Single Crystal X-ray Structure Investigation of $Cu_2ZnSnSe_4$

A. Nateprov[a], **V. Ch. Kravtsov**[a], **G. Gurieva**[b], **S. Schorr**[b]

[a]*Institute of Applied Physics, Academy of Sciences of Moldova,*
Academiei str. 5, Chisinau, MD-2028, Republic of Moldova, alexandr.nateprov@phys.asm.md
[b]*Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn Meitner Platz 1, D-14109, Berlin, Germany*

The crystal structure of $Cu_2ZnSnSe_4$ (CZTSe) has been investigated using two types of structure models known as stannite and kesterite. The single crystal X-ray diffraction study has been performed for two CZTSe single crystals samples obtained by the Bridgman (I) and chemical transport reaction (II) methods. The best refinement was obtained for the model in the space group *I*-42*m*, which suggests that cooper and zinc atoms alternate in the *d* Wickoff position of the space group and statistically occupy it with equal probability.

Keywords: crystal structure, stannite, kesterite, X-ray diffraction.

УДК 548

INTRODUCTION

The $Cu_2ZnSnSe_4$ (CZTSe) compound is known to be a promising material for absorber layers in thin film solar cells since it has the optical band-gap energy of 0.94–1.5 eV and a large optical absorption coefficient. The CZTSSe-based thin film solar cells with the efficiency of 10.1% have been recently manufactured using hydrazine-based solution-processing [1]. However, despite the extensive investigations of bulk and thin films of CZTSe compound, to the best of our knowledge, there are no data on its crystal structure based on single crystal X-ray diffraction measurements. All current investigations of the crystal structure of this compound are based on powder diffraction measurements. From the data obtained earlier elsewhere, two models of crystal structure of CZTSe can be specified, namely, stannite and kesterite. These structures are closely interrelated but belong to different space groups: *I*-42*m* (stannite) and *I*-4 (kesterite) and they differ by cations (Cu and Zn) distribution [2]. First results of powder X-ray refinement [3] suggest that CZTSe crystallizes in the stannite structure. The stannite structure is also confirmed in [4]. However, from X-ray and neutron diffraction investigations, the kesterite structure is considered to be preferable for CZTSe [5, 6], and, what is more, the anti-sites Zn_{Cu} and Cu_{Zn} are detected [6]. Theoretical calculations in [7, 8] predicted that the kesterite structure is the most stable phase for CZTSe, still little difference in the total energy and enthalpy of the formation makes both types of structures possible for CZTSe. In the present research, we are the first to report the details and results of the X-ray investigations of CZTSe single crystals.

EXPERIMENT

Two kinds of single crystals prepared by the Bridgman method and the chemical transport reaction method were used for the present investigation.

The CZTSe crystals are formed via peritectic reactions at 1063K [9], which complicates their preparation by crystallization of the melt. We have prepared crystals of the CZTSe compound using the Bridgman method. Synthesis was carried out in an evacuated and sealed quartz ampoule covered inside with graphite; Cu-99.9999, Zn-99.9999, Sn-99.9999, Se-99.999 were used as the initial elements. In order to avoid a peritectic reaction and appearance of ZnSe as a secondary phase during the crystallization process, both the synthesis of CZTSe from the initial elements and the subsequent crystallization were carried out at the temperature of 50K below the temperature of a peritectic reaction. Moreover, the melt composition used for the crystal growth was slightly displaced from the stoichiometry line of CZTSe of the phase diagram Cu_2SnSe_3 – ZnSe towards Cu_2SnSe_3. The melt cooling rate was 2 K/h. The samples for X-ray measurements were selected from the bottom part of the ingot. The procedure for the preparation of a single crystal using the chemical transport reaction method was similar to [10].

The composition of the sample was tested by EDAX. The content of elements in the samples is given in Table 1.

Table 1. The content of elements in samples

Element, At.%	Cu	Zn	Sn	Se
Sample I	28.91	9.66	13.11	48.32
Sample II	25.22	12.00	13.37	49.42

The X-ray diffraction data were obtained at room temperature using an *Xcalibur E* diffractometer supplied with an EOS CCD space detector and a monochromatic source of Mo*K*α radiation (graphite monochromator). The data were collected and processed using the program CrysAlisPro (Oxford Diffraction Ltd., version 1.171.33.66) and were corrected for the Lorentz and polarization effects and ab-

© Nateprov A., Kravtsov V.Ch., Gurieva G., Schorr S., Электронная обработка материалов, 2013, **49**(5), 70–73.

