

Synthesis and Characterization of Copper Indium Gallium Diselenide (CIGS) Nano-Crystalline Powder using SPEX Mill

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The $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS) ($x = 0.3$) nanocrystalline powder was synthesized by reacting to its constituent elements *i.e.* Copper, Indium, Gallium, and Selenium in a SPEX mill. The SPEX mill is a high-energy mill where the reaction between constituent elements takes place in solid-state to form a nanocrystalline compound powder. SPEX mill consists of tungsten lined hardened steel vials and tungsten carbide balls are used as grinding media. Three different size grinding media was used with ball to charge ratio of 10 : 1. The optimization of milling time was studied to obtain CIGS nanocrystalline powder using SPEX mill. The phase analysis by X-ray diffraction shows the formation chalcopyrite (tetragonal) structure of CIGS after 4 h of high-energy milling with an average crystallite size of 10-13 nm. Raman spectra peak at 174 cm^{-1} confirms the formation of the CIGS phase. The compositional analysis by EDAX confirms the formation of the stoichiometric composition of CIGS. This study reveals that it is possible to synthesize CIGS nanocrystalline powder using SPEX mill.

Keywords: CIGS, Nanocrystalline powder, SPEX mill, EDAX.

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1. INTRODUCTION

CIGS based solar cell belonging to the I-III-VI (I = Cu, III = (In, Ga), and VI = Se) family. This chalcopyrite semiconductor is a promising material for the fabrication of thin-film solar cells because of its high absorption coefficient ($\alpha = 10^5\text{ cm}^{-1}$), a suitable direct bandgap ($E_g = 1.15\text{ eV}$) and long-term stability. CIGS compound has been widely adopted by researchers and it has achieved 22.9 % solar efficiency on 1 cm^2 area by Solar Frontier [1]. Co-evaporation, Sputtering, Metal-organic chemical vapor deposition (MOCVD), Molecular Beam Epitaxy (MBE), inkjet printing, etc. deposition techniques were used by researchers to develop CIGS based solar cells on different types of the substrate such as soda-lime glass, polyimide foil and metallic foil [2, 3]. Mechanochemical route using various types of high-energy mill produces a large quantity of nanocrystalline powder in a short time by physical or/and chemical changes occurring during the process. In the mechanochemical route, the effect of process parameters like milling time and milling speed on the formation of the chalcopyrite structure of CIGS was investigated [4]. The device properties of CIGS based solar cells are critically influenced by the structure and stoichiometric composition of CIGS.

The present research work was carried out to synthesize stoichiometric $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS) ($x = 0.3$) nanocrystalline compound powder by high-energy milling process using SPEX mill. The phase analysis of the high-energy milled CIGS powder was carried out using X-ray diffraction analysis (XRD). The morphology of the powder was studied using a Scanning Electron Microscope (SEM) and the compositional analysis by Energy Dispersive X-ray Spectroscopy (EDS). Raman

spectroscopy was carried out for the structural characterization of CIGS powder.

2. EXPERIMENTAL DETAILS

2.1 Raw Material and Synthesis of CIGS Compound Powder

The high purity elemental powder of Copper, granules of Indium, Gallium, and Selenium was used as starting material. The stoichiometric amount of the powders were taken to obtain Cu:In:Ga:Se of 1:0.7:0.3:2 ratio.

The SPEX mill used for high-energy milling has a capacity of handling $10 \pm 2\text{ g}$ of the powder at a time. It has hardened steel vials lined with tungsten carbide. The grinding media used was tungsten carbide balls of three different diameters *i.e.* $\Phi 5.732\text{ mm}$, $\Phi 10\text{ mm}$, and $\Phi 10.62\text{ mm}$ to maximize the milling efficiency. Prior to milling the vials and grinding media were thoroughly cleaned using acetone in an ultrasonic machine for 10 min. The ball to charge ratio was 10:1.

The stoichiometric ratio (Cu:In:Ga:Se of 1:0.7:0.3:2) of starting powders was hand-mixed for half an hour and then fed into vials. Argon gas was purged in the vials to prevent oxidation of powder during milling. After argon purging the vials were closed and fitted in a frame of SPEX mill. The high-energy milling was carried out at 1200 rpm.

