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Review

XRD and TEM characterizations of the mechanically alloyed $CuIn_{0.5}Ga_{0.5}Se_2$ powders

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ABSTRACT

The $CuIn_{0.5}Ga_{0.5}Se_2$ (CIGS) nanocrystalline powders were prepared by mechanical alloying method. Effect of various milling times and higher milling speed on the structure of CIGS nanoparticles was investigated by X-ray diffraction measurements. The Rietveld method was used to refine the XRD data using the MAUD program. Refinement process reveals that the main phase of the CIGS powders milled for different milling times is of chalcopyrite structure. Milling time dependence of the unit-cell parameters and crystallite size has also been reported. The TEM observations demonstrated that the size of agglomerated CIGS powder is about 140 nm. The EDAX analysis of various grains of the milled powder shows that the compositions vary from one grain to another. However, the global composition was found slightly copper rich.

Contents

1. Introduction

The quaternary semiconductors $Cu(In_{1-x}Ga_x)Se_2$ (CIGS) are important materials for the fabrication of high efficiency solar cells [1]. These semiconductors crystallize in the tetragonal chalcopyrite structure. The latter derives directly from the cubic zinc blend lattice, but with a tetragonal deformation ($\eta = c/2a$) and anion displacement (u) [2]. The technological importance of these compounds as absorber in thin film solar cells is due to their high optical properties. One of the special qualities of CIGS materials is its variable band gap. It increases from 1.02 to 1.66 eV by increasing the Ga/(Ga + In) ratio from 0 to 1 [3]. The energy conversion efficiency of these materials-based solar cells has reached 19.5% (692 mV, 35.2 mA/cm^2, FF 79.9%) at NREL [4]. However, the laboratory scale efficiency is still lower than that of the expected theoretical calculation efficiency (30%) [5]. In the last years, researches tried to use the semiconductors nanocrystals in the solar cells technology. They have demonstrated that the performance of photovoltaic cells may be improved by using nanotechnology during the materials synthesis and device fabrication [6]. For this reason, the CIGS nanoparticles have been studied by several authors. For instance, Chun et al. [7] reported that the spherical CIGS nanoparticles can be obtained by solvothermal route. Ahn et al. [8] investigated the effect of heat treatment in nitrogen atmosphere on the properties of CIGS nanoparticles prepared by a low temperature colloidal route.

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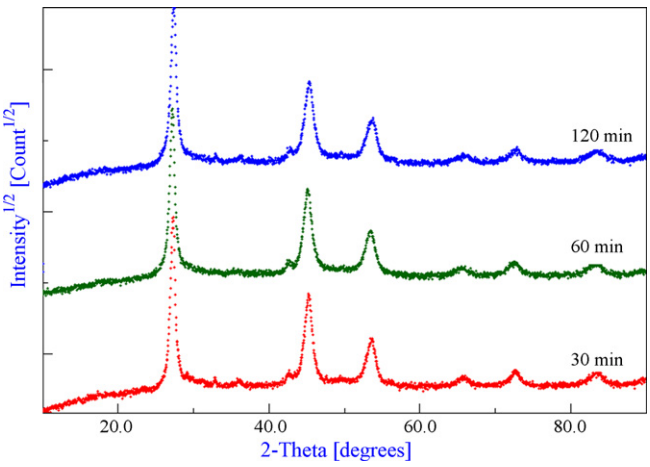

Fig. 1. X-ray diffraction patterns of the $CuIn_{0.5}Ga_{0.5}Se_2$ powders prepared at the milling time of 30, 60 and 120 min.

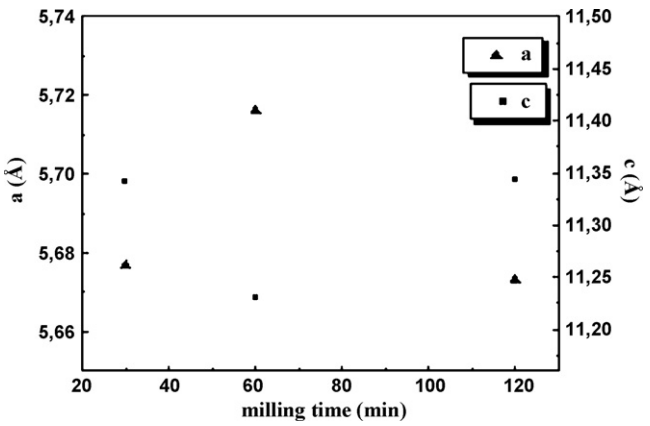

Fig. 3. Effect of milling time on cell parameters.

In this work, we presented a successfully synthesis of the high quality chalcopyrite type CIGS nanoparticles by mechanical alloying (MA) process. The crystal structure of the prepared samples was studied by X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM). The Rietveld method was also used to refine the XRD data using the MAUD program.

