



Optical and structural properties of orthorhombic and tetragonal polymorphs of $\text{Cu}_2\text{CdGeSe}_4$

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ABSTRACT

The quaternary $\text{Cu}_2\text{CdGeSe}_4$ (CCGSe) is a potential absorber material for thin film solar cells. This study presents the results of photoluminescence (PL) and X-ray diffraction analysis of high-temperature and low-temperature CCGSe polycrystals with orthorhombic (space group $Pmn2_1$) and tetragonal (space group $I4_2m$) crystal structure, respectively. Detailed PL analysis revealed different dominating radiative recombination mechanisms for orthorhombic and tetragonal CCGSe.

1. Introduction

$\text{Cu}_2\text{CdGeSe}_4$ (CCGSe) belonging to the group of quaternary copper chalcogenides is a potential absorber material for thin film solar cells. From this group of compounds the record power conversion efficiency of 12.6% is obtained for $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ [1]. However, still limited efficiency compared to other thin film solar cells based on $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$ and CdTe showing efficiencies of 22.9% [2] and 22.1% [3], respectively, is driving the research of other quaternary chalcogenides like $\text{Cu}_2\text{CdGeSe}_4$. CCGSe has p-type conductivity and very promising properties including a band gap energy of about 1.20–1.29 eV [4,5]. Depending on the synthesis conditions, CCGSe can crystallize in orthorhombic structure with a $Pmn2_1$ space group and in stannite tetragonal structure with a $I4_2m$ space group [5,6]. Tetragonal crystal structure was found to prevail at low temperatures ($T < 878$ K) and orthorhombic crystal structure at higher temperatures ($T > 878$ K), the corresponding material is named tetragonal CCGSe (t-CCGSe) and orthorhombic CCGSe (o-CCGSe), respectively [7,8]. According to the first-principles calculations by Zhang et al. [9] the band gap of t-CCGSe is 1.06 eV and of o-CCGSe 1.16 eV. Brik et al. [4] found band gap of 1.2 eV at $T = 300$ K for t-CCGSe from the optical absorption measurements. So, there is a contradiction in the band gap energy values of this compound and more experimental information would be valuable. Moreover, information about the radiative recombination in tetragonal and orthorhombic CCGSe could not be found in the literature. The differences in the optical properties of the t- and o-CCGSe are a subject of the present study. Photoluminescence (PL) spectroscopy is used

together with X-ray diffraction (XRD) to obtain detailed information about the radiative recombination mechanisms in orthorhombic and tetragonal CCGSe.

2. Experimental

In order to produce o-CCGSe and t-CCGSe, previously synthesized CCGSe monocrystalline powder was post-treated in two different ampoules at 1173 K for 2 h followed by slow cooling of the samples to 673 K with the cooling rate ~ 0.2 degree/min. To obtain the o-CCGSe modification, the sample was quenched into water. According to XRD analysis, the sample consisted of a mixture of t- and o-modifications. Therefore, to obtain more pure o-CCGSe, the polycrystalline sample was annealed once again at 873 K for 20 h and cooled by quenching into water. t-CCGSe modification resulted from continuous annealing of the sample at 673 K for 250 h and then cooling to room temperature with the rate ~ 0.5 degree/min. According to Energy Dispersive X-Ray Spectroscopy analysis, the resulting o-CCGSe and t-CCGSe polycrystals had near-stoichiometric composition.

The crystal structure of the studied CCGSe polycrystalline powder was determined by XRD by using a Rigaku Ultima IV diffractometer with monochromatic $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 40 mA operating with the silicon strip detector D/teX Ultra. All samples were studied in the 2θ range of 10–60 deg. with the scan step of 0.02 deg. The phase analysis and lattice parameters calculations were made by using software on the Rigaku's system PDXL2.

A 0.64 m focal length single grating (600 mm^{-1}) monochromator

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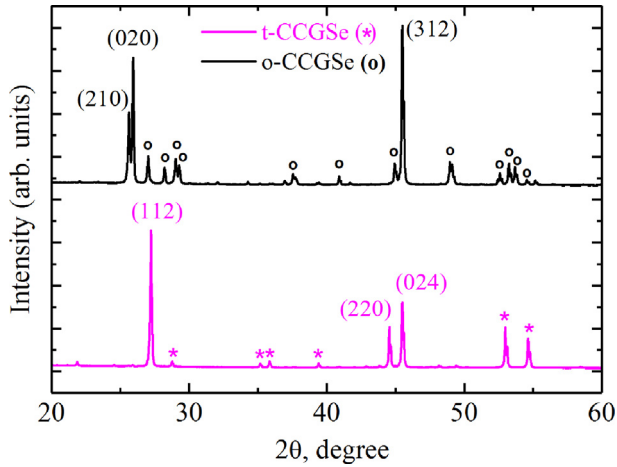


