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Evaluation of semiconductor materials by hydrothermal synthesis

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Abstract. The present work describes the obtaining of semiconductor materials with kesterite structure by a hydrothermal methodology. The obtained kesterite has a structural modification of the conventional $\text{Cu}_2\text{ZnSnS}_4$ structure with the insertion of titanium instead of tin, in order to obtain $\text{Cu}_2\text{ZnTiS}_4$. The precursors of this material, metallic salts of copper, zinc acetate, titanium butoxide and thiourea were added in a hermetic steel reactor, controlling time (24 hours, 48 hours and 72 hours) and temperature ($200^\circ\text{C} - 300^\circ\text{C}$). To evaluate the synthesis, the materials obtained were analysed by different characterization techniques (X-ray diffraction, scanning electron microscopy, solid state impedance). The results show that material with the conditions of synthesis 48 hours and 300°C , exhibit the best textural and electrical results in terms of economy process. The X-ray diffraction analysis shows secondary phases, which can possibly be eliminated with a thermal treatment, since most of the secondary phases (such ZnS and Cu_2S) can be eliminated by combustion in an inert atmosphere. The results showed that the increase in the temperature of synthesis decreases the formation of amorphous agglomerates, improving the morphology of the material. The characterization of the materials showed that the $\text{Cu}_2\text{ZnSnS}_4$ phase is possible to obtain by hydrothermal synthesis.

1. Introduction

With the current energy demand, is necessary the development of efficient and renewable energy systems, in order to mitigate the negative human impact on the environment. Renewable energies are defined as those that are produced from and inexhaustible on a human scale. They are renewed continuously, unlike fossil fuels, of which there are certain quantities or finite reserves, exhaustible in a more or less determined term. Taking advantage of natural resources is the best alternative in the search for substitutes for non-renewable energies, one of the best sources for this purpose is sunlight, so designing materials that allow the conversion of solar energy to electricity is extremely important in the way to optimize devices such as solar cells [1]. The development and implementation of solar energy has generated the need to increase the efficiency of photovoltaic technology which we have access at present, although it is true that most of these systems are based on the use of monocrystalline and polycrystalline silicon cells, currently this film solar cells have attracted great interest due to their high efficiency of energy conversion as they can be deposited on a wide variety of substrates. Materials with a kesterite structure [2] such as $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) and $\text{Cu}_2\text{ZnTiS}_4$ (CZTiS) have recently been studied as an effective absorbent of solar sun at low cost, showing optimal results regarding the band gap and absorption coefficient [12].



In Colombia, the country's energy requirements for 2018 were 69.121 G Wh and the power generation was 68.943 GWh [11]. The problems of supply and reliability in energy terms face difficulties in the country's interconnection network, so alternatives are needed to meet the country's energy requirements. Of the renewable energies, solar energy is the one with the highest growth rate, close to 46%, so this is one of the most recommended to meet the electricity demand in Colombia [11].

In the development of technologies and the research, academic and research growth of the country, the study of renewable energies contributes to the strengthening of these. This research work contributes to the development of these studies, providing information on the results in the study of absorbent materials that allow the conversion of solar energy to electricity, contributing to the engineering of these energy sources. Therefore, the aim of current work is evaluating a hydrothermal synthesis method to obtain materials with $\text{Cu}_2\text{ZnTiS}_4$ structure, which has application as an absorbent material in solar energy devices. This methodology permits to obtain absorbent materials of low cost and high efficiency, using non-toxic and abundant precursors. The synthesis method is evaluated through different physicochemical, morphological and electrical techniques to corroborate the effectiveness in proposed synthesis route.

2. Methodology

The synthesis was developed in a steel stainless autoclave, where the precursors were added in a teflon vessel as shown in Figure 1. The precursors were copper nitrate ($\text{Cu}(\text{NO}_3)_2$), zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$), titanium butoxide ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$) and thiourea ($\text{CH}_4\text{N}_2\text{S}$), all from Sigma-Aldrich, using distilled water as solvent, to solubilize and allow the reaction between precursors and adjusted to obtain 1.0 g of CZTiS at the end of reaction process.



Figure 1. Used reactor in the obtention of $\text{Cu}_2\text{ZnTiS}_4$ powders.

The stoichiometry of the $\text{Cu}_2\text{ZnTiS}_4$ material is not subject to change, so the conditions that are modified in each synthesis are the time and temperature as shown in Table 1. The temperatures were evaluated between 200 °C and 300 °C, with intervals of 25 °C, being 200 °C the temperature with superior results.

