Synthesis and characterization of the Cu$_2$ZnSnS$_4$ system for photovoltaic applications

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Abstract. This paper focuses on the synthesis and characterization of a ceramic material based on the Cu$_2$ZnSnS$_4$ system, through the implementation of a hydrothermal route. For this purpose, we started from nitrate dissolutions in a 1.0mol L$^{-1}$ concentration, which were mixed and treated in a teflon lined vessel steel at 280°C for 48h. The Physicochemical characterization of the solid was evaluated by means of ultraviolet visible spectroscopy (UV-VIS), X-ray diffraction (XRD), Raman spectroscopy, scanning and transmission electron microscopy (SEM-TEM) and solid state impedance spectroscopy (IS). The initial characterization through UV measurements confirms a Band-gap around 1.46eV obtained by the Kubelka-Munk method, which demonstrates the effectiveness of the synthesis method in the obtaining of a semiconductor material. The XRD results confirm the obtaining of a crystalline material of pure phase with tetragonal geometry and I-42m space group. The preferential crystalline orientation was achieved along (2 2 0) facet, with crystallite sizes of nanometric order (6.0nm). The morphological aspects evaluated by means electron microscopy, confirmed the homogeneity of the material, showing specifically a series of textural and surface properties of relevant importance. Finally, the electrical characterizations allow to validate the semiconductor behaviour of CZTS system for development of photovoltaic technologies.

1. Introduction

The research in the field of renewable energies is oriented to the search for new and enhanced systems that not only meet the growing energy demand that the current world requires, but also mitigate the environmental impact caused by the excessive use of fossil fuels used mainly for the generation of conventional energy. In this way, photovoltaic technology becomes an important alternative, since it promises a decreased environmental impact while supplying security and lowers the cost of the energy requirements of modern world [1]. However, photovoltaic technology has not achieved sufficient maturity to allow it to contribute significant energy contributions at the global level. Therefore, it is of the utmost importance to development of new materials that can eventually contribute to the research and development of this technology [2]. Traditionally the manufacture of photovoltaic devices involves the use of materials with high purity, structural perfection and high levels of toxicity. These restrictions have considerably limited the utilization of photovoltaic solar energy. The kesterite (Cu$_2$ZnSnS$_4$) or sulphur of copper, zinc and tin is one of the most interesting materials in the field of renewable energies, mainly due to its interesting photovoltaic properties. The CZTS offers optical and structural characteristics of significant importance for applications in thin film technology. Likewise, it is composed of elements that are not toxic and are readily available in the terrestrial crust [3].
Cu$_2$ZnSnS$_4$ is a quaternary type p semiconductor that has recorded values of Band-gap 1.40 to 1.55eV [4], coefficients of absorption in the visible region of 10$^4$cm$^{-1}$ [5] and efficiencies of around 31 to 33% calculated theoretically [6]. However, the solar cells based on CZTS have managed to reach values of energy conversion efficiencies close to 9.66% in solar panels [7].

In this regard, they have used a great variety of techniques for the development of thin film solar cells based on this material. However, a great part of them involve the use of equipment and routes of complex and costly synthesis that dramatically raise the cost associated with the manufacture of this type of material [8-9]. The hydrothermal synthesis method is an alternative technique to synthesize these materials at low temperatures and low residence times [10-11] that give rise to aggregates with important physical, chemical, and electrical properties [12]. Therefore, the present investigation is focused on the synthesis and characterization of a ceramic material based on Cu$_2$ZnSnS$_4$ system for application in thin film solar technology.

2. Experimental

The Cu$_2$ZnSnS$_4$ material was synthesized by a hydrothermal route in a single stage of reaction, starting from precursor solutions of Cu, Zn and Sn in 1.0mol L$^{-1}$ concentration, together with the addition of thiourea as source of sulphur. The dosage of the reagents is carried out in a stainless steel autoclave, where it were treated under stirring conditions at 280°C for 48h. Once completed the synthesis process, it was obtained a dark precipitate, which was washed repeatedly with absolute ethanol. Subsequently the solid was dried at 100°C (60min) to get the ceramic material.

The characterization by UV-VIS was conducted in a MAPADA UV-VIS 1800PC equipment, between 200 and 1100nm. The morphological characteristics were evaluated by X ray diffraction, in a PANalytical X’pert PRO MPD diffractometer, using the Cu Kα ($\lambda=1.54\AA$) radiation between 10 and 80° 2θ with steps of 0.02°. The X-ray pattern was analysed using the X’Pert High Score software, while the size of crystallite was estimated using the highest diffraction signal by the Debye-Scherrer equation. The evaluation of the purity of the solid and the formation of the crystalline phase was evaluated using Raman spectroscopy in a HR-UV 800 infinity microprobe (Jobin-Yvon) apparatus, equipped with a CCD detector (-70°C) and a laser of 10.7mW. The Raman spectrum of the solid was taken between 100 and 800cm$^{-1}$ projecting a continuous radiation laser of He-Ne, which supplying the excitation line at 632nm. The analysis by scanning electron microscopy (SEM) was performed in a Leica-Zeiss LEO 440 system with an electron gun and an accelerating voltage of 30kV, with analogic and digital image of EDX. The analysis by transmission electron microscopy (TEM), was conducted in a JEOL 2100 microscope with a thermionic gun of LaB$_6$ and an accelerating voltage of 200kV, allowing the obtaining of high-resolution images. Finally, the impedance analyses were performed with an AUTOLAB potentiostat-galvanostat at room temperature, to which the material was compressed in an uniaxial system at 5.0MPa pressure.

