

Solvothermal synthesis of CZTSSe for photovoltaic technology

D. Fraga, R. Martí, T. Lyubenova, L. Oliveira, A. Rey, S. Kozhukharov, J. Carda

Abstract: Solid solution of $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ with kesterite-type structure for low cost thin film solar cell were successfully synthesised by solvothermal route. The influence of different solvents was investigated in order to improve the preparation procedure. The physical properties of CZTS powders together with their structural and microstructural analysis was performed using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX).

Key words: Solar cells, $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$, Solvothermal

INTRODUCTION

Chalcopyrite (CIGS) and Kesterites (CZTS), highlight as one of the most important semiconductors nowadays, due to its unique optical and electrical properties [1,2]. In the last years, an enormous scientific attention of these materials was focused. In particular, the field of thin films technology filed benefits their applications in nonlinear optical materials [3], infrared sensors and lenses [4], and as sources for solar energy conversion.

Kesterites (CZTS) are the most promising candidates for low cost thin film photovoltaics. Recently, there has been an effort to investigate direct band gap $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) and $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) thin films for photovoltaic applications. CZTS and CZTSe are particularly attractive material thanks to it low-cost, earth-abundant elemental composition (Zn and Sn) and have relatively low toxicity [5-9].

In addition, significant record efficiencies (~10%) in this materials are obtained for solid solution of $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ [10]. Different synthesis procedures have been applied for its preparation [11,12]. However, simple and rapid way of preparation, as it is a solvothermal route, is proposed in this work. The physical properties of CZTS particles, such as stoichiometric composition, structure, morphology were studied. Moreover, different synthesis conditions were studied, evaluating the solvent influence to the final compositions of CZTS.

EXPERIMENTAL

For the synthesis, 2 mmol of copper (II) nitrate trihydrate (99%, Aldrich), 1 mmol of zinc nitrate hexahydrate (99%, Fluka) and 1 mmol of tin (IV) chloride pentahydrate (98%, Riedel-de Haën) in different solvents (ethyleneglycol and ethylenediamine) were dissolved, keeping metal cation ratio $\text{Cu}/\text{Zn}+\text{Sn}=0.8$ and $\text{Zn}/\text{Sn}=1.2$ in order to rich stoichiometry composition [10]. Afterwards, 5 mmol of thiourea (99%, Fluka) was loaded into teflon-lined stainless steel autoclave. The mixture was heated to 170 °C for 48 h and then allowed to cool to room temperature naturally.

The precipitate was washed and further calcined and selenized at 500 °C under reducing atmosphere (H_2/N_2) in a tubular furnace. Finally, the products were collected for characterization.

XRD patterns were recorded using a Siemens D5000D X-ray diffractometer in a range from 10 to 70° (2 Theta) with a scan rate of 0.05° and step of 2 s. A Scanning Electron Microscopy (SEM) model JEOL 7001F attached with an energy dispersive X-ray analysis (EDX) was employed to study the morphology and elemental composition of the materials.

RESULTS AND DISCUSSION

The XRD analysis of CZTS powders obtained with ethyleneglycol as solvent (raw and calcined) shows reflections corresponding to the $\text{Cu}_2\text{ZnSnS}_4$ (JCPDS 26-0575) for the non-calcined sample. However, the calcined one suggest solid state solution formation of $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ according to the synthesis design.

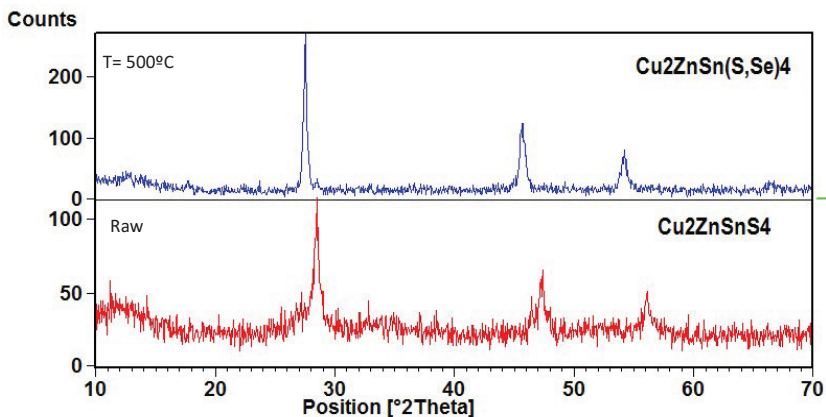


Figure 1. XRD patterns of CZTS (ethyleneglycol), before and after calcination at 500°C.

