ref. [34], we calculated Urbach's energies using Cody's model [35] with temperature, which are smaller as compared to the estimated values in this work, represented by solid squares.

This difference has also been reported in CuInTe<sub>2</sub>, and increases with increasing average phonon energy  $\hbar\omega$  [36].

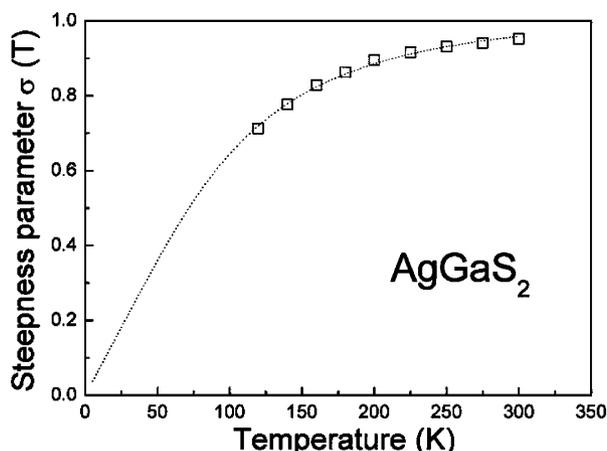


Fig. 3. Plot of the  $\sigma$  parameter as a function of temperature.

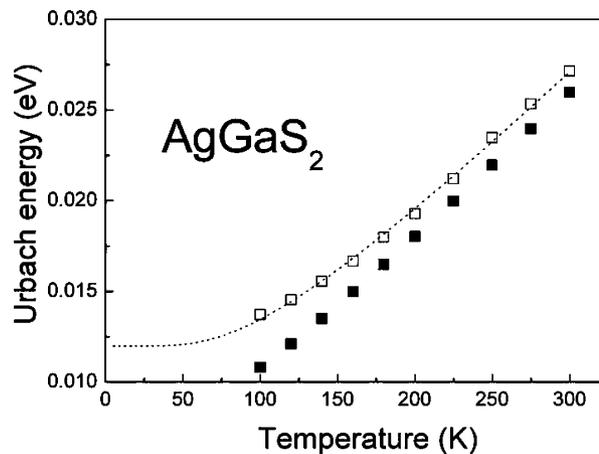


Fig. 4. Urbach energy as a function of temperature. The measured and the calculated Urbach energies using Cody's model with temperature are plotted with the open squares and the solid squares, respectively. The dotted line represents a fit to the measured data with Eq. (6).

To overcome this discrepancy, Cody et al. proposed the following equation, which takes the contribution of structural disorder into account [37]

$$E_U(T) = \frac{E_P}{2\sigma_0} \left[ \chi + \coth \left( \frac{E_P}{2kT} \right) \right], \quad (5)$$

where  $E_P$  is phonon energy and  $\chi$  is a measure of structural disorder. The best fit was obtained with  $\chi = 0.02$  and  $E_P = 24.7$  meV. This phonon energy is very close to that discussed in relation to the steepness parameter with temperature. Furthermore,  $\chi$  obtained from the fit is nearly equal to 0, which is an indication of the high quality of the grown AgGaS<sub>2</sub> single crystals. It was found that the disorder effects due to excessive doping and radiation considerably affects the  $\chi$  value. Highly Cu-doped CdS films with a large  $\chi$  value of 32–58 are good examples to illustrate the relation between  $\chi$  and structural disorder [38]. Hence, a lower  $\chi$  indicates higher crystal quality. Recently, it was found that the Urbach energy in Cu-III-VI<sub>2</sub> compounds is affected by molecularity and stoichiometry. A modified model of Eq. (5) was also proposed [28]

$$E_U(T) = \left( \frac{k_B \Theta_E}{\sigma_0} \right) \left[ \frac{1+N}{2} + \frac{P}{\exp(\Theta_E/T) - 1} \right], \quad (6)$$

where  $N$  is temperature-independent structural disorder, and  $P$  is a thermal phonon modification term.  $\Theta_E$  is Einstein's characteristic temperature and is related by  $\Theta_D = \sim 4\Theta_E/3$ . A tendency is observed from the Cu ternary compounds with various composition ratios, wherein  $N$  decreases with increasing average phonon energy  $\hbar\omega$ , whereas  $P$  increases. Using  $\sigma_0 = 1.03$  and  $\Theta_E = 295$  K obtained above, the experimental data were fitted using Eq. (6). The best fit was obtained with  $N = 0.02$  and  $P = 0.99$ , and is presented by a dashed line in Fig. 4. It should be noted that I-III-VI<sub>2</sub> compounds are composed of two different cations in atomic size related to II-VI compounds, leading to high structural disorder and structural

defect density. Nevertheless, these two values are close to the case of defect-free crystals,  $N = 0$  and  $P = 1$ , which demonstrates the high quality of our grown crystals. Eq. (6) can be also rewritten, using the fitting result, as follows

$$E_U = [\varepsilon_U(t) + \varepsilon_U(X, C)] = 24 \left( \frac{0.99}{\exp(295/T) - 1} \right) + 12 \text{ (meV)},$$

where  $\varepsilon_U(T)$  and  $\varepsilon_U(X, C)$  represent Urbach energies attributed to thermal and structural/compositional disorder, respectively. Accordingly, it is concluded that the effect of thermal disorder is dominant in terms of the variation of the absorption tail at room temperature, rather than thermally induced and structural/compositional disorder. These results are in contrast with that of  $\text{CuInTe}_2$  [36] and  $\text{CuInSe}_2$  [39] compounds, which revealed dominant structural disorder and larger phonon energy than that obtained using Raman spectroscopy. Considering the aforementioned, we can conclude that thermally induced disorder effects largely cause the variation of the absorption edge with temperature.

#### 4. Conclusions

Single crystals of  $\text{AgGaS}_2$  were grown with the Bridgman method, and optical absorption spectra were subsequently measured with temperature. We confirmed that the absorption spectra of  $\text{AgGaS}_2$  obey Urbach's rule. The characteristic Urbach parameters obtained in this work are as follows:  $E_0 = 2.78$  eV, steepness parameter  $\sigma_0 = 1.03$ , and the average phonon energy  $\hbar\omega$  is 25 meV. Hence, it can be concluded that LO-phonon plays an important role in the Urbach tail with temperature in  $\text{AgGaS}_2$ . To explain Urbach's energy with temperature, we adopted a modified version of Cody's model that takes into account structural disorder ( $N$ ) and the thermal term ( $P$ ). The obtained parameters are close to the case of defect-free crystals,  $N = 0$  and  $P = 1$ , which demonstrates the high quality of the grown crystals.

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