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Synthesis and characterization by solid-state impedance spectroscopy of semiconductor Cu_2ZnSnS_4 material for photovoltaic technologies

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Abstract: Current work is focused on the synthesis and characterization of a Cu_2ZnSnS_4 material (Abbreviated CZTS), identified as a potential candidate for the manufacture of photovoltaic cells. The material was obtained by means of a hydrothermal route which permits a simple and economical alternative to synthesize advanced materials for photovoltaic applications. The synthesis of a solid started from corresponding metal nitrates of $Cu(NO_3)_2.6H_2O$, $Zn(NO_3)_2$, $Sn(NO_3)_4.6H_2O$ and thiourea as S source, which were dissolved in deionized water until complete a 1.0mol L⁻¹ concentration. The solution was kept in a Teflon lined steel vessel with magnetic stirring (150 rpm) and treated at 300°C for 12 hours to form the crystalline phase. The initial characterization of solid was done using UV spectroscopy to validate the chemical process and identify the corresponding Band-gap around (1.43eV). The structural characterization by X-ray diffraction, confirmed the presence of nanometric solids (140-260nm). The morphological characterization by SEM analysis evidenced a homogeneous material in the form of micrometric aggregates, by a related synthesis method. Finally, the electrical characterization by means of solid state impedance spectroscopy demonstrated a semiconductor behaviour which evidenced the transport phenomena associated with a Warburg resistance.

1. Introduction

Recently, research related with photovoltaic materials has been focused on the search of new and sustainable energy sources that include non-toxic and abundant materials, with aim of reducing contamination by heavy metals and diminishing greenhouse emissions for the preservation of the atmosphere for future generations [1]. In this context, new materials based on kesterite and stannite structures have been developed for use in new photovoltaic cells. Such quaternary materials based on Cu_2ZnSnS_4 composites (CZTS), represent a real alternative to increase production and expand the photovoltaic technology to other fields of technology [2].

Based on the above, for several years, both the physics and chemistry of materials have focused attention on the progress of new synthesis routes which enable the economic production of CZTS materials in, allowing increased production and diversification of these technologies in the development of unconventional systems and previously un-explored solar energy systems [2]. Current interest is focused on the use of hydrothermal routes of synthesis in one or two-step reaction stages, that preserve and provide morphological characteristics of relevance in design of solar cell materials [4]. Therefore, present work is focused on the synthesis and characterization of a Cu_2ZnSnS_4 material, using a two-step hydrothermal route, allowing the study of the physicochemical properties of solids, to identify key chemical aspects of the synthesis process that allow the modelling of the best conditions to generate the

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highest level of photovoltaic performance. Accordingly, a series of characterization techniques which support the identification of these key aspects opens a wide field of exploration in the design and construction of devices for the generation of clean and renewable energy with low environmental impact [2].

2. Materials and methods

The precursors used to prepare the CZTS system were $Cu(NO_3)_3.3H_2O$, $Zn(CH_3COO)_2$, $SnCl_2$ and SH_4N_2S ; all from Merck. The initial stage corresponded with the amount of each metal cation to reach a 1.0mol L⁻¹ concentration of precursors in deionized water, using KOH as mineralizing agent. The solutions were kept in a Teflon lined steel vessels for 30 minutes with magnetic stirring (250rpm) at room temperature to provide a homogenous reaction medium in each case [3].

The solutions obtained were treated at 300°C for 12 hours to obtain the CZTS powders. The resultant materials present as a dark powder, which was washed in absolute ethanol several times to eliminate by products of the reaction. The solid was dried at 100°C in an electric oven for 3 hours, at the end of which the solid was calcined at 400°C in a tubular furnace for 2 hours using a helium flow (50mL min⁻¹), to promote the crystalline formation of desired material and avoid the possible oxidation of S in the material. The initial characterization of solid was done by means UV measurements in a HP 8453 UV-VIS spectroscope. The characterization by means X-ray diffraction (XRD), was done on a PANalytical X' per PRO MPD difractrometer provided with an ultra-fast X'Celerator detector in Bragg-Brentano configuration, using the Cu K_x radiation (λ =1.54Å). The diffractograms were taken between 10 and 90° 20 and the results were analysed using the X'Pert High Score software and the Rietveld refinement.

