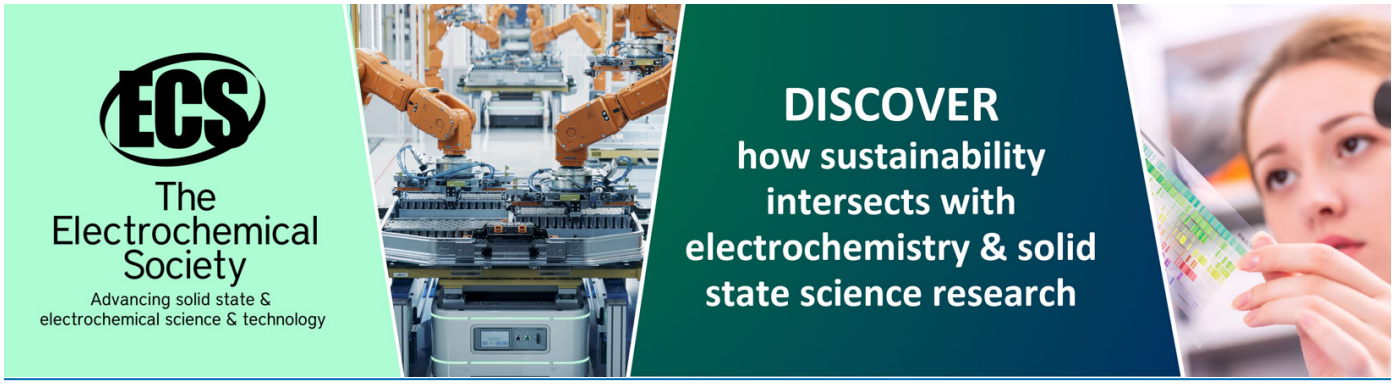
Hydrothermal synthesis and characterization of the semiconductor material Cu_2ZnTiS_4



Hydrothermal synthesis and characterization of the semiconductor material Cu_2ZnTiS_4

H G Pérez Bustos[1], M Patarroyo-Mesa[1], J A Gómez-Cuaspud[1], Y Pineda-Triana[1] and E Vera-López[1]
[1] Universidad Pedagógica y Tecnológica de Colombia, Tunja, Colombia

E-mail: hellem.perez@uptc.edu.co

Abstract. This paper describes the results of the synthesis and characterization of a quaternary semiconductor based on Cu_2ZnTiS_4 (abbreviated CZTiS), using a hydrothermal technique. The results confirm that time (24, 48 and 72 hours) and temperature (250, 275, and 300°C) factors, used in synthesis process, regulate different levels of electrical conductivity in these materials. The results of ultraviolet spectroscopy (UV) analysis, confirm the production of semiconductor solids with Band-gap values around 1.4eV, being coherent with a strong absorption in the ultraviolet region. The X-Ray Diffraction analysis (XRD), confirm that there is an opposite and proportional relationship between the crystal sizes, the reaction times and the synthesis temperature. In all cases, the particle sizes were 50-100nm. The results derived from Scanning Electron Microscopy (SEM), confirm the obtaining of homogenous materials with optimal morphological properties in accordance with synthesis method. Similarly, the composition values derived from the Energy-Dispersion X-ray Spectroscopy analysis (EDS), shown that obtained compositions are in agree with expected values. Finally, the results of electric characterization, confirm that used synthesis parameters show a strong dependence on the conductive behaviour of solids being the most relevant result the shown by the solid obtained at 300°C and 72 hours of reaction in accordance with preliminary works.

