Synthesis of Cu$_2$ZnSnSe$_4$ from nitrate and selenite inks for use as an absorbent layer in the design of solar cells

E A Torres-Barahona$^1$, Y Castellanos-Báez$^1$, J A Gómez-Cuaspud$^1$, E Vera-López$^1$, J B Carda$^2$, and Y Pineda-Triana$^1$

$^1$ Grupo de Integridad y Evaluación de Materiales, Universidad Pedagógica y Tecnológica de Colombia, Tunja, Colombia
$^2$ Departamento de Química Inorgánica y Orgánica, Universitat Jaume I, Castellón de la Plana, España

E-mail: edgar.torres@uptc.edu.co

Abstract. This research was conducted to identify two acceptable precursors and methods of synthesis for the manufacture of photovoltaic cells. The kesterite Cu$_2$ZnSnSe$_4$, a promising material for solar cell applications, was synthesized from metal salts of Cu, Zn, Sn, and Se, by two low-cost routes: the direct dissolution of metal nitrates, and coprecipitation of selenites. In both cases, inks were obtained and deposited as thin-films by the Doctor Blade technique on glass substrates coated with molybdenum. The films were annealed in an oven at 550 °C by 30 minutes. The phases of each thin film were analyzed by X-ray diffraction and Raman scattering. The morphology and the thickness of the layers were observed using a scanning electron microscope. The optical band gap was determined by ultraviolet-visible spectroscopy and the Tauc equation. The results confirmed the main phase of kesterite material, consistent with a tetragonal crystalline system oriented along the plane (1 1 2). These values are consistent with those found by Raman spectroscopy, where the main vibrational mode was identified at 173 cm$^{-1}$ and 196 cm$^{-1}$, characteristic of mode A vibration, and 243 cm$^{-1}$ of mode B vibration; typical of kesterite. Simultaneously, a band gap of 0.89 eV was identified. These results demonstrate the effectiveness of the selenite’s coprecipitation method for synthesis of kesterite, without evidence of secondary phases. This determines the possibility of using this material in solar cell applications.

1. Introduction

Electric power is the most flexible and adequate form of energy for human use. However, it is not a primary form of energy, requiring conversion for its generation. Ideally, this conversion process should be highly efficient, low cost, and friendly to the environment. Better yet, harnessing a renewable energy source. In this sense, one of the most promising sources of renewable energy is solar energy. Much research has been completed into solar energy use in replacing fossil fuels which are associated with problems such as environmental damage and resource limitations. Many researchers have explored alternatives for the development of materials in thin-film solar cell technologies. Colombia, lying near the equator, has strong potential, especially the Atlantico, Orinoquia and Andean regions, for favorable solar irradiation and solar brightness, which exceed the world average [1,2].

Solar energy can occur in different ways. One important method is the direct conversion into electricity by photovoltaic (PV) effect; one of the most promising alternatives. The technological development around the conversion of solar energy into electricity has been taking place with different
approaches. There is also the work with the first-generation photovoltaic solar cells that involve silicon as the semiconductor element and central component of photovoltaic solar panels [3]. Next, there are the thin-film devices with which the economic benefit is essential for the production processes and require less material. Finally, advances in new organic and inorganic absorbent materials, in the cell configuration, and solar concentrators can be cited [4].

To date, the photovoltaic devices of CdTe and Cu(In,Ga)Se$_2$ (CIGS) are two of the most promising absorbent materials to be used as thin film energy absorbers. However, some of its constituent elements, such as Indium and Tellurium, are scarce in the earth's crust, which makes them of limited use and high cost [5]. As an alternative to these materials, the quaternary compound Cu$_2$ZnSnS$_4$ and selenium incorporation as a partial or total substitute for sulfur Cu$_2$ZnSnSe$_4$ (CZTSe) have been investigated. This compound has a crystallographic structure similar to CIGS [6], and its constituent materials are abundant in the earth's crust [7]. Also, it has a bandgap of 1.5 eV and an absorption coefficient of $10^4$ cm$^{-1}$ [8,9], appropriate for a material used as an absorbent in the conversion of solar energy into electricity. The interest in this material is associated with the progress made in the development of high-efficiency solar cells, based on thin films of chalcopyrite semiconductors CIGS. With this compound, the 22.9% efficiency has been reached [10].

