High-Pressure Preparation of High-Density Cu_2ZnSnS_4 Materials *

Yi-Ming Li(李一鸣)[1,2], Li-Xia Qiu(邱利霞)[1], Zhan-Hui Ding(丁战辉)[1**], Yong-Feng Li(李永峰)[1], Bin Yao(姚斌)[1,2**], Zhen-Yu Xiao(肖振宇)[1], Pin-Wen Zhu(朱品文)[1]

[1]*State Key Laboratory of Superhard Material and College of Physics, Jilin University, Changchun 130012*
[2]*Key Laboratory of Physics and Technology for Advanced Batteries (Ministry of Education), College of Physics, Jilin University, Changchun 130012*

(Received 9 March 2016)

High-density Cu_2ZnSnS_4 (CZTS) materials are prepared via the mechanical alloying and high pressure sintering method using Cu_2S, ZnS and SnS_2 as the raw materials. The morphological, structural, compositional and electrical properties of the materials are investigated by using x-ray diffraction, scanning electron microscopy, and energy dispersive x-ray spectroscopy, as well as by the Raman scattering and the Hall Effect measurements. The CZTS synthesized under 5 GPa and 800°C shows a p-type conductivity, with a resistivity of $9.69 \times 10^{-2}\,\Omega{\cdot}cm$ and a carrier concentration of $1.45 \times 10^{20}\,cm^{-3}$. It is contributed to by the large grains in the materials reducing the grain boundaries, thus effectively reducing the recombination of the charge carriers.

PACS: 61.82.Fk, 81.40.Vw, 87.64.Bx DOI: 10.1088/0256-307X/33/7/076101

With the increasing consumption of conventional energy and the increasingly serious environmental crisis, the research and application of solar cells attracted worldwide attention. Up to now, silicon based technology has dominated 80% of the solar cell market of the world. However, silicon is an indirect band gap material and a thick layer (∼200 μm) is needed to absorb an appreciable amount of solar energy. Due to the indirect band gap and the thickness of cells, the next generation of cost-effective high efficiency photovoltaic cells (PVCs) have been investigated. CuInGaSe (CIGS) and CdTe are two highly efficient solar cells, which have been successfully utilized for the development of PVCs. However, these materials are composed of either toxic (Cd) or expensive (In and Ga) rare earth elements. In recent years, Cu_2ZnSnS_4 (CZTS) is one of the promising solar cells due to its semiconductor properties such as p-type conductivity, direct band gaps (1.4–1.5 eV) and high absorption coefficients ($> 10^4\,cm^{-1}$), as well as the abundant and nontoxic constituent elements.[1–3]

In the past few years, the power conversion efficiency of CZTS was enhanced 5.77% in 2007,[4] 9.7% in 2011[5] and 12.6% in 2014.[6] The considerable improvement of the efficiency made it possible that CZTS is one of the future photovoltaic devices. Several successful methods have been established for the preparation of CZTS, such as pyrolysis deposition,[7] pulsed laser deposition,[8] electroplating,[9] co-evaporation,[10] electron beam evaporation,[11] radio frequency magnetron sputter deposition,[12] hybrid spraying,[13] atom beam spraying,[14] hot injecting,[15] spin coating deposition[16] and sol-gel method.[17]

In this Letter, we report the one-step synthesis of high-density CZTS materials under high-pressure conditions. To the best of our knowledge, this is the first time that CZTS has been prepared by the high-pressure sintering method. In addition, the optical and electrical properties of the high-density CZTS have also been studied.