Figure 2 plots the XRD patterns of CZTS powders obtained with ethylenediamine as solvent (initial and calcined). It can be observed that the initial powder exhibit peaks corresponding to the diffraction lines of the $\text{Cu}_2\text{ZnSnS}_4$. On the other hand, the XRD of the calcined powder shows only the present of $\text{Cu}_2\text{ZnSnSe}_4$ that reveal complete substitution of sulfur by selenium in the final composition. Small amount of impurities Cu_2Se was also detected.

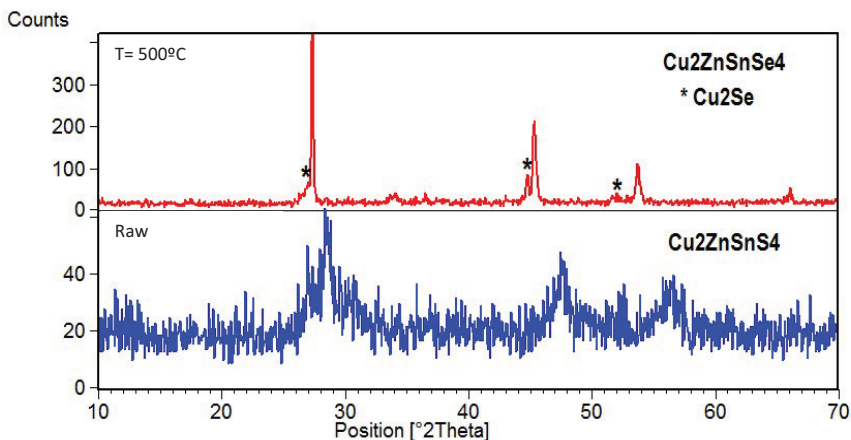


Figure 2. XRD patterns of CZTS (ethylenediamine), before and after calcination at 500°C.

The SEM micrographs (Figure 3 and 4) shows initial CZTS grains with average size of 1 μm , but highly agglomerated. The calcinated sample keeps the same morphology with certain level sintering.

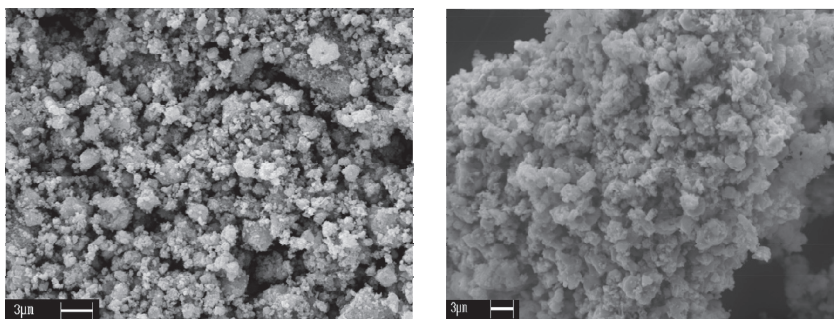


Figure 3. SEM micrographs of CZTS (ethyleneglycol). Image (a) corresponds to the sample before calcinations and (b) after 500°C treatment in a tubular furnace.

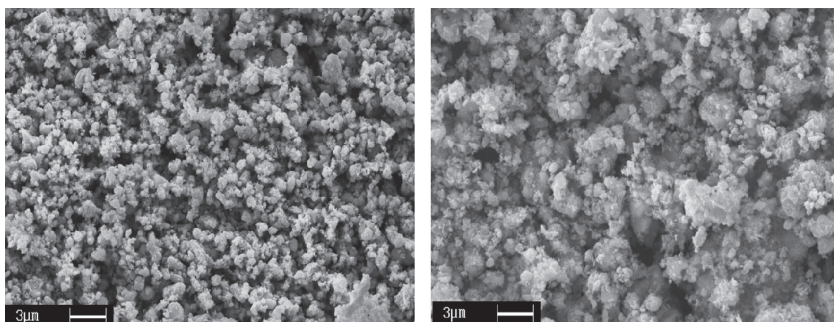


Figure 4. SEM micrographs of CZTS (ethylenediamine). Image (a) corresponds to the sample before calcinations and (b) after 500°C treatment .

The chemical composition of both samples (CZTS with ethyleneglycol and ethylenediamine) have been analyzed by EDX techniques. The results are listed below in Table 1. The analysis of ethyleneglycol's sample displays acceptable homogeneity in both compositions (as-synthesized and calcined), expressed in values corresponding to the theoretical metal cation ratio [10]. However, in the elemental composition of CZTS, prepared by ethylenediamine, it can be observed that both compositions (as-prepared and treated) deviate significantly from the desired stoichiometry.

