Analysis of synthetic profile of CZTS as photovoltaic material obtained with variations of titanium and TiN

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Abstract. Semiconductor type Cu₂ZnTiS₄ (CZTiS) and Cu₂ZnSnS₄ (CZTS), were synthetized starting from a hydrothermal route from precursor powders such as copper, zinc, tin, titanium isopropoxide and tiocarbammide metal nitrates dissolved in deionized water in concentrations of 1molL⁻¹. Dosed and placed in a steel autoclave equipped with a Teflon jacket under magnetic stirring (150rpm) and at a temperature of 300°C for 24 hours in order to promote the formation of the respective ceramic phases. Segregates have been repeatedly washed with ethanol at all times until obtaining crystalline-looking solids. Subsequently, in order to promote the production of pure crystalline phases, the materials were subjected to a second reaction stage in a tubular furnace at 400°C in flow (50mL min⁻¹) for the purpose of Reduce the concentration of secondary phases of sulphides. The characterization of the CZTiS and CZTS materials was performed by X-ray Diffraction (XRD) and Raman spectroscopy where the presence of Kesterite type crystalline structures was confirmed in the two materials revealing that the effect of titanium with a higher ionic radius than tin produces a distortion in the cell of the CZTiS material compared to the report for the CZTS system. The results of Scanning Electron Microscopy (SEM), confirm the regular aggregates obtained with composition consistent with the proposal theoretically and validated by Energy-Dispersion X-ray Spectroscopy (EDX) techniques and comparison between secondary emission spectra and Retro-dispersed.

1. Introduction
In the growing demand for energy consumption that currently lives in the world, the production of energy by means of photovoltaic modules has been one of the most attractive alternatives to solve this problem, currently the photovoltaic modules an expensive silicon base, which opens The field new research of new materials that replace silicon and its more economic view in its manufacture, materials with the structure CZTS and CZTiS result from the most attractive options [1-2].

Both Cu₂ZnTiS₄ (CZTiS) and Cu₂ZnSnS₄ (CZTS), are quaternary material with direct band-like semiconductor properties with a theoretical energy of 1.5eV and a light absorption coefficient of (>104cm⁻¹) in its visible range, theoretically Predict the absorption efficiencies at 32% depending on the dope of the unit cell [3,4].For the synthesis of the materials it was decided to use the routes of chemistry by means of hydrothermal routes (polymerization-combustion, hydrothermal), a technique highly used in the production of materials in glass for the simplicity in its processes and its low cost In order to carry out the process, it was necessary to use precursor solutions in the form of nitrates, chlorides, isopropoxide and acetates, dosed in a sulphur rich solution in order to promote the formation of the desired materials. In order to verify the formation of the kesterite phase, the aggregates obtained by XRD, Raman spectroscopy and SEM are characterized, using a two-material research methodology one with an interaction between them [5].
2. Materials and methods
To obtain kesterite (CZTS), copper nitrate Cu (NO₃)₂, zinc acetate Zn (CH₃COO)₂ and anhydrous tin chloride (SNCL₂) were each used in concentrations of 1mol L⁻¹ dissolved in a solution of tiocarbammide (H₂NCSNH₂) diluted in deionized water 3.3H₂O, for CZTiS-type kesterite, anhydrous tin chloride (SNCL₂) was replaced by titanium isopropoxide (C₃H₇O₄Ti) in equal proportions, each of the solutions was subsequently stirred for 5min to obtain a single solution [8,3].

For the synthesis of each material the respective precursors were dosed in a steel autoclave equipped with a Teflon jacket under magnetic stirring (150rpm) and at a temperature of 300°C for 24 hours in order to promote the formation of the respective compound; The materials obtained at the end of the preliminary stage were washed with absolute ethanol repeatedly until crystalline appearance solids were obtained. Subsequently, in order to promote the preparation of pure crystalline phases, the materials were subjected to a second reaction stage in a furnace at 400°C in He flow (50mL min⁻¹), for the purpose of reduce the concentration of secondary phases of sulphides, as shown in Figure 1 [8,6].

![Diagram of synthesis and characterization](image)

Figure 1. Process of synthesis and characterization of CZTS and CZTiS.

3. Results and discussion
To verify the obtaining of the crystallographic structure, x-ray diffraction tests were performed for each of the aggregates obtained in the synthesis processes of materials CZTS and CZTiS, the samples was identified by X-ray diffraction (XRD, PANanalytical XPert Pro Multi-Purpose Diffractometer, Co Kα, λ=0.1768nm) taking as reference data collection angles ranging from 20° to 80° 2θ (theta), a sufficient range to verify the characteristic peaks of the kesterite phase, in order to make the comparison of theoretical patterns with the experimental ones we used the "Cod" Crystallography Open Database.

The results of the obtained diffraction patterns (Figure 2 and 3) revealed the presence of kesterite mainly in three characteristic peaks attributed to the diffraction planes (1 1 2), (0 2 4) and (1 3 2), together with secondary phases of covellite mainly oriented in the diffraction planes (0 1 3), (1 1 0), (0 1 2) and sulphur present in each of the samples with an orthorhombic and monoclinic crystalline system respectively for CZTS and ZCTiS, two very common structures presented in the formation of sulphur rich compounds, a polymorphic characteristic attributed to the allotropic nature of the sulphur where small changes of temperature or pressure can cause the transition of structure, where in either case the sulphur is forming ring-shaped S₈ molecules (Table 1 and 2) [7].

