

X-ray diffraction studies on the effect of ball-milling speed on the structure of Cu(In,Ga)Se₂ nanoparticles

L. Fu, Y.Q. Guo,^{a)} and S. Zheng

School of Energy Power and Mechanical Engineering, North China Electric Power University, Beijing 102206, China

(Received 30 November 2012; accepted 28 March 2013)

Cu(In,Ga)Se₂ (CIGS) semiconductors were prepared by arc melting and the vacuum solid reaction. CIGS nanoparticles were synthesized by the mechanical alloy method. The influences of various ball-milling speeds on phase structures for CIGS nanoparticles were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The crystal structures and unit-cell parameters of CIGS nanoparticles were determined using TREOR program and the least squares method. A Rietveld structural refinement was used to determine the atomic occupations and atomic numbers of CIGS prepared under various ball-milling speeds. The least size of agglomerated CIGS nanoparticles should be around 200 nm. CIGS nanoparticles milled at various milling speeds with a tetragonal chalcopyrite structure were obtained according to XRD analyses. However, Ga content in CIGS depends on milling speeds. Based on the structural refinements, the unit-cell parameters are $a = 5.693(8)–5.744(9)$ Å and $c = 11.334(9)–11.524(4)$ Å with gallium content ranging from 0.3 to 0.5. The atomic occupations are corresponding to the 4*a* crystal site for Cu atoms, the 4*b* site for In and the 8*d* site for Se. Ga prefers to occupy the 4*b* crystal site. © 2013 International Centre for Diffraction Data. [doi:10.1017/S088571561300033X]

Key words: Cu(In, Ga)Se₂, CIGS, nanoparticles, mechanical milling, Rietveld refinement

I. INTRODUCTION

The copper–indium–gallium–diselenide (CIGS) tetragonal semiconductor has received more attention for its potential application as a prominent thin-film photovoltaic material because of its high optical absorption coefficient, wide absorbing spectrum, and long-term stability (Chandramohan *et al.*, 2010). CIGS solar cells with highest conversion efficiency of 20.3% have been successfully prepared by ZSW Company in Germany (Philip *et al.*, 2011). CIGS thin-film solar cells are of interest in the space power application because of the near optimum band gap for AM0 solar radiation in space. CIGS solar cells are expected to be superior to Si and GaAs solar cells for space missions especially in terms of the performance at the end of low earth orbit (LEO) mission (Dhere and Ghongadi, 2001).

Cu(In,Ga)Se₂ is a I-III-VI semiconducting material with a tetragonal chalcopyrite structure (Chun *et al.*, 2005). Non-vacuum techniques have been used to prepare CIGS films by a process in which water-based inks formulated using nanoparticles of mixed oxides of Cu, In and Ga are used to deposit a precursor layer of fixed Cu/(In + Ga) ratio on a rigid or a flexible substrate of choice using printing techniques and form the CIGS film with an average thickness of 2.5 μm (Kapur *et al.*, 2003). Actually, the preparation methods for CIGS nanoparticles include solvothermal technique (Liu *et al.*, 2012) and low-temperature colloidal technology (Ahna *et al.*, 2007). However, the application of the solvothermal technique is limited to large-scale production because of

its long processing (Gu *et al.*, 2011). As for the low-temperature colloidal process, the toxic Na₂Se had to be one of the starting materials for preparing CIGS nanoparticle. Comparing the two technologies, the mechanical milling method is employed for preparing CIGS with pure elements of copper, indium, gallium and selenium as raw materials for avoiding pollution in the air. This technology takes less time than that of the solvothermal technique. Thus, the mechanical milling technology could be considered as the appropriate method for preparing CIGS nanoparticles (Vidhya *et al.*, 2010). Mechanical milling could induce physical or chemical changes during pulverization, friction and compression between the balls and CIGS powders under high mechanical energy (Bhojan *et al.*, 2009). The grain sizes of agglomerated CIGS powders after ball-milling could be less than 100 nm (Liu and Chuang, 2012). CuIn_{0.5}Ga_{0.5}Se₂ phase could be formed within a very short milling time of 30 min (Benslim *et al.*, 2010).

