

Polarized-thermoreflectance study of the band-edge transitions in $\text{Cu}(\text{Al}_{0.5}\text{In}_{0.5})\text{S}_2$ solar-energy related crystal

Ching-Hwa Ho^{1,2*} and Guan-Tzu Huang²

¹Graduate Institute of Engineering and Department of Electronic Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan

²Department of Materials Science and Engineering, National Dong Hwa University, Shoufeng, Hualien 974, Taiwan
*chho@mail.ntust.edu.tw

Abstract: Polarization dependence of band-edge excitonic transitions in $\text{Cu}(\text{Al}_{0.5}\text{In}_{0.5})\text{S}_2$ [denoted as $\text{Cu}(\text{AlIn})\text{S}_2$] has been characterized using polarized-thermoreflectance (PTR) measurements with $E \parallel \langle 11\bar{1} \rangle$ and $E \perp \langle 11\bar{1} \rangle$ polarizations in the temperature range between 30 and 320 K. The measurements were done on as-grown $\{112\}$ surface of the chalcopyrite crystal. The polarization dependence of the band-edge transitions of $\text{Cu}(\text{AlIn})\text{S}_2$ clearly showed that the E_A exciton is present prominently with $E \parallel \langle 11\bar{1} \rangle$ polarization while the E_B exciton appears significantly only in the $E \perp \langle 11\bar{1} \rangle$ polarized spectra. For the unpolarized spectra, both E_A and E_B features were combined. The E_A feature is closely related to the E_0 transition, while the E_B feature is that of $E_0 + \Delta_0$ transition in the chalcopyrite. The crystal-field splitting energy of Δ_0 of $\text{Cu}(\text{AlIn})\text{S}_2$ at the valence-band top is determined accurately by PTR experiments. Temperature dependences of transition energies of E_A and E_B transitions were analyzed. The band-edge excitons reveal an anomalous temperature-energy shift with increasing the temperatures from 30 to 320 K due to the variation of Cu d electrons' contribution to valence band that affected by the native defects inside $\text{Cu}(\text{AlIn})\text{S}_2$. The PTR technique is more effective in studying the band-edge structure of the chalcopyrite crystal.

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OCIS codes: (160.4760) Optical properties; (300.6380) Modulation spectroscopy; (300.6470) Spectroscopy, semiconductors; (160.6000) Semiconductor materials.

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1. Introduction

Solar energy related materials of I-III-VI₂ (I = Cu, III = In, Ga, Al, and VI = S, Se) family crystals (chalcopyrite phase) are of potential interest for employed in photovoltaic application due to their very high absorption coefficient under sunlight [1,2]. Among these chalcopyrites, sulfide compounds such as Cu(Al,In)S₂, Cu(Al,Ga)S₂, and Cu(Ga,In)S₂ are more environmentally friendly to be free of selenium [3].

Energy band gap is the most important parameter which dominates the main optical-absorption peak of semiconductors. Band-edge structure also determines the optical-absorption behavior in materials. For the sulfide chalcopyrite compounds, CuInS₂ is a smallest-gap material (~1.54 eV) with an absorption peak in the near infrared (NIR) region [4]. On the other hand, CuAlS₂ possesses a largest gap of ~3.55 eV [5] with its main absorption peak located near ultra-violet (UV) region. To improve photoelectric-conversion efficiency of the solar-cell devices, cascaded thin-film solar cell made by I-III-VI₂ family with different band gaps may present high conversion yield due to the combination of absorption peak responses in the NIR, UV, and visible portions. For a cascaded thin-film solar cell by using the Cu(Al,In)S₂ series, CuInS₂ may employ in the NIR region, CuAlS₂ should be dominant in the UV portion, while Cu(AlIn)S₂ may play a best role for optoelectronic conversion in the visible range due to its middle-composition characteristic in between the end members of CuInS₂ and CuAlS₂. Although Cu(AlIn)S₂ is expected to have an absorption-peak response in the visible region the experimental evaluation on the band-edge structure of the mixed-crystal chalcopyrite has not yet been reported.