Table 1 shows the reaction conditions of three materials: Material 1 (M1), Material 2 (M2), Material 3 (M3), of which results are presented.

Table 1. Synthesis conditions for obtention of $\text{Cu}_2\text{ZnTiS}_4$.

Material	Temperature (°C)	Time (h)
Material 1 (M1)	300	24
Material 2 (M2)	300	48
Material 3 (M3)	300	72

The obtained materials at the end of hydrothermal process were washed with absolute ethanol and dried at 110 °C in a convection oven. In order to consolidate a pure phase of material and eliminate the

secondary phases, a thermal treatment is carried out at 550 °C under nitrogen atmosphere (50 mL min^{-1}), in order to achieve a reducing atmosphere, because the presence of oxygen facilitates the formation of TiO_2 avoiding the formation of secondary phases in final material.

After synthesis process, the evaluation of the materials was carried out. The structural analyzes were carried out by X-ray diffraction (XRD), in a PANALytical X'pert PRO MPD equipment, using the $\text{CuK}\alpha$ ($\lambda = 1.54186 \text{ \AA}$) radiation, between $20^\circ 2\theta$ and $90^\circ 2\theta$ with steps of 0.02° . The scanning electron microscopy analysis (SEM) were developed in an JEOL 2100 microscope, equipped with a LaB_6 thermionic gun and an acceleration voltage of 200 kV to promote the obtention of high-resolution images. The electrical analyzes were developed in an AUTOLAB potentiostat-galvanostat equipment between 1.0 Mhz and 10.0 Mhz, using tablets of 10 mm diameter and 1 mm thickness, obtained at 5.0 Mpa of pressure. The data were adjusted and corrected by a reference cell to avoid noise in the acquisition of the data.

3. Results and analysis

The X-ray results allows the identification of the phases present in CZTiS material, which allows to evaluate the effectiveness in proposed methodology. The presence of secondary is mainly associated with sulfides or oxides of copper and zinc [4]. The Figure 2 shows the diffractograms for the three materials studied in this paper.

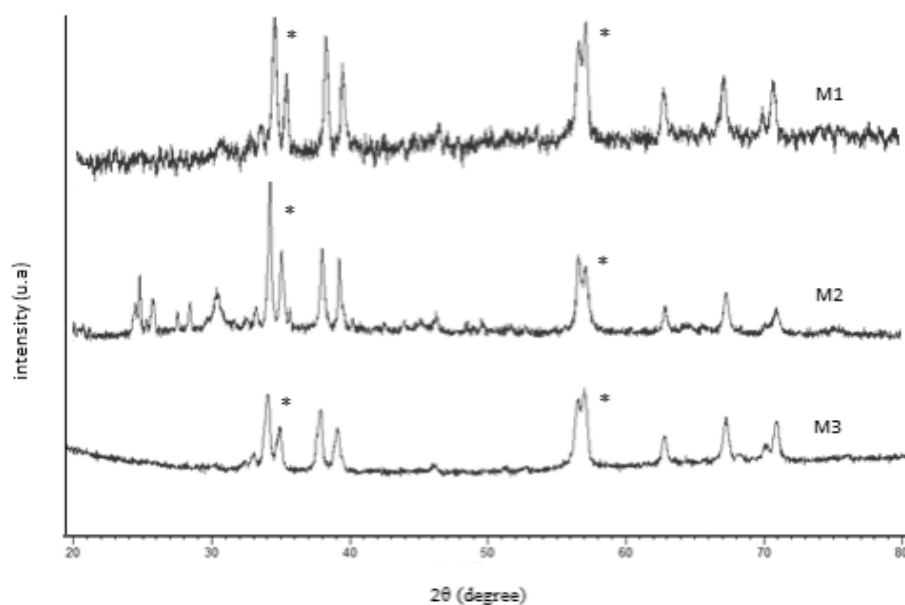


Figure 2. X-ray diffraction pattern for M1, M2 and M3 materials with $\text{Cu}_2\text{ZnTiS}_4$ structure.

