Study of point defects in wide-bandgap Cu2CdGeS4 microcrystals by temperature and laser power dependent photoluminescence spectroscopy

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Study of point defects in wide-bandgap Cu$_2$CdGeS$_4$ microcrystals by temperature and laser power dependent photoluminescence spectroscopy.

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Abstract

We present temperature and laser power dependent photoluminescence (PL) study of high quality wide-bandgap Cu$_2$CdGeS$_4$ microcrystals. At T=10 K three PL bands were detected at about 1.919 eV (#1), 1.855 eV (#2) and 1.748 eV (#3). The temperature and laser power dependencies indicate that the properties of PL bands can be explained by donor-acceptor pair model, where the #1 and #2 bands result from a recombination between distant pairs involving the same shallow acceptor V$_{Cu}$ with $E_A \approx$ 30 meV and different deep donor defects. The #3 PL band originates from the deep donor-deep acceptor pair recombination where the depth of deep acceptor defect is more than 157 meV. Detailed analysis of the PL spectra show the absence of deep potential or band gap fluctuations in this material making it suitable for photovoltaic applications.

Keywords: photoluminescence, donor-acceptor pairs, defects, Cu$_2$CdGeS$_4$, wide bandgap.

1. Introduction

Earth-abundant, inexpensive and non-toxic materials for thin film solar cell technologies are attracting considerable attention due to the growing need for environmentally friendly and sustainable sources of renewable energy. Thin film solar cells have the key benefit of their dimensionality, having thickness of a fraction of
crystalline silicon solar cells making them appealing in terms of cost factor with minimum material usage. The most advanced thin film solar cell technologies today are Cu(In,Ga)Se₂ (CIGS), CdTe, and organic-inorganic hybrid perovskites. All of them have achieved over 20% conversion efficiency on the laboratory scale. Although reaching high solar cell device efficiencies, these materials face various problems limiting their wider commercial availability, high cost being one of these issues. Therefore, the search for cheaper materials based on abundant elements has directed the scientific community to kesterite compounds such as Cu₂ZnSnS₄, Cu₂ZnSnSe₄ and Cu₂ZnSn(S,Se)₄. These semiconductors have a direct band gap, high absorption coefficient values exceeding 10⁴ cm⁻¹, p-type conductivity and a tailored band gap in the range of 1.0—1.5 eV [1]. Unfortunately, the record conversion efficiency of kesterite solar cells is still below 13% [2].

As a possible solution to increase the efficiency of thin film solar cells, the tandem structures are recommended, where the top cell has a larger band gap and thus expands the spectral sensitivity range of a single junction solar cell toward higher photon energies. This tandem structure concept is well known for thin film solar cells based on group III-V compound semiconductors and is mostly used for space applications. However, the tandem cell concept can also be used for other solar cells. Latest studies have shown that the Cu₂ZnGe(S,Se)₄ compound could be a good candidate for top cell in Si–wafer-based devices [3]. Theoretical calculations have also shown that by using Cu₂ZnSnS₄/ Cu₂ZnSnSe₄ tandem structures even the efficiency of kesterite solar cells can be increased up to 22% [4]. However, the band gap energy of Cu₂ZnSnS₄ is only 1.5 eV and in many cases that is too low for the top cell. Therefore, a direct larger band gap compound for the top cell is needed having a natural p-type conductivity, high absorption coefficient and is preferably with low concentration of intrinsic defects. It is known that in Cu₂ZnSnS₄ the defect concentration is usually relatively high causing potential (and band gap) fluctuations and reducing the carrier mobility and lifetime [5][6][7]. Our recent studies have shown that the average depth of potential fluctuations due to charged defects in an orthorhombic quaternary compound Cu₂CdGeSe₄ is smaller than in kesterites- only about 20 meV [8][9]. It is expected that similar relatively small potential fluctuations are also present in orthorhombic Cu₂CdGeS₄ (CCGS) compound and due to higher band gap energy, it can be used as a top cell in various tandem structures or as a photoelectrode in photoelectrochemical (PEC) water splitting devices. Unfortunately,
there is very little information about defect properties of CCGS. In quaternary compounds even a small deviation from the stoichiometric composition lead to the formation of intrinsic point defects (vacancies, anti-sites, and interstitials), which significantly influences the electrical and optical properties of the material. As a member of I$_2$–II–IV–VI$_4$ family, the orthorhombic CCGS (space group: $Pmn2_1$) has a crystal structure similar to that of kesterite-structured Cu$_2$ZnSnS$_4$ [10][11][12][13][14]. Reported band gap energy of CCGS varies from 1.85 eV [13] to 2.05 eV [11]. It has already been used as a counter electrode material in dye-sensitized solar cells [15]. In this paper we present first experimental results of defect structure of CCGS studied by temperature and laser power dependent photoluminescence spectroscopy (PL). Low temperature PL is one of the easiest and most sensitive techniques to study the defect structure of semiconductor materials while temperature and laser power dependencies usually give information about the nature of recombination processes.

