Impedance spectroscopy in photovoltaic materials of Cu$_2$ZnSnS$_4$ (CZTS) and use of the KK transform

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Abstract. The article presents some details about the synthesis and evaluation of photovoltaic materials related with the Cu$_2$ZnSnS$_4$ system (abbreviated CZTS), using a hydrothermal route that provide the optimal way to synthesize the proposed materials. The ceramic was obtained starting from corresponding metal nitrates and thiourea as sulphur source in stoichiometric amounts. Corresponding reagents were dosed in a steel Teflon lined vessel and treated at different temperatures to evaluate the effect of external variables in synthesis process. The structure was evaluated by means scanning electron microscopy (SEM) and X-ray diffraction. The electrical characteristics were evaluated by solid state spectroscopy using a statistical analysis coupled with a simple model fitted to the data of electrical conductivity of the material as function of synthesis temperature, for this, the mathematical formulation of the impedance was analyzed, with the use of the Kramers-Kronig transform (KK), (mathematical equations that describe the relationship between the real and imaginary parts of certain complex functions analytic) as well as documentation and research related with the subject of this article. The results show a good behavior of the material, showing that the higher synthesis temperatures promotes a corresponding increase in the electrical conductivity in accordance with previous works [1].

1. Introduction

For the synthesis of photovoltaic cells of low cost and good performance is necessary a constant research and laboratory test, which in many cases are expensive due to consumption of analitical reagents of high purity, which could be improved by the use of mathematical modelling and techniques of formulation that can validated the processes. So, in this work, we explore the correspondence between experimental and modeled data related with the synthesis of Cu$_2$ZnSnS$_4$ system, in terms of influence of the time and synthesis temperature, using as control parameter the electrical impedance as dependant variable by means a Kramer-Kronig transform equations.

The electrical impedance spectroscopy is a technique to collect experimental data, which can be given a proper interpretation regarding the material under study, this interpretation depends on how the data are analyzed. This technique consists in apply an electrical disturbance sinusoidal (voltage or current) to the material under study, this makes always is present some strange factor or noise that can influence the measurements [2, 3] is here where the transformed Kramer-Kronig do their work, as these purely mathematical equations help validate the reliability of the data and correct decision making. The Nyquist plot represents the impedance in a complex plane, and The Bode plot represents the impedance in function of the frequency. To consider the impedance as a vector, it allows that you can manipulate as a complex number, so its magnitude will be $|Z| = \frac{V_0}{I_0}$ and phase angle $\phi$. 

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1.1. Obtaining mathematical impedance

Suppose that a current flows through a circuit formed by a resistance, an inductor and a capacitor in series, the circuit is fed with a sinusoidal voltage, and there is not presence of transient phenomena, wherewith the system is linear and the current the permanent regime is also sinusoidal with the same frequency as that of the original source, well now, if the current amplitude and the phase gap that may have regarding the voltage of fed, is not known, then, supply voltage is \( V = V_0 \cos(\omega t) \), the current will be of the form \( I = I_0 \cos(\omega t + \varphi) \), where \( \varphi \) is an unknown gap. With this, the equation to be solved is: \( V_0 \cos(\omega t) = V_R + V_L + V_C \).

\( V_R, V_L, V_C \) are the voltages between the ends of the resistance, inductance and capacitor. Applying Ohm’s law, the definition of inductance and condenser is obtained:

\[
V_0 \cos(\omega t) = RI_0 \cos(\omega t + \varphi) - \omega LI_0 \sin(\omega t + \varphi) + \frac{1}{\omega C} I_0 \sin(\omega t + \varphi) \tag{1}
\]

Where \( I_0 \) y de \( \varphi \) they must be found and the equation must satisfy all values of \( t \).

Suppose now that an identical circuit is fed by another source of sinusoidal voltage which begins with a quarter period delayed, then the voltage will be \( V = V_0 \cos(\omega t - \frac{\pi}{2}) = V_0 \sin(\omega t) \), then, the solution will also have the same delay and the current will be: \( I = I_0 \cos(\omega t + \varphi - \frac{\pi}{2}) = I_0 \sin(\omega t + \varphi) \). The equation of the second circuit will be:

\[
V_0 \sin(\omega t) = RI_0 \sin(\omega t + \varphi) + \omega LI_0 \cos(\omega t + \varphi) - \frac{1}{\omega C} I_0 \cos(\omega t + \varphi) \tag{2}
\]

Performing some mathematical calculations you get to: \(^{(1)}\) \( I_0 e^{j \varphi} = \frac{V_0}{R + j \omega L + \frac{1}{j \omega C}} \).

The current amplitude and phase gap is observed in \(^{(1)}\) and must be equal to the module and argument of complex number on the right side.