The raw materials used in this work were copper sulfide (Cu_2S, 99.99%), zinc sulfide (ZnS, 99.99%) and tin disulfide (SnS_2, 99.8%) powders. The molar ratio of Cu_2S, ZnS and SnS_2 was fixed at 1:1:1 according to the reaction

$$Cu_2S + ZnS + SnS_2 \rightarrow Cu_2ZnSnS_4. \quad (1)$$

The mixtures were mechanically milled under Ar atmosphere in a P-7 ball mill machine (Fritsch Ltd., Germany) with stainless steel balls and vessel. The weight ratio of ball to powder was maintained at 5:1, and the rotation speed is 300 rpm. The 10 h milled blends were pressed into a pellet ($\Phi 6 \times 4$ mm) and loaded into a cubic anvil high-pressure apparatus (DS-029a-type). The sample was heated to 800°C for 30 min when 5 GPa was applied, and finally quenched to room temperature. The temperature was monitored by using a thermocouple and the pressure was given by a calibration curve that was established by determining the applied loads corresponding to the phase transformation pressures of Bi (I→II, 2.55 GPa; III→V, 7.50 GPa).

The structures and grain size of the samples were characterized by an x-ray diffractometer (XRD,

*Supported by the National Natural Science Foundation of China under Grant Nos 10874178, 11074093, 61205038 and 11274135, the National Found for Fostering Talents of Basic Science under Grant No J1103202, the Ph.D. Programs Foundation of Ministry of Education of China under Grant No 20120061120011, the Open Project of State Key Laboratory of Superhard Materials of Jilin University, and the State Key Laboratory of Inorganic Synthesis and Preparative Chemistry of Jilin University.

**Corresponding author. Email: dingzh@jlu.edu.cn; binyao@jlu.edu.cn

© 2016 Chinese Physical Society and IOP Publishing Ltd

D/Max-IIIA, Japan) and a scanning electron microscope (SEM, JSM-6700 F, JEOL). Raman spectroscopy was conducted on a Renishaw InVia Raman spectrometer by using an excitation wavelength of 532 nm. The electronic properties of the samples were measured by using the Lakeshore 7707 Hall measurement system at room temperature.

Figure 1 shows the XRD patterns of the mixed powders of Cu_2S, ZnS and SnS_2 milled for different times. After milling for 2 h, the intensities of diffraction peaks of ZnS, SnS_2 and Cu_2S decrease obviously while the corresponding full width half-maximum (FWHM) increases, as shown by curve b in Fig. 1, implying that the grain size of raw powders decreases continually during the milling process. When the milling time is over 4 h, the diffraction peak intensities of SnS_2 and Cu_2S decrease continually, however, three peaks at $2\theta = 28.6°$, 47.6° and 56.5°, which were once attributed to the ZnS diffraction peaks, become stronger than ever (curves c–e in Fig. 1). As it is known that during the milling process the particles of raw materials are deformed, cold welded and fractured due to high energy collision, there is no possibility for ZnS crystal growth during this process, thus we deduce that a new phase has been formed. Since the three peaks accord well with the (112), (220) and (312) crystal plane diffraction peaks of Cu_2ZnSnS_4 (CZTS, JCPDS No.26-0575), respectively, it is believed that CZTS has been formed in this stage. After milling for 10 h, only four peaks at $2\theta = 28.62°$, 32.37°, 47.48° and 56.46° are shown by curve f in Fig. 1, those peaks attributed to the (112), (200), (220) and (312) crystal plane diffraction peaks of CZTS, respectively. This result indicates that the single phase CZTS has been formed finally.

