SYNTHESIS OF Cu₂ZnSnS₄ BY MECHANICAL ALLOYING METHOD FOR THERMOELECTRIC APPLICATION

Bui Duc Long[1)*], Nguyen Van Khanh[1)], Duong Ngoc Binh[1)], Le Hong Thang[1)], Le Thi Bang[1)], Suhana Binti Mohd Said[2)]

[1)]School of Materials Science andEngineering, Hanoi University of Science and Technology, No.1 Dai Co Viet, Hanoi, Vietnam
[2)]Department of Electrical Engineering, Faculty of Engineering, University of Malaya, Malaysia

[*]Corresponding author: email: long.buiduc@hust.edu.vn, Tel.:+84 24 3868 0355, School of Materials Science and Engineering, Hanoi University of Science and Technology, No.1, Dai Co Viet Street, Hai Ba Trung, Hanoi, Vietnam

Abstract

Quaternary chalcogenide Cu₂ZnSnS₄ is a potential candidate for thermoelectric (TE) application due to a number of advantages including containing only non-toxic and abundant elements, high Seebeck coefficient and low thermal conductivity. In this study, Cu₂ZnSnS₄ was synthesized using mechanical alloying method from Cu, Zn, Sn and S powders. In order to study the effect of milling duration on the formation of Cu₂ZnSnS₄, different milling duration of 2, 4, 12 and 16 h were carried out. As the results, Cu₂ZnSnS₄ wasstarted to form after milling for 12 h. The formation of Cu₂ZnSnS₄ was completed after 16 h of milling. In addition, Cu₂ZnSnS₄ nanoparticles were obtained after 16 h of milling with the particle distribution mostly in the range of 50 - 60 nm.

1 Introduction

Alarming environment and energy crisis associated with insatiable demand of energy from fossil fuel sources,which has resulted in efforts of seeking clean and sustainable energy sources. It has been estimated that two-thirds of the primary energy from fossil fuels consumed by humans is wasted, with mostof it being waste heat[1-3]. The recovery of huge amount of wasted heat not only has a significant influence on the efficiency of energy consumption,but also reduces the global greenhouse gas emission.Thermoelectric generators (TEGs), which are capable of generating electricity directly from waste heat sources by Seebeck effect,have emerged as a novel technology for recovering waste heats from automobiles, industrial sectors and home cooking etc. TEGs are solid-state devices, which areholding a number of advantages over conventional powder generators, such as silent operation,no moving parts, reliable durabilityand no gas emission [4-6]. However, currently TEGs still exist some main drawbacks including low efficiency and high cost of TE materials, which are primary factors restricting for large-scale applications [7-9].

The performance of a type of TE materials is evaluated by the dimensionless figure of merit *ZT*, ($ZT = \sigma S^2 T / \kappa$, where S, σ, κ are Seebeckcoefficient, electrical conductivity and thermal conductivity, respectively). *T* is the absolute average temperature between the hot and the cold sides of TEGs. A high efficiency TE material, therefore, should possess a high Seebeck

coefficient(S), high electrical conductivity (σ) in combination with low thermal conductivity (κ). Although the commercial TE materials have a ZT value of 1.0, however, TE devices require a ZT of 3.0 to be a competitive candidate in practical applications [10].

Among potential TE materials studied for middle range temperature application, quaternary chalcogenide Cu_2ZnSnS_4 (CZTS) has recently received a great interestfrom scientist due high stability in air, high melting temperature, low thermal conductivity, high Seebeck coefficient, and particularly containing only non-toxic and earth abundant elements [11, 12].The synthesis of CZTS has been studied through a number of methods, such as, sputtering [13], thermal evaporation [14], solution phase reaction [15], sol–gel [16] and spray pyrolysis [17]. However, these methods either require particular equipment for complicated process and low production mass. Hence, it is challenging to develop facile and cost-effective methods, which are capable oflarge-scale production.

In this study, kesterite CZTSwas synthesized using a simple method which is mechanical alloyingofCu, Zn, Sn and Spowders. The formations of CZTS, morphology and particle sizes of milled powders were investigated.