2. Methodology

The CZTS material was obtained by the implementation of a hydrothermal route, starting from nitrate solutions in 1.0mol L\(^{-1}\) concentration and solid thiourea as S source, all from Merck. The systems in each case were treated under magnetic stirring conditions (100rpm) and subjected to different time and thermal treatments (200, 220, 240, and 260°C), in a teflon lined stainless steel autoclave. The obtained material as a black precipitate was washed several times using absolute ethanol and acetone to achieve a rapid drying of it. As second stage, the solids were calcined at 400°C in a tubular furnace under helium flow (20ml min\(^{-1}\)) for two hours, to remove volatile impurities and consolidate the crystalline phase. The obtained solid was characterized by X-ray diffraction (XRD), on a PANalytical X’pert PRO MPD equipment provided with an ultra-fast X’celerator detector in Bragg-Brentano configuration, using the Cu K\(\alpha\) radiation (\(\lambda=1.54\)Å). The diffractograms were taken between 10 and 90° 2\(\theta\) and the results were analyzed using the X’Pert High Score software.

The morphological evaluation of solid 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 of the material was evaluated using the solid state impedance spectroscopy technique (IS), in a GAMRY potentiostat-galvanostat instrument between 1 and 10MHz for which a set of pellet samples, were obtained using a pressure of 5.0Mpa and a constant diameter of 10mm and a thickness of 0.8mm. Each sample was tested five times to avoid mistakes in the numerical information of impedance.

3. Analysis and results

The morphological characteristics of solid, initially was evaluated by means scanning electron microscopy at different magnifications, the images in Figure 1, confirm the obtention of homogeneous aggregates of regular morphology in accordance with works in which is clear that hydrothermal treatment configure specific characteristics of similar compositions based on CZTS materials.
Figure 1. Scanning electron microscopy (SEM), of CZTS materials at different magnifications.

The structural characterization by XRD measurements confirm the obtention of a pure CZTS phase related with a tetragonal classification in accordance with 00-026-0575 PDF card with crystal group I-42m(121) and cell parameters $a=5.427$ angstrom and $b=10.848$ angstrom. As shown in Figure 2, the XRD pattern confirm that in all cases the second stage of calcination provide an optimal way to obtain the crystalline phase.

![XRD pattern](attachment:image.png)

Figure 2. Structural characterization by XRD of CZTS materials.

The Figure 2 XRD is the pattern of representative CZTS system obtained by hydrothermal method in two reaction stages.

The electrical characterization by solid-state impedance spectroscopy shown in Figure 3, confirm a typical behavior of materials in terms of Nyquist and Bode plots.

The obtained impedance data took into account the different temperatures of synthesis of the material (independent variable), and the maximum values of the impedance modules of each test, Table 1, finding with them the material conductivity (inverse of the maximum impedance) Table 2, leaving as fixed effects the synthesis time and material ($\text{Cu}_2\text{ZnSnS}_4$). To these data were made a statistical analysis of variance, obtaining a favorable correlation factor as shown in the Table 3.

As $F_0>1$ the treatments provided (temperature levels) are actually the factor greatest influence on the dependent (electrical response) variable, also as $F_0>F$, the independent variable ($T$) of the experiment is 95% probability of success the most influential on the value of the dependent variable.
Table 1. Impedance spectroscopy (CZTS) to different temperatures.

| T C | Registry 1 | Registry 2 | Registry 3 | Registry 4 | Registry 5 |
|-----|------------|------------|------------|------------|------------|
| 220 | 5977.77    | 7080.79    | 7472.18    | 7325.91    | 7540.15    |
| 240 | 3610.41    | 4316.57    | 4750.21    | 4811.20    | 5112.52    |
| 260 | 1243.05    | 1552.35    | 2028.25    | 2296.49    | 2684.89    |

Table 2. CZTS conductivity material at different temperatures in °C.

| T C | Registry 1 | Registry 2 | Registry 3 | Registry 4 | Registry 5 |
|-----|------------|------------|------------|------------|------------|
| 220 | 1.67       | 1.41       | 1.34       | 1.36       | 1.33       |
| 240 | 2.77       | 2.32       | 2.11       | 2.08       | 1.96       |
| 260 | 8.04       | 6.44       | 4.93       | 4.35       | 3.72       |

4. The KK transform
The Kramers-Kronig relations are mathematical equations that describe the relationship between the real and imaginary parts of complex analytic functions (Defined functions on an open subset of the complex plane \( \mathbb{C} \) with values in \( \mathbb{C} \) and differential at each point, that further, they can be...
Table 3. Statistical analysis of the electrical conductivity of the material CZTS.

| Source of variation | Sum of squares | Degrees of freedom | mean squares | $F_0$ Value | P  |
|---------------------|---------------|--------------------|--------------|-------------|----|
| Temperature levels  | $4.65 \times 10^{-7}$ | 2                  | $2.32 \times 10^{-7}$ | 22.05       | < 0.01 |
| Error               | $1.26 \times 10^{-7}$ | 12                 | $1.05 \times 10^{-8}$ |             | F(0.05) = 4.47 |
|                     |               |                    |              | F(0.01) = 5.95 |
| Total               | $5.91 \times 10^{-7}$ | 14                 |              |             |    |

described by its Taylor series) in the complex upper half plane [4]. These relationships are used to calculate the real and imaginary parts of responses in physical systems in a linear, causal, estable process and finite impedance [5,6].