The detailed analyzes using the X'Pert® High Score software and the comparison with the ICDD database, allowed to establish that solids exhibit a crystalline system I-42m (1 2 1) with cell parameters $a = 0.5427$, $b = 0.5427$, $c = 1.0848 \text{ nm}$ with preferential crystalline orientation along (1 1 2) facet in all cases [5]. In the spectrum are clear characteristic signals related with the kesterite structure (*), which are observed between 30 and $40^\circ 2\theta$, showing a shift of the conventional kesterite. Previous results are produced by the introduction of titanium in the structure [6] and the main signals are observed with a light shift in position suggesting the presence of secondary phases such as metal sulphurs (Cu_2S and Cu_2TiS_3). It is possible to analyze by X-ray diffraction that diffraction pattern intensity increases as function of time synthesis, improving the purity of obtained compounds too.

The SEM images for $\text{Cu}_2\text{ZnTiS}_4$ materials at 300°C at different synthesis times show a distribution of agglomerated particles of small crystals, where sub-micrometric particles prevail. The formed

agglomerates can be distributed evenly through the proposed heat treatment. The Figure 3 corresponds to the SEM analyzes for M3 material, which showed the best morphological results, respect to expected results [7]. The increases in the synthesis temperature, allow the obtention of optimal morphological results [8]. The micrograph reported in Figure 3 was performed with a magnification of 2 micrometers.

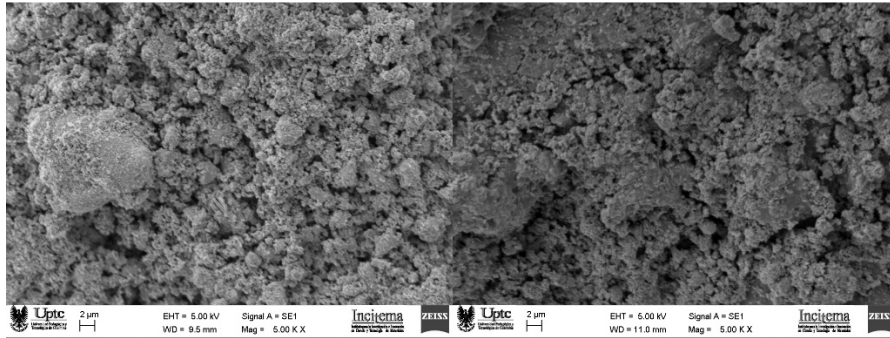


Figure 3. SEM images for $\text{Cu}_2\text{ZnTiS}_4$ materials at different magnifications.

The impedance results, represented in the Nyquist diagram of Figure 4, show favorable results in terms of semiconductor behavior, these values were calculated using the inverse of the maximum values of the impedance modules.

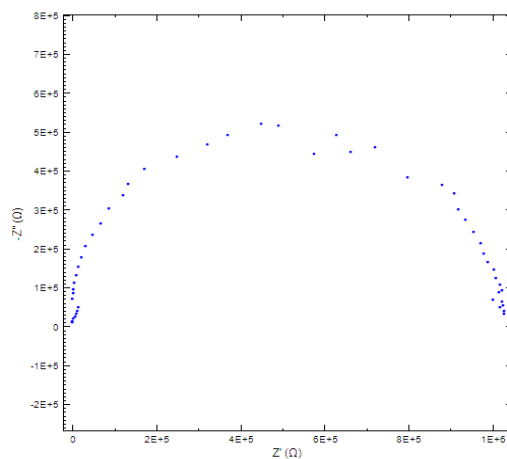


Figure 4. Nyquist diagram for $\text{Cu}_2\text{ZnTiS}_4\text{-M2}$.

The M2 sample, exhibit conductivity values of approximately $8 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$, evidencing a conductivity in the range of semiconductors and a better electrical response than conventional kesterite. The impedance results, allow to conclude that temperature is the main influencing factor in the electrical response of such materials. Is clear that elevated temperatures improve the conductivity values [9], as well as afore mentioned M2 material, since the time is a key factor in terms of economy process for potential industrial application of current results.

4. Conclusions

The studied methodology, replies to the main objective of $\text{Cu}_2\text{ZnTiS}_4$ materials, where the traditional kesterite structure was modified with the incorporation of titanium, using a hydrothermal synthesis route. The main results confirm the effectiveness of proposed synthesis route and evidence the effect of time synthesis in morphological and electrical properties of solids. Current results are optimal for potential application in design of photovoltaic devices using $\text{Cu}_2\text{ZnTiS}_4$ as main absorbent layer. In terms of obtained materials, is clear that M2 material is the most recommended, for studies and photovoltaic applications.

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