2   Experimental procedure

For preparation of CZTS precursor, Cu (99.5%,−100 mesh, Strem Chemicals), Zn(99.9%,−325 mesh, Strem Chemicals), Sn (99.5%, −100 mesh, Alfa Aesar), and S (99.5%, −325 mesh, Alfa Aesar) powders were used as starting materials. Mixtures of powders with the stoichiometric ratio of 2:1:1:4 were milled using Fritsch Planetary Mono Mill Pulverisette 6 classic line for various milling durations of 2, 4, 12and 16h under Ar atmosphere. The ball to powder ratio and the milling speed were of 10:1 and 300 rpm, respectively. In order to minimize contamination of milled powders, the mill media and container were made of zirconia oxideand no process control agents were added into the mixtures.

The phase transformation after ball milling was analyzed using X-ray diffractometer (Bruker D8 Advance, CuKαradiation, 1.54059 Å). The surface morphologies of the mixed powders and milled powders were studied by field-emission scanning electron microscope (FE-SEM) (Hitachi S-4800).For particle size distribution analysis, random 50 particles from each image were measured using ImageJ software.

3   Results and discussion

In the present work, the effect of milling duration on the phase transformation of milled CZTS powders was investigated by using differentmilling duration of 2, 4, 12and16 h, whilst other parameters remained constant. The XRD patterns of a raw mixture of Cu, Zn, Sn and S powders, and milled powders are shown in **Fig. 1**.

The XRD pattern of the mixedpowder shows a number of sharp peaks attributed to the elemental powders of Cu, Zn, Sn and S. After 2 h and 4 h of milling, the XRD peaks of elemental powders of Cu, Zn, Sn and S were broadened and the intensity of peaks was decreased due to the refinement of the crystallites and the increase in lattice strain [18]whilst no obvious peaks of CZTS appeared.After milling for 12 h, most XRD peaks of the starting powders disappeared except a peak of Cu. Besides, it can be seen that four primary peaks were appeared, which are attributed to the diffraction of the planes (112) (200) (220) (312) of CZTS. This indicates that the formation of CZTS has been taken place. After a prolonged milled duration of 16 h, all peaks of elemental powders were disappeared, whilst there were only peaks of CZTS present. The

crystal structure of CZTS has been completed with the appearance of primary peak attributed to the planes (332). It can be concluded that the mixture of powders has been mechanically alloyed completely after 16 h of milling.The formation of CZTS in our experiment was taken place in a shorter milling duration compared to which were reported by Pareek *et al.*[19]and Wang *et al.*[20]. Pareek *et al.* reported that pure CZTS was synthesized completely from starting elemental powders after ball milling for 30 h with the rotation speed of 450 rpm andthe ball-to-powder weight ratio of 5:1, whilst Wang *et al.* reported that the formation of CZTS was completed after milling for 20 h at 50 Hz frequency with the rotation speed of 300 rpm and at the same ball-to-powder weight ratio of 5:1. These above mentioned differences could be primarily attributed to the differences in milling process variables including ball-to-powder weight ratio, model of milling machine, the molar ratio of elemental powders and the particle sizes of powders (the manufacturers of the source powders are different in the present work and the literatures).
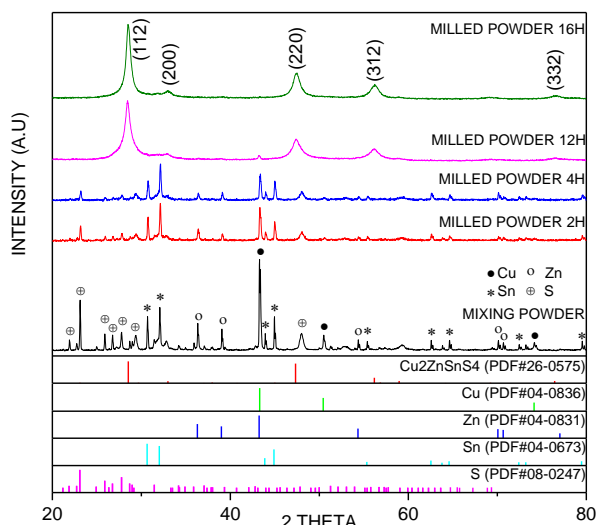

Fig. 1 XRD patterns of mixing powder and milled powders at different duration

During ball mill, the mixture of powder particles is repeatedly flattened, cold-welded, fractured and rewelded. The formation mechanism of CZTS during high-energy ball mill is attributed tothe diffusion process, which takes place when particles are cold-welded together. Heavy plastic deformations during milling createa variety of crystal defects such asdislocations, vacancies, stacking faults, and increasethe grain boundaries, and so, enhances the diffusion process.In addition, slightly temperature raise during milling further aids the diffusion process; consequently, true compound is formed.The specific times required to develop a given structure in any system depends on the initial particle size, characteristics of the ingredients,and the operating parameters of the equipment [21-23].

