Construction, study and mathematical modelling of the electrical behavior of CZTiS photovoltaic material as function of time and synthesis temperature

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Abstract. This work reports the obtaining, study and mathematical modeling of a photovoltaic material type CZTiS (Cu₂ZnTiS₄), in function of two thermodynamic variables such as temperature and hydrothermal synthesis time. The obtention the materials had to be validated through the implementation of characterization techniques such as X-Ray Diffraction (XRD) and solid state Impedance Spectroscopy (IS). The results of the characterization, allowed to confirm in all cases the obtention of the materials, with a crystalline structure concordant with a tetragonal geometry space group of I-42m, a preferential crystalline orientation in the plane (1 1 2), with crystal sizes in the nanometric order (5-6nm). The electrical characterization, showed a semiconductor behavior of the solids concordant with values of conductivity that can be modeled by the analysis of variance and verified through the Kramers-kronig transform. The information obtained confirms that the temperature variable is the most strong influence in the electrical behavior of the CZTiS material, which is in agreement with similar works evaluated with alternative techniques [1].

1. Introduction

The type CZTiS (copper, zinc, titanium, sulfur) made in the Uptc and obtained by a synthesis process using a hydrothermal pathway is a low cost alternative of semiconductor that has been evaluated with the possibility of using as material for construction of photovoltaic cells. The optical and electrical properties with kesterite structure achieved in this research show that CZTiS has an acceptable electric behavior. The CZTiS has been manufactured using this technique, analyzed and validated using statistical and mathematical methods such as variance and the Kramers-Kronig equations in order to find a cost-effective process and where possible replace other high-cost techniques such as those mentioned in [2]. The temperatures and times used in this work (250, 275, 300°C and 24, 48 and 72 hours) served to mathematically model the electrical behavior of the studied material, as well as to compare the results of the characterization with works that used temperatures of 473K a 773K, with 100K intervals and investigations with temperatures of 500 to 575°C at 25°C intervals and different techniques as can be seen in [2, 3]. The mathematical model found allowed to interpolate and predict the conductivity of the material at different temperatures.

The X-Ray Diffraction (XRD) was used to characterize the manufactured product, from which
it was possible to obtain information that corroborated the type of material sought CZTiS \((\text{Cu}_2\text{ZnTiS}_4)\), on the other hand, by means of The electrical Impedance Spectroscopy (SI), a technique used to collect experimental data, which consists of applying a sinusoidal electrical disturbance (voltage or current) to the study material, obtained numerical information used to perform the analysis of the variance and for the treatment of the data by means of the Kramers-Kronig transforms, in this stage several impedance tests were carried out since due to the applied voltage and to strange factors there can be some type of noise or error that influences the measurements [4–6].

2. Methodology
The preparation of the CZTiS material started from the respective precursors in the form of Cu and Zn nitrates, titanium isopropoxide and thiourea, which were stoichiometrically dosed in a teflon vessel with magnetic stirring and deposited in an steel autoclave. The synthesis temperatures were established according to the thermodynamic criteria to form the respective kesterite phase (250, 275 and 300°C). Likewise, the time values were established at 24, 48 and 72 hours, being these variables the main factors to be evaluated in the present work. At the end of each process the materials were obtained as a black precipitate, which was washed with absolute ethanol repeatedly to reduce the effect of impurities generated in the process. Subsequently, the materials were dried for 80 minutes in an electric oven at a temperature of 100°C, obtaining the respective materials in each case in the form of a compact powder. The solids were characterized by XRD on PANalytical X’pert pro MPD equipment, equipped with an X’celerator detector in Bragg-Bretano configuration, using the Cu Kα \((\lambda=1.54\text{Å})\). The diffractograms were taken between 10 and 90°and the results were analyzed using the X’Pert High Score software. The solid state impedance spectroscopy (IS) analyzes were performed on a GAMRY potentiostat-galvanostat between 1 and 10MHz obtaining numerical information from the set of samples, which were uniaxially compacted at 10Mpa with a diameter of 10mm and a thickness of 1.0mm. Four measurements were performed on each sample to verify the reproducibility of the data and each analysis was corrected by a reference cell to avoid noise in the determinations.