This paper characterizes the experimental band-edge structure of Cu(Al_{0.5}In_{0.5})S₂ chalcopyrite crystal by performing polarized-thermoreflectance (PTR) spectroscopy in the temperature range between 30 and 320 K. The PTR had been proven to be a powerful tool for studying band-edge characteristic of anisotropic crystalline materials [6]. In this study, the PTR measurements were carried out on as-grown {112} face of the chalcopyrite. Two transition features of E_A and E_B that corresponding to the interband transitions of $\Gamma_{4V} \rightarrow \Gamma_{1C}$ and $\Gamma_{5V} \rightarrow \Gamma_{1C}$ are respectively detected in the PTR spectra of E || <11 $\bar{1}$ > and E \perp <11 $\bar{1}$ > polarizations. The optical selection rule of Cu(AlIn)S₂ crystal clearly indicates that the E_A feature is forbidden with the E \perp <11 $\bar{1}$ > polarization, whereas the E_B feature is not allowed with the optical measurement along E || <11 $\bar{1}$ > polarized orientation. The energies of band-edge transitions of E₀ (E_A) and E₀ + Δ_0 (E_B) are determined to be 2.192 and 2.267 eV at 300 K. Temperature dependence of transition energies of E₀ and E₀ + Δ_0 from the temperature-dependent analysis of PTR spectra for Cu(AlIn)S₂ is evaluated. The dependency shows an abnormal S-shape energy variation with increasing the temperatures from 30 to 320 K. This result also renders a maximum turnover temperature of Cu(AlIn)S₂ located at 170 K. The occurrence of anomalous temperature-energy shift of the chalcopyrite may closely related to the native defects inside Cu(AlIn)S₂.

2. Experiment

Single crystals of Cu(Al_{0.5}In_{0.5})S₂ solid solution were grown by chemical vapor transport (CVT) method using ICl₃ as a transport agent. All the starting materials (by stoichiometric weight of each element) and the transport agent were sealed in an evacuated quartz ampoule. The growth temperature was set as 850 °C \rightarrow 750 °C with a gradient of -5°C/cm. The reaction kept 280 hrs for producing large single crystals. Detailed procedure of CVT was described elsewhere [7]. The as-grown crystals showed slightly dark-red colored and

transparent with a maximum size up to $8 \times 1.5 \times 1 \text{ mm}^3$. Figure 1 shows the crystal morphology of the as-grown $\text{Cu}(\text{AlIn})\text{S}_2$ crystal. The $\{112\}$ face seems to be the favorite as-grown surface of the crystals. Electron probe microanalysis showed a slight chalcogen deficiency in the crystals. The stoichiometric composition for all elements inside the crystal is matched to a reasonable standard error of the original stoichiometry. X-ray diffraction measurements confirmed the chalcopyrite phase of the solids. The X-ray pattern was analyzed and the lattice parameters were determined to be $a = 5.44 \text{ \AA}$ and $c = 10.80 \text{ \AA}$, respectively.

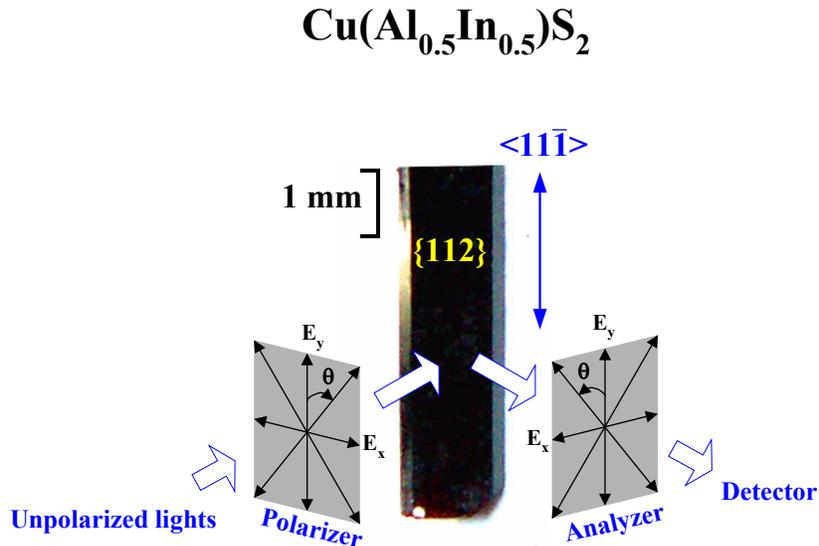


Fig. 1. The crystal morphology and measurement arrangement of PTR experiments for $\text{Cu}(\text{Al}_{0.5}\text{In}_{0.5})\text{S}_2$.