Fig. 1. XRD patterns of o- and t-CCGSe polycrystals. The dominating peaks are labelled with the corresponding indices, rest of the peaks belonging to the respective phase are marked with symbols.

and the 442 nm line of a He-Cd laser with different power were used for the PL measurements. For PL signal detection a Hamamatsu InGaAs detector was used. A closed-cycle helium cryostat was employed to measure temperature dependencies of the PL spectra at temperatures from 10 K to 300 K.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of o- and t-CCGSe are presented in Fig. 1. The t-CCGSe was found to crystallize in tetragonal structure with space group $\bar{4}2m$ and o-CCGSe in orthorhombic structure with space group $Pmn2_1$. Small traces of t-CCGSe were found in o-CCGSe sample. From the diffraction patterns the following lattice parameters were determined: $a = 0.5747$ nm and $c = 1.1055$ nm for t-CCGSe and $a = 0.8071$ nm, $b = 0.6883$ nm and $c = 0.6607$ nm for o-CCGSe. The obtained crystal structures and lattice parameter values are in correspondence with the data reported by Gulay et al. [6].

3.2. Photoluminescence analysis

The PL spectra of t-CCGSe and o-CCGSe polycrystals measured at $T = 10$ K are presented in Fig. 2. The PL spectrum of o-CCGSe at $T = 10$ K consists of three PL bands at 1.027 eV, 1.146 eV and 1.218 eV. The PL spectrum of t-CCGSe includes only one asymmetric PL band at 1.053 eV. Due to the asymmetric shape of the PL bands, the experimental spectra were fitted with an empirical asymmetric double sigmoid function [10]. The PL bands have a steeper decline at high-energy side and a nearly temperature independent incline at the low-energy side that is common in multinary semiconductors with band tails [10,11,12]. The temperature and laser power dependencies were measured for both spectra and following information on the radiative recombination mechanisms in t-CCGSe and o-CCGSe was obtained.

Fig. 3 presents the temperature and laser power dependencies of the PL spectrum of o-CCGSe. Due to the low intensity of the PL band at 1.027 eV, detailed analysis of this PL band was not conducted. Due to the match of this PL band position with the PL band detected in t-CCGSe and considering that the XRD analysis showed traces of t-CCGSe in the o-CCGSe sample, we propose that this PL band originates from t-CCGSe phase. The analysis of the PL band at 1.146 eV in o-CCGSe is submitted as a separate publication and is not presented here.

The high-energy PL band at 1.218 eV in o-CCGSe has not been detected before. Strong dependence of the PL band at 1.218 eV on

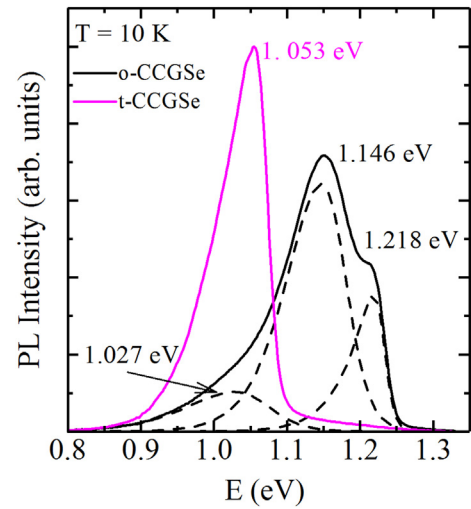


Fig. 2. PL spectra of t-CCGSe and o-CCGSe polycrystals measured at $T = 10$ K together with the PL band positions determined from the fitting of the spectra. The fitting for the PL spectrum of o-CCGSe is shown with dashed lines.

temperature and laser power i.e. on carrier concentration suggests that the recombination behind this PL band involves localized carriers, electrons in potential wells and holes in acceptor states. In so-called highly doped materials, this type of recombination is possible if donors form clusters involving several defects [12]. In this case potential wells that are deep enough for electrons to be localized are formed and due to the bending of the bands near a donor cluster, as the separation r between the donor cluster and the acceptor states decreases, the energy of acceptor states increases. The temperature dependence of the peak position of the PL band at 1.218 eV is presented in Fig. 4 showing continuous shift towards higher energies with increasing temperature. At low temperatures holes occupy acceptor states that are far from the cluster and the peak position of the PL band has a lowest value. When the temperature increases, holes have enough energy to move closer to the donor cluster and the peak position of the PL band starts to move towards higher energy as can be seen in Fig. 4. This is typical tail-to-impurity (TI) emission, see [11,12,13]. It is known, that the TI recombination behaves like a donor-acceptor pair recombination where the energy of the radiative recombination is determined by