2. Experimental procedure

In order to prepare the alloys required for these studies, a mixture of appropriate amounts of Cu, In, Ga and Se with a high purity of 99.999 (Balzers) were weighted to get a stoichiometric composition of $CuIn_{0.5}Ga_{0.5}Se_2$, then ball milled in a vial with balls. Both the vials (45 ml in volume) were in stainless steel. The powders were sealed in the vials under a pure argon atmosphere. The mechanical alloying procedure was done in a planetary ball milling set (Pulvérisette 7) at room temperature. The Powder/balls weight ratio was 1/30. The rotational speed (disc rotational velocity) was fixed at 300 tr/mn and the milling time was fixed at 30, 60 and 120 min.

X-ray diffraction data were collected by a D501 SIEMENS diffractometer with Cu-K_α radiation (λ_α = 1.542056 Å) at room temperature. The samples were scanned from 10 to 90° 2θ with a step size of 0.04°. We also used the MAUD procedure [9] for microstructure XRD analysis, based on RietVeld [10] method combined with Fourier analysis, which is well adapted for broadened diffraction peaks. This version permits a more detailed analysis of the material since it can take in account the anisotropy of shape of diffraction coherent domains and of micro-deformations [11]. The RietVeld's method was successfully applied for determination of the quantitative phase abundances of the mixture powders. There is a simple relationship between the determined individual scale factor, considering all refined structural parameters of individual and multi phases of the sample, and the phase concentration in the mixture. The weight fraction for each phase was obtained from the refinement relation as adopted earlier [12]. TEM micrographs were obtained with

