

Crystallographic and optical properties of $\text{Cu}_2\text{ZnSn}_{1-x}\text{Ge}_x\text{Se}_4$ solid solution

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1. Introduction

The efficiency of $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) thin-film solar cells has reached more than 20% [1]. Recently, EMPA achieved a new record efficiency of 20.4% for CIGS thin-film solar cells on flexible polymer foils. However, mass production of CIGS solar cells is limited by availability of the rare metals In and Ga. $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is anticipated as a rare-metal-free absorber material for thin-film solar cells. An IBM group fabricated $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ (CZTSSe) solar cells with an efficiency of 11.1% by the hybrid coating process [2]. Recently, Purdue University reported a $\text{Cu}_2\text{Zn}(\text{Sn}_{1-x}\text{Ge}_x)(\text{S,Se})_4$ (CZTGSSe) solar cell with an efficiency of 6.8% using a nanocrystal paste coated with a doctor-blading technique and annealed under a selenium atmosphere [3].

We prepared Cu deficient $\text{Cu}_{2(1-x)}\text{ZnSnSe}_4$ and characterized their crystal structures by XRD and XAFS [4]. Then, we characterized their optical properties. The band gaps of the CZTSSe solid solutions were determined from diffuse reflectance spectra of the powders and transmittance spectra of the films [5]. The band gap (E_g) of the $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ solid solution linearly increases from 1.05 eV for CZTSe ($x=0.0$) to 1.51 eV for CZTS ($x=1.0$).

In this study, we synthesized $\text{Cu}_2\text{Zn}(\text{Sn}_{1-x}\text{Ge}_x)\text{Se}_4$ ($x=0.0-1.0$) powder and characterized the crystallographic structure and optical properties.

2. Experimental Procedures

2.1 Fabrication of Cu_2GeSe_3 powder

Starting materials of elemental powders Cu, Zn, Sn, Ge, and Se were weighed to give a molar ratio of Cu:Zn:Sn:Ge:Se = 2: 1: 1-x: x: 4. The $\text{Cu}_2\text{Zn}(\text{Sn}_{1-x}\text{Ge}_x)\text{Se}_4$ (CZTGSe) powder was synthesized from elemental powders by planetary ball milling (Fritsch premium line P-7) under a rotational speed of 800 rpm and a milling period of 20 min. The powder was synthesized by post-annealing at 600°C for 5 h in an N_2 gas atmosphere.

2.2 Characterization of $\text{Cu}_2\text{Zn}(\text{Sn}_{1-x}\text{Ge}_x)\text{Se}_4$ powder

The phase in the synthesized CZTGSe powder was identified by X-ray diffraction. The crystal structure of CZTGSe was analyzed by Rietveld refinement. X-ray diffraction measurements for Rietveld analysis were performed using an X-ray diffractometer (Rigaku RINT 2400) equipped with a rotating-anode source and a curved graphite monochromator. The diffraction data were collected at a step width of 0.04° (2θ) and a counting time of 4 s for each

step over a 2θ range from 5 to 120° .

The optical properties of the CZTGSe were characterized by UV-Vis-NIR spectroscopy (JASCO; V-670). The band gap energy of CZTGSe powder was determined by a diffuse reflectance spectrum.

3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of $\text{Cu}_2\text{Zn}(\text{Sn}_{1-x}\text{Ge}_x)\text{Se}_4$ ($x=0.0-1.0$) synthesized by milling the elemental powders and post-annealing at 600°C. The diffraction peaks of the CZTGSe solid solutions are shifted to the higher angle side with increasing Ge content.

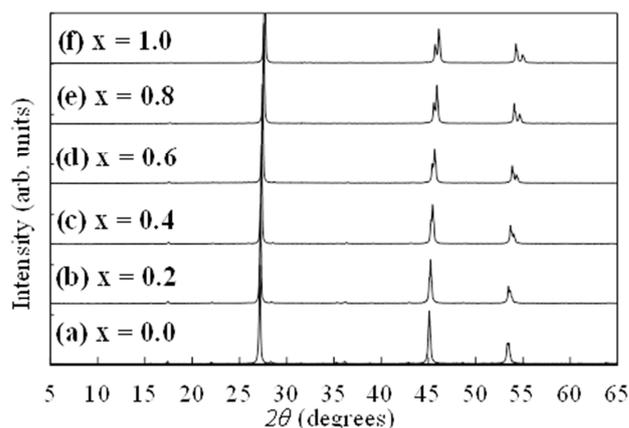


Fig. 1 X-ray diffraction patterns of $\text{Cu}_2\text{Zn}(\text{Sn}_{1-x}\text{Ge}_x)\text{Se}_4$ powder synthesized by milling the elemental powders and post-annealing at 600°C.