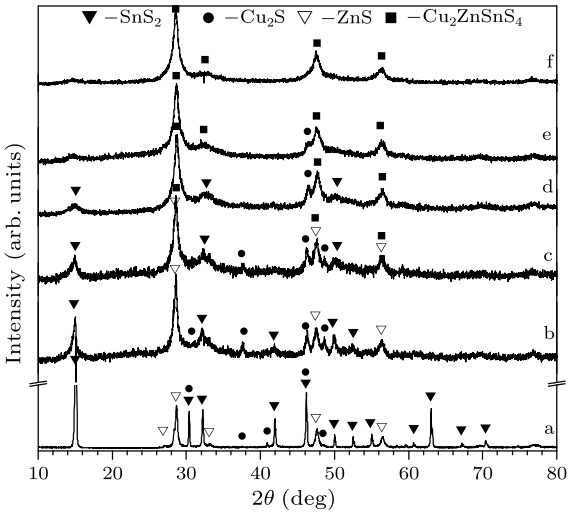

Fig. 1. XRD patterns for the mixtures of Cu_2S, ZnS and SnS_2 with molar ratio of 1:1:1 milled for (a) 0 h, (b) 2 h, (c) 4 h, (d) 6 h, (e) 8 h and (f) 10 h.

Although the CZTS has been formed, it is difficult to prepare high-density materials by ball mill. The raw powders are ground and welded continually during the milling process, thus the as-milled powder samples are very loose and there could be many defects (such as Cu or Zn vacancies) or holes in the obtained CZTS nanocrystal materials. The defects or holes of the sample, as well as the nanocrystal grain size, impact the performance of the CZTS solar cell, which could greatly improve the recombination possibility of the carriers. To enhance the crystallinity and density of the CZTS materials, the high-pressure annealing process was performed using the 10 h milled samples as precursors. Figure 2 shows the XRD patterns of the samples synthesized at 5 GPa and 800℃. The diffraction peaks at $2\theta = 18.2°$, 28.56°, 33.12°, 38.1°, 47.4°, 56.2°, 69.24° and 76.48° are observed in Fig. 2, which belong to (101), (112), (200), (211), (220), (312), (008) and (332) plane diffractions of CZTS, respectively. The tiny diffraction peaks (in Fig. 2) at $2\theta = 26.7°$, 30.8°, 49.6°, 51.9°, 59°, and 78.9° belong to (100), (101), (110), (103), (201), and (210) plane diffractions of ZnS(JCPDS No.80-0007), respectively. They are from the remaining reactants ZnS crystal. Based on Archimedes' principle, the density of the CZTS sample obtained by the high pressure sintering (HPS) method has been measured, which is 4.45 g/cm^3. According to the standard density data of CZTS (4.54 g/cm^3), the density for the obtained CZTS sample is 98%. The average grain sizes of CZTS synthesized by ball mill and HPS are compared, which are calculated with the diffraction data by using the Scherrer formula. The grain size of CZTS prepared by milling is 10 nm, while it is 40 nm for the HPS. High temperature is beneficial for the further growth of the crystal, meanwhile the evaporation of Sn and S elements are restricted under high pressure, and in favor of obtaining CZTS crystal with stoichiometry.

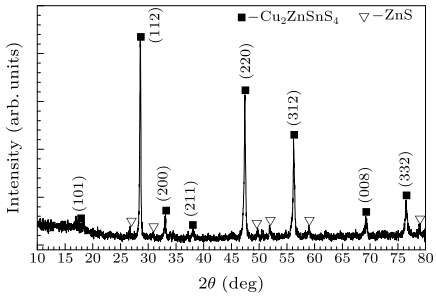

Fig. 2. XRD patterns of the samples synthesized at 5 GPa and 800℃.

To further identify the CZTS phase, the Raman scattering measurement was performed for the milled mixture and the sample synthesized at 5 GPa and 800℃, the Raman spectra are shown in Fig. 3. Two peaks (~227 and ~310 cm^{-1}) can be observed for the 2 h milled sample, as shown by curve a in Fig. 3, which may correspond to the TO mode of ZnS nanoparticles

and the LO mode of SnS_2, respectively.[18,19] A new peak ($\sim$329 cm^{-1}) appears in the 4 h milled sample spectrum (curve b in Fig. 3), and it becomes stronger with the increasing milling time (curves b–e in Fig. 3). The strong peak at $\sim$330 cm^{-1} shown by curve f in Fig. 3) of the sample synthesized by the HPS method is in good agreement with the reported Raman spectra of Kesterite CZTS.[20] The Raman spectra results further confirm our deduction that CZTS is formed after 4 h milling the mixtures, and high quality single phase CZTS has been synthesized at 5 GPa and 800℃.