There is an important characteristic to be noted in the XRD data of milled powders after 12 h and 16 h of milling that is a slight peak shift to lower or higher 2θ values in the samples, which corresponds with result reported in previous paper [19]. This phenomenon can be due to the presence of a large amount of defects, lattice strain and disorder, which usually results in peak shift, in milled powders after a long milling duration, as seen in **Fig. 2**.
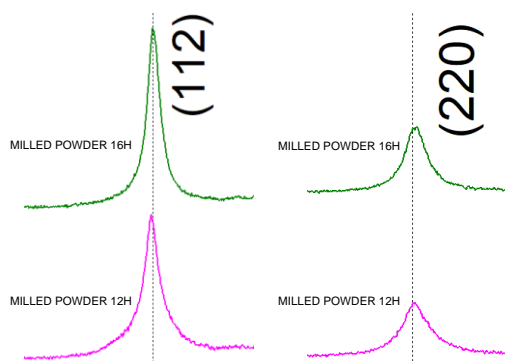
Fig. 2 Zoomed-in of XRD pattern of two main peaks of milled powders in small ranges of 2θ (left) from 25 to 30° and (right) from 45 to 50°

Morphologies of the mixture powders before and after milling at different duration were investigated using SEM, as shown in **Fig. 3**. It can be seen in **Fig. 3 (a)** that particles of raw element powders separated completely or loosely contact which can be observed clearly in distinguishable shape. However, the powder particles started to be plastically deformed and get cold-welded after 2 h of milling although some un-welded particles still existed, as illustrated in **Fig. 3 (b)**. After 4 h of milling, the cold-welding and fracturing processes continued to take place leading to microstructural refinement, as shown in **Fig. 3 (c)**. At this milling duration, the distribution of particle sizes can be observed in a large range.
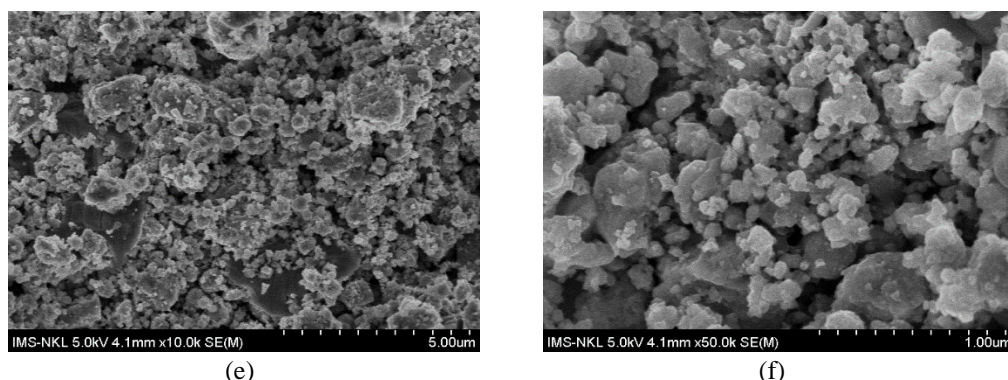

(a)

(b)

(c)

(d)