In this study, CIGS semiconductors have been prepared by vacuum arc melting and the vacuum solid state reaction method, and CIGS nanoparticles were synthesized using a high energy ball mechanical milling. The influence of ball-milling speeds on phase structures in Cu(In,Ga)Se₂ nanoparticles is studied. The goal of this study could supply valuable references for large-scale production of CIGS solar cells.

II. EXPERIMENTAL

The metals of copper granules (>99.95% Sigma Aldrich), indium powders (>99.999% Aldrich), fine chips of gallium (>99.99% Aldrich) and non-metal selenium (>99.9% Aldrich) were used as the starting materials. The precursor Cu–In and Cu–Ga binary alloys with nominal compositions CuX (X = In,

^{a)}Author to whom correspondence should be addressed. Electronic mail: yqguo100@yahoo.com.cn

Ga) were prepared using vacuum arc melting in an atmosphere of ultra-pure argon gas, and followed by sealing these precursors and nonmetallic Se in an evacuated quartz tube for solid state reaction in a furnace at 400–500 °C for several weeks.

CIGS bulks for mechanical milling process were broken and followed by hand grinding in a glove box with high-purity nitrogen atmosphere. A wet milling technique was used to prepare CIGS nanoparticles by putting the mixtures of CIGS powders and anhydrous alcohol with a volume of 13 ml and milling balls into a grinding tank. Two sealed tanks in glove box were taken out and fixed in tanking holders for the milling process at room temperature. The milling time was 10 h and the rotational speeds were fixed at 460, 480, 500 and 520 r/min, respectively. In order to prevent the nanoparticles oxidation in air, the nanoparticles were taken out in the glove box.

The microstructures of CIGS nanoparticles were analysed by a scanning electron microscopy (SEM; JSM6010LA). X-ray diffraction intensity data used for crystal structure analysis were collected by a Rigaku diffractometer with rotating anode and an 18-kW X-ray generator $\text{CuK}\alpha_1$ radiation ($\lambda_{\alpha_1} = 1.54056 \text{ \AA}$) and a graphic monochromator for diffracted beams were used. A step-scanning mode was adopted with a scanning step of $0.02^\circ/2 \text{ s}$ and scan 2θ from 10 to 80° . The phases in CIGS were analysed with Jade5.0 and PDFWIN programs. The unit-cell parameters were determined using TREOR and a least-squares method. After normalization, the diffraction data were analysed by using Rietveld's powder diffraction profile-fitting technique to determine the atomic parameters.

III. RESULTS AND DISCUSSION

A. SEM analysis

The main purpose of this work is to obtain CIGS nanoparticles by a simple process such as mechanical milling

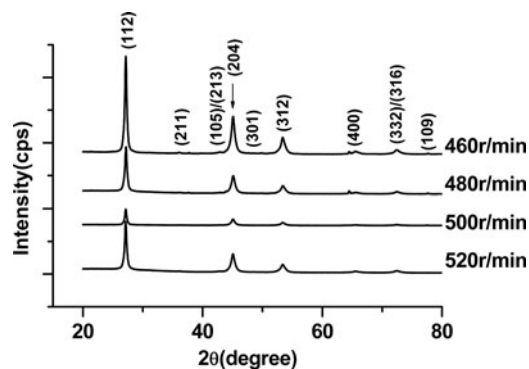


Figure 2. X-ray diffraction patterns of CIGS powders prepared at the milling speed of 460, 480, 500 and 520 r/min.

synthesis and to study the influence of ball-milling on the structure of the prepared CIGS nanoparticle. Figure 1 shows the morphologies of CIGS powders, the particle sizes with 200 nm are observed. The grain size of the CIGS powders decreases with increasing milling speed. However, the large agglomerates of CIGS nanoparticles present (see Figures 1 (c) and (d)) with speed more than 500 r/min. It might be because of the high surface energy of the nanoparticles and strong van der Waals and Coulomb force between the grains. However, if there is obvious agglomeration among CIGS powders, the nanoscale of CIGS prepared will not be displayed.

