Hydrothermal synthesis of a photovoltaic material based on 
CuIn_{0.5}Ga_{0.5}Se_{2}

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Abstract. The present work report, the synthesis and characterization of the CuIn_{0.5}Ga_{0.5}Se_{2} system (abbreviated CIGS), by the implementation of a hydrothermal route, in order to obtain a solid with appropriate properties in terms of surface, morphological and texture properties for potential applications in the design of photovoltaic cells. The synthesis was carried out using the corresponding stoichiometric quantities (Cu:In:Ga:Se 1:0.5:0.5:2), which were mixed in a Teflon vessel under stirring conditions. The homogeneous solution was treated in a steel autoclave at 300°C for 72 hours at the end of which the resulting material was characterized by X-Ray Diffraction (XRD) and Rietveld refinement. The results of the structural characterization allowed to confirm the obtaining of a chalcopyrite type structure, with a I-42 d (122) structure and cell parameters a=0.570, b=0.570, c=1.140nm, α=90, β=90, γ=90° oriented along (1 0 4) facet, detecting the presence of a secondary phases, related with CuInSe and CuIn metallic selenides, derived from synthesis process. The structural refinement allowing to validate the obtaining of a nanometric crystalline material (10-20nm) for potential applications in field of photovoltaic technology.

1. Introduction

The current photovoltaic industry has found in ternary and quaternary materials derived from CuInSe_{2} (CIS) and CuIn_{0.5}Ga_{0.5}Se_{2} (CIGS) chalcopyrite compounds, promising materials for the effective conversion of solar energy, due to its semiconductor behaviour and band-gap value of approximately 1.45eV, with conversion levels around 19.2% [1-4]. These materials can be synthesized by a series of physical routes such as Physical Vapor Deposition (PVD), Chemical Vapor Deposition (CVD), Pulsed Laser Deposition (PLD) and other techniques related with the use of high vacuum conditions in which the stoichiometric control of elements is not the most effective or simple, reason why the obtaining of these compounds only is available under extreme reaction conditions [6]. Although the efficiency values in materials obtained by physical synthesis methods is around 21.7-22.6%, nowadays the use of chemical synthesis methods based on liquid solution reactions, get allow solids with a high degree of purity and provide an excellent composition control up to atomic or molecular level as in the case of sol-gel, controlled precipitation or solvothermal methodologies among others [5].

In the specific case of hydrothermal synthesis method, several advantages over other synthesis routes are possible, since is possible to generate a better dissolution of the used precursors under controlled conditions of reaction, which only depend of time and synthesis temperature as the main thermodynamic parameters with an optimal stoichiometric control [6,7]. As result of previous advantages related with the use of hydrothermal methodology for the production of advanced materials, the objective of current
work is focused on the obtaining of a \( \text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2 \) photovoltaic material, under 300°C and 72 reaction hours, with the aim to provide a simple methodology to development of photovoltaic materials at micro or nanometric scale for potential application in solar technology.

2. Experimental

The procedure used in this work to perform the synthesis of CIGS material start with the corresponding dissolution of the metal precursors of copper acetate \( \text{Cu(CH}_3\text{COO)}_2 \), indium nitrate \( \text{In(NO}_3)_3 \), gallium acetylacetonate \( \text{Ga(C}_5\text{H}_8\text{O}_2)_3 \) and metallic selenium \( \text{Se} \), all from Sigma-Aldrich. The reagent addition order was established in terms of the corresponding dissolution constants in a ratio \( (1:0.5:0.5:2) \). The adjust of the pH was performed with concentrated nitric acid around 1.0 until a homogeneous mixture was obtained. The solution was deposited in a Teflon vessel under stirring conditions (250rpm) and placed in a steel autoclave in which the system was sealed and held under a temperature of 300°C for 72 hours. At the end of the process, the system was cool to room temperature, then a green solid precipitate was recollected and washed with absolute ethanol, in order to remove the remnant impurities. The solid was dried at 90°C for 6 hours in an electric oven and grounded in an agate mortar for characterization process. The structural characterization of material was performed by X-ray diffraction in a PANalytical X’Pert PRO-MPD equipment, using a Pixel detector between 10° and 90°, with a Cu Ka source of 1.54Å. The corresponding refinement was performed by the Rietveld routine and the GSAS software in order to analyse the crystalline structure of the material and its main crystalline parameters.

3. Results and discussion

The X-ray diffraction pattern of CIGS obtained material is shown in Figure 1, in which is possible to observe the main signal indexed along \((1\ 0\ 4)\) facet.