(e)   (f)
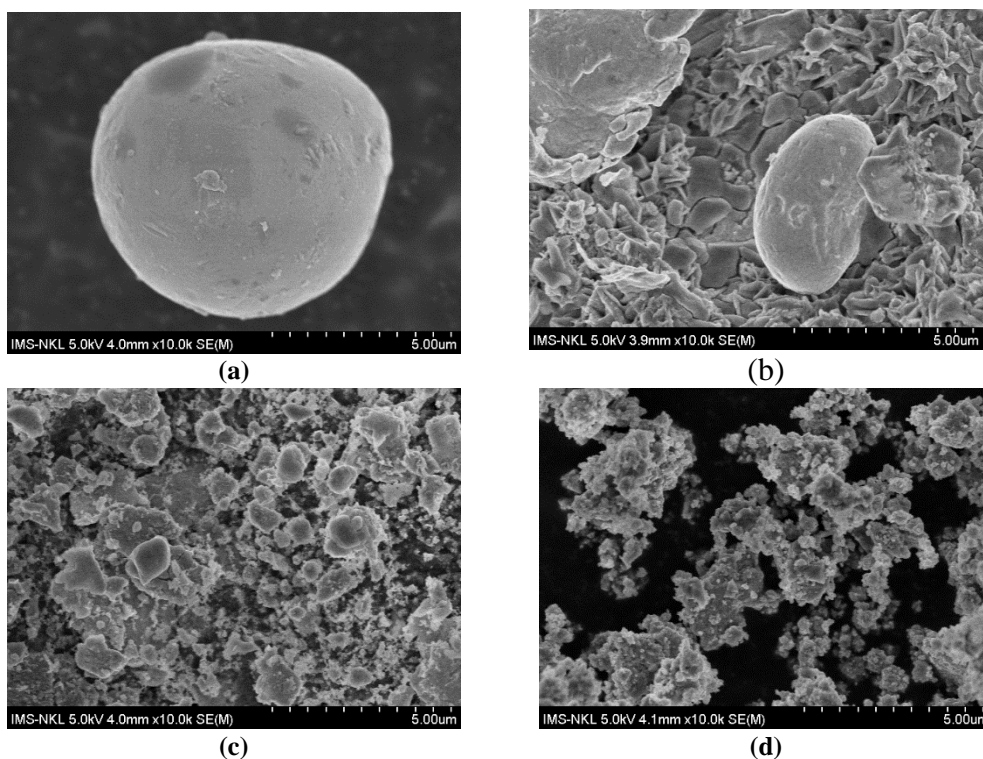
Fig. 3 SEM morphologies of (a) raw powder mixture and milled powders after (b) 2 h, (c) 4 h, (d) 12 h and (e) 16 h of milling. Image (f) is SEM morphology of 16 h milling with high magnification (50,000 X)

After milling for long duration of 12 h and 16 h, the particles continued to cold-weld and fracture but the tendency to fracture predominates over cold-welding. As the results,numbers of small particles wereincreased, **Fig. 3 (d),(e)**. With high magnification SEM image (**Fig. 3(f)**), it can be clearly seen that the powder particles of 16 h milling became round shapes and the distribution of particle sizes is mostly in the range of 50 - 60 nm, as seen in **Fig. 4**.
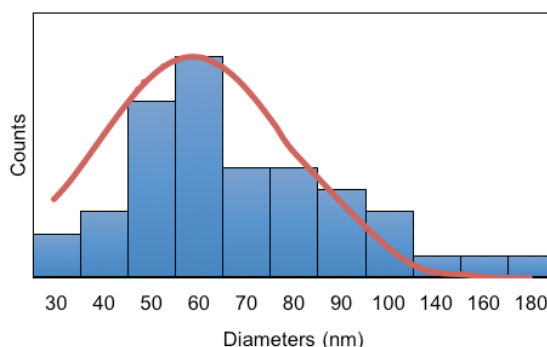

Fig. 4 The distribution of particle size of milled CZTS after 16 h milling

4   Conclusions

In this research, kesterite CZTS was synthesized using mechanical alloying method from Cu, Zn, Sn and S powders. After milling of 12 h, the CZTS phase was formed. Single phase of CZTS was obtained completely after 16 h of milling. The milled powderswere obtainedin nanosized with the particle distribution mostly in the range of 50 - 60 nm after 16 h of milling.

References

[1] R. Ovik, B. D. Long, M. C. Barma, M. Riaz, M. F. M. Sabri, S. M. Said, R. Saidur: Renewable & Sustainable Energy Reviews, Vol. 64, 2016, p. 635–659, http://dx.doi.org/10.1016/j.rser.2016.06.035

[2] X. Zhang, L.D. Zhao: Journal of Materiomics Vol.1, 2015, p. 92-105, http://dx.doi.org/10.1016/j.jmat.2015.01.001

[3] Y. Wu, S.W. Finefrock, H. Yang: Nano Energy Vol. 1, p. 651-653, http://dx.doi.org/10.1016/j.nanoen.2012.08.001