$$Z'(\omega) = Z'(\infty) + \frac{2}{\pi} \int_{0}^{\infty} \frac{xZ''(x) - \omega Z''(\omega)}{x^2 - \omega^2} dx$$

$$Z'(\omega) = Z'(0) + \frac{2\omega}{\pi} \int_{0}^{\infty} \left( \frac{\omega}{x} \right) \frac{Z''(x) - Z''(\omega)}{x^2 - \omega^2} dx$$

$$Z''(\omega) = -\frac{2\omega}{\pi} \int_{0}^{\infty} \frac{Z'(x) - Z'(\omega)}{x^2 - \omega^2} dx$$

$$\Phi(\omega) = \frac{2\omega}{\pi} \int_{0}^{\infty} \frac{\ln |Z(x)|}{x^2 - \omega^2} dx$$

Where $Z'(\omega)$ and $Z''(\omega)$ are the real and imaginary parts of the impedance at a given frequency; $\omega$ and $x$ are the angular frequencies; $Z'(x)$ and $Z''(x)$ are continuous functions that provide the real and imaginary parts of the impedance, respectively, in function of the angular frequency ($x$) with $0 < x < \infty$; $Z'(0)$ and $Z''(\infty)$ everyone, is the component real at zero and infinite frequency, that is to say, when $x \to 0$ and $x \to \infty$; $|Z(x)|$ is the module and $\Phi(\omega)$ It is the phase angle for the angular frequency $x = \omega$ [7]. well now, using Equations (3) to (6) It can transform the real part of the impedance in the imaginary part and viceversa. [8,9].

4.1. Testing process for data reliability

The appropriate procedure for use the KK and can validate the data, is calculate the imaginary part of the impedance from the values of the real part measured experimentally, in this case the Equation used is (5), the results obtained from this equation are compared with the results of the imaginary part experimentally measured, confirming the validity of the data. It also can find the real part of the impedance from the data of the imaginary part experimentally measured, in this case the Equation would be used (3). The process just mentioned have a difficulty, it is that you must first adjust to one or several polynomials experimental data of $Z'$ o $Z''$ with $\omega$, later replace in the corresponding equation KK and integrate numerically, however, there is another way to validate the data without having to perform the previously mentioned process, that, further, always satisfies equations KK, this method is known as measurement models, which they are used by general equivalent circuit. (Maxwell circuits or Voigt). One advantage is that it can be used in a general model for a wide variety of systems. The impedance components at a given frequency for parallel RC circuit are given by
\[ Z'(\omega_i) = R_1 + \sum_{k=2}^{M} \frac{R_k}{1 + (\omega_i \tau_k)^2} \]  

(7)

\[ Z''(\omega_i) = -\sum_{k=1}^{M} \frac{\omega_i R_k \tau_k}{1 + (\omega_i \tau_k)^2} \quad \text{con} \quad \tau_k = [\omega_k]^{-1} \]  

(8)

The procedure for calculating the components ‘transformed’, is as follows: for obtain the imaginary components from the real components, the experimental values of the real component \( Z' \), the angular frequency and the time constant \( \tau_k \) for each frequency in the Equation (7), are substituted and a system of linear equations is established for \( R_k \), which is solved to obtain the values of \( R_k \), later, these are substituted in the Equation (8) for obtain at the same time the imaginary components transformed \( (Z''(\text{trans})) \), these values \( (Z''(\text{trans})) \) are compared with the experimental data \( (Z'') \), through the imaginary residual calculus \( (\Delta'') \) for each freency.

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

(9)

5. Mathematical model for data conductivity of the CZTS material

Realized the analysis with the data described in Table 2, a mathematical model of the electrical conductivity of the material was adjusted, (inverse of the average of the maximum impedance) in function of the synthesis temperature, using the least squares method [10]. The model describes the electrical behavior of photovoltaic CZTS material in function of the temperature with good approximation as shown in Figure 4.

\[ \sigma(T) = 8.219 \times 10^{-3} - 7.667 \times 10^{-5} T + 1.812 \times 10^{-7} T^2 \]  

(10)

Figure 4. Curve fitted to the conductivity data of CZTS material at 220, 240 and 260°C.
6. Conclusions
The characterization of the material properties, by SEM and XRD techniques, allow to validate the obtention of a pure phase of Cu$_2$ZnSnS$_4$ material in terms of a two stage hydrothermal synthesis process. The electrical characterization of solid obtained at different synthesis temperatures confirm a semiconductor behavior in which the impedance response may be modelled by a fitted set of equations in terms of kramers-kronig equations, confirming that exist a dependence between synthesis temperatures and impedances responses in obtained solids. So, its clear that conductivity of CZTS materials with the characteristics and process described above, show a strong dependence with the synthesis temperature, according with nyquist and bode plots, which permit us to validate the impedance data and confirm the accuracy of the methodology with excellent approximations. Finally is clear that the implementation of Fourier transforms, can improve the model and interpret the dynamics associated with the system.

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