Table 1. EDX elemental compositional analysis of CZTS powders.

		Atomic %					Atomic ratio	
		S%	Se%	Sn%	Zn%	Cu%	Cu/(Zn+Sn)	Zn/Sn
Ethyleneglycol	Raw	32.90	-	15.33	13.91	37.86	1.29	0.71
	Calcined and Selenized	17.10	24.50	12.76	15.32	30.31	1.07	1.20
Ethylenediamine	Raw	45.88	-	12.23	8.36	33.53	1.61	0.70
	Calcined and Selenized	2.83	43.27	13.58	9.16	31.17	1.30	0.70

CONCLUSIONS

CZTSSe powders with kesterite structure have been prepared by solvothermal synthesis. The influence of different solvents was investigated. The use of ethyleneglycol favors the formation of kesterite solid solution $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ with better homogeneity, due to greater chemical reactivity of the system, while the addition of ethylenediamine demonstrated the formation of $\text{Cu}_2\text{ZnSnSe}_4$ together with certain amount of impurities.

Insignificant microstructural variations have been observed for both samples as analogous morphology displays the use of ethylenglycol and ethylenediamine as solvents.

REFERENCES

- [1] K. Ramasamy, M.A. Malik, P. O'Brien, Chem. Commun., 48 (2012), 5703-5714
- [2] S. Siebentritt, S. Schorr, Prog. Photovolt: Res. Appl., 20 (2012), 512-519
- [3] K. Jamshidi-Ghaleh, M. Karimi, Optics Communications, 281 (2008), 5561-5565.
- [4] S.Thangavel, S. Ganesan, S. Chandramohan, P. Sudhagar, Y. S. Kang, C.-H.Hong, Journal of Alloys and Compounds, 495 (2010) 234-237.
- [5] Q. Guo, H.W. Hillhouse, R. Agrawal, J. Am. Chem. Soc., 131 (2009), 11672-11673.
- [6] Q. Guo, G. Ford, W. Chang, B. Walker, E. Stach, H.W. Hillhouse, R. Agrawal, J. Am. Chem. Soc., 132 (2010), 17384-17386.
- [7] H. Wei, W. Guo, Y. Sun, Z. Yang, Y. Zhang, Materials Letters, 64 (2010), 1424-1426.
- [8] M. Wei, Q. Du, D. Wang, W. Liu, G. Jiang, C. Zhu, Materials Letters, 79 (2012), 177-179.
- [9] T. Rath, W. Haas, A. Pein, R. Saf, E. Maier, B. Kunert, F. Hofer, R. Resel, G. Trimmel, Solar Energy Materials & Solar Cells, 101 (2012), 87-94.
- [10] T. K. Todorov, K. B. Reuter, D. B. Mitzi, Advanced Materials 22 (2010) E156-E159.
- [11] Y. Li Zhou, W. Zhou, Y. Du, M. Li, S. Wu, Materials Letters, 65 (2011), 1535-1537.
- [12] M. Cao, Y. Shen, Journal of Crystal Growth, 318 (2011), 1117-1120.

About the authors:

Diego Fraga Chiva, PhD student, Department of Inorganic and Organic Chemistry, Jaume I University (Castellón, Spain), Phone: +34 964 72 82 34, E-mail: fraga@uji.es.

Rafael Martí Valls, PhD student, Department of Inorganic and Organic Chemistry, Jaume I University (Castellón, Spain), Phone: +34 964 72 82 34

Teodora Stoyanova Luybenova, PhD, Department of Inorganic and Organic Chemistry, Jaume I University (Castellón, Spain), Phone: +34 964 72 82 34

Leonardo Ladeira de Oliveira, PhD, Department of Inorganic and Organic Chemistry, Jaume I University (Castellón, Spain), Phone: +34 964 72 82 34

Aitor Rey, PhD student, Department of Inorganic and Organic Chemistry, Jaume I University (Castellón, Spain), Phone: +34 964 72 82 34

Stephan Kozhukarov, PhD, LAMAR Laboratory, University of Chemical Technology and Metallurgy, Sofia (Bulgaria)

Juan Bautista Carda, PhD, Department of Inorganic and Organic Chemistry, Jaume I University (Castellón, Spain), Phone: +34 964 72 82 47, E-mail: carda@uji.es

The paper is reviewed.