The milled powder was characterized at a regular interval of 1 h during the milling process by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray spectroscopy (EDS) and Raman Spectroscopy. The milled powder was character-

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ized for phase analysis using X-ray diffraction (XRD), Bruker AXS, D8 advance diffractometer makes, Cu-K α radiation with wavelength 1.541 Å, at 40 kV and 40 mA. Measurements were made for 2θ values over 20°-80° with an increment angle of 0.05°. The morphology of the milled powder was studied using SEM Hitachi S-3400N with a resolution of 3.0 nm High Vacuum Mode and 4.0 nm Variable Pressure Mode. The compositional analysis of milled powder was carried out using the Bruker EDS System. The XFlash silicon drift detector (SDD) for energy dispersive spectrometry combines high count-rates up to 275,000 CPS. It uses Quantax software for mapping signals. Structural analysis was carried out using micro-Raman model STR 500 with Nd-YAG laser as a source with 532 nm wavelength and Peltier cooled CCD detector equipped with a Nikon microscope.

3. RESULTS AND DISCUSSIONS

3.1 X-ray Diffraction Analysis

The multiple X-ray diffraction patterns of the CIGS powder milled for 1, 2, 3 and 4 h are shown in Fig. 1. The preferred orientation of the CIGS milled powder was observed with diffraction peaks for crystallographic planes (112), (211), (220) / (204), (312), (400), and (332) / (316). The inter-planar spacing 'd' values are matching with the standard JCPDS card 35-1102. This confirms the formation of the chalcopyrite (tetragonal) structure of CIGS after 4 h of high-energy milling.

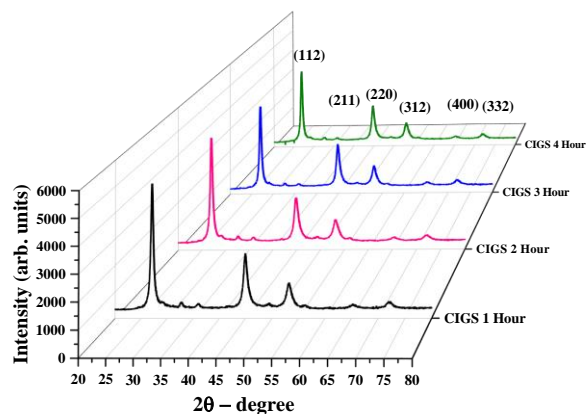


Fig. 1 – X-ray diffraction profile of CIGS milled powder after 1, 2, 3 and 4 h of milling

It is observed that with increase in milling time from 1 h to 4 h, the intensity of X-ray diffraction peaks decreases and the broadening of peak takes place. This is due to the formation of the nanocrystalline CIGS phase with milling. During milling flattening, fracturing and welding of powder particles lead to the formation of the nanocrystalline phase [5, 6]. The values of FWHM (Full Width Half Maximum) of diffraction peak is related to the average crystallite size of the milled powder. Using the Scherrer formula crystallite size 'D' was calculated [7]. Table 1 gives the crystallite size of milled CIGS powder for 2, 3 and 4 h. The average crystallite size ranges between 10 nm and 13 nm.

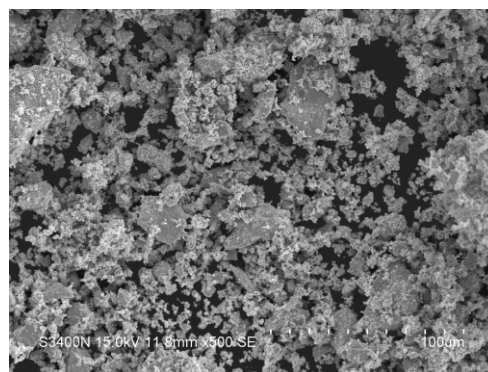
Table 1 – Crystallite size of CIGS milled powder at different milling time

Milling time (h)	2θ (deg.)	d-spacing (nm)	FWHM (radian)	Crystallite Size (D) (nm)	Average Crystallite Size (nm)
2	26.969	0.330	0.0091	17.478	13
	44.854	0.202	0.0153	10.936	
	53.095	0.172	0.0157	11.005	
3	26.971	0.333	0.0095	16.743	10
	44.795	0.202	0.0158	10.590	
	53.019	0.172	0.0191	9.044	
4	27.071	0.329	0.0094	16.920	12
	44.917	0.202	0.0153	10.936	
	53.182	0.172	0.0190	9.101	

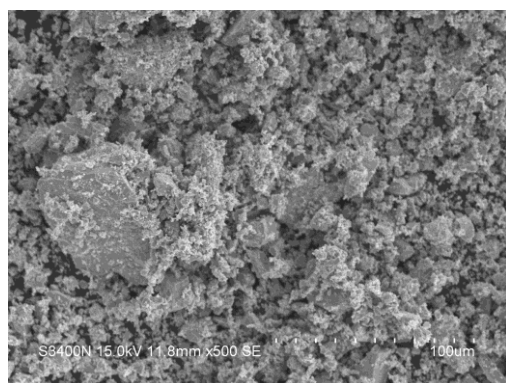
The lattice parameter of milled powders was ' a ' = 5.71 ± 0.02 Å and ' c ' = 11.430 ± 0.02 Å which matches with literature values and indicates the formation of the tetragonal structure of CIGS milled powder [8].