The PTR experiments were carried out in the energy range of 1.8 to 2.8 eV. An 150 W tungsten-halogen lamp filtered by a PTI 0.2 m monochromator provided the monochromatic light. The reflected light of the sample was detected by an EG&G type HUV-2000B silicon photodiode and the signal was recorded from an EG&G model 7265 dual phase lock-in amplifier. A pair of visible-dichroic-sheet polarizers with the measured range of 700-400 nm was employed in the PTR measurements of $\text{Cu}(\text{AlIn})\text{S}_2$. The representative scheme for the sample placement and measurement arrangement of PTR is demonstrated in Fig. 1. The experiments were done on the $\{112\}$ face. The angular-dependent polarized measurements were carried out with the linearly polarized light setting at $E \parallel \langle 11\bar{1} \rangle$ ($\theta = 0^\circ$) or $E \perp \langle 11\bar{1} \rangle$ ($\theta = 90^\circ$) polarized orientation. For thermal perturbation of the samples, a quartz plate acted as the heat sink. The quartz plate was coated with a winding path of golden tracks as the heating element. The shape of the golden path was formed by a copper mask. The detailed experimental procedure of TR was described elsewhere [6]. The measurements were done in the temperature range between 30 and 320 K with a temperature stability of about 0.5 K or better. A RMC model 22 closed-cycle cryogenic refrigerator equipped with a model 4075 digital thermometer controller facilitated the temperature dependent measurement.

3. Results and discussion

Figure 2 shows the PTR spectra of $E \parallel \langle 11\bar{1} \rangle$ ($\theta = 0^\circ$) and $E \perp \langle 11\bar{1} \rangle$ ($\theta = 90^\circ$) polarizations for $\text{Cu}(\text{AlIn})\text{S}_2$ at (a) 300 K, and (b) 30 K, respectively. The dashed lines are the experimental data and open-circle lines are the least-square fits to a Lorentzian line-shape function appropriate for the interband transitions expressed as [8,9]:

$$\frac{\Delta R}{R} = \text{Re} \left[\sum_{i=1}^2 A_i^{\text{ex}} e^{j\phi_i^{\text{ex}}} (E - E_i^{\text{ex}} + j\Gamma_i^{\text{ex}})^{-2} \right] \quad (1)$$

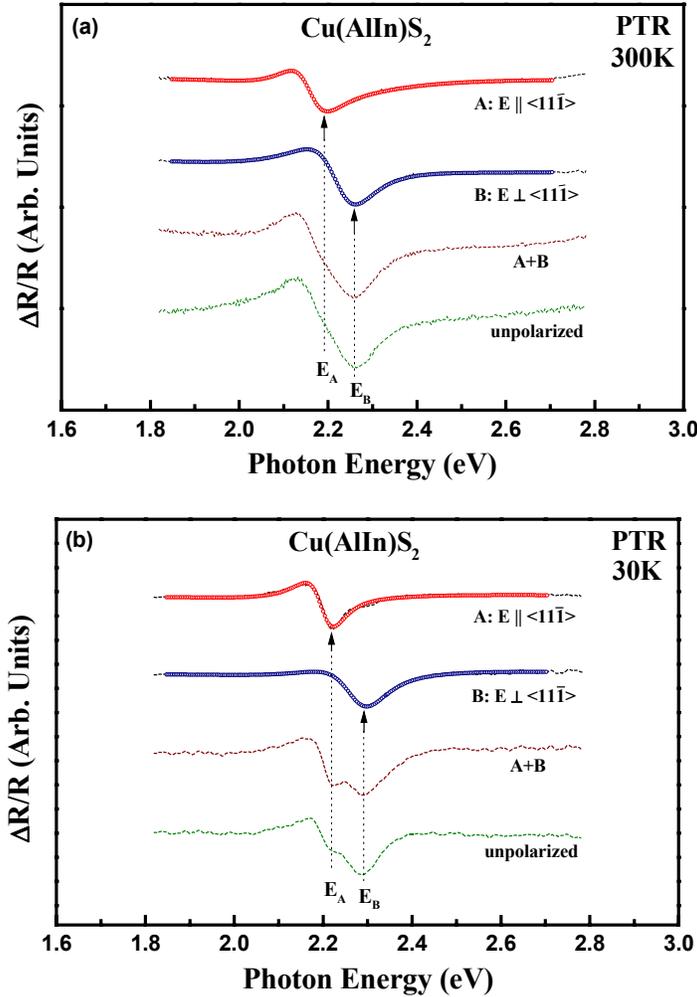


Fig. 2. Experimental PTR spectra of Cu(AlIn)S₂ at (a) 300 and (b) 30 K along E || <111> and E ⊥ <111> polarizations. The dashed lines are experimental data and open-circle lines are least-square fits to Eq. (1). The obtained transition energies are indicated by arrows.