As a contribution to technological development in photovoltaic solar energy, inks of CZTSe material were synthesized by two different routes: by dissolution of metal salts and by coprecipitation of selenites, with the purpose of characterizing them and determining their viability in the application of photovoltaic solar cells. It is found that the route followed from selenites presents favorable conditions for the formation of thin films with crystals belonging to the main phase of kesterite, as shown by the results of characterization by X-ray diffraction (XRD), Raman and ultraviolet-visible spectroscopy (UV-Vis).

2. Experimental

The absorbent material type CZTSe has been synthesized to obtain a stoichiometry Cu$_{1.8}$ Zn$_{1.2}$ SnSe$_4$ that provides Cu/(Zn + Sn) = 0.82 and Zn/Sn = 1.2 ratios. It is done taking into account that these proportions, for a copper-poor and zinc-rich stoichiometry have superior photovoltaic properties [11-13]. For this, copper (II) nitrate trihydrate (Cu(NO$_3$)$_2$.3H$_2$O), zinc nitrate hexahydrate (Zn(NO$_3$)$_2$.6H$_2$O), tin (IV) chloride pentahydrate (SnCl$_4$.5H$_2$O), and selenium dioxide (O$_2$Se), all with purity above 99% were used. The synthesis was made by two different routes: by the dissolution of salts in acid medium and by coprecipitation of selenites.

In the first case, the solution was made in 5.0 ml of acid, using magnetic stirring until a homogeneous and transparent ink was obtained, shown in Figure 1. This ink (II) was deposited on a glass/Mo substrate by the Doctor Blade method. Taking into account that a thickness between 1 and 2 is necessary to guarantee a good absorption performance [14], 6, 8, and 10 layers were applied with drying cycles at 100°C for 5 min. It was found that 6 layers are suitable for a thickness of about 2 µm.

![Figure 1. CZTSe ink in acid medium.](image)

The second case was made based on a preliminary reference [12]. In this process, the precursors were dissolved in 150 ml of deionized water, utilizing magnetic stirring until a homogeneous solution was
obtained. Later, ammonia was added until a pH = 6, maintaining the agitation. With the pH reached, coprecipitated selenites were collected, then washed three times with deionized water and one with ethanol to remove impurities. Then they were dried at 60 °C for one hour. The precipitated selenites can be seen in Figure 2.

From selenites, a second ink (I2) was prepared with a weight ratio of 65% ethanol, 20% selenites and 15% diethanolamine (DEA), the latter as a dispersing agent. This ink was homogenized by ultrasound. In this case, two layers applied on glass/Mo substrates by Doctor Blade method, drying each at 400°C for 1 minute, were enough to reach an average thickness of 2.35 µm. The samples thus obtained were subjected to a process of thermal treatment under a nitrogen atmosphere in which 99% elemental selenium was evaporated. The samples were annealed at 550 °C for 30 min., in a system designed for this process; time and temperature were defined according to references that indicate that the process at this temperature and time favor the formation and growth of the grain in the synthesized material [15]. Figure 3 shows the thin film layers deposited.

3. Results and discussion
The morphology of the samples was taken by scanning electron microscopy (SEM), in a Carl Zeiss equipment EVO – MA10. Figure 4 shows representative surface and cross-section SEM images of I1 thin-film. A superficial heterogeneous compound with secondary phases was noted; the cross-section shows a compact mass with good contact with the substrate. By EDX attached to SEM, the elemental composition ratios Cu/(Zn + Sn) = 0.7 and Zn/Sn = 0.85 were obtained, and they are far from starting relationships. Secondary phases, mainly of SnSe, were identified.
Figure 5 shows the surface and cross-section SEM images of I2 thin-film. The surface image shows larger, densely packed grains. The cross-section shows a good interface between the CZTSe and Mo layer. The elemental composition ratios Cu/(Zn + Sn) = 0.84 and Zn/Sn = 1.08 are similar to original relationships.