The crystallographic structures of the CZTGSe solid solution samples were analyzed by Rietveld analysis using X-ray diffraction data. The crystal structures were refined on the basis of the tetragonal kesterite-type crystal structure [space group: $I\bar{4}$ (No.82)]. The refined lattice parameters of CZTSe ($x=0.0$) are $a=5.685(4)$ Å, $c=11.329(6)$ Å, and $c/a=1.99$. The determined u_x , u_y , and u_z are 0.240(6), 0.245(8), and 0.127(4), respectively. These are in good agreement with the reported values (ICSD# 95117). The final values of the R factors are $R_{\text{wp}}=4.52\%$ and $R_p=3.45\%$. For $\text{Cu}_2\text{ZnGeSe}_4$ (CZGSe) ($x=1.0$), the refined lattice parameters are $a=5.608(4)$ Å, $c=11.037(2)$ Å, and $c/a=1.97$. The determined u_x , u_y , and u_z are 0.259(0), 0.254(7) and 0.122(9), respectively. The final values of the R factors are $R_{\text{wp}}=4.48\%$ and $R_p=3.30\%$. Since the R_{wp} and R_p of the fitting pattern of Rietveld analysis were small values, we con-

sidered the reliability of the crystal structure refinement of CZTGSe is to be high. The refined lattice parameters of a , c and c/a of CZTGSe solid solutions are shown in Fig. 2(a)-(c). Both lattice constants a and c of the CZTGSe solid solution linearly decrease with increasing Ge content. This is because the covalent radius of germanium (1.24 Å) is smaller than that of tin (1.40 Å).

The reflectance spectra of the CZTGSe solid solution powders shown in Fig. 3(a) were measured by NIR-VIS-UV spectroscopy. The absorption edge shifts to the lower wavelength side with increasing Ge content. The band gaps of the CZTGSe solid solution powders were determined from the reflectance spectra. We plotted the $[F(R)hv]^2$ vs hv [shown in Fig. 3(b)].

Figure 4 shows the E_g values of the CZTGSe solid solution determined from the reflectance spectra. The determined band gaps of the CZTGSe solid solution powders with $x=0.0, 0.2, 0.4, 0.6, 0.8,$ and 1.0 are 0.99, 1.07, 1.14, 1.20, 1.29, and 1.35 eV, respectively. The E_g of the CZTGSe solid solution linearly increases from 0.99 eV for

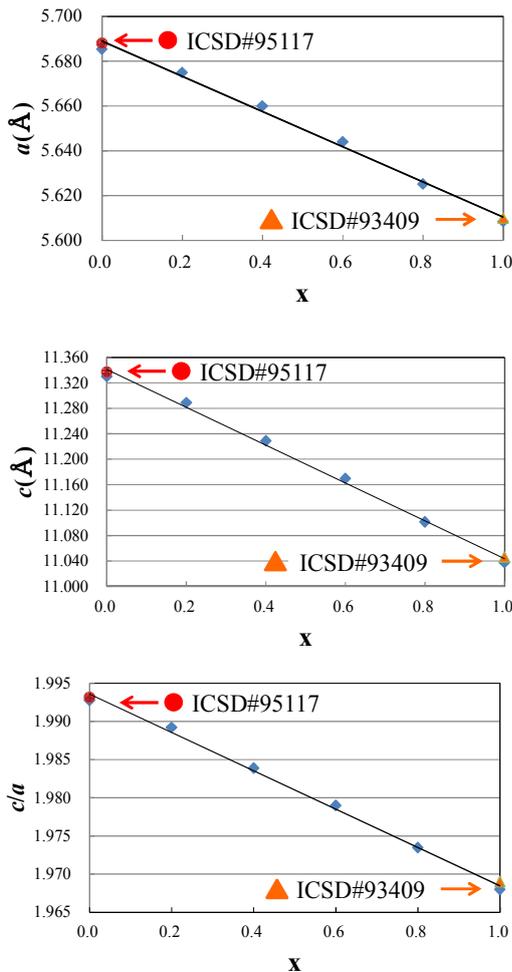


Fig. 2 Lattice parameters a , c , and c/a of CZTGSe solid solution with the tetragonal kesterite-type crystal structure determined by Rietveld refinement.

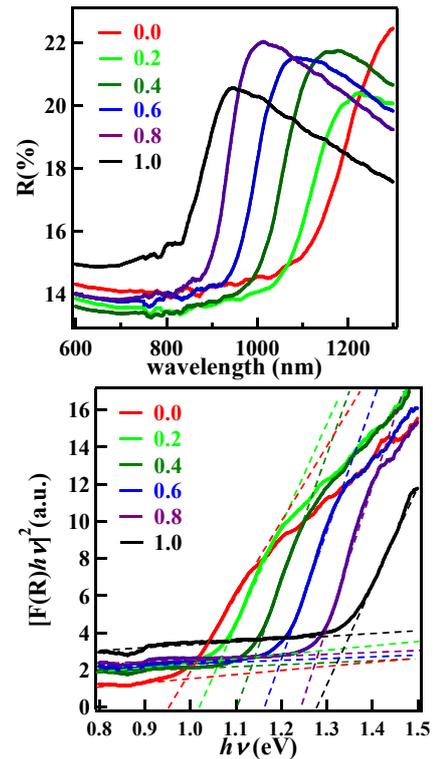


Fig. 3 Diffuse reflectance spectra (a) and $[F(R)hv]^2$ vs. hv plot (b) of CZTGSe powders ($x=0.0-1.0$)

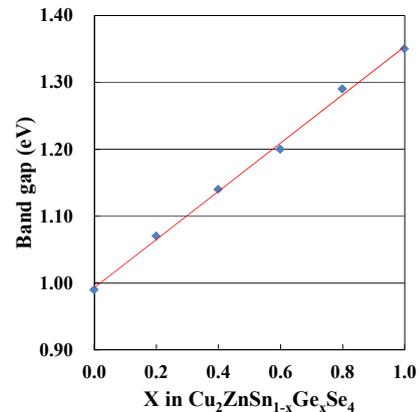


Fig. 4 Band gap energy of the CZTGSe solid solution determined from the reflectance spectra.

CZTSe ($x=0.0$) to 1.35 eV for CZGSe ($x=1.0$).

Acknowledgements

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