where A_i^{ex} and ϕ_i^{ex} are the amplitude and phase of the lineshape, and E_i^{ex} and Γ_i^{ex} are the energy and broadening parameter of the interband transition. As shown in Fig. 2, two transition features of E_A and E_B combine together in the unpolarized spectra of Cu(AlIn)S₂ at 30 and 300 K. The polarization dependence of band-edge transitions of Cu(AlIn)S₂ clearly indicates that the E_A feature is merely present in the E || <111> polarization while the E_B feature appears prominently only in the E ⊥ <111> polarized spectra. The unpolarized spectrum can be regarded as the random superposition of the PTR spectra with E || <111>

and $E \perp \langle 11\bar{1} \rangle$ polarizations. This situation can be evident from the similar spectral line shape of A + B (i.e. linear combination of two polarized spectra) and unpolarized TR spectra in Fig. 2. Transition energies of the E_A and E_B features in Fig. 2 can be analyzed by fitting the PTR spectra to Eq. (1) that obtained transition energies are indicated with arrows. The values of E_A and E_B at 300 K (30 K) are respectively 2.192 ± 0.008 eV (2.222 ± 0.005 eV) and 2.267 ± 0.008 eV (2.292 ± 0.005 eV). This result also determines an uniaxial crystal-field splitting energy (i.e. $E_B - E_A$) of $\Delta_0 = 75$ meV at 300 K and $\Delta_0 = 70$ meV at 30 K, respectively.

The crystal structure of I-III-VI₂ family is a chalcopyrite form. The chalcopyrite lattice crystallizes in a tetragonal structure with its unit cell approximately doubles the size of a zinc-blende unit cell (e.g. ZnS) along the *c*-axis. The sub-unit cells of chalcopyrite are essentially the zinc-blende type. The main difference in between a zinc-blende and an I-III-VI₂ unit cell is the unequal bond lengths of $R_{I-VI} \neq R_{III-VI}$ due to different atomic sizes of I and III cations contributed to the I-VI and III-VI bonds. Therefore copper incorporation to the valence band (E_V) is the main distinction in chalcopyrite [CuInS₂, CuAlS₂, and Cu(AlIn)S₂] with respect to the general zinc-blendes [10,11]. The main contribution of valence band for the chalcopyrite is coming from Cu 3*d* – S 3*p* hybridizations. One consequence of *p*-*d* hybridization is *p*-*d* repulsion. The *p*-*d* repulsion makes a substantial upward repulsion to lift up S *p*-like $\Gamma_{15}(p)$ states, which also reduces the band gap of the chalcopyrite compounds relative to their II-VI zinc-blende binary analogs. Because the raise of the S 3*p* states by *p*-*d* repulsion, the sulfur *p* electrons are hence entering into the conduction band [10]. The band-gap transition of Cu(AlIn)S₂ is therefore determined by the *p* → *p* transition of sulfur. The sulfur *p* → *p* transition is an “intra-atomic” transition in the I-III-VI₂ compounds. This type of band gap differs from that of the binary II-VI zinc-blendes, which belong to the “inter-atomic” transition. A compound with band gap of “intra-atomic” transition has a special character in contrast to that of the “inter-atomic” band gap. The specialty is very high absorption coefficient for the chalcopyrite to be utilized as the solar-cell material. The *p*-*d* hybridization in valence band also achieves the separation of S 3*p* Γ_{15} band into $\Gamma_{4V}(p)$ and $\Gamma_{5V}(p)$ located at the E_V maximum by crystal field splitting. For CuInS₂, the E_V top is Γ_{5V} (i.e. $\Gamma_{5V} > \Gamma_{4V}$) [10]. It is claimed to be contradict to the other chalcopyrites (i.e. CuGaS₂, CuAlS₂) with the E_V maximum located at Γ_{4V} [10]. The Γ_{4V} and Γ_{5V} bands at the E_V top can be respectively identified by the polarization-dependent optical measurements using $E \parallel \langle 11\bar{1} \rangle$ and $E \perp \langle 11\bar{1} \rangle$ polarizations [2]. The PTR spectra of Cu(AlIn)S₂ shown in Fig. 2 clearly indicates that the transition energy of E_A with $E \parallel \langle 11\bar{1} \rangle$ polarization is lower than that of E_B with $E \perp \langle 11\bar{1} \rangle$ polarization. It lends an evidence that the band-edge nature of E_V for Cu(AlIn)S₂ is similar to that of CuAlS₂ with $\Gamma_{4V} > \Gamma_{5V}$ located at the valence-band top [5]. Figure 3 depicts the band-edge structure of Cu(AlIn)S₂ determined by PTR measurement at 300 K. The band gap is determined by S *p*→*p* transition. The presence of E_A (E_0) and E_B ($E_0 + \Delta_0$) is attributed to the valence-band splitting in Cu(AlIn)S₂, which caused by the uniaxial crystal field. The crystal-field splitting Δ_0 is 75 meV for Cu(AlIn)S₂, which is dissimilar to $\Delta_0 \approx 154$ meV for CuAlS₂ [5] and $|\Delta_0| \approx 22$ meV for CuInS₂ [12,13] due to different amount of uniaxial stress (i.e. different crystal field) existed in the chalcopyrites with the stoichiometric variation of aluminum and indium composition from CuAlS₂ to CuInS₂. For the conduction band (E_C) of Cu(AlIn)S₂, the lowest band is Γ_{1C} , and which is determined by the antibonding S 3*p** [11]. The E_C edge usually exists an excitonic level starting from the principal quantum number of $n = 2$ below Γ_{1C} due to its *p*-state character. The E_0 and $E_0 + \Delta_0$ are assigned as the band-edge transitions of $\Gamma_{4V} \rightarrow \Gamma_{1C}$ and $\Gamma_{5V} \rightarrow \Gamma_{1C}$, respectively.