1. Introduction

The world's largest source of energy throughout history has been through the exploitation of fossil resources (oil and coal), which have allowed high levels of energy production with respect to the amount of matter used and the amount of energy obtained [1]. However, despite their good efficiency in responding to global energy needs, this type of energy generates two main problems: one, non-renewable energy and two, generate toxic greenhouse gases to the detriment of the quality of life of many people and the environment in general. At present, the percentage of fossil resources available for its exploitation is exhausted, which means that in a few decades it will not be possible to respond to the global energy demand through this type of resources, in addition to the restrictions that present the problem environmental. It is for this reason that the search for new sources of clean and self-sustaining energy generation is especially important, especially those related to the use and use of solar energy. In this context, the use and use of solar energy through the use of solar panels, which basically use the photoelectric effect as a mechanism of electrical generation through materials of a semiconductor nature, have shown an important evolutionary process since its inception as panels of Silicon to alternative materials of low cost and toxicity, among which are the Kesterite type based on quaternary systems type Cu_2ZnSnS_4 (Abbreviated CZTS), which have allowed good conversion levels and a notable reduction in production costs. Although these materials have achieved good results,

efficiency processes remain low compared to traditional silicon materials, which is why the possibility of incorporating new elements into the basic structure such as titanium, that allow to reduce the values of band-gap, maintaining the efficiency of the system. One of these materials is called CZTiS (Cu_2ZnTiS_4) which consists of a semiconductor material in which the traditional tin has been replaced by titanium in the same stoichiometric proportions. This type of material, therefore, became a very promising material for the development of new photovoltaic devices, because it reduces the band gap values of the traditional CZTS up to 5% around 1.5eV. Based on the above, the present work proposes the synthesis and characterization of this type of material (CZTiS), by a route of hydrothermal synthesis that allows obtaining better experimental conditions for the obtaining of a pure phase, that will be reflected in the improvement in Conductivity and reaction conditions, taking into account the variables time and temperature [7-9].

2. Experimental

For the synthesis of the photovoltaic material of Cu_2ZnTiS_4 through a hydrothermal route, was started from the corresponding precursors of the material in stoichiometric quantities in the form of Copper nitrate ($Cu(NO_3)_2$), Zinc acetate ($Zn(CH_3COO)_2$), Titanium butoxide ($C_{16}H_{36}O_4Ti$), Thiourea (CH_4N_2S), all from Sigma-Aldrich commercial house. The precursors were metered stoichiometrically in aqueous medium to obtain 1.0g of material. The mixture of the components was made in a Teflon vessel and taken to a steel autoclave, where the temperature conditions were adjusted in each case (24, 48 y 72 hours). The systems were maintained under specific reaction conditions, simultaneously varying both time and temperature of synthesis, obtaining a total of nine samples as indicated in Table 1. After the synthesis process, each solid was repeatedly washed with absolute ethanol to remove possible impurities generated in the synthesis process. At the end, the solids were dried in an oven at 110°C for 2 hours.

Table 1. Parameters established for the synthesis of photovoltaic materials type CZTiS.

Material	Reaction temperature (°C)	Time of synthesis (h)
CZTiS	250	24
CZTiS	250	24
CZTiS	250	24
CZTiS	275	48
CZTiS	275	48
CZTiS	275	48
CZTiS	300	72
CZTiS	300	72
CZTiS	300	72

In order to analyse the morphological, structural and electrical properties of the materials obtained, different characterization techniques were used, such as visible ultraviolet spectroscopy (UV-VIS) were used in a scanning range of 190-1000nm in a spectrophotometer UV-VIS Mapada Instruments 8000 PC. Structural analyses were made by X-Ray Diffraction (XRD), in an equipment PANALytical X´pert PRO MPD, using radiation Cu Kα (λ=1.54186Å) between 20 and 90° 2θ with steps of 0.02°. The diffraction patterns were analysed using X'Pert software High Score. Analyses of infrared spectroscopy were made in a Perkin-Elmer FTIR equipment between 4700 and 500cm^{-1}. Scanning Electron Microscopy analysis (SEM) were developed in an JEOL 2100 equipment endowed with a LaB_6 thermionic barrel, an acceleration voltage of 200kV and a CCD camera that allows to obtain images of high resolution. X-ray Photoelectron Spectroscopy (XPS) analysis, were performed on a surface characterization platform XPS/ISS/UPS-