The formation of the secondary phases is mainly attributed to the electronegativity of the elements since in the period of composition of the acetate of copper and zinc acetate carried out at temperatures higher than 200°C, the sulphur tends to react more easily with elements such as copper or tin due to its...
high electronegativity, in this way the formation of secondary phases in the compound is highly probable; The effect of annealing in an inert atmosphere at 400°C shows positive results for obtaining kesterite as the only compound present, but previous studies report that to obtain a single phase of CZTS we will need a temperature higher than 500°C in an atmosphere of He+H2S (5%) favouring not only the consolidation of the phase but also it could lead to increase in its crystallinity and grain size [8,12].

![Figure 2. X-ray diffraction pattern obtained synthesis of CZTS.](image1.png)

![Figure 3. X-ray diffraction pattern obtained synthesis of CZTiS.](image2.png)

**Table 1.** Species found in CZTS diffraction patterns.

| Compound name | Ref cod. | Crystal system | Chemical formula |
|---------------|----------|----------------|-----------------|
| Kesterite     | 96-900-4751 | Tetragonal     | Cu2.0Zn1.0Sn1.0S4.0 |
| Covellite     | 96-900-8390 | Hexagonal      | Cu1.0S1.0       |
| Sulfur        | 96-901-1363 | Orthorhombic  | S1.0            |

**Table 2.** Species found in CZTiS diffraction patterns.

| Compound name | Ref cod. | Crystal system | Chemical formula |
|---------------|----------|----------------|-----------------|
| Kesterite     | 96-900-0010 | Tetragonal     | Cu2.0Zn1.0Sn1.0S4.0 |
| Covellite     | 96-900-8390 | Hexagonal      | Cu1.0S1.0       |
| Sulfur        | 96-901-1363 | Orthorhombic  | S1.0            |

In the two x-ray diffraction spectra, there are notable differences, where the most important is the displacement of the CZTiS spectrum with respect to the CZTS of 0.321 degrees at the 2θ (theta) position which can be observed in Figure 4. This behaviour in the patterns is due to the tin atom was replaced by the titanium atom in the unit cell the interplanar distances thereof are modified [9], resulting in different diffraction planes for the two materials.

![Figure 4. Comparison patterns obtained with theoretical patterns of each compound present in the sample.](image3.png)
Even though the titanium atom has a higher atomic radius than the tin atom so it would expect its crystalline cell to increase in size, the shift of the right diffraction peak reflects that the cell size for the CZTiS type kesterite is lower than that of the kesterite type CZTS [4]. Raman spectroscopy was performed in order to further verify the presence of kesterite phase in the two samples obtained, the results show in Figure 5 that both spectra have significant peaks centred in 287cm⁻¹ [10], this characteristic is attributed to a result of the vibration of the sulphur atoms present in the kesterite, the position of the most intense resonance peak present in the spectrum of CZTS at 338cm⁻¹ is consistent with other investigations carried out for results obtained in synthesis of CZTS type materials; For the main signal present in the spectrum related to the CZTiS appears a resonance peak in the position 440cm⁻¹ a very specific characteristic of the material since it presents a considerable deviation in the position of the primordial line of Raman with respect to the main peak Raman Presented in traditional CZTS type materials, which could be due to a difference in the interactions of resonant photons and to the repulsion of the states of photonic interference that the structure presents[11].

![Raman Spectra](image)

**Figure 5.** Raman spectra of materials obtained in CZTS and CZTiS synthesis, showing the main vibrational modes of each sample.

For each of the tests was taken micrographs at 5000X using the scanning electron microscope, the photos obtained are presented in Figures 6 and 7.

![Micrographs](image)

**Figure 6.** CZTS sample morphology set at 400°C.  
**Figure 7.** CZTiS sample morphology set at 400°C.
The results of the two materials show a morphology of irregular agglomerates with sizes varying from 10 to 120 nm, it is observed that the reaction in two stages homogenizes the material maintaining similar sizes in the two cases of synthesis, small formations of crystals in circular form, generally observed in materials synthesized with high concentrations of thiocarbammide, the solvent can generate colloids which generates an effect of inhibitor in the growth of aggregates [8,7].

The analyses carried out by EDX made to CZTS and CZTiS material demonstrate an elemental composition homogeneous to the general stoichiometry of the kesterite where the levels of tin prove to be a little lower thanks to the formation of secondary phases such as copper sulphides type covellite confirmed in the spectrum by x-ray diffraction (see Figures 8 and 9).

![Figure 8. Chemical composition by EDX of CZTS.](image)

![Figure 9. Chemical composition by EDX of CZTiS.](image)

4. Conclusions
The synthesis of the crystallises kesterite phase type is possible to carry out by means of hydrothermal routes but taking into account that one of the crucial parts to decrease the secondary phases depend directly of the second phase of heating at higher temperatures than the first one.

The synthesis of the CZTiS ceramic phase demonstrates significant changes in its crystallinity since the shift of the x-ray diffraction peaks shows a smaller size in its unit cell.

Although the atomic volume size of titanium is greater than that of tin, the unit cell of the CZTiS type kesterite is less than the CZTS type kesterite, which means that the distances between atoms are smaller, a characteristic that may favour the band of conduction of electrons in the material.

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