[4] C. R. S. Rodrigues, T. Machado, A. L. Pires, B. Chaves, F. S. Carpinteiroa, A. M. Pereira: Applied Thermal Engineering, Vol. 138, 2018, p. 319–324, http://dx.doi.org/10.1016/j.applthermaleng.2018.04.046

[5] S. LeBlanc: Sustainable Materials and Technologies Vol.1–2, 2014, p. 26–35, https://doi.org/10.1016/j.susmat.2014.11.002

[6] G. J. Snyder, E. S. Toberer, Nature, Vol. 7, 2008, p. 105-114, http://dx.doi.org/10.1038/nmat2090

[7] T. Kvackaj, R. Bidulsky, A. Kovacova, J. Ileninova, J. Bidulska: Acta Metallurgica Slovaca, Vol. 20, 2014, No. 4, p. 397-404, https://doi.org/10.12776/ams.v20i4.438

[8] W. He, G. Zhang, X. X. Zhang, J. Ji, G. Li, X. Zhao: Applied Energy Vol. 143, 2015, p. 1-25, https://doi.org/10.1016/j.apenergy.2014.12.075

[9] M. Ibańez et al.: Chemistry Materials, Vol. 24, 2012, p. 562−570, http://dx.doi.org/10.1021/cm2031812

[10] X. Zhang, L. D. Zhao: Journal ofMateriomics, Vol. 1, 2015, p. 92-105, http://dx.doi.org/10.1016/j.jmat.2015.01.001

[11] M. L. Liu, F. Q. Huang, L. D. Chen, I. W. Chen: Applied Physics Letter, 94, 2009, p. 202103, http://dx.doi.org/10.1063/1.3130718

[12] A. Nagaoka, T. Masuda, S. Yasui, T. Taniyama, Y. Nose: Applied Physics Express, Vol. 11, 2018, p.051203, https://doi.org/10.7567/APEX.11.051203

[13] T. P. Dhakal, C. Peng, R. Reid Tobias, R. Dasharathy, C. R. Westgate: Solar Energy, Vol. 100, 2014, p. 23–30, http://dx.doi.org/10.1016/j.solener.2013.11.035

[14] C. Shi, G. Shi, Z. Chen, P. Yang, and M. Yao: Materials Letters, Vol. 73, 2012, p. 89–91, http://dx.doi.org/10.1016/j.matlet.2012.01.018

[15] H. Yang, L. A. Jauregui, G. Zhang, Y. P. Chen, and Y. Wu: Nano Letters, Vol. 12, No. 2, 2012, p. 540–545, http://dx.doi.org/10.1021/nl201718z

[16] B. L. Guo, Y. H. Chen, X. J. Liu, W. C. Liu, A. D. Li: AIP Advance, Vol. 4, No. 9, 2014, p. 097115, http://dx.doi.org/10.1063/1.4895520

[17] M. Aono, K. Yoshitake, H. Miyazaki: Physica Status Solidi (c), Vol. 10, No. 7–8, Aug. 2013, p. 1058–1061, http://dx.doi.org/10.1002/pssc.201200796

[18] C. Suryanarayana: Progress in Materials Science, Vol. 46, No. 1–2, 2001, p. 1–184, http://dx.doi.org/10.1016/S0079-6425(99)00010-9

[19] D. Pareek, K. R. Balasubramaniam, P. Sharma: Materials Characterization, Vol. 103, 2015, p. 42–49, http://dx.doi.org/10.1016/j.matchar.2015.03.014

[20] Y. Wang and H. Gong: Journal of Alloys Compounds, Vol. 509, No. 40, 2011, p. 9627–9630, http://dx.doi.org/10.1016/j.jallcom.2011.07.041

[21] C. Suryanarayana: Progress in Materials Science, Vol. 46, 2001, p. 1-184, https://doi.org/10.1016/S0079-6425(99)00010-9

[22] M. Besterci, F. Dobeš, T. Kvačkaj, K. Sülleiová, B. Ballóková,O. Velgosová, Acta Metallurgica Slovaca, Vol. 20, 2014, No. 3, p. 326-340, http://dx.doi.org/10.12776/ams.v20i3.307

[23] T. Kvackaj, A. Kovacova, J. Bidulska, R. Bidulsky, R. Kocisko: Archives of Metallurgy and Materials, Vol. 60, 2015, No. 2A, p. 605-614, https://doi.org/10.1515/amm-2015-0180

Acknowledgements