3. Results and discussion

The material obtained was evaluated by UV-VIS spectroscopy between 190-1100nm (see Figure 1). The Band-gap values were calculated from the inflection points, using the more characteristic wavelength providing a value around 1.46eV, which allow concluding that the dominant phase in the material corresponds to Cu$_2$ZnSnS$_4$ phase. The obtained values of Band-gap, permit to compare current result with the optimal value around 1.5eV and evaluate the effectiveness in the synthesis process. The slight decrease in assignation of wavelength and therefore in the calculation energy values could be attributed to the presence of Cu$_2$SnS$_3$ phase in the material, according to previous studies Malerba et al., this phase can be corrected by light thermal treatments not greater than 500°C [13].

The X-ray analysis, confirm the obtention of the Cu$_2$ZnSnS$_4$ system in a kesterite phase, showing a clear tetragonal geometry and a preferential crystal orientation along (2 2 0) facet. The estimation of the crystallite size was made by the Debye-Scherrer equation using the highest signal of the spectrum, resulting in a value around 5.46nm. In the Figure 2 is observed the main signals associated to the
CZTS system. These representative signals of material in kesterite phase show a great similarity with the works published recently by Vanalakar et al. [14]. The signals located at 34.3°, 37.1°, 62.2° 2θ are directly related with the formation of covalite (CuS), this secondary phase is associated with the low temperatures in the synthesis process, however it can be eventually corrected with subsequent thermal treatments as has been previously documented by Agawane et al. [15].

The characterization by Raman spectroscopy shown in the Figure 3, allow to highlight a strong signal around 289cm⁻¹ associated to the main mode vibrational asymmetric mode of the CZTS system in the kesterite phase [16]. Of equal way, this technique confirms the presence of other signals with lower intensity located at 225cm⁻¹ (SnS), 326cm⁻¹ (Cu₂SnS₃), 346cm⁻¹ (ZnS) and 475cm⁻¹ (CuS₂), which are linked to the formation of intermediate compounds. The existence of a low peak located at 326cm⁻¹, is associated with the tetragonal phase of Cu₂SnS₃, the formation of this phase in the structure is probably caused by the strong presence of Cu²⁺ cation in the material [17]. Of this form, the consolidation of secondary phases is a consequence of the incomplete conversions of sulphides during the synthesis process [18]; therefore, a progressive increase in the synthesis temperature could improves the morphological, structural and optical characteristics of CZTS material [15].

The analysis by scanning electron microscopy (Figure 4), show the obtaining of a material conformed by conglomerates distributed homogeneously. The morphology of the material allows to
identify a solid formed by aggregates with irregular spherical geometry. According to Wang et al. [19], the morphology of the material is improved with the increases in the synthesis temperature since is a key factor in the consolidation of appropriate kinetic mechanisms in the formation of crystalline phases [19,20]. In addition, the chemical composition of CZTS nanoparticles using the energy dispersive of X-rays spectroscopy (EDX), permit to validate an excellent relationship between proposed and obtained composition (Table 1). The data show an optimal correlation between Cu/Zn/Sn/S elements in a 2:1:1:4 proportion, this corroborates the absence of contaminants in the solid, allowing appreciate the grade of purity of the material.

| Percentage values by weight (%) | Cu   | Zn   | Sn   | S    | Total |
|--------------------------------|------|------|------|------|-------|
| Experimental                  | 28.65| 15.69| 26.89| 28.77| 100   |
| Theoretical                   | 28.91| 14.87| 27.03| 29.18| 99.99 |

On the other hand, the morphology and surface characteristics of the material were investigated using transmission electron microscopy (TEM), as shown in the Figure 5. The results show that nanoparticles have a diameter around 5-6nm with interplanar distances of 0.70nm, current data confirm the results obtained from previous size analysis performed by the Debye-Scherrer equation.

The electrical response of the material was evaluated using solid-state impedance spectroscopy, the results confirm that the material presents a semiconductor behaviour, all resistivity values are values near to 50000Ω. The semicircle in Figure 6, show a region controlled by charge transfer processes, which show the way in which the charge carriers react during the potential change and its relation with the generation of electric power [21].

![Figure 5. Transmission electron microscopy images for the CZTS system.](image)

![Figure 6. Impedance diagram for the CZTS system.](image)

The Figure 7 show the equivalent circuit, modelled for the CZTS system taking as reference the impedance shown in Figure 6, which is consistent with a constant phase element (CPE). In this case, the experimental values conform a value of n=1.1. In this way, the use of the CPE allows make an excellent fit of the experimental data because it takes into account the independent gap of frequency between the alternate potential and its response in terms of current. Therefore, the results derived from the electrical circuit demonstrated that the material presents a superficial heterogeneity, resulting in a superficial roughness. This physical phenomenon is probably related to the presence of the minority of covalite phase in the structure of the material, responsible for a notable decline in the process of transfer of load on the material. These data are consistent with the results previously obtained through the analytical techniques described above [22, 23].
4. Conclusions

The CZTS material obtained by means a hydrothermal route, showed physicochemical features of marked importance in the field of photovoltaic applications. The results of X-ray diffraction showed that the material are composed of nanometric particles (5-6nm), which agree with the transmission electron microscopy results. The obtained Band-gap value (1.46eV), allow to classify the solid as a semiconductor material in accordance with previous works. In this form, the synthesis method permits the obtaining of a material with a characteristic morphology textural and optical properties, for potential use as absorbent layer in photovoltaic devices.

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