ACenteno SPECS. The platform provided with an energy analyser PHOIBOS 150 2D-DLD and a lightning source X Al Kα monochrome (FOCUS 500) was operated at 200W. The passing energy of the hemispherical analyser was set at 100 eV for the general and 60eV spectra for high resolution spectra. The surface load compensation was controlled with a flood pistol (dispositive FG 15/40-PS FG500) operated at 58μA and 1.5eV. The spectra were analysed with the program CasaXPS (Casa Software Ltd) using the CasaSSI GL 15 library for values R.S.F. a Shyrley baseline was used for this purpose. (BE) was corrected using the C*1s* at 284eV. Finally, the electrical analyses were developed in a potentiostat-galvanostat AUTOLAB between 1 and 10Mhz using Tablets of 10mm and 1mm of thickness obtained at 5.0Mpa of pressure. The data were adjusted and corrected by a reference cell to avoid noise in the acquisition of the data.

3. Results and discussion

The formation of Cu_2ZnTiS_4 materials can be described under the hydrothermal reaction conditions by the following half-reactions describing the three-step process identified in equations (1), (2) and (3).

$$2\,Cu_{(l)} + \frac{1}{2}\,S_{2(s)} \rightarrow Cu_2S_{(s)} \quad (1)$$

$$Cu_2S_{(s)} + TiS_{2(s)} \rightarrow Cu_2TiS_{3(s)} \quad (2)$$

$$Cu_2TiS_{3(s)} + ZnS_{(s)} \rightarrow Cu_2ZnTiS_{4(s)} \quad (3)$$

After the synthesis process under controlled temperature and time conditions, the obtained materials were repeatedly washed with absolute ethanol and dried in an oven at 110°C for 2 hours before the physicochemical characterization processes were performed.

The results of the UV-VIS spectrophotometry analysis on the different samples suspended in ethylene glycol between 190-1000 allowed determining the corresponding inflection points for each system to determine the band gap values using equation 4. In all cases the value Average was 1.40eV in agreement with the obtaining of semiconductor materials. In spite of this, it is clear that there is a proportionality relationship between the synthesis temperature and the band gap value, with the highest values being for the solid of the highest reaction temperature [11].

$$E = \frac{h\,c}{\lambda} \quad (4)$$

These results are in agreement with those obtained by T. E. Manjulavalli, *et. al*. [2], who has reported prohibited band gap for these same systems between 1.37 and 1.6eV, with efficiency values of around 0.16%. The results of infrared spectroscopy in all the samples allowed to identify that the materials show absence of organic phases related to free and derived sulphur species that could affect the performance of the systems. Signals identified around 800-1000cm^{-1}, Correspond to typical signals associated with the characteristic M-S and M-O vibrations present by the potential formation of Cu and Zn metal sulphides [3].

The X-ray results of the samples synthesized and shown in Figure 1, make it possible to determine that by varying the reaction conditions, more defined signals are generated for the highest reaction time and temperature (300°C-72h), this being due to the remarkable improvement the crystallinity of the samples. The detailed analyses using the X'Pert® High Score program and the comparison with the ICDD database, allowed to establish that the materials present a crystalline system *I-42m* (1 2 1) with cell parameters *a*=0.5427, *b*=0.5427, *c*=1.0848nm with preferential crystalline orientation along the plane (1 1 2) in all the Cases as shown in Figure 2. Additionally, the presence of secondary

phases such as ZnS, Cu_2S and Cu_2TiS_3, which decrease the percentage of synthesis efficiency of $Cu_2ZnTiS_4$and are made more noticeable at low temperatures and reaction times, is identified.