The morphological characterization was performed by scanning electron microscopy (SEM), in a Leica-Zeiss LEO 440 electron gun equipment with an accelerating voltage of 30kV and the electrical and conductivity properties were evaluated using the solid state impedance spectroscopy technique (IS), in a GAMRY potentiostat-galvanostat instrument between 1 and 10MHz over 10mm pellets compacted in uniaxial form at 5.0Mpa pressure with a 10mm diameter and 1mm standard thickness, to avoid variations in measurements.

3. Results and discussion

The initially UV measurements provided information regarding the main electron transitions related with the CZTS composition as shown in Figure 1.



Figure 1. UV spectrums with corresponding Band-gap energy values obtained from general scan between 190-1100nm,

The Band-gap values were obtained using the Kubelka Munk technique, providing a value of 1.55eV, in accordance with a semiconductor material. Additionally, evident was a strong absorption phenomena around the 220nm zone in which the solid has the capacity to absorb the most energetic portion of UV radiation. The structural characterization of solid by X-ray diffraction confirmed the presence of the

main diffraction signals of CZTS in a tetragonal (Figure 2) system oriented along $(0\ 1\ 1)$, $(0\ 0\ 2)$ and $(0\ 2\ 0)$ facets, as the most intense signals (Figure 3). A rise in temperature in the second thermal treatment of material provided more definitive evidence of a corresponding elimination of secondary phases associated with villaminite and wursite as shown in Figure 3.



Figure 2. Comparison CZTS X-ray patterns obtained with the simulated patterns of secondary phases.



Figure 3. Quantitative analysis of CZTS powders obtained by Rietveld refinement, show the incidence of villaminite and wursite.

A detailed analysis of the XRD results demonstrate that differences exist in the size of crystallites after the second stage of reaction as shown in Figure 4. The crystal sizes were determined using the Scherrer equation as follows:

$$D = K\lambda/\beta \cos\theta \tag{1}$$

Where λ is the wavelength generated by the copper source supplying radiation to the sample, K is a constant close to 1 and θ is the angle corresponding to the main diffraction signal, resulting in a crystallite size around 140nm to CZTS sample before thermal treatment and 260nm for the sample

annealed at 400°C. These results could be important in determination of electric properties, since these results mean that resistance values due to grain boundaries in the material annealed at 400°C exhibit a better electrical response in terms of the effectiveness of carriers transfer [12].



Figure 4. Crystallite size of CZTS materials obtained at 300 and 400°C.

Figure 5 (a) and (b), shows the images obtained by the scanning electron microscopy (SEM) at identical magnification, with clear evidence of the development of homogeneous powders with a typical morphology related with the synthesis process [4]. The diameter of CZTS semispherical particles changes from 2.8 to 3.2μ m with increasing temperature from 300 to 400°C, indicating that thermal treatment in CZTS solid strongly influenced the crystal growth. Therefore, the morphology was found to be dependent upon the synthesis conditions as well as the reaction time.



Figure 5. Morphology of the CZTS sample obtained in (a) one-step and (b) two-step reaction stages.

Finally, the electrical characteristics of CZTS powders were evaluated by solid-state impedance in a cell adapted and modified for this purpose. This characterization enabled the establishment of a semiconducting behaviour with conductivity levels around 5.4×10⁴S. The interpretation of the data needs the study of the Nyquist plots, which was adjusted to a transfer function (impedance), where in addition to the classic elements such as resistors or elements of constant phase, it was necessary to define an electronic equivalent circuit to fit the electrochemical response of material as shown in Figure 6. The identification of a Warburg (W) resistance in the system obtained at low frequencies, confirmed that the materials display a transfer phenomenon attributed mainly to the presence of heterogeneous surfaces and polymorphisms, which increase the tortuosity of electric charge carriers as has been established in preliminary works [10,11].



Figure 6. Nyquist plot of CZTS material obtained at 400 °C.

4. Conclusions

The current work confirms how the development of a second thermal treatment in the hydrothermal synthesis of CZTS powders, provides a more efficient tool for the design of more effective photovoltaic materials. The UV measurements, evidence the obtaining of a material with an optimal Bang-gap (1.55eV), which permit the ideal absorption in the UV region. The XRD characterizations confirm the obtaining of a crystalline material in tetragonal configuration with presence of secondary phases of villaminite and wursite, which could be eliminated by a thermal treatment in the second stage of reaction. The morphological results demonstrate that temperature promotes the obtaining of solids with a crystal size around 260nm, reflecting a strong dependence with the electrical behaviour. The implementation of the solid-state impedance spectroscopy to validate the electrical characteristics of CZTS powders was effective enabling the study of semiconductor materials for photovoltaic applications.

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