$$E = E_e - E_h + \frac{e^2}{\epsilon r} \quad (1)$$

where E_e and E_h are the energy of the electron in the potential well and the energy of the hole in the acceptor state, at the distance r from the cluster, respectively, and ϵ is the dielectric constant. The peak position of the TI band E_{max} can be calculated as [11]:

$$E_{max} = E_g^0 - E_a - \gamma - kT \ln(G) + 2\sqrt{(kT)^2 \ln(G) + kT\gamma} \quad (2)$$

where E_g^0 is the bandgap energy of the undoped “ideal” semiconductor at $T = 0$ K, E_a is the ionisation energy of the acceptor, γ is the root-mean-square depth of potential fluctuations, $G = N_c/n$ where N_c is the effective density of states of the conduction band, n is the concentration of electrons in the conduction band, T is the temperature and k is the Boltzmann constant. The estimated value of γ is 20 meV obtained from the slope of the low-energy side of the PL band at 1.146 eV according to [11]. An exponential incline of this PL band at low energy side $I(E) \sim \exp\left(-\frac{E}{\gamma}\right)$ results from the exponential shape of the density of states function [11].

Temperature dependence of the peak position of the TI band together with its theoretical dependence calculated using Eq. (2) with different values of G is presented in Fig. 4. To study the influence of the carrier concentration on the behavior of the PL emission, the laser

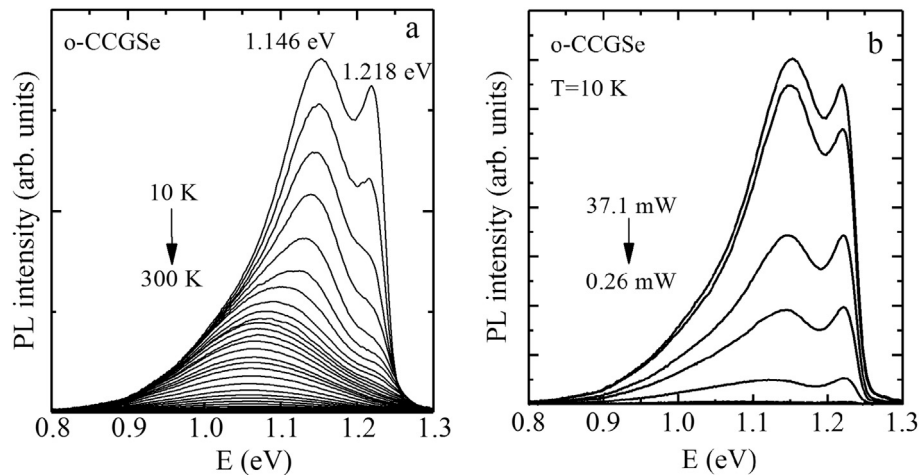


Fig. 3. (a) Temperature and (b) laser power dependencies ($T = 10$ K) of the PL spectrum of orthorhombic CCGSe.

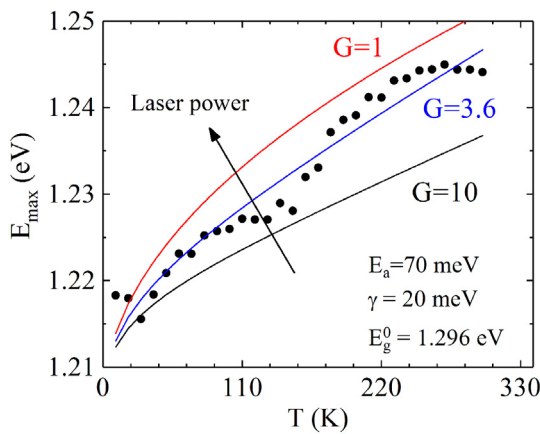


Fig. 4. Temperature dependence of the peak position of the TI band (dots) and the theoretical dependence calculated using Eq. (2) with different values of G (solid lines).

power dependence of the spectrum was measured at temperatures $T = 10$ K (see Fig. 3b) and $T = 100$ K. The low temperature laser power dependence resulted in the 1.5 meV/decade shift of the PL band at 1.218 eV towards higher energies with increasing laser power. At $T = 100$ K a larger shift of 10 meV/decade was obtained. This is in accordance with the theoretical behavior of the TI-band presented in Fig. 4 showing larger shift of the PL band with increasing injection level and temperature. From the fitting with Eq. (2) $G = 3.6$ and $E_g^0 = 1.296$ eV are obtained for the studied o-CCGSe. The ionisation energy of the acceptor $E_a = 70$ meV is determined from the temperature dependence of the PL spectrum presented in Fig. 3a using following Eq. [14]: $I(T) = I/[1 + A_1 T^{3/2} + A_2 T^{3/2} \exp(-E_a/kT)]$, where I is the integral intensity of the PL band, A_1 and A_2 are process rate parameters and E_a is the thermal activation energy. The detected acceptor defect with ionisation energy of 70 meV taking part in the radiative recombination behind the PL band at 1.218 eV in o-CCGSe could be Cu_{Cd} .