Table 2. Results of refinement and experimental details for I and II single crystals of CZTSe

Sample	I	II
Empirical formula	Cu_2Se_4SnZn	Cu_2Se_4SnZn
Formula weight	626.98	626.98
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Tetragonal	Tetragonal
Space group	*I*-42*m*	*I*-42*m*
Unit cell dimensions	$a = b = 5.6884(3)$ Å $c = 11.3472(13)$ Å	$a = b = 5.6954(17)$ Å $c = 11.3475(6)$ Å
$c/2a$	0.9974	0.9962
Volume	367.17(5) Å^3	368.09(2) Å^3
Z	2	2
Density (calculated)	5.671 Mg/m^3	5.657 Mg/m^3
Absorption coefficient	32.012 mm^{-1}	31.933 mm^{-1}
$F(000)$	548	548
Crystal size	0.10 x 0.06 x 0.03 mm^3	0.08 x 0.06 x 0.02 mm^3
Theta range for data collection	3.59 to 32.42°	3.59 to 32.49°
Index ranges	$-8<=h<=8$, $-8<=k<=8$, $-17<=l<=17$	$-8<=h<=8$, $-8<=k<=8$, $-17<=l<=17$
Reflections collected	4583	5165
Independent reflections	378 [R(int) = 0.0771]	381 [R(int) = 0.1563]
Completeness to θ_{max}	100.0 % (θ_{max} = 32.42°)	100.0 % (θ_{max} = 32.49°)
Max. and min. transmission	0.4468 and 0.1420	0.5676 and 0.1844
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	378 / 0 / 14	381 / 0 / 16
Goodness-of-fit on F^2	1.004	1.000
Final R indices [$I>2\sigma(I)$]	$R1 = 0.0234$, $wR2 = 0.0487$	$R1 = 0.0367$, $wR2 = 0.0913$
R indices (all data)	$R1 = 0.0304$, $wR2 = 0.0508$	$R1 = 0.0458$, $wR2 = 0.0991$
Absolute structure parameter	0.00(3)	-0.02(4)
Extinction coefficient	0.0426(13)	0.0097(10)
Largest diff. peak and hole	1.221 and -1.134 e. Å^{-3}	1.457 and -1.226 e. Å^{-3}

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for CZTSe

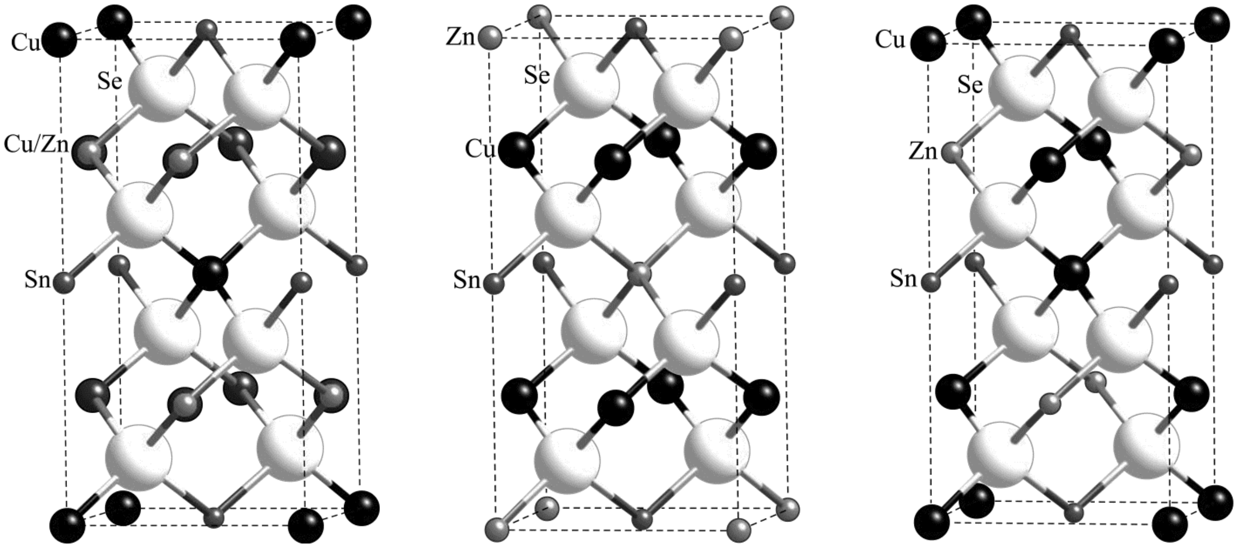
Atom	Wickoff position/Site occupation factor	x	y	z	U(eq)
Cu(2)	2*a* / 0.125	0	0	0	19(1) [21(1)]
Cu(1)	4*d* / 0.125	0	5000	2500	17(1) [27(4)]
Zn(1)	4*d* / 0.125	0	5000	2500	17(1) [13(3)]
Sn(1)	2*b* / 0.125	5000	5000	0	13(1) [15(1)]
Se(1)	8*i* / 0.5	7416(1) [7417 (1)]	7416(1) [7417(1)]	6287(1) [6289(1)]	12(1) [14(1)]