![Figure 5. Thin-film from ink I2, (a) surface morphology, (b) cross section.](image)

The average thickness of the thin film for the case of I1 was 2.48 µm and 2.15 µm for I2, these values were higher than programmed.

In order to determine the crystallinity of the thin-films, a PANalytical X'pert PRO-MPD device, equipped with an Ultra-fast X'Celerator detector in Bragg-Brentano arrangement, using the CuKα radiation (λ = 1.54186 Å) between 10 and 80° with steps of 0.02° was used. Figure 6 shows the diffraction spectra of the selenized samples I1 and I2.

![Figure 6. XRD spectra of thin films of I1 and I2.](image)

The results show a crystalline structure typical of CZTSe phase. The strongest signal, located at 27.2° (2θ), has been assigned to the plane (1 1 2) of the CZTSe phase ([JCPDS 052 – 0868]), as well as the planes (1 0 1), (2 0 4), (3 1 2), (3 1 6), (4 0 0), and (0 0 8), present in all the characterized samples. These results coincide with the results published by other authors who use different methods [16-18]. The molybdenum signal corresponds to the value of 47.2° and 69.4°, the last one not perceptible in Figure 6. The slight variations in the elemental composition between the CZTSe precursor and the films obtained from the two methods can be attributed to the fact that the I1 ink forms secondary phases of SnSe ([JCPDS 052 – 0868]), which corroborates the SEM observations.

As a complement to the observations by XRD, Raman spectroscopy was used to establish the existence of secondary phases. Figure 7 shows the Raman spectra of the same samples. This analysis was done with the use of a Raman spectrometer, XDR Smart Raman, equipped with a diode laser of
785 nm. For the thin film I1, the Raman spectra shows the existence of the desired material structure, with signals at 172 and 194 cm\(^{-1}\), which is consistent with the previous XRD spectrum. The shift presented from 197 to 194 cm\(^{-1}\) of the principal peak, was related to the atomic order of the crystalline structure [19]. A 236 cm\(^{-1}\) signal attributable to SnSe can also be seen, similar to that observed by SEM and other early reports [20]. In the spectrum for the I2 Thin-film, the signals observed at 173, 196, and 243 cm\(^{-1}\) were attributed to the compound CZTSe without other secondary phases [21]. A peak of lower intensity is observed at 291 cm\(^{-1}\), which has been attributed to mode E of MoSe\(_2\) [22].

The optical absorptions of the CZTSe after annealing samples were measured using UV-Vis spectroscopy, using a HACH DR6000 UV – VIS system. The band gap energies can be estimated by the related curve of \((\alpha \cdot h \cdot v)^2\) versus photon energy [23]. From the extrapolated linear portion, it is shown that the band gap of these CZTSe films are 1.6 eV for thin-films with I1, and the results are shown in Figure 8, the Figure 9 shows for films I2 a band gap of 0.89 eV.

These values identify that a bandgap for ink I2 is within acceptable range for a semiconductor material to be used as an absorbent material in photovoltaic devices. These conclusions are verified by earlier research [24,25].

4. Conclusions

In this work, absorbent layers of CZTSe were synthesized by two methods: by direct dissolution of the precursors, and by coprecipitation of selenites. After the annealing, via X-ray diffraction and Raman spectroscopy, it was identified that the absorber layer by direct dissolution of the precursors contains secondary phases in a higher proportion than that developed from selenites. Alternately, that obtained from selenites was constituted by large grains and of homogeneous aspect, although it also contains secondary phases of MoSe\(_2\), which is recommended to be eliminated from a chemical process (etching). The bandgap measurements also show a better result for selenites with a value of 0.89 eV compared to 1.66 eV for the other sample. It can be inferred that the delegated films belong to the CZTSe structure and can be obtained by these methods. However, the use of the selenite method is of greater purity and apt to be applied to the development of photovoltaic cells.