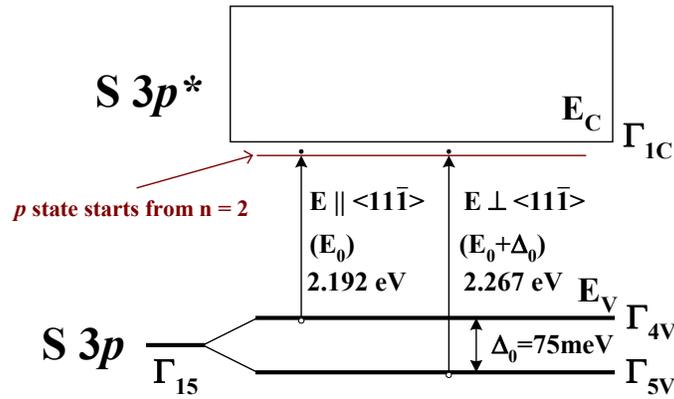


Fig. 3. The representative scheme of band-edge structure of $\text{Cu}(\text{AlIn})\text{S}_2$ by PTR experiments at 300 K.

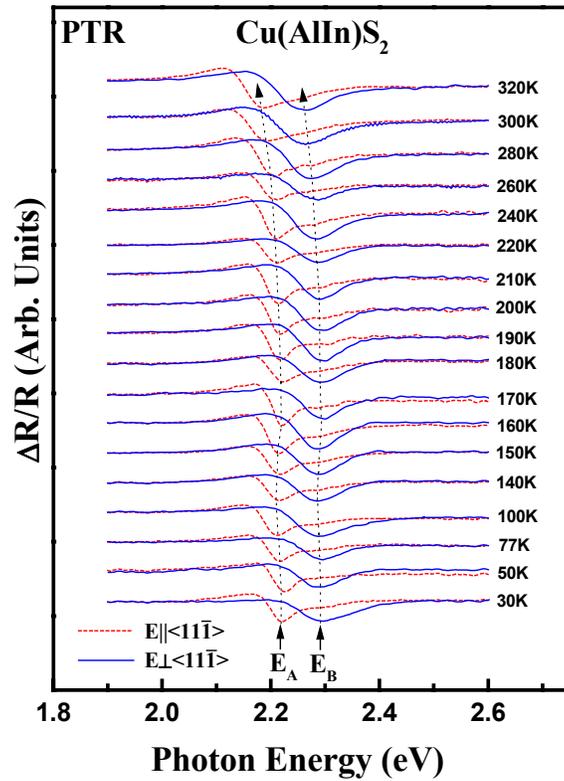


Fig. 4. Temperature-dependent PTR spectra of $\text{Cu}(\text{AlIn})\text{S}_2$ between 30 and 320 K. The dashed lines are the experimental data with $E \parallel \langle 11\bar{1} \rangle$ polarization and solid lines are those of the $E \perp \langle 11\bar{1} \rangle$ polarized spectra.

Temperature dependent PTR spectra of $\text{Cu}(\text{AlIn})\text{S}_2$ in the temperature range of 30-320K are shown in Fig. 4. The dashed lines are the PTR spectra with $E \parallel \langle 11\bar{1} \rangle$ polarization and the solid lines are the experimental data of $E \perp \langle 11\bar{1} \rangle$ polarized spectra. The optical selection rule applied to the valence band of Γ_{4V} and Γ_{5V} clearly indicates that the E_A transition is forbidden in the $E \perp \langle 11\bar{1} \rangle$ polarization while the E_B feature is not allowed in the $E \parallel \langle 11\bar{1} \rangle$ polarized spectra. The temperature-dependent PTR spectra of $\text{Cu}(\text{AlIn})\text{S}_2$ in Fig. 4 can be analyzed by the Lorentzian line-shape function using Eq. (1) (not showing fitted curves) and the obtained transition energies of E_A and E_B are indicated by arrows and are interconnected by dotted lines to show their temperature-variation trace from 30 to 320 K. As the temperature is raised, the E_A and E_B features demonstrate a slowly energy red-shift behavior with increasing the temperatures from 30 to 140 K. Whereas the E_A and E_B features reveal anomalous blue shift with the temperatures increased from 140 to 170 K. For $T > 170$ K, the temperature-energy variation of the band-edge transitions in $\text{Cu}(\text{AlIn})\text{S}_2$ recovers to normal behavior of general semiconductors. An anomalous S-shape temperature-energy shift for E_A and E_B is found with the increase of temperatures from 30 to 320 K (see Fig. 4), where a maximum turnover temperature of about 170 K is occurred. The occurrence of abnormal temperature-energy shift of $\text{Cu}(\text{AlIn})\text{S}_2$ may come from the native defects such as V_{Cu} and V_{S} inside $\text{Cu}(\text{AlIn})\text{S}_2$ to alter the symmetry center of the chalcopyrite lattice points when the temperature is changed. This consequence reduces the contribution of copper d electrons in the valence band, which increases the band gap of $\text{Cu}(\text{AlIn})\text{S}_2$ near the turnover temperature. Although the temperature of $\text{Cu}(\text{AlIn})\text{S}_2$ increases from 140 to 170K the energies of the E_A and E_B features still present anomalous blue shift due to somewhat reduction of p - d repulsion in the temperature range to increase band gap. This situation had also been found in an as grown sulfur-deficient CuInS_2 crystal ($E_g \approx 1.54$ eV) with the turnover temperature of 120 K [12]. For the sulfur-annealed sample, the anomalous blue-shift effect is small [12]. The anomalous temperature-energy shift of the band gap of $\text{Cu}(\text{AlIn})\text{S}_2$ may cause by copper vacancy (V_{Cu}) and sulfur vacancy (V_{S}) inside the crystal to reduce the d electrons' contribution in the valence band (i.e. reduce the p - d repulsion to enlarge gap). The V_{S} may come from sulfur deficiency of the crystal while V_{Cu} is caused by the deficiency of copper similar to the native copper vacancies that frequently detected in CuAlS_2 [14]. For the CuAlS_2 , the maximum turnover temperature had been evaluated to be about 210 K [5], which is higher than those of $\text{Cu}(\text{AlIn})\text{S}_2$ and CuInS_2 .