sorption [11]. The structure was refined by the full matrix least squares method on F^2 with anisotropic displacement parameters using the program SHELXL [12].

RESULTS AND DISCUSSION

Best results of the structure refinement for both samples were obtained for the model in the space group *I*-42*m* and are summarized in Tables 2 and 3.

Table 2 shows that the sample prepared from melt (I) has a $c/2a$ value closer to 1 than sample (II) prepared using chemical transport. The ideal stannite and kesterite structures should have $c/2a$ ratio $c/2a = 1$ [7], thus the sample prepared from melt corresponds better to the ideal model. Best final R indices in both cases were obtained on the assumption that cooper and zinc atoms alternate in *d* Wickoff position of the unit cell and statistically occupy it



(a) (b) (c)

Fig. 1. Final (a), stannite (b) and kesterite (c) models of CZTSe structure.

with equal probability and other Cu atoms are situated in 2a position (Table 3, Fig. 1).

U(eq) are defined as one third of the trace of the orthogonalized U^{ij} tensor. Data for II are given in square brackets when it differs from I.

As follows from Table 3, the difference in structural parameters of I and II do not exceed three standart deviations.

The data are deposited as CIF files at the Fachinformationszentrum Karlsruhe, Eggenstein-Leopoldshafen, 76344 Germany (fax: +49 7247808666; E-mail: crysdata@fiz-karlsruhe.de); CSD#424774); the data can be obtained by addressing the Fachinformationszentrum and giving the CSD number.

Table 4. Final *R* values for different models

Sample I			
Model	Stannite	Kesterite (Conv.)	Kesterit (Desord.)
Final *R* indices [*I*>2sigma (*I*)]	*R*1=0.0263 *wR*2 = 0.0659	*R*1 = 0.0292 *wR*2 = 0.0558	*R*1 = 0.0291 *wR*2 = 0.0556
R indices (all data)	*R*1 = 0.0339 *wR*2 = 0.0693	*R*1 = 0.0399 *wR*2 = 0.0601	*R*1 = 0.0399 *wR*2 = 0.0599
Sample II			
Model	Stannite	Kesterite (Conv.)	Kesterit (Desord.)
Final *R* indices [*I*>2sigma (*I*)]	*R*1= 0.0384 *wR*2 =0.1051	*R*1 = 0.0442 *wR*2 = 0.0964	*R*1 = 0.0445 *wR*2 = 0.0972
R indices (all data)	*R*1 = 0.0481 *wR*2 = 0.1150	*R*1 = 0.0575 *wR*2 = 0.1028	*R*1 = 0.0579 *wR*2 = 0.1037

The best model of a structure has been obtained for the space group *I*-42*m*, but the arrangement of Cu atoms is similar to the kesterite structure. However, it does not match the conventional kesterite (space group *I*-4) structure with independent 2*c* and 2*d* positions because in the space group *I*-42*m* the corresponding four 4*d* positions are equivalent (Fig. 1a).

The refinement procedure has been also carried out for the conventional stannite (space group *I*-42*m*) model (Fig. 1b) and two kesterite (space group *I*-4) models: conventional model (Fig. 1c) and a similar model when 2*c* and 2*d* positions are statistically occupied by copper and zinc with equal probability. The results are listed in Table 4.

Thus X-ray data on single crystals confirm the earlier neutron diffraction measurements [6] of kesterit-like structure of CZTSe. At the same time it should be noted that the best model of refinement suggests the *I*-42*m* space group for CZTSe.