B. XRD analysis

The XRD patterns of CIGS nanoparticles with various milling speeds are shown in Figure 2. According to ICDD cards of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ solid solutions ($x = 0.3-0.5$), the main phase of these samples prepared is $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$

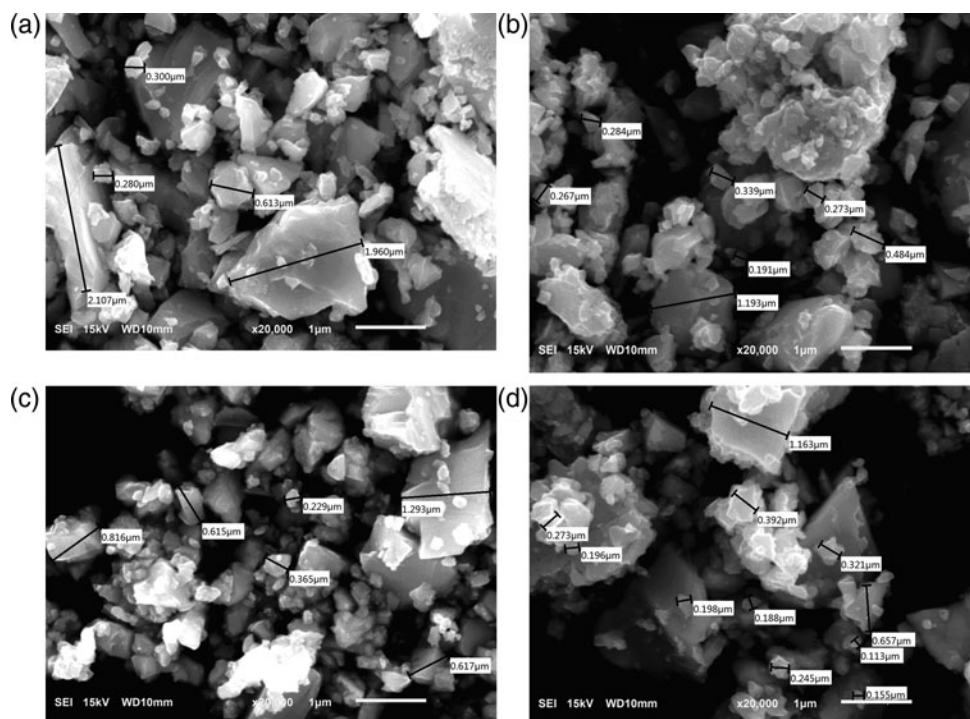


Figure 1. SEM images of CIGS nanoparticles prepared at the milling speed of (a) 460, (b) 480, (c) 500 and (d) 520 r/min.

TABLE I. Milling speed dependence of unit-cell parameters determined by TREOR.

Milling speeds (r/min)	$a(\text{\AA})$	$c(\text{\AA})$	$V(\text{\AA}^3)$
460	5.690(5)	11.327(8)	366.81
480	5.690(3)	11.309(5)	366.19
500	5.695(8)	11.330(7)	367.60
520	5.691(0)	11.358(9)	367.89

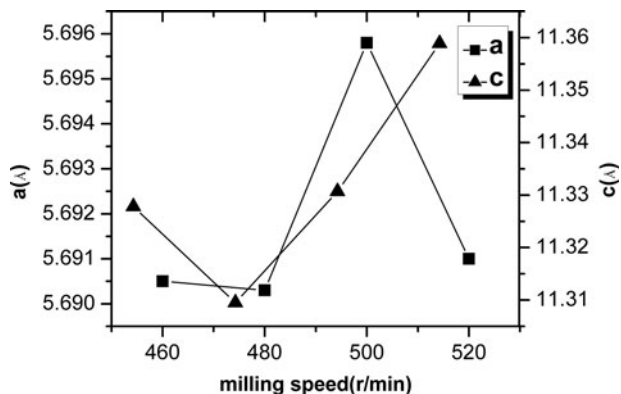


Figure 3. The ball milling speed dependence of unit-cell parameters (a and c).