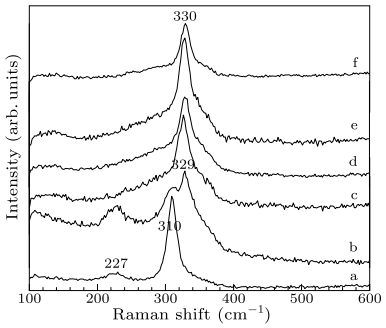

Fig. 3. Raman spectra of the samples milled for (a) 2 h, (b) 4 h, (c) 6 h, (d) 8 h, (e) 10 h and (f) synthesized at 5 GPa and 800℃, respectively.

Morphology is one of the most important parameters that allow the determination of the modification of properties of materials due to the phenomena. Figure 4 shows the surface morphology images of the CZTS synthesized at 5 GPa and 800℃. The samples have compact morphology and are composed of large size grains and well-defined boundaries. The size of the compact grains ranges from 500 nm to 1 μm. The conversion efficiency of the solar cells increases with an increase in the grain size of the absorber layer material, due to the fact that it is important to both the minority carrier diffusion length and the recombination potential in polycrystalline CZTS solar cells. Therefore larger grains are required for the fabrication of highly efficient solar cells.

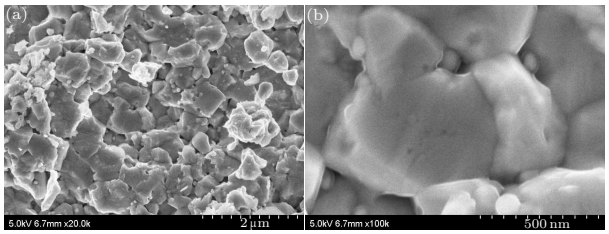

Fig. 4. SEM image of the samples synthesized at 5 GPa and 800℃.

Table 1. The composition of the CZTS obtained by the HPS method.

Element	wt%	at.%
SK	25.99	45.77
SnL	26.77	12.74
CuK	27.76	24.67
ZnK	19.48	16.82

Table 2. Room-temperature electrical properties of the CZTS synthesized by the HPS method.

Field (T)	Resistivity (10^{-2} Ω·cm)	Hall coefficient (10^{-2} cm^3/C)	Type	Carrier density (10^{20} cm^{-3})	Hall mobility (10^{-1} cm^2/(V·s))
0.3	9.69	4.30	p	1.45	4.44
0.6	9.69	2.70	p	2.31	2.78
0.9	9.69	3.02	p	2.07	3.12
1.2	9.69	1.87	p	3.34	1.93

Table 1 lists the chemical compositions of CZTS measured by EDS. The ratios of S/(Cu+Zn+Sn), Cu/(Zn+Sn) and Zn/Sn are 0.844, 0.834 and 1.32, respectively. The results show that the obtained polycrystalline CZTS are S-poor, Cu-poor and Zn-rich, respectively. Table 2 lists the electrical properties of the CZTS synthesized under 5 GPa and 800℃. The high-density polycrystalline CZTS exhibited a p-type conductivity, the room-temperature resistivity (9.69×10^2 Ω·cm) matches well with the reported data (0.1–3.8 Ω·cm).[21,22] It is worth noting that the carrier density (1.45×10^{20} cm^3) is about 100 times higher than the reported device quality CZTS thin films (4.96×10^{18} cm^3).[22] The well electrical performance of CZTS contributed to the fact that the large grains in the materials reduce the grain boundaries, thus effectively reduce the recombination of the charge carriers. This material therefore can be considered for single junction solar cells.

