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$CuSbSe_2$ as a Promising Earth-Abundant Photovoltaic Absorber Material: Synthesis and Structural Properties

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In this work Chalcostibite $CuSbSe_2$, a promising non-toxic and earth-abundant absorber was synthesized using a mechanical alloying (MA) or ball milling process and studied the structural and phase evolution. The collected sample has been successfully characterized by XRD, Raman, FE-SEM and EDS. From the XRD results analysis, it was found that $CuSbSe_2$ single phase was formed in 8 hours of milling. Raman shifts of 198, 222 and 259cm^{-1} for as-milled $CuSbSe_2$ had been recorded. EDS exhibits three strong peaks confirming the purity of the sample by detecting only Cu, Sb and Se element respectively. The main purpose of this research is to provide information on direct synthesis of single phase synthesis of chalcostibite $CuSbSe_2$ single phase at room temperature by wet ball milling process, which has been successfully prepared in a short duration for the first time.

Keywords: Ball milling, $CuSbSe_2$, X-ray diffraction, Raman scattering.

1. Introduction

Ternary $CuSbSe_2$ Chalcostibite is an emerging solar absorber material for thin film solar cells due to its low band gap (1-1.5 ev) and high absorption coefficient ~ 10^4 cm^{-1}. Currently, some of the most studied thin film solar cell technologies are $Cu(In,Ga)Se_2$, CdTe, CIGS and the hybrid organic-inorganic perovskites non-stabilized[1]. The solar cells of CdTe and CIGS have shown demerits in terms of high cost of Indium and Gallium in CIGS and toxicity of cadmium in CdTe which are both ineluctable factors that shorten their commercial quantity of CdTe and CIGS absorber materials [2]. However, the scarcity of materials and the elemental toxicity in some of them may limit their environmental benefits. Thus, emerging photovoltaic (PV) absorber materials with potential low toxicity and earth-abundant advantages are of gaining more attention, including CU_2O [3], Sb_2Se_3 [4], Cu_3N [5], SnS [6], [7], $ZnSnN_2$ [8], $BiFeO_3$ [9], $CuTaN_2$ [10] and $Cu_2ZnSn(S,Se)_4$ (CZTSSe) [11]. The ternary $CuSbSe_2$ material, which belongs to orthorhombic system and space group Pnma, has a 2-D double-layered structure with six-membered heterorings of Sb_2CuSe_2 and $SbCu_2Se_3$, where Cu atom has a one-sided tetrahedral coordination with four Se atoms and Sb atom is coordinated to three Se atoms to form a $SbSe_3$ trigonal pyramidal geometry [12]. It has a bandgap of 1.05 eV and displays potential applications in infrared detectors, photovoltaic devices and solar absorbers. [13], [14], Moreover, it also has an intrinsically very low thermal conductivity and seems to be a potential thermoelectric material for middle temperature application. However, no consideration has been paid to its medium temperature thermoelectric performance yet [15], [16]. Infact, in compared with several popular thermoelectric materials in medium temperature range, such as PbTe, [17], filled skutterudites [18] and In_4Se_3 [19]. $CuSbSe_2$ constituent element are very cheap, and it will be more competitive if its thermoelectric performance is comparable to those conventional materials. Currently, due to the poor electrical properties, the thermoelectric performance of $CuSbSe_2$ is still very poor; In addition, it is mainly fabricated by vacuum melting, which acquires high temperature and long-time annealing [15], [16], the time and energy-consuming process is also of much concern to be solved.

Nowadays, mechanical alloying (MA) is being considered for the synthesis of intermetallic compound and several thermoelectric compounds due to its versatile nature. Firstly, ball milling leads to particle size reduction in combination with homogeneous mixing. The energy imparted from milling media enables self-propagating chemical reactions, which leads to the formation of new phase that is different from the starting phases.

In this work, mechanical alloying (MA), was employed to synthesize chalcostibite $CuSbSe_2$ compound which has been successfully prepared in a short duration for the first time. The main purpose of this research is to provide information on direct synthesis of single phase $CuSbSe_2$ at room temperature by wet ball milling process.