3.2 Scanning Electron Microscopy (SEM)

The as-blended powder prior to milling and the 4 h milled CIGS powder morphology is shown in Fig. 2a and Fig. 2b, respectively. Fig. 2a shows that the copper powder particles are spongy in nature and have a high tendency to agglomeration whereas Selenium has plate-like morphology. It is difficult to observe the presence of Gallium and Indium in SEM due to their small quantity. Fig. 2b shows that milling leads to diffusion of different powder particles at the atomic level and it is difficult to distinguish individual powder particles after 4 h of milling.



a



b

Fig. 2 – Scanning Electron Micrograph of as-blended (a) and 4 h milled (b) CIGS powder

3.3 Raman Spectroscopy

The structural change occurring during milling was also confirmed by Raman Spectroscopy. Fig. 3 shows the Raman spectra of CIGS milled powder after 4 h of milling. The Raman spectra were recorded using an excitation wavelength of 532 nm. In the Raman spectra, the intense peak at 174 cm^{-1} indicates A1 mode for $\text{A}^{\text{I}}\text{B}^{\text{III}}\text{C}^{\text{VI}}$ chalcopyrite compound [9, 10]. Hence, it confirms the formation of CIGS chalcopyrite structure after 4 h of high-energy milling.

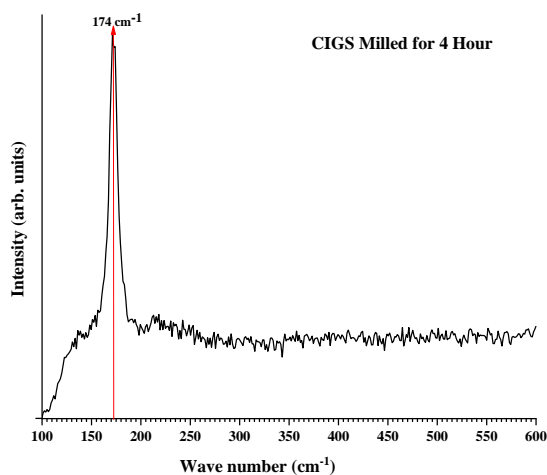


Fig. 3 – Raman Spectra of CIGS milled powder after 4 h of milling

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3.1 Energy Dispersive X-ray Spectroscopy (EDS)

Fig. 4 shows the EDS pattern of CIGS milled powder after 4 h of milling. It shows the presence of Copper, Indium, Gallium, and Selenium elements only. EDAX analysis gives the values of $\text{Cu}/(\text{In} + \text{Ga}) = 1.12$, $\text{Ga}/(\text{In} + \text{Ga}) = 0.31$ and $\text{Se}/(\text{Cu} + \text{In} + \text{Ga}) = 1.005$ [11, 12].

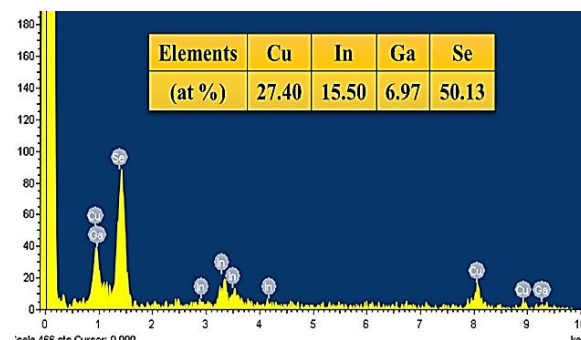


Fig. 4 – The EDS pattern of the synthesized CIGS powder after 4 h of milling

4. CONCLUSIONS

High-energy milling of elemental Copper, Indium, Gallium, and Selenium in SPEX mill leads to solid-state reaction between constituent powder particles, which in turn gives the formation of Copper Indium Gallium Di-Selenide (CIGS) nanocrystalline powder. X-ray Diffraction analysis of milled powder indicates that after 4 h of high-energy milling a single-phase CIGS phase having a tetragonal structure with lattice parameter ' a ' = $5.71 \pm 0.02\text{ \AA}$ and ' c ' = $11.430 \pm 0.02\text{ \AA}$ was formed. The average crystallite size of nanocrystalline CIGS powder was 12 nm. Raman spectroscopy confirms the formation of chalcopyrite CIGS structure. The Energy-dispersive X-ray Spectroscopy (EDS) of 4 h milled CIGS powder confirms the formation of compound of $\text{Cu}_1\text{In}_x\text{Ga}_{(1-x)}\text{Se}_2$ (CIGS), where $x = 0.7$.

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