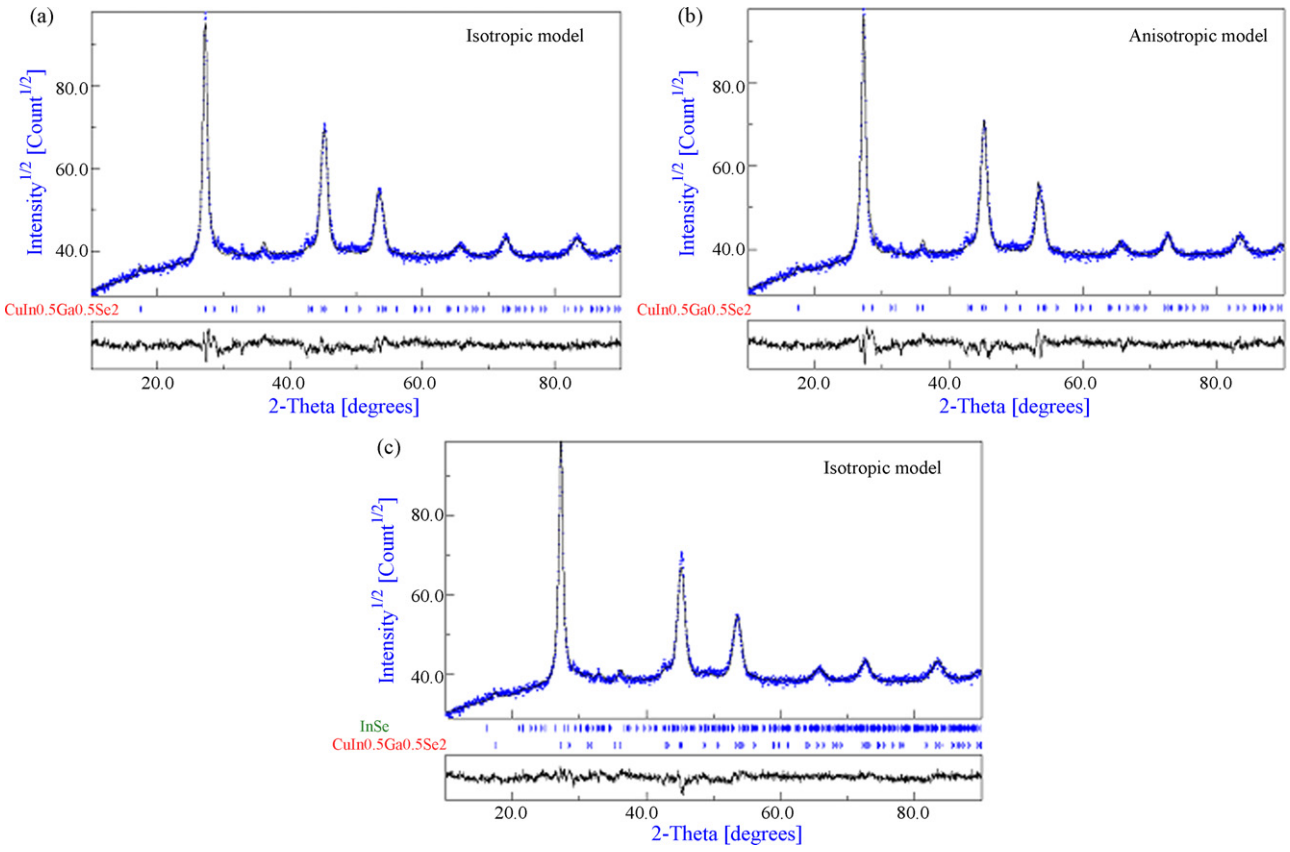

Fig. 2. Maud refinement of the XRD data of the $CuIn_{0.5}Ga_{0.5}Se_2$ powders milled for 30 min (a) and (b) model with 1 component and (c) with 2 components.

a JEOL 2010 CX transmission electron microscope operating with beam energy of 200 keV. The specimens for TEM measurement were prepared by placing the milled powder (dispersed in ethanol solution) in ultrasonic bath for 5 min then depositing a drop of solution on a carbon coated copper grid. Scanning transmission electron microscope (STEM) analysis was also carried out to quantify the concentrations of the constituents.

3. Results and discussion

3.1. XRD analysis

The main purpose of this work was to obtain $CuIn_{0.5}Ga_{0.5}Se_2$ nanoparticles by a simple process such as mechanosynthesis. This process is a dry milling technique in which elemental material mixtures are repeatedly welded, fractured, and rewelded in a controlled atmosphere, under a highly energetic ball charge, to prepare $CuIn_{0.5}Ga_{0.5}Se_2$ powders at various milling times. Fig. 1 shows the evolution of the X-rays diffractograms as a function of milling time. From these patterns, the $CuIn_{0.5}Ga_{0.5}Se_2$ phase formation occurs after 30 min of milling. As milling time progresses (60, 120 min), no phase change has been detected. We can say that the phase formation is done very quickly, and increase in the milling duration leads to homogenization.

The diffraction spectra accompanied by refinement results for $CuIn_{0.5}Ga_{0.5}Se_2$ powders milled for 30 min are illustrated in Fig. 2. In the first stage of refinement, X-ray spectra of $CuIn_{0.5}Ga_{0.5}Se_2$ are presented together with the calculated one, when we explored the isotropic and anisotropic model as a microstructure model (Fig. 2(a) and (b)). A good overlapping of the experimental (dots) and calculated (full line) peaks have been observed and no difference between isotropic and anisotropic model was revealed. In the second stage, the X-ray diffraction spectrum of $CuIn_{0.5}Ga_{0.5}Se_2$ is fitted with combination of two phases (Fig. 2(c)). It is clear that the best fit is obtained when we introduce two components using isotropic model. The evolution of cell parameters (a and c) with the milling periods is presented in Fig. 3. It is noticed that the cell volume is constant. This confirmed the homogeneity of the powder after 30 min of milling.

Table 1
Quantitative analysis of samples.

Milling time	Crystallite size (nm)	Phases (%)	
		$CuIn_{0.5}Ga_{0.5}Se_2$	InSe
30 min	20.2	90	10
60 min	16.4	95	5
120 min	14.5	92	8

Table 2
Atomic position of elements.

Atom	Occupancy	*x*	*y*	*z*	*B* factor
Cu	1.113	0	0	0	1.543
In/Ga	0.607	0	0	1/2	0.624
Se	0.83	0.22	1/4	1/8	1.898

The quantitative analysis obtained by MAUD program is given in Table 1. No remarkable effect of milling time on crystallite size has been observed. The final values reached after the different milling times are almost the same (16.4 ± 0.2). On the basis of the above XRD results, the complete mixing of elemental Cu, In, Ga and Se materials leads to the formation of $CuIn_{0.5}Ga_{0.5}Se_2$ phase after 30 min of milling. Nevertheless, the best refinement of XRD patterns is achieved when we introduced an additional binary phase (InSe). This phase appears in the milled powder at all periods of milling according to refinement results with lower proportions less than 10%.

Table 2 presents the atomic position, occupation factor and isotropic thermal parameter (*B*) of elements of the $CuInGaSe_2$ phase. These values agree very well with those of Refs. [13,14],