3. Analysis and results
Initially, the CZTiS materials were characterized by XRD, obtaining the presence of characteristic crystalline structures and associated with the pure tetragonal phase of kesterite and identified with PDF card 00-026-0575, with space group \(I-42m\) (1 2 1) and cell parameters \(a=5.427\text{ angstrom}\) and \(b=10.848\text{ angstrom}\), as shown in Figure 1. In all cases, there is no evidence of relevant structural variations related to this crystalline phase.

Figure 1. Structural characterization by XRD of CZTiS material.
The results of the electrical characterization of the materials, in the form of Nyquist and Bode diagrams, show a favorable semiconductor behavior in agreement with preliminary works [7]. And as shown in Figure 2. The data of these diagrams were collected and analyzed by means of the Kramers-Kronig equations, with the final purpose of validate the proposed method related to the analysis of the impedances as a function of thermodynamic parameters of temperature and time of synthesis. The data were analyzed taking into account the proposed variables, recording the maximum values of the impedance modules in each test, as indicated in Table 1.

![Nyquist and Bode diagrams](image)

**Figure 2.** Nyquist and Bode diagrams for 24-48h and 275-300°C.

To find the conductivity of the material, was used the inverse of the maximum values of the impedance modules of each test, as indicated in Table 2. These data were statistically analyzed by the variance obtaining a correlation factor for temperature and time, as well as the interaction of these two variables, in order to check which of these is the factor that most influences the conductivity of the material as is indicated in the Table 3.

As $F_0 > 1$, of the treatments provided (time and temperature), which has the greatest influence on the conductivity of the material is the temperature, it is also observed that the temperature correlation factor is greater than $F$, that is, $F_{0(T)} > F$, so with this variable the experiment has a 97% of success. Although the correlation factor of the time variable is close to 1, it has little influence on the conductivity of the material.
### Table 1. Impedance spectroscopy (CZTiS) to different times and temperatures.

| T (°C) | Registry 1 | Registry 2 | Registry 3 | Registry 4 | Time in h |
|--------|------------|------------|------------|------------|-----------|
| 300    | 769.74     | 3787.87    | 530.85     | 3562.81    | 24        |
| 300    | 3024.25    | 2643.64    | 6017.47    | 2154.54    | 48        |
| 300    | 3938.44    | 500.37     | 8765.01    | 6431.26    | 72        |
| 275    | 8412.06    | 8944.22    | 8294.3     | 15535.48   | 24        |
| 275    | 9475.23    | 7151.24    | 12359.13   | 10023.38   | 48        |
| 275    | 1785.34    | 8421.64    | 11432.14   | 8941.36    | 72        |
| 250    | 16463.65   | 6275.14    | 13612.17   | 16707.95   | 24        |
| 250    | 18688.88   | 8761.5     | 14672.51   | 10172.35   | 48        |
| 250    | 13036.76   | 10594.106  | 19903.7    | 18164.13   | 72        |

### Table 2. CZTiS conductivity material at different times and temperatures.

| T (°C) | Registry 1 | Registry 2 | Registry 3 | Registry 4 | Time in h |
|--------|------------|------------|------------|------------|-----------|
| 300    | 1.29 × 10^{-3} | 2.64 × 10^{-4} | 1.88 × 10^{-3} | 2.80 × 10^{-4} | 24        |
| 300    | 3.30 × 10^{-4} | 3.78 × 10^{-4} | 1.66 × 10^{-4} | 4.46 × 10^{-4} | 48        |
| 300    | 2.53 × 10^{-4} | 1.99 × 10^{-3} | 1.14 × 10^{-4} | 1.55 × 10^{-4} | 72        |
| 275    | 1.19 × 10^{-4} | 1.12 × 10^{-4} | 1.20 × 10^{-4} | 6.43 × 10^{-5} | 24        |
| 275    | 1.055 × 10^{-4} | 1.398 × 10^{-4} | 8.09 × 10^{-5} | 9.97 × 10^{-5} | 48        |
| 275    | 5.60 × 10^{-4} | 1.187 × 10^{-4} | 8.74 × 10^{-5} | 1.118 × 10^{-4} | 72        |
| 250    | 6.07 × 10^{-5} | 1.59 × 10^{-4} | 7.34 × 10^{-5} | 9.83 × 10^{-5} | 24        |
| 250    | 5.35 × 10^{-5} | 1.14 × 10^{-4} | 6.81 × 10^{-5} | 5.98 × 10^{-5} | 48        |
| 250    | 7.67 × 10^{-5} | 9.43 × 10^{-5} | 5.02 × 10^{-5} | 5.50 × 10^{-5} | 72        |