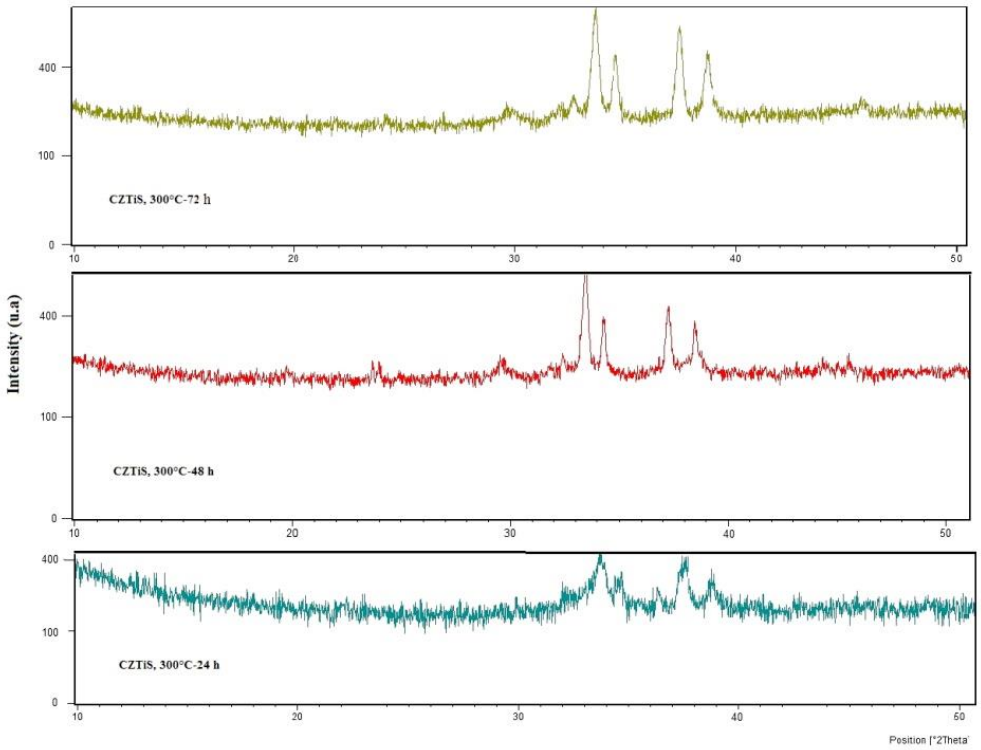


Figure 1. X-ray diffraction pattern for CZTiS systems under different reaction times and the maximum temperature studied-300°C.

The results of the analysis by scanning electron microscopy (SEM) allowed us to validate the identified morphological results and the surface characteristics of the synthesized materials as can be seen in the images of Figure 2. The results shown for the most representative materials of each series determine that the proposed synthesis method provides a series of surface features of interest with a heterogeneous grain distribution. According to the work of *Wang et. al.,* [3] the morphology of the materials is improved with increases in the temperatures of synthesis, since the formation of amorphous agglomerates is dramatically reduced reason why the obtained results correspond with the expected results. [4]

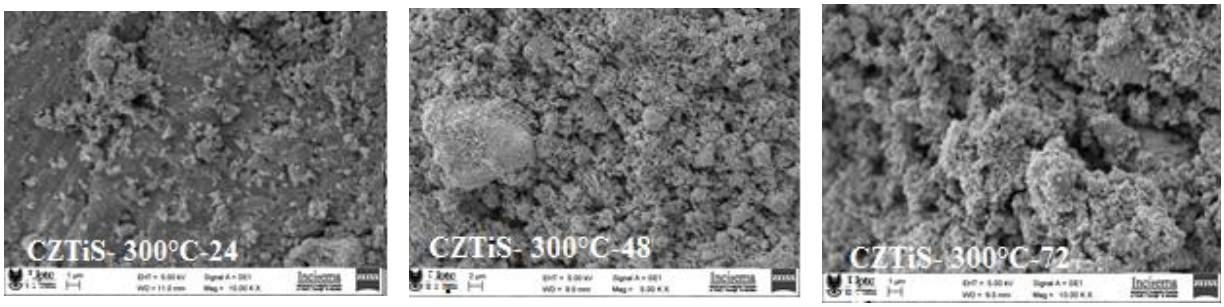


Figure 2. Scanning electron micrographs for CZTiS materials obtained at 300°C under different reaction time conditions.