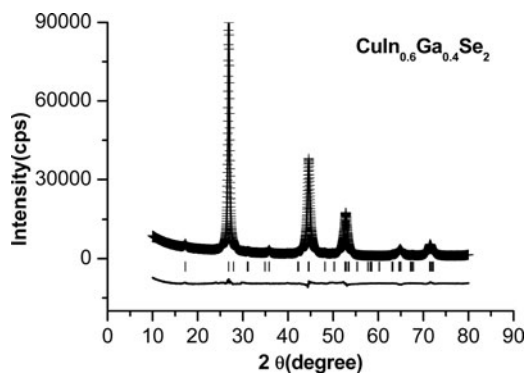


Figure 4. The refined XRD patterns of $\text{CuIn}_{0.6}\text{Ga}_{0.4}\text{Se}_2$ nanopowders milled at 500 r/min.

with $x < 0.5$ with space group of $I\bar{4}2d$. At a low speed, small amount of impurity phase Cu_7Se_4 presents. With increasing milling speed, the content of impurity phase decreases.

When the milling speed reaches 520 r/min, the Cu_7Se_4 phase disappears. As a result, the increase of rotational speed is beneficial for formation of a pure CIGS phase. It might be that fast rotation speed supplies high energy for pushing the chemical reaction for forming pure phase among copper granules, selenium and indium powders and fine chips of gallium.

TREOR and a least squares method were used to determine the planar indices and lattice parameters. The results are listed in Table I. The unit-cell parameters (a and c) dependence of milling speeds are shown in Figure 3. It is noticed that the lattice parameters and cell volume are sensitive to the milling speeds. The relation between the unit-cell parameters and milling speeds is not linear. The unit-cell parameters are minimum at a speed of 480 r/min. The diffraction characteristic peaks of (1 1 2), (2 0 4), (3 1 2), (4 0 0) and (3 3 2)/(3 1 6) planes in the chalcopyrite structure appear for the CIGS samples at various milling speeds. By increasing the milling speed, the diffraction peak of (1 1 2) shows a disordered change, and its 2θ angle values are corresponding with 27.153° for milling at 460 r/min, 27.193° for milling at 480 r/min, 27.153° for milling at 500 r/min and 27.141° for milling at 520 r/min. According to the indexed results of planar indices, the unit-cell parameters a and c decrease with increasing diffraction angle 2θ , thus, the peak position of (1 1 2) plane is found to shift to the higher angle as reported by Olejnicek *et al.* (2010). The unit-cell parameters are related to the atomic radius. Since the atomic radius of Ga (0.61 Å) is less than that of In (0.81 Å), thus, it implies that low rotation speeds are beneficial for enhancing Ga content in CIGS and the possibility of Ga substitution for In decreases with increasing milling speed.

C. Rietveld structure refinement

The typical refinement X-ray diffraction patterns of $\text{CuIn}_{0.6}\text{Ga}_{0.4}\text{Se}_2$ nanopowders milled at 500 r/min are shown in Figure 4. The “+” points represent the experimental data; the line represents the calculated pattern, and the lowest line indicates the difference between the calculated and experimental pattern. A good overlapping of the experimental and calculated peaks has been observed. The pattern factor $R_p = 3.42(7)\%$ and the weighted pattern factor $R_{wp} = 4.50(5)\%$.

Table II lists the structural parameters, atomic positions and residual R factor of $\text{CuIn}_{0.6}\text{Ga}_{0.4}\text{Se}_2$. The results agree very well with those of TREOR. On the basis of the results,

TABLE II. The refined structural parameters of CIGS nanoparticles milled with a speed of 500 r/min.