### Table 3. Variance analysis of the electrical behavior of the material CZTiS.

| Source of variation | Sum of squares | Degrees of freedom | Mean squares | $F_0$ Value |
|---------------------|----------------|--------------------|--------------|-------------|
| Synthesis time      | 2.63 × 10^{-7} | 2                  | 1.315 × 10^{-7} | 0.766 < 0.01 |
| Synthesis temperature | 2.19 × 10^{-6} | 2                  | 1.095 × 10^{-6} | 6.387 < 0.01 |
| Interaction         | 4.86 × 10^{-7} | 4                  | 1.215 × 10^{-7} | 0.709 < 0.01 |
| Fault               | 4.63 × 10^{-6} | 27                 | 1.714 × 10^{-7} | $F_{0.05:4:27}=2.73$ $F_{0.05:2:33}=3.27$ |
| Total               | 7.57 × 10^{-6} | 35                 |              |             |

### 4. Application of Kramers Kronig transforms

These equations relate the real and imaginary part of a complex analytic function [8]. Now well, as the impedance is formed by a real part (resistance) and an imaginary part (reactance), these equations (KK) can be used to calculate and verify the experimental data of the impedance spectra of the CZTiS material [9,10]. Therefore, making use of the KK equations, it is possible to transform the complex part of the impedance in the imaginary part and reciprocally [11,12].
4.1. How to verify the reliability of the data

The literature evidences several ways to validate the experimental data of a system; one is adjusting several or a polynomial of $Z'$ or $Z''$ with $\omega$ and replacing them in the corresponding equations of KK and integrating numerically. Another way is making use of the models of measurement, these are used by means of general equivalent circuits (Maxwell or Voigt circuits) and always comply with the KK. The component equations of the impedance for a given frequency in a parallel circuit are: [13].

\[
Z'(\omega_i) = R_1 + \sum_{k=2}^{M} R_k \frac{\omega_i}{1 + (\omega_i \tau_k)^2} \tag{1}
\]

\[
Z''(\omega_i) = -\sum_{k=1}^{M} \frac{\omega_i R_k \tau_k}{1 + (\omega_i \tau_k)^2} \cot t_k = (\omega_k)^{-1} \tag{2}
\]

The easier way to calculate the transformed components is: 1. Find the imaginary components from the real ones, for this the real experimental values $Z'$, the values of the angular frequency and the time constant $\tau_k$ are replaced for each frequency in the equation (1), this allows to establish a system of linear equations in $R_k$, 2. Once this system is established, it is solved to obtain the values corresponding to $R_k$, 3. These values are replaced in the equation (2) obtaining of this way the transformed imaginary components, which will be noticed $Z''(\text{trans})$. 4. The $Z''(\text{trans})$ values are compared with the imaginary experimental data ($Z''$) by imaginary residuals ($\Delta''$) for each frequency, as shown in the following equation.

\[
\%(\Delta'')_i = \frac{Z''(\text{trans})_i - Z''_i}{|Z_i|} \times 100 \tag{3}
\]

5. Mathematical model for data conductivity of the CZTiS material in function of the time and temperature of synthesis

Using the data from the Table 2, it was possible to fit a mathematical model capable of describing the electrical behavior of the CZTiS material as a function of time and temperature of synthesis, the model was adjusted using the method of least squares [14], the obtained surface verifies that the experimental data remains closely or are on the graph, as evidenced in the Figure 3.

\[
C(t, T) = 3.74 \times 10^{-4} - 1.158 \times 10^{-6}t - 5.85 \times 10^{-8}T - 1.30 \times 10^{-9}t \ast T \tag{4}
\]