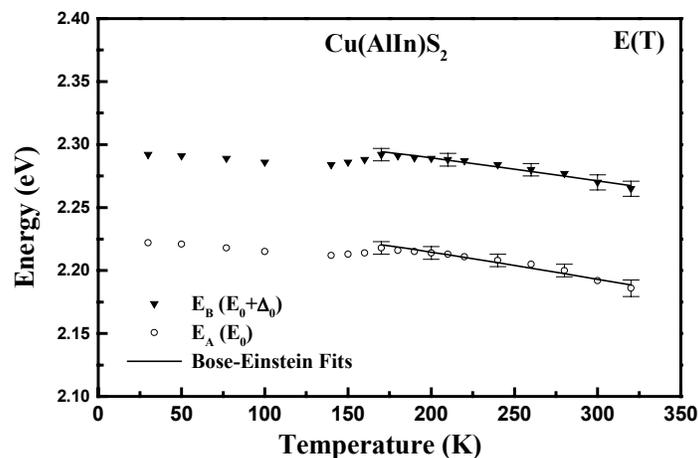


Fig. 5. Temperature dependences of transition energies of E_A (E_0) and E_B ($E_0 + \Delta_0$) in $\text{Cu}(\text{AlIn})\text{S}_2$.

Temperature dependence of transition energies of E_A (E_0) and E_B ($E_0 + \Delta_0$) features obtained by the PTR measurements of 30-320 K are depicted in Fig. 5. The solid lines (above 170 K) are fitted to a Bose-Einstein expression $E_i(T) = E_{iB} - a_{iB} \cdot \{1 + 2/[\exp(\Theta_{iB}/T) - 1]\}$, where i is the respective transition feature, a_{iB} represents the strength of the electron (exciton)-phonon interaction and Θ_{iB} corresponds to the average phonon temperature. The fitted values of E_{iB} , a_{iB} and Θ_{iB} of $\text{Cu}(\text{AlIn})\text{S}_2$ are 2.334 ± 0.003 eV, 28 ± 5 meV, and 240 ± 40 K for $E_0 + \Delta_0$ transition, and 2.267 ± 0.003 eV, 34 ± 5 meV, and 245 ± 40 K for E_0 transition, respectively. These values are available for the estimate of transition energies into higher temperature range when the solar-cell material is operated under sunlight with $T > 300$ K. The temperature-energy shift of E_A and E_B features in Fig. 5 also reveals approximately parallel temperature dependence due to their similar valence-band origin that coming from the sulfur $p \rightarrow p$ transition.

4. Conclusions

Polarization-dependent band-edge transitions of $\text{Cu}(\text{Al}_{0.5}\text{In}_{0.5})\text{S}_2$ are evaluated by temperature-dependent PTR measurements in the temperature range between 30 and 320 K. The optical selection rule applied to the valence band of the chalcopyrite is clearly demonstrated in the PTR spectra of $\text{Cu}(\text{AlIn})\text{S}_2$. The energy values of E_0 and $E_0 + \Delta_0$ at 300 K are respectively determined to be 2.192 ± 0.008 eV and 2.267 ± 0.008 eV. The crystal-field splitting energy between Γ_{4V} and Γ_{5V} is determined to be $\Delta_0 = 75$ meV at 300 K, which is lying in between those of CuInS_2 and CuAlS_2 . The temperature-energy shift of the band-edge transitions in $\text{Cu}(\text{AlIn})\text{S}_2$ shows an anomalous S-shape variation with increasing the temperatures from 30 to 320 K. It is due to the native defects such as V_{Cu} and V_{S} in $\text{Cu}(\text{AlIn})\text{S}_2$ to alter the symmetry center of the chalcopyrite lattice points when the temperature is changed. The maximum turnover temperature for the abnormality of $\text{Cu}(\text{AlIn})\text{S}_2$ is about 170 K. It is lying in between the turnover temperatures of CuInS_2 and CuAlS_2 in the same chalcopyrite series of $\text{Cu}(\text{Al},\text{In})\text{S}_2$. From the experimental analyses of PTR, it can be inferred that both the crystal-field splitting energy (Δ_0) and maximum turnover temperature for the $\text{Cu}(\text{Al}_{1-x}\text{In}_x)\text{S}_2$ ($0 \leq x \leq 1$) series may be simultaneously determined by the uniaxial crystal field existed in the chalcopyrite lattice.

Acknowledgments

The authors would like to acknowledge the financial support from the National Science Council of Taiwan under the grant No. NSC 98-2221-E-011-151-MY3.