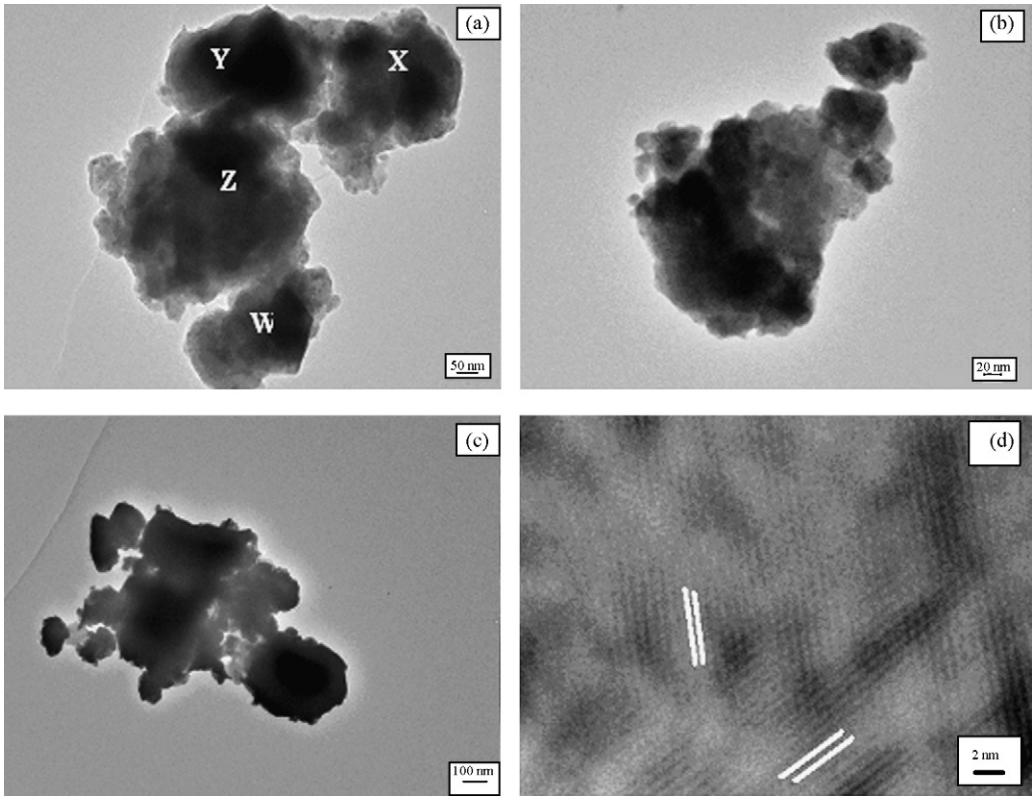

Fig. 4. TEM images of 4 different grains of $CuIn_{0.5}Ga_{0.5}Se_2$ powder milled for 120 min.

Table 3

Grain	[Cu] at.%	[In] at.%	[Ga] at.%	[Se] at.%	[Cu] ([In] + [Ga])	[Ga] ([In] + [Ga])
X	30.6	15.4	11.7	42.6	1.13	0.43
Y	22.3	38.5	5.3	33.9	0.51	0.12
Z	25.5	17.5	17.0	40.0	0.74	0.49
W	37.3	5.2	3.7	53.8	4.19	0.41

where they reported anion position values of 0.2232 and 0.2271 respectively.

3.2. MET observations

Detailed TEM observations of three different grains of the milled $CuIn_{0.5}Ga_{0.5}Se_2$ powder for 120 min are presented in Fig. 4(a)–(c). It observed that powder grain is composed of large agglomerate states of many particles with average grain size of 140 nm. In Fig. 4(d) we present a higher-magnification image of another grain of the milled powder. The clear lattice fringes confirm that the nanoparticle powder is crystalline in nature. As well as the figure reveals two directions of atomic arrangement. The calculated distances between two successively fringes are 1.95 and 3.25 Å, corresponding to the (2 0 4) and (1 1 2) planes of the CIGS chalcopyrite structure respectively.

The chemical composition of the constituents in the different regions, indicated by the letters (X, Y, Z and W) in Fig. 4 (a), are collected in Table 3. It is found that the elemental composition differs from one grain to another. Some grains (X and W) are copper rich which consequently results in a deficiency of selenium in grain X, indium and gallium in grain W. This may be attributed to the use of copper grid in TEM analysis. As well as, a remarkable excess of indium has been detected in grain Y. The global composition (Cu: 30.31 at.%, In: 16.12 at.%, Ga: 10.96 at.% and Se: 42.43 at.%) corresponds to the chemical formula: $Cu_{1.21}In_{0.64}Ga_{0.43}Se_{1.69}$ revealing a small deviation from the ideal composition.

4. Conclusion

In this paper, the $CuIn_{0.5}Ga_{0.5}Se_2$ nanoparticle powders have been successfully synthesized by mechanical alloying method. The refinement process of X-ray diffraction results confirms the existence of chalcopyrite structure as the main phase and reveals that the formation of $CuIn_{0.5}Ga_{0.5}Se_2$ phase occurs at short milling time (30 min) with high milling speed. The average grain size obtained from TEM observations is found of about 140 nm. However, inhomogeneous distribution of elemental constituents has been detected in individual grain.

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