Figure 3. Curve fitted to the conductivity data of CZTiS material at 250, 275, 300°C and times of 24, 48, 72h.
6. Conclusions
The characterization of the properties of the material, using X-Ray Diffraction (XRD) technique, allowed to verify the obtention of a material type CZTiS and the quality of the same. The shape of the Nyquist diagrams showed good electrical behavior of the material, since the material is not as resistive. With the inverse of the maximum impedance modulus, an appreciable value of the conductivity could be obtained, as can be seen in the Table 2. The model fitted to the conductivity data was made possible by the different impedance spectra of the material, this model was adjusted by the method of least squares. The statistical analysis of the variance allowed to detect that the factor that predominates in the manufacture of this type of materials is the synthesis temperature. It is observed that the conductivity of the CZTiS material manufactured with the characteristics and process described above is linked to the synthesis temperature and very little to the reaction time of the material. The Kramers-Kronig equations are of a lot importance to validate the impedance data, with this it is possible to ensure the validity of the process. The construction of a model and the adjustment of the conductivity data obtained through the impedance spectra allow us to interpolate and to know point approximations of the electrical behavior of the CZTiS material.

References
[1] Suryawanshi M P, Shin S W, Agawane G L, Gurav K V, Ghorpade U V, Hong C W, Gaikwad M A 2015 A Promising Modified SILAR Sequence for the Synthesis of Photoelectrochemically Active CuZnSnS4 (CZTS) Thin Films Israel Journal of Chemistry 55 1-6
[2] Nuttee Khottoommee, et al. 2015 Structural and optical properties of Cu2ZnSnS4 films deposition by screen coating technique of sol-gel process SNRU Journal of Science and Technology 7(2) 100-105
[3] Shin S W, et al. 2015 A chemical approach for synthesis of photoelectrochemically active Cu2ZnSnS4 (CZTS) thin films Solar Energy 110 221-230
[4] Becerra R A 2016 Síntesis y caracterización de películas delgadas de Cu2ZnSnS4 depositadas por CBD, asistida con membrana de difusión (Colombia: Universidad Nacional de Colombia)
[5] Boukamp B A 1993 Practical application of the Kramers-Kronig transformation on impedance measurements in solid state electrochemistry Solid State Ionics 62 131-141
[6] Antaño L Q R 1997 Aplicación de un algoritmo basado en un modelo de medición para la detección de errores en las mediciones experimentales de impedancia (México: Universidad Autónoma Metropolitana-Iztapalapa)
[7] Patarroyo M, Vera E, Pineda Y, Gómez J 2017 Impedance spectroscopy in photovoltaic materials of Cu2ZnSnS4 (CZTS) and use of the KK transform Journal of Physics: Conf. Series 786 012014
[8] Urquidi-Macdonald M Real S, Macdonald D D 1986 Application of Kramers-Kronig transforms in the analysis of electrochemical impedance data II transformations in the complex plane Journal of the Electrochemical Society 133(10) 2019-2024
[9] Matthew E, Orazem M 1991 On the Application of the Kramers-Kronig relations to evaluate the consistency of electrochemical impedance Data The Electrochemical Society Inc 138(1) 67-76
[10] Dambrowski J 2013 Validation of impedance-data and of impedance-based modeling approach of electrochemical cells by means of mathematical system theory The 39Th Annual Conference Of The IEEE Industrial Electronics Society (Vienna) (USA: IEEE) 1-7
[11] Bayer M H, Schneider I A 2013 Application of the Kramers Kronig relations to locally resolved impedance data of polymer electrolyte fuel cells Journal of Electroanalytical Chemistry 689 42-45
[12] León C, Martín J M, Santamaria J, Skarp J, González D G, Sánchez Q F 1996 Use of Kramers-Kronig transforms for the treatment of admittance spectroscopy data of p-n junctions containing traps (USA: American Institute of Physics) 7830-7837
[13] Boukamp B A 1995 A linear Kronig-Kramers transform test for admittance data validation The Electrochemical Society Inc. 142 6
[14] Montgomery D C 2004 Diseño y análisis de experimentos (USA: Limusa Wiley)