2. Experimental

The commercially available CdS powder (5N purity), elemental Ge powder (5N purity), S powder (5N purity) and self-synthesized CuS (5N purity) were used as reaction precursors to synthesize Cu$_2$CdGeS$_4$ micro-crystalline powder. Potassium iodide (ultra dry, 4N purity) was used as a molten salt medium. The mass ratio of precursors and salt was 1:1. The starting materials were mixed and loaded into the quartz ampoule in the glovebox to avoid contaminations by air. The ampoule was sealed and then placed into the muffle furnace. The furnace was heated at a rate of 0.5 K/min to 973 K and then maintained for 120 hours. After cooling naturally to room temperature (RT), the as-synthesized powder was removed from ampoule by deionized water. Then, powder was repeatedly washed, dried and sieved to narrow fractions between 38-125 µm, see Fig. 1. All CCGS microcrystals had a p-type conductivity as determined by the hot probe method. This type of microcrystals are often used in so-called monograin layer solar cells [16].
Fig 1. SEM image of CCGS microcrystals.

The crystal structure of the studied CCGS was determined by X-ray diffraction (XRD) using a Rigaku Ultima IV diffractometer with monochromatic Cu Ka1 radiation (\(\lambda=1.5406\) Å) at 40 kV and 40 mA operating with the silicon strip detector D/teX Ultra. The lattice constants were determined using the Rietveld refinement procedure by Rigaku PDXL version 1.4.0.3 software.

The elemental composition of microcrystals was determined by Energy Dispersive X-ray spectroscopy (EDX). The EDX analysis was performed on Zeiss Merlin high-resolution scanning electron microscope equipped with the Bruker EDX-XFlash6/30 detector. Bulk composition of micro-crystalline powder was measured by EDX from polished crystals. According to EDX results, the average composition of synthesized microcrystals was: Cu (25.1 at. %), Cd (12.8 at. %), Ge (12.0 at. %), S (50.0 at. %).

A 0.64 m focal length single grating (600 mm\(^{-1}\)) monochromator 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 R632 PMT was used. A closed-cycle helium cryostat (Janis CCS-150) was employed to measure temperature dependencies of the PL spectra at temperatures from 10 K to 300 K. The crystals under study were glued with cryogenic grease on the cold finger of the cryostat. The laser spot size for these measurements was 200 \(\mu\)m in diameter. The sample temperature was controlled using the LakeShore 321 temperature controller.
Raman and micro-PL measurements were carried out using a Horiba LabRAM HR800 Micro- Raman system equipped with a cooled multichannel CCD detection system in the backscattering configuration with a spectral resolution better than 1 cm\(^{-1}\). A YAG: Nd laser (wavelength \(\lambda = 532\) nm) was used for excitation. The laser spot size was about 2 \(\mu\)m in diameter.

3. Results and discussion

Fig. 2 shows the resulting X-ray powder diffractogram for the quaternary compound Cu₂CdGeS\(_4\). Cu₂CdGeS\(_4\) was found to crystallize in the orthorhombic structure (space group \(Pmn2_1\); ICDD PDF 00-043-1387) with respective lattice parameters \(a = 7.7050\) Å, \(b = 6.5598\) Å and \(c = 6.3025\) Å being in correspondence with data reported by other groups [17] [10]. According to XRD, the Cu₂CdGeS\(_4\) powder contains less than 1 % hexagonal CdS (space group \(P6_3mc\); ICDD PDF 01-074-9663) as a secondary phase.

![X-ray diffraction pattern of Cu₂CdGeS₄ microcrystals. Reference ICDD card data for CCGS and CdS are also shown.](image)

Fig. 2. X-ray diffraction pattern of Cu₂CdGeS₄ microcrystals. Reference ICDD card data for CCGS and CdS are also shown.