In summary, using the mechanical alloying and high pressure sintering technique, we have synthesized high-density Cu_2ZnSnS_4 (CZTS) materials. The obtained polycrystalline CZTS synthesized under 5 GPa and 800℃ shows a p-type conductivity, with a resistivity of 9.69×10^{-2} Ω·cm and a carrier concentration of 1.45×10^{20} cm^{-3}. This is contributed to by the fact that large grains in the materials will reduce the grain boundaries, thus will effectively reduce the recombination of the charge carriers. Therefore, it can be considered to be used as the absorbing layer for solar cells.

References

[1] Katagiri H, Saitoh K, Washio T, Shinohara H, Kurumadani T and Miyajima S 2001 *Sol. Energy Mater. Sol. Cells* **65**

141
[2] Tang D, Wang Q L, Liu F Y, Zhao L B, Han Z L, Sun K W, Lai Y Q, Li J and Liu Y X 2013 *Surf. Coat. Technol.* **232** 53
[3] Chen S Y, Gong X G, Aron W and Wei S H 2011 *Physics* **40** 248
[4] Jimbo K, Kimura R, Kamimura T, Yamada S, Maw W S, Araki H, Oishi K and Katagiri H 2007 *Thin Solid Films* **515** 5997
[5] Mitzi D B, Gunawan O, Todorov T K, Wang K and Guha S 2011 *Sol. Energy Mater. Sol. Cells* **95** 1421
[6] Abelenda A, Sánchez M, Ribeiro G M, Fernandes P A, SaloméP M P, da Cunha A F, Leitão J P, da Silva M I N and González J C 2015 *Sol. Energy Mater. Sol. Cells* **137** 164
[7] Tanaka K, Kato M and Uchiki H 2014 *J. Alloys Compd.* **616** 492
[8] Wozny S, Wang K and Zhou W 2013 *J. Mater. Chem.* A **1** 15517
[9] Li Y, Yuan T, Jiang L, Su Z and Liu F 2014 *J. Alloys Compd.* **610** 331
[10] Tanaka T, Kawasaki D, Nishio M, Guo Q and Ogawa H 2006 *Phys. Status Solidi* C **3** 2844
[11] Araki H, Mikaduki A, Kubo Y, Sato T, Jimbo K, Maw W S, Katagiri H, Yamazaki M, Oishi K and Takeuchi A 2008 *Thin Solid Films* **517** 1457
[12] He J, Sun Lin, Zhang K Z, Wang W J, Jiang J C, Chen Y, Yang P X and Chu J H 2013 *Appl. Surf. Sci.* **264** 133
[13] Azimi H, Hou Y and Brabec C J 2014 *Energy Environ. Sci.* **7** 1829
[14] Katagiri H 2012 *The 3rd International Conference on Photonics* p 345
[15] Ou K L, Fan J C, Chen J K, Huang C C, Chen L Y, Ho J H and Chang J Y 2012 *J. Mater. Chem.* **22** 14667
[16] Todorov T and Mitzi D B 2010 *Eur. J. Inorg. Chem.* **2010** 17
[17] Su Z H, Sun K W, Han Z L, Cui H T, Liu F Y, Lai Y Q, Li J, Hao X J, Liu Y X and Green M A 2014 *J. Mater. Chem.* A **2** 500
[18] Trajić J, Kostić R, Romčević N, Romčević M, Mitrić M, Lazović V, Balaž P and Stojanović D 2015 *J. Alloys Compd.* **637** 401
[19] Wang C R, Tang K B, Yang Q and Qian Y T 2002 *Chem. Phys. Lett.* **357** 371
[20] Pani B and Singh U P 2013 *J. Renewable Sustainable Energy* **5** 053131
[21] Kala S, Kaur H, Rastogi, Singh V N and Senguttuvan T D 2016 *J. Alloys Compd.* **658** 324
[22] Shin S W, Pawar S M, Park C Y, Yun J H, Moon J H, Kim J H and Lee J Y 2011 *Sol. Energy Mater. Sol. Cells* **95** 3202