![Figure 1. XRD experimental and theoretical pattern of the \( \text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2 \) material, obtained at 300°C for 72 hours.](image)

The detailed analysis of XRD results, confirm the presence of secondary phases of \( \text{CuInSe} (*) \) and \( \text{CuSe} (#) \), due to reaction conditions. The crystalline structure related with the pure phase of \( \text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2 \) is around 85.7%, while the 14.3% is related with the presence of secondary phases. According to E. Romero et al. [10], the effect of an acid medium could propitiate the formation of \( \text{CuInSe} \) phase due to stability related with these elements contrary to gadolinium effect, that preserves as isolated oxide species in form of \( \text{Ga}_2\text{O}_3 \) [11]. The main diffraction signal of experimental CIGS material is located along \((1\ 0\ 4)\) facet, indicating a structural variation with respect to theoretical value of \((1\ 1\ 2)\), this effect is provoked by the gallium cation and its composition level in obtained material, taking into account that the refined \( \text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2 \) structure only could be compared with the
CuIn$_{0.7}$Ga$_{0.3}$Se$_2$ reference structure, generating a shift of the signal towards the left and promoted by the change in the atomic radius of the Gallium in the structure in accordance with previous reports [1,15].

The analysis of the 14.3% of impurities shown in Table 1, by means the Rietveld refinement permit to corroborate the presence of another compounds bonded in obtained CIGS material as follows:

| Compound                        | Percentage |
|---------------------------------|------------|
| CuIn$_{0.5}$Ga$_{0.5}$Se$_2$    | 85.7%      |
| NaNO$_3$                        | 6.6%       |
| Cu$_2$O                         | 1.1%       |
| Cu$_6$Ga$_{17}$O$_{68}$         | 1.2%       |
| Na$_2$SeO$_3$                   | 3.1%       |
| InO$_3$                         | 0.8%       |
| CuInSe$_2$                      | 1.4%       |

The above results observed in the material synthesis affect the performance of the reaction since the undesirable products can affect the electrical performance of material, although some authors [12,14], has been established that the necessity of a second thermal stage could reduce the presence of this secondary phases to increase the presence of a pure crystalline phase of CIGS, its employ in current work was not considered due to necessity of know the synthesis methodology to future works related with the obtaining of selenides. In this context, must to be considered that the hydrothermal synthesis pathway need to be tested in alkaline medium because the effects of mass transfer can improve getting a more effective crystalline growth of the desired material in accordance with previous works [7,13].

The analysed structure using the X´Pert High Score software in the ICDD databases and based on the 85.7% of the obtained material, permit to confirm the presence of a chalcopyrite-type structure, corresponding with a $I4_2d$ (1 2 2) structure with cell parameters $a=0.570$, $b=0.570$, $c=1.140$nm, $\alpha=90$, $\beta=90$, $\gamma=90^\circ$ oriented along (1 0 4) facet. With this data was possible to obtain the corresponding unit cell and expected X-ray diffraction pattern based on experimental data as shown in Figure 2 [9].

![Figure 2. Unit cell and expected X-ray diffraction pattern of CuIn$_{0.5}$Ga$_{0.5}$Se$_2$ material.](image)

The structural data obtained by ELMIX software and Rietveld refinement is shown in Table 2, using the GSAS software, permit to validate the obtaining of a prevalent crystalline phase of CuIn$_{0.5}$Ga$_{0.5}$Se$_2$ material with its main expected diffraction signals, in accordance with experimental pattern for potential applications in field of photovoltaic cells.
Table 2. Main structural parameters obtained for CuIn$_{0.5}$Ga$_{0.5}$Se$_2$ material by ELMIX and GSAS software.

| Crystal system | CuIn$_{0.5}$Ga$_{0.5}$Se$_2$ | Space group | I -42d (1 2 2) | Cell Volume (Å$^3$) | 370.39 |
|---------------|-----------------------------|-------------|----------------|---------------------|--------|
| Lattice parameters | | | | | |
| a (Å) | 5.7000 | α | 90.0000 |
| b (Å) | 5.7000 | β | 90.0000 |
| c (Å) | 11.4000 | γ | 90.0000 |

| Atomic positions | Cu | In | Ga | Se |
|-----------------|----|----|----|----|
| X               | 0.00000 | 0.00000 | 0.00000 | 0.24260 |
| Y               | 0.00000 | 0.00000 | 0.00000 | 0.25000 |
| Z               | 0.50000 | 0.00000 | 0.00000 | 0.12500 |

4. Conclusions

By means of the hydrothermal synthesis route obtains of a CuIn$_{0.5}$Ga$_{0.5}$Se$_2$ material is performed, with a purity level around 85.7% with presence of a secondary phases, which could be reduced by the implementation of a second thermal stage or development of a longer reaction time. The X-ray diffraction data and the Rietveld refinement allows to confirm the obtaining of a chalcogenide phase for use as photovoltaic material in solar cell technology with the use of a scalable and easy procedure without necessity of extreme vacuum conditions or sophisticated equipment.

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