The results show that the different characteristic elements of the material (Cu, Zn, Ti, S) exhibit signals. The results of XPS results on CZTiS type materials with reaction conditions of 300°C and 72 hours of reaction Characteristics, which allow analysing the oxidation states in which the constituent elements are found as indicated in Figure 3. The copper signals, confirm a state of oxidation Cu^{2+}, while those of zinc are attributed to the presence of Zn^{2+}, with a characteristic bonding energy at 1046 and 1023eV. For its part, titanium shows a typical bonding signal at 459 and 468eV related to the presence of an oxidation state 4^{+}, while in the case of sulphur the presence of two signals at 163 and 168 eV determining their presence in form of metal sulphide with a defined oxidation state and in the form of S^{2-}, which allows to validate the preliminary characterization results and to confirm the presence of the crystalline structure sought. In the case of sulphur results, it should be noted that secondary phases such as sulphides (mainly zinc or copper) may be present, which explain the slight modifications in bond energy compared to preliminary works [5,6,10].

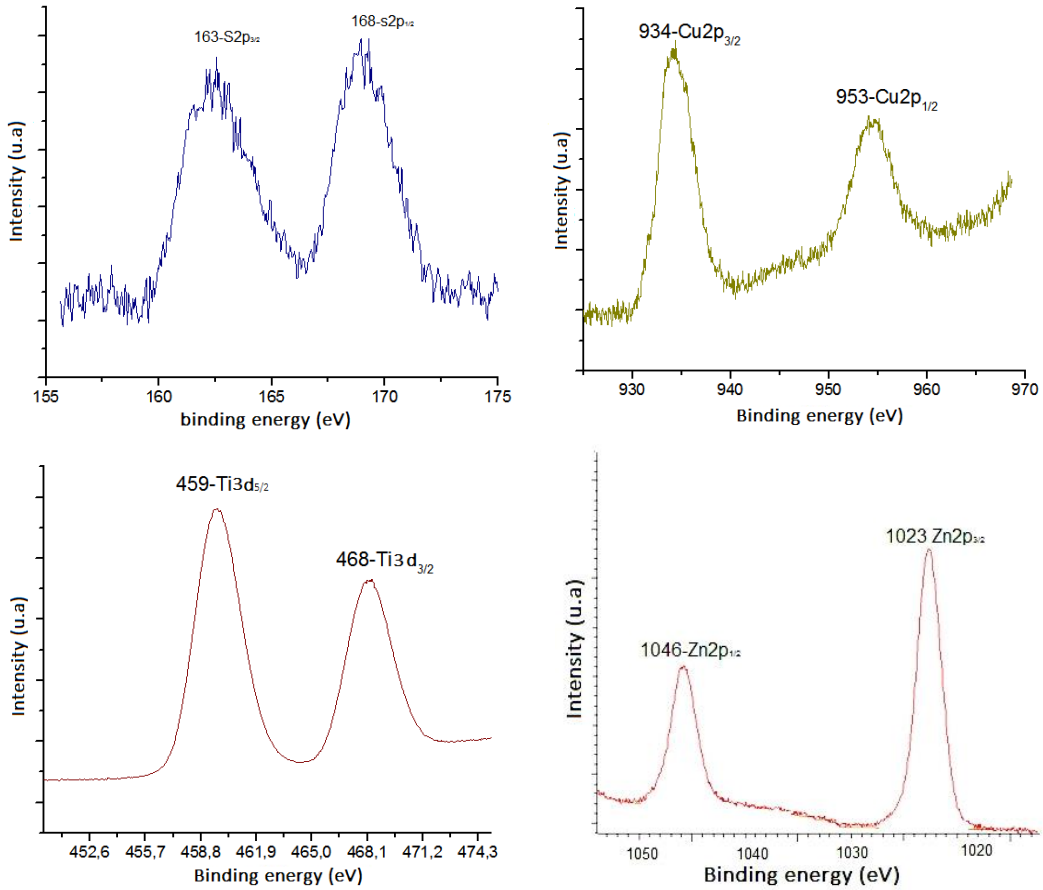


Figure 3. XPS spectra for the material synthesized under the highest reaction conditions.