Raman spectroscopy was used to analyze the phase composition of CCGS microcrystals, see Fig. 3. While the relative Raman intensity was slightly different, all
crystals showed similar peaks. This compound was previously studied by Fourier transform infrared spectroscopy (FTIR) [18] and by low-temperature polarized Raman spectroscopy [10]. Our measured Raman peaks are in good correlation with previously reported vibrational modes in CCGS, see Table 1. The full width at half maximum (FWHM) of the most intense 356 cm\(^{-1}\) Raman peak is only 4.3 cm\(^{-1}\) and this rather small value indicates a good crystal quality of our microcrystals.

![Fig. 3. Room temperature Raman spectra of different CCGS microcrystals.](image)

Table 1. Strongest vibrational modes in \(\text{Cu}_2\text{CdGeS}_4\) (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>This work</th>
<th>FTIR data [18]</th>
<th>Raman data [10]</th>
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We also measured a RT micro-PL from our crystals. The typical PL spectrum is presented in Fig. 4. The PL band has a slightly asymmetrical shape with a peak position at $E_{\text{max}}=1.97$ eV. The same emission was also detected in [10], where it was assigned to the band-to-band transition. As a first approximation the peak position of the PL band can be an estimation of the room temperature band gap energy of CCGS: $E_g \approx E_{\text{max}} - (1/2)kT = 1.967$ eV.

![PL spectrum](image)

**Fig. 4.** Room temperature micro-PL spectrum measured from single Cu$_2$CdGeS$_4$ microcrystal. The inset shows the micro-PL spectrum from the microcrystal where CdS was dominating.

In some CCGS crystals, a weak PL band at around 1.75 eV was observed. The 1.75 eV band was more noticeable in separate crystals where CdS was dominating, see the inset in Fig. 4. According to XRD measurements, a small fraction of CdS is present in our CCGS and although majority of CdS is concentrated on separate crystals (detected also by EDX and Raman), some residues of CdS can also be found on the surface of CCGS microcrystals. Thus, the faint emission at 1.75 eV is proposed to originate from the deep defects in CdS. It is known that Cu doped CdS shows PL emission in the same spectral region [19][20] and it is probable that we indeed have traces of CdS doped with Cu.
The low temperature PL spectrum of CCGS shows 3 peaks, see Fig. 5, at 1.919 eV (#1), 1.855 eV (#2) and 1.748 eV (#3). All PL peaks have slightly asymmetrical shape and therefore the best fitting of experimental PL spectra was achieved by using split Pearson VII function. The same function was used for all measured PL spectra.

Fig. 6 represents the laser power and temperature dependent behavior of PL spectra.
Fig. 6. Laser power (a) and temperature dependent (b) PL of Cu$_2$CdGeS$_4$ microcrystals.

By increasing the laser power, the shape of the PL spectra did not show any dramatic changes, i.e. the integrated intensity $\Phi$ of all peaks increase almost linearly with laser power, see Fig. 7 (a).

Fig. 7. Integrated intensity $\Phi$ (a) and peak position (b) of PL bands as a function of laser power at $T = 11K$. The solid line for $m = 1$ is included for comparison.
The experimental data can be fitted by the simple power law of the form $\Phi \propto L^m$, where $\Phi$ is the PL integrated intensity, $L$ is the excitation laser power and $m$ is a dimensionless exponent. It is well known that for an excitation laser photon with an energy exceeding the band gap energy the coefficient $m$ is generally $1 < m < 2$ for the free- and bound-exciton emission, and $m \leq 1$ for free-to-bound and donor–acceptor pair recombinations [21]. Thus, the obtained value of $m \approx 1$ for all bands is a sign that all measured PL bands are related to defects and do not have an excitonic nature. At the same time, all PL bands show a certain blue-shift with laser power, see Fig. 7 (b). The blue-shift is typical for donor-acceptor (DA) pairs with different distances between donor and acceptor defects in the crystal lattice. The rate of this blue shift is usually higher for DA pairs with shorter distances. Accordingly, the #1 PL band with a smallest blue-shift of 11 meV per decade of laser power must be related to shallow defects with longest distances between donor and acceptor defects. Sometimes very deep donor and acceptor defects can form DA pairs with a shortest allowed distance between them [22][23]. These deep donor-deep acceptor (DD-DA) pairs usually do not show any blue-shift with laser power [24][25]. At the same time, the blue-shift is possible when these DA pairs have slightly different distances between deep donor and deep acceptor defects. Calculated closest interatomic distances in the CCGS lattice are in the ranges 0.2243-0.2320 nm for Ge-S sites, 0.2250-0.2326 nm for Cu-S sites and 0.2520-0.2537 nm for Cd-S sites [14]. These small differences are sufficient to create blue-shift of DD-DA PL bands and can also cause a small asymmetry of PL bands. The blue-shift of PL bands, however, can be caused also by other reasons. In kesterites, for example, wide PL bands at low temperature usually show similar blue-shift with laser power [26] due to high concentration of charged defects, when band tails appear. Typical recombination in kesterites involves holes localized in valence band tail and the blue shift of PL bands is caused by redistribution of holes between tail states [27][28]. Our CCGS crystals show quite narrow PL band (#1) quite close to the estimated band gap energy. This type of emission is practically impossible in compounds where band tails overlap with shallow defect states. Therefore, the DA pair model seems to be more acceptable to explain the blue-shift of PL bands in the studied CCGS microcrystals.
Fig. 8. Arrhenius plots for PL bands derived from the temperature dependencies of the PL spectra of CCGS microcrystals. Solid lines present the fitting with the theoretical expression (1).

The thermal activation energies for the bands obtained from the Arrhenius plot (Fig. 8) where the dependence of \( \ln \Phi(T) \) versus \( 1000/T \) was fitted by using the theoretical expression for discrete energy levels [29]:

\[
\Phi(T) = \Phi_0 /[1 + A_1 T^{3/2} + A_2 T^{3/2} \exp(-E_A/kT)]
\]

(1)

where \( \Phi \) is an integrated intensity of the PL band, \( A_1 \) and \( A_2 \) are the process rate parameters and \( E_A \) is the thermal activation energy. As predicted by the fast quenching of the PL bands #1 and #2 with temperature (see Fig. 6(b)) quite small thermal activation energies \( E_A(#1) = 34 \pm 3 \) meV, \( E_A(#2) = 27 \pm 6 \) meV were obtained. The deepest PL band (#3) shows the thermal activation energy of \( E_A(#3) = 157 \pm 6 \) meV. Small activation energies indicate that relatively shallow defect levels are involved in the recombination processes for PL bands #1 and #2.

All PL bands show a certain redshift with increasing temperature, see Fig. 9. The low temperature band gap energy of CCGS is currently not known, but we assume that, like in most quaternary compounds where the band gap energy is increasing with decreasing of temperature, it must be slightly higher than 2 eV.
Fig. 9. Temperature dependence of the peak positions of the PL bands in CCGS microcrystals.

By combining the thermal activation energies and PL peak positions we are able to generate a low temperature recombination model for CCGS, see Fig. 10.

Fig. 10. The low temperature recombination model for CCGS microcrystals.
According to this model we see, that all PL bands are associated with relatively deep donor levels in the range of 50-120 meV. PL bands #1 and #2 show very comparable thermal activation energies and therefore we propose that they are related to the same shallow acceptor defect. It is known that in kesterites, the most probable shallow acceptor defect is V_{Cu} [30] and it is likely that the same defect is present also in CCGS. The nature of deeper acceptor and donor defects is currently not known and will be a task for future studies. The shallow acceptors detected in this material provide a proof that typical for ordinary kesterites potential or band gap fluctuations play insignificant role in CCGS. Hence, the wide band gap CCGS might very well represent a material that may be used as an absorber in top cells of tandem solar cells or in PEC devices.

4. Conclusion

In conclusion, the results of a detailed photoluminescence study on Cu_{2}CdGeS_{4} microcrystals are presented. Radiative recombination in Cu_{2}CdGeS_{4} microcrystals was studied by temperature and laser power dependent photoluminescence spectroscopy that revealed the origin for the detected low-temperature PL bands at 1.919 eV (#1), 1.855 eV (#2) and 1.748 eV (#3) as donor-acceptor pair recombination. #1 and #2 PL bands include more distant donor-acceptor pairs with relatively shallow acceptor (probably V_{Cu}) and deep donor defects. The #3 PL band results from the deep donor - deep acceptor recombination. The manifestation of shallow acceptor defects shows that this material does not have deep potential or band gap fluctuations and could be used in photovoltaic applications.

Acknowledgements

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References


Figure captions:

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