2. Experimental Procedure

The elemental powder of Cu, Sb and Se were taken in stoichiometry ratio of 1:1:2. Elemental powders of Cu (99.99%), Sb (99.99%) and Se (99.99%) were weighed and mixed, and then subjected to MA in a planetary ball mill. The mechanical alloying process was performed at a speed of 500 rpm and toluene was added as process control agent using stainless vials and balls. The balls to powders weight ratio was kept at 15:1. The sample was milled for 8 hours, during the process, some powders were extracted for characterization from the vial at a certain interval to study the phase evolution. The mechanically alloyed powders were consolidated by hot-pressing at 673K for 1h under a pressure of 120 MPa. The direction of rotation was reversed after every 2 hours of the run. The $CuSbSe_2$ phase formation was detected by high-resolution X-ray diffraction (X-pert pro diffractometer) Cu Kα radiation (λ=0.15418nm), Raman scattering spectroscope (Raman Microscope) with an Olympus microscope equipped with a 100X magnification lens and in the backscattering configuration. The excitation source was a green Argon ion laser operated at 532 nm and 220 mW output powers. The morphology and the elemental composition of the samples were examined by Field Emission Scanning Electron Microscope (FET Quanta USA) operated at 30 kV at a magnification of 10,000X. The Energy Dispersive X-ray analysis (EDAX) were recorded in the binding energy region of 0 to 16 KeV.

3. Results and Discussions

XRD measurements were done on $CuSbSe_2$ powder samples collected during different stages of the synthesis. Figure 1 shows the XRD patterns of the as-milled $CuSbSe_2$ by wet milling. It can be seen from the figure that at 2 hours of milling, $CuSbSe_2$ started forming with $CuSe_2$ and CuSe have been detected being the main phases. At 4 hours of milling both peaks belonging to $CuSe_2$ and CuSe increased in intensity as compared to those milled for 2 hour. After prolonging the milling time to 6 hours, the aimed ternary compound $CuSbSe_2$ appears along with the gradual disappearance of the "transition phase" Cu_3SbSe_4. When the milling time is further prolonged to 8 hours, no obvious change in the XRD pattern can be found. It can be concluded that the formation steps for the ternary chalcostibite compound $CuSbSe_2$ are as follows: In the initial stage of MA, the reaction between Cu and Se results in the formation of binary compounds (CuSe and Cu_2Se); with increasing the milling time, the refined Sb powder is gradually involved in the reaction with Cu and Se to form the ternary chalcostibite compound Cu_3SbSe_4 ($Cu_{1.5}Sb_{0.5}Se_2$) and ultimately $CuSbSe_2$ after a complete consumption of the Sb component. During the MA process, Cu_3SbSe_4 forms in the middle process and then evolves to the targeted $CuSbSe_2$ compound as a "transition phase". Similar process was also reported in some other ternary semiconductors [20]. All the peaks in the powder pattern were indexed with reference to the available XRD pattern for $CuSbSe_2$ (ICDD No. 04-008-2357).

The crystallite size was calculated using equation,

$$D = \frac{0.9\times\lambda}{\beta\times\cos\theta} \quad \text{..... (1)}$$

Where D is the crystallite size, λ is the wavelength of the radiation, β is the FWHM in radians and θ is the Bragg's angle.

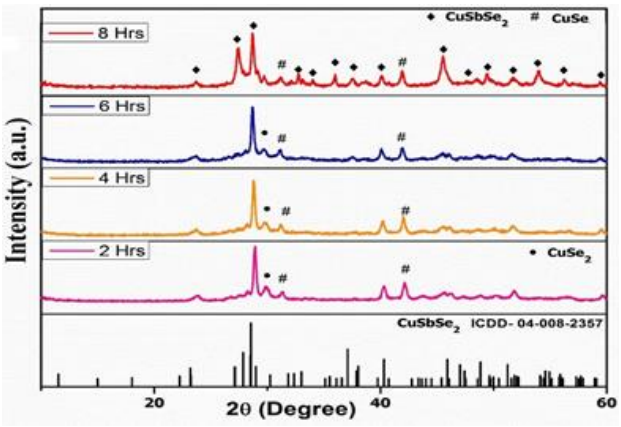

Fig. 1: Typical XRD pattern for as-milled $CuSbSe_2$

Further analysis for phase formation in the as-milled $CuSbSe_2$ was done by Raman spectroscopy studies. Raman spectroscopy is a non-destructive characterization technique with minimal sample requirement. The peak positions or Raman shift in the collected spectra gives information about the corresponding phase, whereas the shape of the peak and intensity indicates crystalline nature of the sample. Raman spectrum of the wet as-milled $CuSbSe_2$ powder is shown in Figure 2. Raman

investigation shows the existence of Cu_2Se at 198 cm^{-1}, Sb-Se stretching mode peak at 259 cm^{-1} and $CuSbSe_2$ at 222 cm^{-1} could be identified. The Raman spectra of $CuSbSe_2$ indicate high purity of the as-milled $CuSbSe_2$ material.