CONCLUSIONS

To summarize, the X-ray diffraction investigation of single crystals has been carried out for two samples of CZTSe prepared using the Bridgman and chemical transport reaction methods. The most suitable model that fits for both samples has been obtained in *I*-42*m* space group. A better refinement was obtained for the CZTSe single crystal prepared using the Bridgman method. The final model of the structure suggests that 2a Wickoff positions of the unit cell are occupied by Cu atoms and *d* positions are statistically occupied by copper and zinc atoms with equal probability. This model has main features of the kesterit structure, but belongs to the *I*-42*m* space group unlike the conventional kesterit structure with the *I*-4 space group.

ACKNOWLEDGMENTS

The authors thank Professor E. Arushanov for his valuable remarks and Dr. V. Tezlevan for sample II preparation. The financial support from the projects

STCU no. 5402 and IRSES PVICOKEST (Grant Agreement no. 269167 is acknowledged.

REFERENCES

1. Barkhouse D.A.R., Gunawan O., Gokmen T., Todorov T.K., Mitzi D.B. Device Characteristics of a 10.1% Hydrazine-processed $Cu_2ZnSn(Se,S)_4$ Solar Cell. *Progress in Photovoltaics: Research and Applications*, **20**, (2012), 6–11.
2. Hall S.R., Szymanski J.T. and Stewart J.M. Kesterite, $Cu_2(Zn,Fe)SnS_4$, and Stannite, $Cu_2(Fe,Zn)SnS_4$, Structurally Similar but Distinct Minerals. *Canadian Mineralogist*, **16**, (1978), 131–137.
3. Olekseyuk I.D., Gulay L.D., Dydchak I.V., Piskach L.V., Parasyuk O.V., and Marchuk O.V. Single Crystal Preparation and Crystal Structure of the $Cu_2Zn/Cd,Hg/SnSe_4$ Compounds. *J. of Alloys Compd*., **340**, (2002), 141–145.
4. Wibowo R.A., Kim W.S., Munir B., and Kim K.H. Growth and Properties of Stannite-Quaternary $Cu_2ZnSnSe_4$ thin Films Prepared by Selenization of Sputtered Binary Compound Precursors. *Advanced Material Research*, **29–30**, (2007), 79–82.
5. Siebentritt S. and Schorr S. Kesterites – a Challenging Material for Solar Cells. *Progress in Photovoltaics: Research and Applications*, (2012), **20**, 512–519.
6. Schorr S. The Crystal Structure of Kesterite Type Compounds: A Neutron and X-ray Diffraction Study. *Solar Energy Materials and Solar Cells*, **95**, (2011), 1482–1488.
7. Persson C. Electronic and Optical Properties of Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$. *J. Appl. Phys.*, **107**, (2010), 053710.
8. Maeda T., Nakamura S. and Wada T. Phase Stability and Electronic Structure of In-free Photovoltaic Semiconductors, $Cu_2ZnSnSe_4$ and Cu_2ZnSnS_4 by First-principles Calculation. *Mater. Res. Soc. Symp. Proc.* Vol.1165, (2009), 1165–M04-03.
9. Olekseiuk I.D., Dudchak I.V., Piskach L.V. Fazovi Ravnovagi v Kvazipotriinii Sistemi Cu_2Se-ZnSe-Cu_2SnSe_3. *Fizika i chimiya tverdogo tila*, **2**, (2001), 195–200.
10. Nitsche R., Sargent D. F. and Wild P. Crystal Growth of Quaternary Chalcogenides by Iodine Vapour Transport. *J. Cryst. Growth* **1** (1967) 52–53.
11. Clark R.C., Reid J.S. The Analytical Calculation of Absorption in Multifaceted Crystals. *Acta Cryst. A*, **51**, (1995), 887–897.
12. Sheldrick G.M. A Short History of SHELX. *Acta Cryst. A*, **64**, Part 1, (2008), 112.

Received 20.07.12

Реферат

Кристаллическая структура соединения $Cu_2ZnSnSe_4$ была исследована с использованием в качестве прототипов двух структур: кестерита и станнита. Рентгеноструктурные измерения проведены на монокристаллах, полученных методом Бриджмена (I) и методом химических транспортных реакций (II). Наилучшее совпадение получено для модели с пространственной группой *I*-42*m* и в предположении, что атомы меди и цинка с равной вероятностью распределения занимают *d* Wickoff позиции пространственной группы.

Ключевые слова: кристаллическая структура, станнит, кестерит, рентгеноструктурный анализ.