References

[1] Checa F, et al. 2015 Potencial natural para el desarrollo fotovoltaico en Colombia (Colombia: Universidad Cesmag) p 52
[2] Instituto de Hidrología, Meteorología y Estudios Ambientales / Unidad de Planeación Minero Energética (IDEAM/UPME) 2015 Atlas de radiación solar (Colombia: Instituto de Hidrología, Meteorología y Estudios Ambientales)
[3] Hoffmann W 2017 Photovoltaics for sustainable electricity and buildings ed A Sayigh (Brighton: Springer) p 78
[4] Luque A, and Hegedus S 2011 Handbook of photovoltaic science and engineering (Chichester: J Wiley & Sons Ltd) p 402
[5] Jiang M, and Yan X 2013 Solar cells: Research and application perspectives ed A Morales-Acevedo (Croatia: InTechOpen) p 107
[6] Goodman C 1958 The prediction of semiconducting properties in inorganic compounds Journal of Physics and Chemistry of Solids 6 305
[7] Wadia C, et al. 2009 Materials availability expands the opportunity for large-scale photovoltaics deployment Environmental Science & Technology 43 2072
[8] Prashant R, et al. 2018 Advanced ceramic and metallic coating and thin film materials for energy and environmental applications ed J Zhang, Y Gil Jung (USA: Springer) p 121
[9] Orletskii I, et al. 2016 Optical properties and mechanisms of current flow in Cu2ZnSnS4 films prepared by spray pyrolysis Physics of the Solid State 58 1058
[10] Martin A, et al. 2019 Solar cell efficiency tables (Version 53) Prog Photovolt: Res Appl 27 3
[11] Zhang Y, et al. 2016 Afacile non-vacuum-based Cu2ZnSnSe4 superstrate solar cell with 2.44% device efficiency Physica Status Solidi A 213 1324
[12] Calvet I, et al. 2015 Development of photovoltaic ceramic tile based on CZTSSe absorber Mater. Lett. 161 636
[13] Fella C, et al. 2012 Cu2ZnSnSe4 absorbers processed from solution deposited metal salt precursors under different selenization conditions Physica Status Solidi 209 1043
[14] Heriche H, et al. 2015 Thickness optimization of various layers of CZTS solar cell J. New Technol. Mater. 4 27
[15] Tanaka T, et al. 2006 Fabrication of Cu 2 ZnSnS 4 thin films by co-evaporation Physica Status Solidi C 3 844
[16] He J, et al. 2018 Compositional dependence of photovoltaic properties of Cu2ZnSnSe4 thin film solar cell: Experiment and simulation Sol Energy 159 572
[17] Kim S, et al. 2018 Characterization of CBO and defect states of CZTSe solar cells prepared by using two-step process Curr. Appl. Phys. 18 191
[18] Wang W, et al. 2016 Preparation of high efficiency Cu2ZnSn(S,Se)4 solar cells from novel non-toxic hybrid ink J. Power Sources 335 84
[19] Liu S, et al. 2013 Preparation of Cu2ZnSnSe4 absorber layer by nonvacuum method Jpn. J. Appl. Phys. 52 1
[20] Dimitrievska M, et al. 2015 Influence of compositionally induced defects on the vibrational properties of device-grade Cu2ZnSnSe4 absorbers for kesterite based solar cells Appl. Phys. Lett. 106 073903
[21] Guc M, et al. 2013 Polarized Raman scattering analysis of Cu2ZnSnSe4 and Cu2ZnGeSe4 single crystals J. Appl. Phys. 114 193514
[22] Tomndorf P, et al. 2013 Photoluminescence emission and Raman response of monolayer MoS2, MoSe2, and WSe2 Optics Express 21 4909
[23] Khadka D, et al. 2015 A Nonvacuum Approach for fabrication of Cu2ZnSnSe4(In2S3) thin film solar cell and optoelectronic characterization J. Phys. Chem. 119 12226
[24] Ferhati H, and Djeffal F 2018 Graded band-gap engineering for increased efficiency in CZTS solar cells Opt. Mater. 76 393
[25] Ahn S et al 2010 Determination of band gap energy (Eg) of Cu2ZnSnSe4 thin films: On the discrepancies of reported band gap value Appl. Phys. Lett. 97 1