Normal formula	$\text{CuIn}_{0.6}\text{Ga}_{0.4}\text{Se}_2$			
Crystal system	Body-centred tetragonal			
Space group	$I\bar{4}2d$ (122)			
Lattice parameter(Å)	$a = 5.698(9)$, $c = 11.348(9)$			
Cell volume(Å ³)	368.58			
R_p (%)	3.427			
R_{wp} (%)	4.505			
Atom	Occupancy	x	y	z
Cu	4.00	0	0	0
In	2.73	0	0	1/2
Ga	1.27	0	0	1/2
Se	8.00	0.234(5)	1/4	1/8
Refined formula	$\text{CuIn}_{0.68}\text{Ga}_{0.32}\text{Se}_2$			

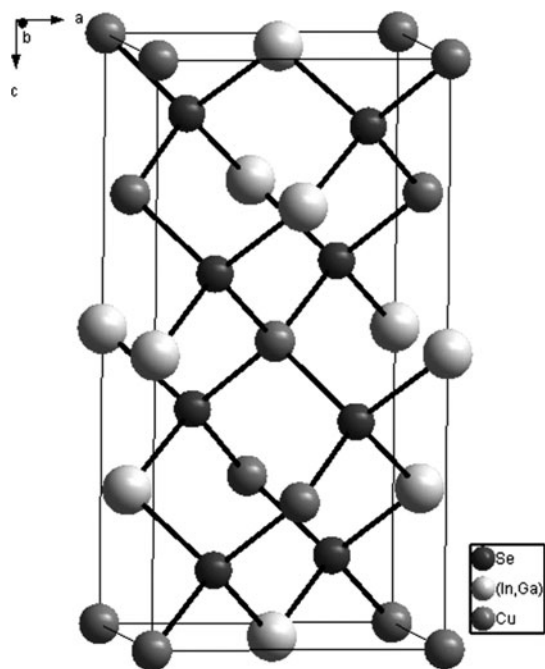


Figure 5. The crystal structural frame of $\text{CuIn}_{0.6}\text{Ga}_{0.4}\text{Se}_2$ with chalcopyrite structure.

TABLE III. Bond length (BL) in $\text{CuIn}_{0.6}\text{Ga}_{0.4}\text{Se}_2$.

Atom	Atom	BL(Å)
Cu	–4Se	2.411(4)
In(Ga)	–2Se	2.513(3)
Se	–2In(Ga)	2.513(3)
	–2Cu	2.411(4)

the space group of $\text{CuIn}_{0.6}\text{Ga}_{0.4}\text{Se}_2$ phase is $I\bar{4}2d$, and the unit-cell parameters are $a = 5.698(9)$ Å and $c = 11.348(9)$ Å.

According to the refined results, the crystal structure of $\text{CuIn}_{0.6}\text{Ga}_{0.4}\text{Se}_2$ is drawn by Diamond software, as shown in Figure 5. The nearest bond lengths in $\text{CuIn}_{0.6}\text{Ga}_{0.4}\text{Se}_2$ are listed in Table III.

IV. CONCLUSION

CIGS nanoparticles have been successfully prepared using mechanical milling technology. Based on XRD analyses, the main phase in CIGS nanoparticles milled at various rotation speeds is $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ solid solution with a chalcopyrite structure. The unit-cell parameters are $a = 5.693(8)–5.744(9)$ Å, $c = 11.334(9)–11.524(4)$ Å for Ga content ranging from 0.5 to 0.3. The phase structures are related to the rotation speed. CIGS single phase is obtained with a speed more than 500 r/min. it implies that the low rotation speeds is beneficial for enhancing Ga content in CIGS and the possibility of Ga substitution for In decreases with increasing milling speed. The least grain size observed from SEM is around 200 nm. The grain size of the CIGS powders decreases

with increasing milling speed. However, the large agglomerates of CIGS nanoparticles present with speed more than 500 r/min. It might be because of the high surface energy of the nanoparticles and strong van der Waals and Coulomb force between the grains. The milling speed plays an important role in preparation of CIGS nanoparticles. The high purity CIGS nanoparticles could be prepared by further optimization of milling speed.

