



## Strathprints Institutional Repository

**Yakushev, M.V. and Forbes, I. and Mudryi, A.V. and Grossberg, M. and Krustok, J. and Beattie, N.S. and Moynihan, M. and Rockett, A. and Martin, R.W. (2015) Optical spectroscopy studies of Cu<sub>2</sub>ZnSnSe<sub>4</sub> thin films. *Thin Solid Films*, 582. pp. 154-157. ISSN 0040-6090 , <http://dx.doi.org/10.1016/j.tsf.2014.09.010>**

This version is available at <http://strathprints.strath.ac.uk/55983/>

**Strathprints** is designed to allow users to access the research output of the University of Strathclyde. Unless otherwise explicitly stated on the manuscript, Copyright © and Moral Rights for the papers on this site are retained by the individual authors and/or other copyright owners. Please check the manuscript for details of any other licences that may have been applied. You may not engage in further distribution of the material for any profitmaking activities or any commercial gain. You may freely distribute both the url (<http://strathprints.strath.ac.uk/>) and the content of this paper for research or private study, educational, or not-for-profit purposes without prior permission or charge.

Any correspondence concerning this service should be sent to Strathprints administrator: [strathprints@strath.ac.uk](mailto:strathprints@strath.ac.uk)

# Optical Spectroscopy Studies of $\text{Cu}_2\text{ZnSnSe}_4$ Thin Films

M.V. Yakushev<sup>a,b\*</sup>, I. Forbes<sup>c</sup>, A.V. Mudryi<sup>a,d</sup>, M. Grossberg<sup>e</sup>, J. Krustok<sup>e</sup>, N.S. Beattie<sup>e</sup>,

M. Moynihan<sup>e</sup>, A. Rockett<sup>f</sup>, and R.W. Martin<sup>a</sup>

<sup>a</sup>Department of Physics, SUPA, Strathclyde University, G4 0NG Glasgow, UK.

<sup>b</sup>URFU and Ural Branch of RAS, 620002 Ekaterinburg, Russia.

<sup>c</sup>Northumbria Photovoltaics Applications Centre, Northumbria University, Ellison Building, Newcastle upon Tyne NE1 8ST, UK.

<sup>d</sup>Scientific-Practical Material Research Centre of the National Academy of Science of Belarus, P.Brovki 19, 220072 Minsk, Belarus.

<sup>e</sup>Tallinn University Technology, Ehitajate tee 5, Tallinn 19086, Estonia.

<sup>f</sup>University of Illinois, Urbana, IL 61801, USA.

\*M.V. Yakushev. Tel.:+44-141-548-3374; fax: +44-141-552-2891.

E-mail address: michael.yakushev@strath.ac.uk

## Abstract

$\text{Cu}_2\text{ZnSnSe}_4$  thin films were synthesised by selenisation of magnetron sputtered metal precursors. The band gap determined from the absorption spectra increases from 1.01 eV at 300 K to 1.05 eV at 4.2 K. In lower quality films photoluminescence spectra show a broad, low intensity asymmetric band associated with recombination of free electrons and holes localised on acceptors in the presence of spatial potential fluctuations. In high quality material the luminescence band becomes intense and narrow resolving two phonon replicas. Its shifts at changing excitation power suggest donor-acceptor pair recombination mechanisms. The proposed model involving two pairs of donors and acceptors is supported by the evolution of the band intensity and spectral position with temperature. Energy levels of the donors and acceptors are estimated using Arrhenius quenching analysis.

Keywords:  $\text{Cu}_2\text{ZnSnSe}_4$ ; thin films; defects; photoluminescence; absorption.

## 1. Introduction

$\text{Cu}(\text{InGa})\text{Se}_2$ -based solar cells are currently leading amongst thin film photovoltaic (PV) devices in terms of conversion efficiency and stability. However low estimated reserves of indium and gallium as well as their high costs can cause problems for wide scale fabrication of such cells. Therefore growing attention has made the related semiconductor compound  $\text{Cu}_2\text{ZnSnSe}_4$  (CZTSe) [1], attractive as an Earth-abundant alternative. The crystalline lattice of CZTSe is similar to the chalcopyrite structure of  $\text{Cu}(\text{InGa})\text{Se}_2$ , where In/Ga are substituted by alternating zinc (Zn) or tin (Sn) [1]. The electronic properties of CZTSe are also similar to  $\text{Cu}(\text{InGa})\text{Se}_2$  providing an opportunity to use for the CZTSe-solar cells a number of technological solutions, originally developed for  $\text{Cu}(\text{InGa})\text{Se}_2$ . The reported conversion efficiency record for CZTSe-based solar cells exceeds 12% [2] making them potential candidates for the large-scale production of thin film PV. However the level of knowledge on CZTSe is very low. Although p-type doping is believed to be achieved by intrinsic defects [1], very little experimental evidence on their nature can be found in the literature [3,4,5].

In this report we present an optical spectroscopy study of thin films of CZTSe, demonstrate how improvements in the structural quality of the material influences their photoluminescence (PL) spectra narrowing the width of the PL bands, revealing their fine details and providing an opportunity to gain more information on the defect energy levels and their nature. Using optical

transmission spectra the band gap energy has been determined at 4.2 K and compared with the room temperature value.

## 2. Experimental details

Thin p-type conductivity films of CZTSe were fabricated by selenisation of precursors, deposited by magnetron sputtering of high-purity (5N) elemental targets of Cu, Zn and Sn on either Mo-coated or bare soda-lime glass substrates kept at room temperature. The selenisation was carried out for 15 min at 530°C in a mixture of argon and Se vapour. More details on the synthesis and results of basic characterisation of the films including: scanning electron microscopy (SEM), wavelength dispersive X-ray microanalysis (WDX), X-ray diffraction (XRD), Raman spectroscopy and optical transmission at room temperature have been reported earlier [5]. Films with a thickness of 700 nm show good lateral homogeneity of the elemental composition with the ratios of the elements  $[\text{Cu}]/[\text{Zn}+\text{Sn}] = 1.05$ ,  $[\text{Se}]/[\text{Cu}+\text{Zn}+\text{Sn}] = 0.91$ ,  $[\text{Zn}]/[\text{Sn}] = 0.94$ , in other words a small excess of copper and deficiency of zinc and selenium. The X-ray diffraction (XRD) patterns and Raman spectra revealed distinct peaks of CZTSe suggesting that the material is free from secondary phases. The photoluminescence (PL) measurements were carried out using a 1 m focal length single grating monochromator and the 514 nm line of a 100 mW  $\text{Ar}^+$  laser for excitation. Either a closed-cycle or liquid helium cryostat was used for temperature resolved PL

measurements. The PL signal was detected by either an InGaAs photomultiplier tube (PMT). The accuracy of the spectral position measurements was of about 0.2 meV. More experimental details can be found in ref. [5].

### 3. Results and Discussion

To clarify the band gap energy ( $E_g$ ) optical absorption spectra  $\alpha(h\nu)$  have been determined at 4.2 K using both optical transmission and reflection data as described in [6]. For direct allowed transitions  $\alpha(h\nu)$  can be represented as  $\alpha=A(h\nu - E_g)^{1/2}/h\nu$ , where A is a constant and the band gap is  $E_g$ . Fig. 1(a) shows the dependence of  $\alpha(h\nu)$  on photon energy  $h\nu$  at 4.2 K and compares it with that of measured at 300 K as reported earlier [5].

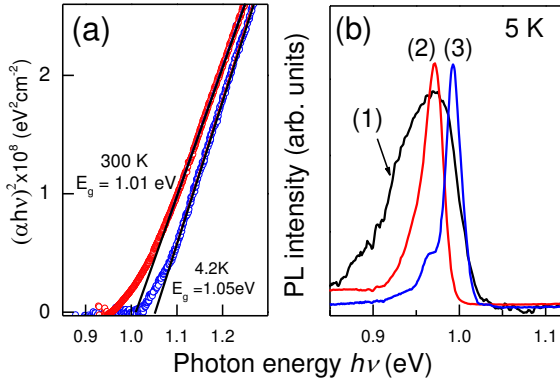


Fig. 1. The dependence of  $(\alpha h\nu)^2$  on photon energy  $h\nu$  at 4.2 and 300 K (a); (1), (2) and (3) are normalised PL spectra measured in three CZTSe films at 5 K (b).

The band gap of 1.05 eV is determined at 4.2 K by extrapolating the linear part of  $(\alpha h\nu)^2$  to the photon energy axis  $h\nu$ . It demonstrates a significant increase of 40 meV in comparison to that at 300 K. Such increases are considered to be due to thermal contraction of the lattice and electron-phonon coupling [7]. No thermal dependencies of the band gap of CZTSe can be found in the literature as yet however in the chalcopyrite compounds  $\text{CuInSe}_2$  and  $\text{CuGaSe}_2$  such shifts are reported to be 20 meV and 42 meV, respectively [8].

Although all the examined films demonstrate similar x-ray diffraction patterns, elemental composition and absorption spectra their PL emission at 5 K reveals quite different types of spectra as shown in Fig. 1(b). An explanation could be that PL is significantly more sensitive to defect types and concentrations as well as to structural quality than x-ray diffraction, WDX and absorption techniques so small variations in elemental compositions unseen by these three methods can cause dramatic changes in the PL spectra.

PL spectra of some films have an asymmetric, low intensity and broad PL band with the maximum at 0.98 eV labelled in Fig. 1(b) as (1). Its full width at half maximum (FWHM) is of about 90 meV. The low energy slope of this band at 0.9 eV is modified by water absorption. Variations in the excitation intensity (laser power density from 1 to 20  $\text{Wcm}^{-2}$ ) do not change the band spectral position.

Other films reveal a much sharper and higher intensity PL band, labelled in Fig. 1(b) as (2), with the maximum also at 0.98 eV and the FWHM of 30 meV. Changes in

the laser power density from 1 to 5  $\text{Wcm}^{-2}$  shift the spectral position of this line (j-shift) with a rate of  $j = 7$  meV per decade of excitation power density as can be seen in Fig. 2(a). The band intensity quenches at temperatures of 40 K as shown in Fig. 2(b). The band with a maximum at 0.99 eV and FWHM is of 0.16 meV, shown in Fig. 1(b) as (3), represents the third type of PL spectrum. Its intensity significantly exceeds that of (1) and (2). Fig.2(c) shows this band shifting with a rate of  $j = 3$  meV per decade of excitation intensity change. The low energy slope of the band (3) shows peak (3)<sub>LO</sub> at 0.96 eV. This peak was assigned to the first phonon-assisted replica of the band (3) shifted by a longitudinal optical (LO) phonon with energy of 28 meV [5]. The band quenches at temperatures of 60 K as shown in Fig. 2(d).

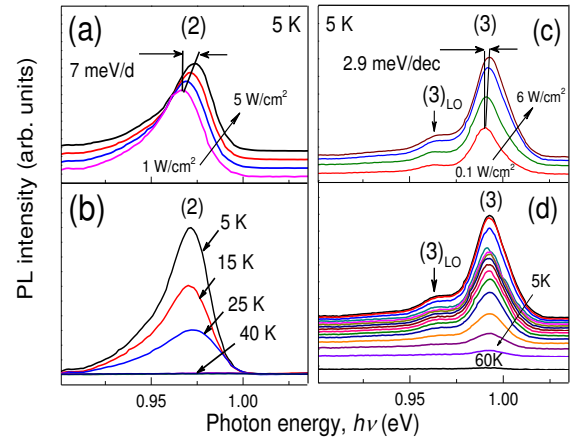


Fig. 2. Excitation intensity dependence of the type (2) PL spectra (a), temperature dependence of the type (2) PL spectra (b), excitation intensity dependence of the type (3) PL spectra (c), temperature dependence of the type (3) PL spectra (d).

The excitation intensity and temperature dependence analysis of PL bands help to identify recombination mechanisms and the nature of defects associated with these bands.

The dependence of the band (3) PL intensity  $I$  on the excitation power density  $P$  has been fitted with  $I \sim P^\gamma$ , where the determined power coefficient  $\gamma \approx 0.8$  suggests that this band is due to defects with energy levels in the band gap [9]. Band (1) has an asymmetric shape with the high-energy slope steeper than the low-energy one. At changing excitation laser power density from 1 to 20  $\text{Wcm}^{-2}$  this band does not change its shape. Jagomägi et al. [10] observed a PL band with similar characteristics in highly doped  $\text{CuInTe}_2$  single crystals. It was assigned to a free-to-bound recombination (FB) of electrons from the conduction band and holes localised at an acceptor affected by spatial potential fluctuations. In multinary compounds spatial non-uniformity of the elemental composition on a micro-scale can result in the formation of charged defects. At high concentrations such defects create potential fluctuations broadening the defect levels in the band gap and forming band tails. A semiconductor is heavily doped if the average distance between the defects is smaller than the Bohr radius. In semiconductors with effective electron masses  $m_e$  significantly smaller than that of holes  $m_h$  (in CZTSe with kesterite structure a theoretical ratio of the masses

$m_h/m_e \approx 2.7$  [11]) this condition is satisfied for donors at much lower concentrations than acceptors. Thus we can expect electrons to be free in the conduction band whereas heavier holes are more likely to be localised at acceptors. PL bands in heavily doped ternary and quaternary semiconductors with chalcopyrite structure exhibit such a characteristic asymmetric shape [10,12]. The spectral shape of the band (1) as well as its excitation intensity behaviour suggest that the films are heavily doped and the band can be assigned to the recombination of electrons in the conduction band and holes localised at an acceptor [9,11]. Grossberg et al. [3] reported a similar band at 0.946 eV in the PL spectra of CZTSe. This band has also been assigned to a FB recombination. The ionisation energy  $E_a \approx 70$  meV of the involved acceptor has been estimated from temperature quenching analysis. The similarity of the band (1) shape and proximity of its spectral position to that reported in [3] suggests that similar acceptor type defects can be responsible for the band (1).

Band (2) is significantly more intense and narrower than (1). Both are indications of an improvement of the structural quality and reduction of non-radiative recombination due to lower defect concentrations. The shifts of the band to higher energies with increasing excitation power suggest a donor-acceptor pair (DAP) type of recombination [13]. The band maximum spectral position  $h\nu_{\max}$  can be found as:  $h\nu_{\max} = E_g - (E_a + E_d) + e^2/\epsilon r$ , where  $E_d$  and  $E_a$  are the donor and acceptor ionisation energies, respectively,  $r$  is the distance between the donor and acceptor and  $\epsilon$  is the static dielectric constant. The last term represents the Coulomb interaction between the donor and acceptor. Once the excitation power rises the average distance between them becomes smaller increasing the Coulomb interaction energy and  $h\nu_{\max}$ . The evolution of the PL spectra with temperature increase from 5 K to 40 K is shown in Fig. 2(b). An Arrhenius temperature quenching analysis assuming one recombination channel determines an activation energy of  $30 \pm 3$  meV which is an estimate of the ionisation energy of a related defect. The strongly asymmetric shape of the band (2) and significant rate of the j-shift however could be indications of a FB related transition, similar to that of (1) but with a lower average depth of potential fluctuation [10].

Band (3) is significantly more intense and narrow than (2) suggesting a better structural quality of the material due to lower defect concentrations. The j-shift of 3 meV per decade for (3) indicates that this band is associated with a DAP recombination. This shift is smaller than 7 meV per decade for (2) demonstrating that the level of compensation in the (3)-type films is lower. Due to the smaller FWHM in (3) phonon assisted transitions as well as an excitonic feature appear in the PL spectra [5].

A model including a single DAP recombination channel has been proposed in ref. [5] to interpret band (3). This model, based on temperature quenching analysis at temperatures above 10 K, suggested the presence in the type (3) films an acceptor level at 27 meV from the valence band and a donor level at 7 meV from the conduction band.

Temperature quenching analysis from 5 K, carried in the present study, demonstrates a remarkable two stage quenching shown in Fig. 3(a). Neither one nor two recombination channel quenching explain such behaviour. The best fit of the experimental data points is achieved assuming three recombination channels:

$$I(T) = \frac{I_{01}}{1 + A_1 \exp\left(-\frac{E_{a1}}{kT}\right)} + \frac{I_{02}}{1 + A_2 \exp\left(-\frac{E_{a2}}{kT}\right) + A_3 \exp\left(-\frac{E_{a3}}{kT}\right)} \quad (1)$$

where  $k$  is the Boltzmann constant whereas  $I_0$  (PL intensity at the lowest temperature),  $E_a$  (activation energy) and  $A$  (the process rate parameter) are fitting parameters. The determined activation energies  $E_{a1} = 7 \pm 2$  meV,  $E_{a2} = 13 \pm 2$  meV,  $E_{a3} = 27 \pm 3$  meV are estimates of energy distances of the defect levels from either conduction (if the defect is a donor) or valence (if the defect is an acceptor) band.

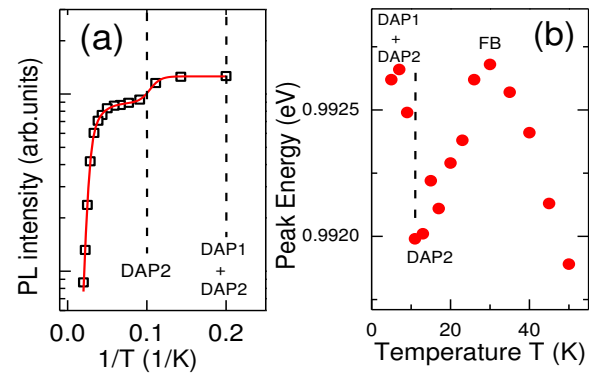


Fig.3. Arrhenius plot of the band (3) intensity quenching,  $\square$  experimental data,  $—$  fitted line (a), dependence of the band (3) spectral position on temperature (b).

To interpret the quenching we propose a model including two DAP recombinations. At 5 K band (3) represents emission from two DAP1 and DAP2 which have close spectral positions and therefore are not resolved in the PL spectra in Fig. 2(d). Temperature, increasing from 5 to 10 K, ionises the first acceptor in DAP1 and quenches this band leaving in the spectrum DAP2 at a slightly lower energy. This quenching stage is described by the first term of Eq. (1) associated with the acceptor level at 13 meV above the valence band. This interpretation is supported by the band (3) spectral shift towards lower energies as shown in Fig. 3(b). At 10 K the band (3) represents only DAP2. The donor level in DAP2, at 7 meV below the conduction band, ionises as temperature rises from 10 to 30 K transforming DAP2 into FB, recombination of free electrons with holes localised at the second acceptor at 27 meV above the valence band. It is supported by the gradual shift of (3) to higher energy. This acceptor is probably also associated with the bands (1) and band (2) acceptor levels in the PL spectra of the lower quality films. Ionisation of the second acceptor takes place at temperatures above 30 K. The donor associated with DAP1 does not participate in emission after the ionisation of the first acceptor. Therefore we cannot determine its ionisation energy using quenching analysis. Taking in account the proximity of the spectral

positions of DAP1 and DAP2 its level could be 20 meV below the conduction band.

Our analysis demonstrates that this material contains a number of different types of very shallow defects, donors as well as acceptors. The elemental composition and absorption spectra are not sensitive to examine these defects whereas PL is a better technique for their analysis. Significantly more information can be gained by studying high structural quality material with low defect concentration. At high concentrations the width of the emission bands increases whereas their intensity drops due to rising non-radiative recombination processes making difficult accurate optical spectroscopy measurements.

## Conclusion

The band gap, determined from absorption spectra, increases from 1.01 eV at 300 K to 1.05 eV at 4.2 K. PL spectra of CZTSe films show different types of bands: a broad asymmetric low intensity band at 0.98 eV, not shifting with changing excitation power and assigned to free-to-bound recombination of electrons from the conduction band and holes localised at an acceptor affected by spatial potential fluctuations. At lower defect concentration the band increases its intensity and narrows resolving two phonon assisted transitions and excitonic features. Excitation power shifts the band at rates of 7 or 3 meV per decade, suggesting donor-acceptor pair (DAP) recombination mechanisms. For the highest quality films a model including two DAP transitions is proposed, energy levels of the donors and acceptors are determined using an Arrhenius quenching analysis. The evolution of the band spectral position with temperature supports the model.

## Acknowledgements

This work was supported by the EPSRC (SUPERGEN II "PV21", EP/F029624/2 and EP/H5 0009X/1), BRFFR (F13IC-018), the US Civilian Research & Development Foundation (CRDF Global) and the Ural Branch of RAS (RUE2-7105-EK-13), RFBR (14-02-00080, 13-03-96032, 12-U3-1006, 14-03-00121), Estonian Science Foundation Grant G9369.

## References

- [1] S. Siebentritt and S. Schorr, Kesterites - a challenging material for solar cells, *Prog. Photovolt. Res. Appl.* 20 (2012) 512-519.
- [2] W. Wang, M.T. Winkler, O. Gunawan, T. Gokmen, T. K. Todorov, Y. Zhu, D. B. Mitzi, A 12.6%  $\text{Cu}_2\text{ZnSnS}_x\text{Se}_{4-x}$  (CZTSSe) solar cell is presented with detailed device characteristics, *Advanced Energy Materials* (2013), doi:10.1002/aenm.201301465.
- [3] M. Grossberg, J. Krustok, K. Timmo, M. Altsaar, Radiative recombination in  $\text{Cu}_2\text{ZnSnSe}_4$  monograins studied by photoluminescence spectroscopy, *Thin Solid Films* 517 (2009) 2489-2492.
- [4] M. J. Romero, H. Du, G. Teeter, Y. Yan, and M. M. Al-Jassim, Comparative study of the luminescence and

- intrinsic point defects in the kesterite  $\text{Cu}_2\text{ZnSnS}_4$  and chalcopyrite  $\text{Cu}(\text{In,Ga})\text{Se}_2$  thin films used in photovoltaic applications, *Phys. Rev. B* 84 (2011) 165324-1-5.
- [5] F. Luckert, D. I. Hamilton, M. V. Yakushev, N. Beattie, G. Zoppi, M. Moynihan, I. Forbes, A. V. Karotki, A. V. Mudryi, M. Grossberg, J. Krustok and R. W. Martin, Optical Properties of High Quality  $\text{Cu}_2\text{ZnSnSe}_4$  Thin Films *Appl. Phys. Lett.* 99 (2011) 062104-1-3.
- [6] A.V. Mudryi, V.F. Gremenok, I.A. Victorov, V.B. Zalesski, F.V. Kurdesov, V.I. Kovalevski, M.V. Yakushev, R.W. Martin, Optical Characterisation of  $\text{CuInSe}_2$  Thin Films Synthesised by Two-Stage Selenisation Process, *Thin Solid Films* 431/432 (2003) 193-196.
- [7] A.V. Mudryi, V.F. Gremenok, A.V. Karotki, V.B. Zalesski, M.V. Yakushev, F. Luckert, R.W. Martin. Structural and optical properties of thin films of  $\text{Cu}(\text{In,Ga})\text{Se}_2$  semiconductor compounds, *Journal of Applied Spectroscopy* 77 (2010) 371-377.
- [8] K.P.O'Donnell and X. Chen. Temperature dependence of semiconductor band gaps, *Appl. Phys. Lett.* 58 (1991) 2924-2926.
- [9] T. Schmidt, K. Lischka, W. Zulehner, Excitation-power dependence of the near-band-edge photoluminescence of semiconductors, *Phys. Rev. B* 45 (1992) 8989-8994.
- [10] A. Jagomagi, J. Krustoka, J. Raudojaa, M. Grossberga, M. Danilsona, M. Yakushev, Photoluminescence studies of heavily doped  $\text{CuInTe}_2$  crystals, *Physica B.* 337 (2003) 369-374.
- [11] C. Persson, Electronic and optical properties of  $\text{Cu}_2\text{ZnSnS}_4$  and  $\text{Cu}_2\text{ZnSnSe}_4$ , *J. Appl. Phys.* 107 (2010) 053710-1-8.
- [12] J. Krustok, H. Collan, M. Yakushev and K.Hjelt, The role of Spatial Potential Fluctuations in the Shape of the PL Bands of Multinary Semiconductor Compounds, *Physica Scripta*, T79 (1999) 179-182.
- [13] R. Dingle, Radiative Lifetimes of Donor-Acceptor Pairs in p-type Gallium Arsenide, *Phys. Rev.* 184 (1969) 788-796.