The PL spectrum of t-CCGSe includes only one asymmetric PL band at 1.053 eV (Fig. 2). A peak position shift of 13 meV/decade was determined from the laser power dependence of this PL band at $T = 10$ K. The thermal quenching of the PL emission can be divided into two regions: low-temperature quenching process with no clear activation energy and high-temperature quenching with activation energy of $E_a = 103 \pm 4$ meV (see Fig. 5a). Two temperature regions showing different dominating processes can also be seen in the temperature dependence of the half-width and the peak position of this PL band (Fig. 5b). The low-temperature ($T < 50$ K) process can be attributed to

the thermal redistribution of electrons between the localized energy levels near the conduction band edge shifting the PL peak to lower energies with increasing temperature. At higher temperatures ($T > 50$ K) the localized energy levels are emptied and the recombination will continue through the band states. The behavior of the PL band in the high temperature region corresponds to the band-to-impurity (BI) recombination involving acceptor states with the ionisation energy of about 103 meV. In the case of BI recombination, the peak position $E_{\text{max}} = E_g - E_a$, where E_g is a bandgap energy and E_a is a thermal quenching activation energy [11]. Considering that $E_{\text{max}}(T = 10 \text{ K}) = 1.053$ eV and $E_a = 103$ meV, the E_g at $T = 10$ K should be about 1.156 eV that is in very nice correlation with the band gap energy obtained from the quantum efficiency measurements of the solar cells based on LT-CCGSe ($E_g = 1.14$ eV at $T = 300$ K [15]).

To summarize, the detailed analysis of the PL emission of t- and o-CCGSe shows significant difference in the radiative recombination processes in comparison to most studied multinary kesterite compound $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ giving the less studied material CCGSe an opportunity to overcome the factors limiting the efficiency of the CZTSSe based solar cells.

4. Conclusions

Radiative recombination mechanisms dominating in tetragonal and orthorhombic CCGSe were studied and were found to have different origin. The PL spectrum of t-CCGSe includes one PL band at 1.053 eV showing different behavior at low and high temperatures. The low-temperature ($T < 50$ K) process is attributed to the thermal redistribution of electrons between the localized energy levels near the conduction band edge. At higher temperatures ($T > 50$ K) BI recombination involving acceptor states with the ionisation energy of about 103 meV is dominating.

The PL spectrum of o-CCGSe includes three PL bands at 1.027 eV, 1.146 eV and 1.218 eV from which the PL band at 1.218 eV is not been observed before. This PL band is found to originate from TI recombination involving an acceptor defect with ionisation energy of about 70 meV and electrons localized in potential wells created by clusters of donor defects.

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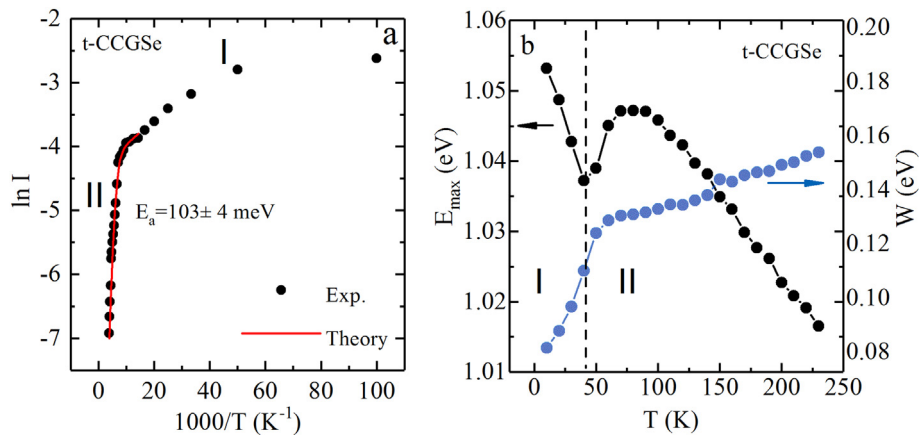


Fig. 5. (a) Arrhenius plot showing the two thermal processes (regions I and II), and (b) temperature dependence of the PL band peak position E_{max} and half-width W for t-CCGSe.

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