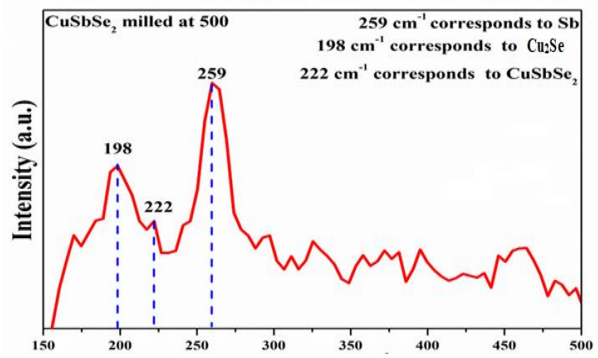

Fig. 2: Typical Raman spectrum for as-milled $CuSbSe_2$

Field emission scanning electron microscope (FESEM) were taken to study the surface morphology of the sample, with a machine (FET Quanta USA using ImageJ software packaage) at an accelerating voltage of 30kv. SEM images of the samples shows a high quality of the material with confirmed formation of $CuSbSe_2$ material separated in the form of bulk, the material showed a smooth surface morphology with a clear grain boundaries. The image appears to be agglomerated and amorphous in nature. In order to complete the FESEM observation and measurement, Energy dispersive x-ray spectrum was obtained (EDS in fig.4). EDS were taken with (Bruker USA) exhibiting three strong peaks confirming the purity of the sample by detecting only Cu, Sb and Se element respectively. From the EDS images techniques the atomic ratio of elemental Cu, Sb and Se was confirmed closed to 1:1:2 as expected from stoichiometry ratio and atomic weight percentage of 50.34, 24.64 and 25.02 respectively with Se the main component of the sample as it has error of 2.23. Elemental composition analysis of the atomic weight (At %), unnormalised concentration (Unn C wt. %) and normalised concentration (Norm C wt. %) of as-milled $CuSbSe_2$ are tabulated in Table 1.

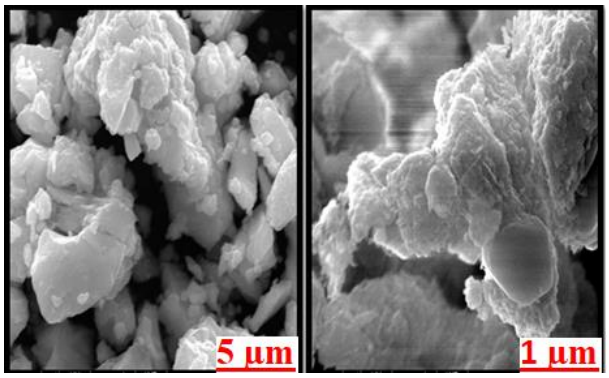

Fig. 3: FE-SEM micrographs of the wet as-milled (8 hours) sample

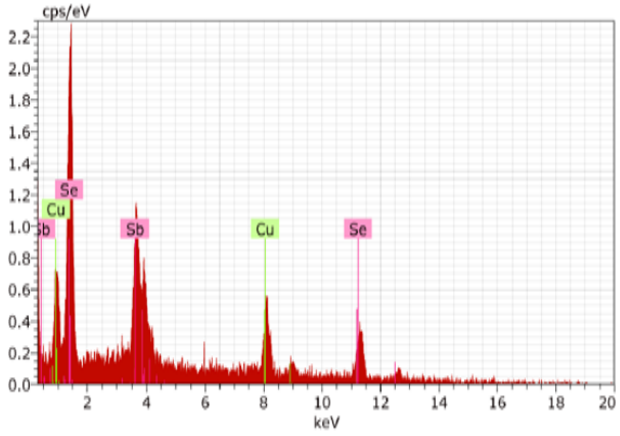

Fig. 4: EDS spectrum of as-milled $CuSbSe_2$

Table 1: Elemental composition of the wet as-milled sample

Element	Atomic No.	Series	Unn. C (wt. %)	Norm. C (wt. %)	Atomic. (At. %)	Error (1 sigma) (wt. %)
Se	34	K- series	45.49	46.41	50.34	2.23
Sb	51	L-series	34.33	35.02	24.64	1.21
Cu	29	K-series	18.20	25.02	25.02	0.78
Sum			**98.02**	**100.00**	**100.00**	

4. Conclusion

$CuSbSe_2$ single phase have been synthesized successfully for the first time by mechanical alloying (MA) under different ball milling conditions. Results of the experiment and theoretical investigation of the phase evolution and optical properties of as-milled $CuSbSe_2$ have been revealed. XRD and Raman analysis, reveals that the resulting as-milled $CuSbSe_2$ are amorphous in nature. SEM and EDS images shows a good coverage and the presence of purely $CuSbSe_2$ compound. