Cu$_2$Zn$_{1-x}$Cd$_x$Sn(Se$_{1-y}$S$_y$)$_4$ solid solutions as absorber materials for solar cells

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Cu$_2$Zn$_{1-x}$Cd$_x$Sn(Se$_{1-y}$S$_y$)$_4$ monograin powders with different x- and y-values were prepared from binary compounds in the liquid phase of flux material (KI) in evacuated quartz ampoules. All the materials had uniform composition and p-type conductivity. PL spectra (10 K) of the as grown Cu$_2$Zn$_{1-x}$Cd$_x$Sn(Se)$_4$ monograin powders showed one PL band with peak position around 0.85 eV which shifted linearly to the lower energy side with increasing Cd content. Cu$_2$ZnSnS$_4$ material showed asymmetrical PL band at 1.31 eV attributed to band-to-tail recombination. RT Raman spectra of Cu$_2$ZnSnSe$_4$ revealed two main peaks at 196 cm^{-1} and 173 cm^{-1} and a third less intensive peak with varying peak position in the region 231–253 cm^{-1}. Raman spectra of Cu$_2$ZnSnS$_4$ showed an intensive peak at 338 cm^{-1} and additional peaks at 287 cm^{-1} and 368 cm^{-1}. Narrow sieved fractions of grown powders were used as absorber materials in monograin layer (MGL) solar cell structures: graphite/Cu$_2$Zn$_{1-x}$Cd$_x$Sn(Se$_{1-y}$S$_y$)$_4$/CdS/ZnO. The best so far solar cell that was based on the Cu$_2$Zn$_{0.8}$Cd$_{0.2}$SnSe$_4$ had open circuit voltage 422 mV, short circuit current 12 mA/cm^2 and fill factor 44%.

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196 cm⁻¹ and 173 cm⁻¹ and a third less intensive peak with varying peak position in the region 231–253 cm⁻¹. Raman spectra of Cu_2ZnSnS_4 showed an intensive peak at 338 cm⁻¹ and additional peaks at 287 cm⁻¹ and 368 cm⁻¹. Narrow sieved fractions of grown powders were used as absorber materials in monograin layer (MGL) solar cell structures: graphite/ $Cu_2Zn_{1-x}Cd_xSn(Se_{1-y}S_y)_4$/CdS/ZnO. The best so far solar cell that was based on the $Cu_2Zn_{0.8}Cd_{0.2}SnSe_4$ had open circuit voltage 422 mV, short circuit current 12 mA/cm² and fill factor 44%.

1 Introduction Quaternary compounds Cu_2ZnSnS_4, $Cu_2ZnSnSe_4$ and $Cu_2CdSnSe_4$ are new interesting semiconductor materials for absorber layer in thin film solar cells. The most of their elemental constituents are abundant on the earth's crust and they have semiconductor properties such as p-type conductivity, direct band gaps and high absorption coefficients ($>10^4$ cm⁻¹) [1]. Almost all investigations on solar cells are based on Cu_2ZnSnS_4 absorbers. The overview of progress in Cu_2ZnSnS_4 thin film solar cell development has been given by Katagiri [2]. The highest conversion efficiency of Cu_2ZnSnS_4 solar cells is till now 5.74% [3]. The methods for thin film production such as sputtering and PVD in the case of quaternary materials lead to inhomogeneous composition of layers [4, 5]. As a rule, monograin growth in molten fluxes results in homogeneous material. In our previous report [6], we showed, that $Cu_2ZnSnSe_4$ monograin powders with tailored chemical composition could be prepared by isothermal recrystallization of initial binary compounds in molten fluxes. $Cu_2ZnSnSe_4$ powder crystals grown in molten KI had tetragonal shape with rounded grain edges. By XRD analysis the powders had stannite structure (space group I4̄2m).

The ZnO/CdS/$Cu_2ZnSnSe_4$/graphite monograin layer solar cells had low fill factors (25–30) and the barrier height of their p–n junction was around 250 mV [6]. The present research was performed with the aim to gain better understanding of the reasons of low efficiency of $Cu_2ZnSnSe_4$ monograin layer solar cells by comparing the properties of absorber materials on the base of solid solutions $Cu_2Zn_{1-x}Cd_xSn(Se_yS_{1-y})_4$. Therefore $Cu_2Zn_{1-x}Cd_xSnSe_4$ monograin materials with $x = 0$, 0.2, 0.33, 0.5 and $Cu_2ZnSn(Se_{1-y}S_y)_4$ powders with $y = 1$, 0.5, 0 were prepared and studied.

2 Experimental

2.1 Powder preparation The $Cu_2Zn_{1-x}Cd_xSn(Se_yS_{1-y})_4$ powder materials were synthesized from CuSe(S), ZnSe(S), CdSe(S) and SnSe(S) precursors in molten KI. The binary compounds in stoichiometric relation of $Cu_2Zn(Cd)SnSe(S)_4$ and KI were mixed and ground in planetary ball mill. The mixture was degassed and sealed into quartz ampoules. The recrystallization temperature was 1000 K. Crystal size was controlled by the temperature and duration of the recrystallization process. Crystals

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of the synthesized powders were released from flux by washing with deionized water. More details about this process can be found elsewhere [8]. Polycrystalline Cu_2SnSe_3 was synthesized by melting of CuSe and SnSe in a vacuum ampoule at 1170 K.

2.2 Characterization The bulk composition of powders was determined by energy dispersive spectroscopy (EDS). The shape and surface morphology of crystals were studied with the help of high-resolution scanning electron microscope (SEM) Zeiss ULTRA 55. Photoluminescence (PL) was excited by a He−Cd laser with the wavelength of 441 nm. Powder samples were mounted inside a closed cycle He cryostat ($T = 9-300$ K). The PL spectra were recorded with a computer-controlled SPM-2 grating monochromator ($f = 0.4$ m). The signal was detected with an InGaAs detector using the conventional lock-in technique. The room temperature (RT) micro-Raman spectra were recorded by using a Horiba LabRam HR high-resolution spectrometer equipped with a multi-channel detection system in the backscattering configuration. The incident laser light with the wavelength of 532 nm was focused on samples within a spot of 1 μm in diameter and the spectral resolution of the spectrometer was about 0.5 cm^{-1}.

2.3 Solar cell preparation Narrow granulometric fractions of the grown powders were used as absorber material in MGL solar cell structures: graphite/$Cu_2Zn_{1-x}Cd_xSn(Se_yS_{1-y})_4$/CdS/ZnO [6, 7]. $Cu_2Zn_{1-x}Cd_xSn(Se_yS_{1-y})_4$ powder crystals were covered with CdS thin layer by chemical bath deposition. For MGL formation a monolayer of sieved, nearly unisize grains was bound into a thin layer of epoxy resin, so that the contamination of upper surfaces of crystals with epoxy was avoided. After polymerization of epoxy, ZnO window layer was deposited onto front side of MGL by RF-sputtering. Solar cell structures were completed by vacuum evaporation of $1-2$ μm thick In grid contacts onto the ZnO window layer. After glueing the structures on glass substrates, the back contact area of crystals covered with epoxy was opened by etching epoxy with H_2SO_4 followed by an additional abrasive treatment. The back contact was made using graphite paste.

3 Results and discussion
3.1 Powder preparation and characterization
$Cu_2Zn_{1-x}Cd_xSnSe_4$ materials were prepared with $x = 0$, 0.2, 0.33, 0.5 and $Cu_2ZnSn(Se_{1-y}S_y)_4$ powders with $y = 1$, 0.5, 0. EDS scanning over polished individual powder crystals showed homogeneous distribution of constituent elements.

Ratio of Cu to other metals Cu/Zn(Cd) + Sn was $0.85-0.9$, Zn/Sn = 1.04 and Se/metals ratio ≥1. PL spectra of pure $Cu_2ZnSnSe_4$ ($x = 0$) and Cu_2ZnSnS_4 ($y = 1$) are presented in Fig. 1. The PL spectrum of Cu_2ZnSnS_4 (see Fig. 1) is similar to that one described by Tanaka et al. [9]. They attributed the detected broad PL band between

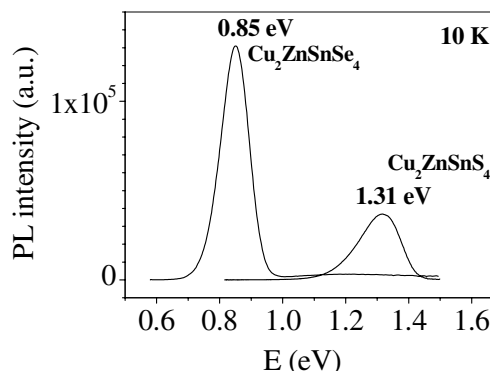**Figure 1** PL spectra of $Cu_2ZnSnSe_4$ and Cu_2ZnSnS_4 monograin powders.

$1.1-1.45$ eV to donor−acceptor pair recombination. The asymmetrical shape of this band and our temperature and excitation power density dependant measurements of this band showed that the PL band might also originate from band-to-tail (BT) recombination as it was observed in ternaries [10]. A blue shift of the PL band of magnitude about 15 meV per decade with excitation power density was detected while in the case of DA pair recombination the shift is usually smaller. Details of these measurements will be published elsewhere. The PL spectrum of $Cu_2ZnSnSe_4$ shows one nearly symmetrical band with the band maximum at 0.85 eV. The peak position hv_{max} (see Fig. 2) and the full width of half maximum (FWHM) of the band shifted with increasing Cd content in $Cu_2Zn_{1-x}Cd_xSnSe_4$ linearly to lower energy side: from $hv_{max} = 0.85$ eV ($x = 0$) to 0.77 eV ($x = 0.5$) and from FWHM = 0.09 eV ($x = 0$) to 0.078 eV ($x = 0.5$), correspondingly. By Matsushita et al. [11] the band gap value of $Cu_2ZnSnSe_4$ is 1.44 eV and observed PL emission at 0.85 eV cannot originate from this compound. We tried to identify the possible source of this band by Raman measurements. RT Raman spectra of $Cu_2Zn_{1-x}Cd_xSnSe_4$ revealed two main peaks at 196 cm^{-1} and 173 cm^{-1} (see Fig. 3), which positions did not change noticeably with x, and a third, less intensive peak with varying peak position in the region of 231–253 cm^{-1}. In this region there were peaks in all Raman spectra of $Cu_2Zn_{1-x}Cd_xSnSe_4$ materials. From initial binary compounds, SnSe does not have Raman peaks
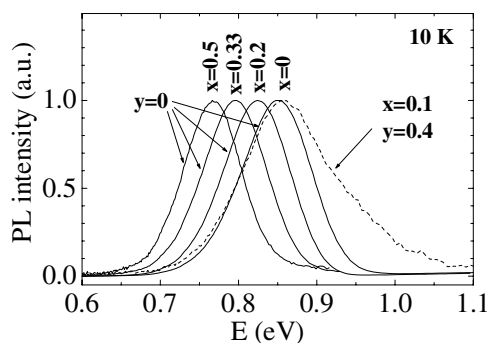

Figure 2 PL spectra of $Cu_2Zn_{1-x}Cd_xSn(Se_{1-y}S_y)_4$.

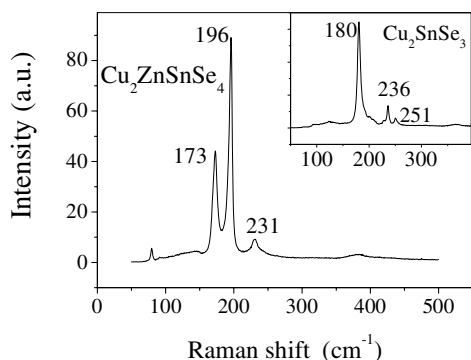**Figure 3** Raman spectrum of $Cu_2ZnSnSe_4$ monograin powder. Raman spectrum of polycrystalline Cu_2SnSe_3 is shown in the upper right corner.

in this region, but ZnSe has a peak at 253 cm^{-1} and CuSe at 260 cm^{-1}.

Cu_2SnSe_3 is the most probable ternary compound in this system. In Cu_2SnSe_3 spectra there are also Raman peaks in the above-mentioned region (see Fig. 4). At the moment the attribution of the Raman peaks in the region of $231-253$ cm^{-1} remains questionable and Raman spectra do not give base for unambiguous identification of the bright PL emission at 0.85 eV. The PL spectrum of Cu_2SnSe_3 showed one asymmetrical band at 1.33 eV and so excluded this compound also from the list of probable source of 0.85 eV PL band. The Raman spectra of Cu_2ZnSnS_4 showed the most intensive peak at 338 cm^{-1} and the other peaks at 287 cm^{-1} and 368 cm^{-1} (see Fig. 4) that are close to the values found in [12].

3.2 Solar cell characterization Quantum efficiency (QE) curves of solar cells on the base of Cd containing $Cu_2Zn_{1-x}Cd_xSnSe_4$ showed a shift to the longer wavelengths with increasing Cd content as it is seen in Fig. 5. The highest value of open circuit voltage ($V_{oc} = 422$ mV) was achieved with $Cu_2Zn_xCd_{1-x}SnSe_4$ material with $x = 0.2$ (see Fig. 6). By Matsushita et al. the band gap values of $Cu_2ZnSnSe_4$ and $Cu_2CdSnSe_4$ are 1.44 eV and 0.96 eV correspondingly [11]. The temperature dependence of V_{oc}
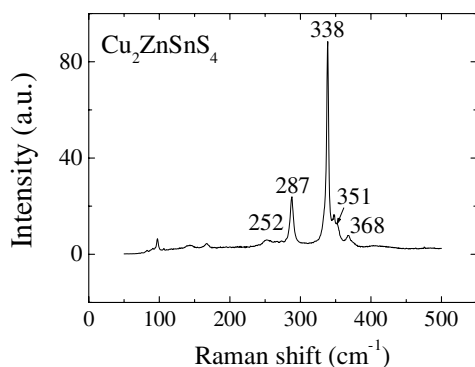

Figure 4 Room temperature Raman spectrum of Cu_2ZnSnS_4 monograin powder.

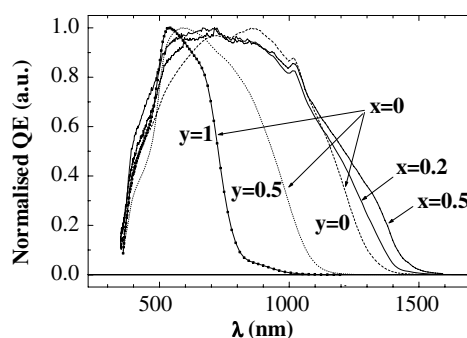**Figure 5** Normalized spectral response curves of $Cu_2Zn_{1-x}Cd_xSn(Se_{1-y}S_y)_4$ solar cells.

gave the barrier height of the junction $\Phi = 758$ meV. This value is much lower than that one possible with an absorber material with the band gap value being a little bit lower than 1.44 eV, as it should be for $Cu_2Zn_xCd_{1-x}SnSe_4$ with $x = 0.2$. PL spectra of $Cu_2ZnSnSe_4$ (see Fig. 2) showed a band with the band maximum at 0.85 eV. The measured PL spectrum of used SnSe showed the PL band maximum at 0.67 eV. At the same time the QE curves showed a regular shift with increasing Cd content (with increasing x) to the longer wavelength region and with increasing sulphur content (with increasing y) to the shorter wavelength side (see Fig. 5). Considering all these facts we assume that a narrow band gap compound or a solid solution formed on the surface of $Cu_2Zn_{1-x}Cd_xSnSe_4$ limits the efficient work of solar cells at the moment. It is also possible that $Cu_2ZnSnSe_4$ itself has smaller than given in [11] band gap value. Further investigations should clarify the origin of the PL band of $Cu_2ZnSnSe_4$ at 0.85 eV.

4 Conclusions $Cu_2Zn_{1-x}Cd_xSn(Se_{1-y}S_y)_4$ monograin powders were synthesized and characterised by PL and Raman measurements. The results of PL and Raman measurements combined with solar cell parameters enabled to conclude that a narrow band gap compound or a solid solution formed on the surface of $Cu_2Zn_{1-x}Cd_xSnSe_4$ limits the efficient work of solar cells or $Cu_2ZnSnSe_4$ itself has lower than 1.44 eV bandgap.
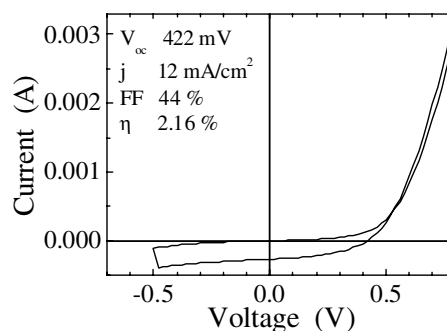

Figure 6 $I-V$ curve of $Cu_2(Zn_{0.8}Cd_{0.2})SnSe_4$ MGL solar cell. The efficiency is given to the active area of solar cell.

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