Finally, the electrical characterization by solid state impedance spectroscopy allowed the determination of a semiconductor behaviour along the series of materials obtained at a higher temperature, which allowed the determination of values of conductivity of 1.29×10^{-3}, 7.98×10^{-3} and $4.46 \times 10^{-4} S \cdot cm^{-1}$ for the samples obtained at 24, 48 and 72 hours respectively. The results were validated by mathematical refinement processes and correspond to the expected conductive behaviour in this type of solids, in agreement with the work developed by L. Wang *et. al*. [5], according to which the temperature is the most critical factor and not the reaction time the most Influences the conductivity values [12].

4. Conclusions

The synthesis methodology used in the production of CZTiS photovoltaic materials was successful in that it allowed obtaining materials with relevant properties in terms of composition, structure and electrical performance, being the results of the samples obtained at higher times and temperatures of Synthesis (300°C 72 hours). The results of infrared and ultraviolet spectroscopy confirmed the achievement of semiconductor materials with a band gap around 1.5eV for potential applications with little evidence on the presence of sulphates in the materials obtained. The structural results evaluated by X-ray diffraction confirm the presence of a crystalline phase consistent with the CZTiS material with evidence of secondary phases associated with sulphides, which can be corrected by the development of subsequent thermal stages in agreement with preliminary works. Finally, the results of X-ray Photoelectron Spectroscopy (XPS) and electric characterization allow us to infer that the semiconductor response of materials, especially those obtained under the most extreme reaction conditions, is based on the expected chemical composition for these solids. Although the analyses show that the best composition results are obtained using the highest temperature and the highest reaction time due to the consolidation of a better kesterite type phase, it is clear that all can be improved to the extent that Subsequent heat treatment processes are implemented that reduce the presence of the secondary crystalline phases for their potential use as a photoabsorbent layer in photovoltaic devices.

References

[1] N. Asim, K. Sopian, S. Ahmadi, Kasra Saeedfar, M. A. Alghoul, Omidreza Saadatian, Saleem H. Zaidi 2012 *Renewable and Sustainable Energy Reviews* **16(8)** 5834–5847
[2] A. Kannan, T. Manjulavalli and J. Chandrasekaran 2016 *Procedia Engineering* **141** 15– 22
[3] J. Wang, P Zhang, X Songa, L Gao 2015 *RSC Adv.* **5** 1220-1226
[4] W. Huang, C. Tseng, S. Chang Solvothermal 2012 *Langmuir* **288** 496–501
[5] S. M. Camara, L.Wang and X. Zhang 2013 *Nanotechnology* **24** 495401
[6] J. M. Skelton, A. J. Jackson, M. Dimitrievska, S.K. Wallace, and A. Walsh 2015 *APL Materials* **3(4)** 041102
[7] D. Pardo and L. Bailón 2006 *Fundamentos de Electrónica Digital* (España: Universidad de Salamanca)
[8] Todorov 2008 *Preparación y estudio de películas delgadas con aplicaciones fotovoltáicas* (España: Universitat JAUME I) pp 20-29
[9] H. Dana, C. Hurlbut and C. Klein 2006 *Manual of Mineralogy* (New York: John Wiley & Sons, Inc) pp 73-87
[10] S. Chen, X. Gong, A.Walsh 2009 *Applied Physics Letters* **94** 041903
[11] R. Marti Valls, E. Barrachina, D. Fraga, I. Calvet, T. Stoyanova and J. Bautista 2015 Práctica de laboratorio *Síntesis y depósito de capas fotoabsorbentes tipo CIGS para dispositivos fotovoltáicos* (España: Universitat Jaume I) pp 37-40
[12] J. Balenzategui Manzanares 2008 Módulo: Gestión Eficiente de la Energía. *Fundamentos de la conversión fotovoltáica: la célula solar* (España: Escuela de Organización Industrial) pp7-11