ACKNOWLEDGEMENTS

This study was supported by the National Natural Science Foundation of China (Grant No. 11274110). The authors appreciate the research group of Prof. Dr. Y.H. Ren in New York City University and their cooperation institute in Sun Harmonics Ltd in Hangzhou, China for providing vacuum nano-material synthesis equipments for preparing CIGS nanoparticles.

- Ahna, S. J., Kim, K. H., Chun, Y. G., and Yoon, K. H. (2007). "Nucleation and growth of Cu(In,Ga)Se_2 nanoparticles in low temperature colloidal process," *Thin Solid Films* **515**, 4036–4040.
- Benslim, N., Mehdaoui, S., Aissaoui, O., Benabdeslem, M., Bouasla, A., Bechiri, L., Otmani, A., and Portier, X. (2010). "XRD and TEM characterizations of the mechanically alloyed $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ powders," *Journal of Alloys and Compounds* **489**, 437–440.
- Bhojan, V., Subramaniam, V., Alatorre, J. A., and Asomaza, R. (2009). "Mechano-chemical Synthesis, Deposition and Structural Characterization of CIGS," *MRS Proceedings*, 1210, 1210-Q03-10 doi: 10.1557/PROC-1210-Q03-10.
- Chandramohan, M., Velumani, S., and Venkatachalam, T. (2010). "Experimental and theoretical investigations of structural and optical properties of CIGS thin films," *Mater. Sci. Eng. B* **174**, 205–208.
- Chun, Y.-G., Kim, K.-H., and Yoon, K.-H. (2005). "Synthesis of CuInGaSe_2 nanoparticles by solvothermal route," *Thin Solid Films* **480–481**, 46–49.
- Dhere, N. G. and Ghongadi, S. R. (2001). "CIGS₂ Thin Film Solar Cells on Stainless Steel Foil," *MRS Proceedings*, 668, H3.4 doi: 10.1557/PROC-668-H3.4.
- Gu, S.-I., Shin, H.-S., Yeo, D.-H., Hong, Y.-W., and Nahm, S. (2011). "Synthesis of the single phase CIGS particle by solvothermal method for solar cell application," *Curr. Appl. Phys.* **11**, S99–S102.
- Kapur, V. K., Bansal, A., Le, P., and Asensio, O. I. (2003). "Non-vacuum processing of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ solar cells on rigid and flexible substrates using nanoparticle precursor inks," *Thin Solid Films* **431**, 53–57.
- Liu, C. P. and Chuang, C. L. (2012). "Fabrication of CIGS nanoparticle-ink using ball milling technology for applied in CIGS thin films solar cell," *Powder Technol.* **229**, 78–83.
- Liu, Y., Kong, D. Y., Li, J. W., Zhao, C., Chen, C. L., and Brugger, J. (2012). "Preparation of Cu(In,Ga)Se_2 thin film by solvothermal and spin-coating process," *Energy Proc.* **16**, 217–222.
- Olejnick, J., Kamler, C. A., Mirasano, A., Martinez-Skinner, A. L., Ingersoll, M. A., Exstrom, C. L., Darveau, S. A., Huguenin-Love, J. L., Diaz, M., Ianno, N. J., and Soukup, R. J. (2010). "A non-vacuum process for preparing nanocrystalline $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ materials involving an open-air solvothermal reaction," *Solar Cells* **94**, 8–11.
- Philip, J., Dimitrios, H., Erwin, L., Stefan, P., Roland, W., Richard, M., Wiltraud, W., and Michael, P. (2011). "New world record efficiency for Cu(In,Ga)Se_2 thin-film solar cells beyond 20%," *Prog. Photovolt. Res. Appl.* **19**, 894–897.
- Vidhya, B., Velumani, S., Arenas-Alatorre, J. A., Morales-Acevedo, A., Asomoza, R., and Chavez-Carvayar, J. A. (2010). "Structural studies of mechano-chemically synthesized $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ nanoparticles," *Mater. Sci. Eng. B* **174**, 216–221.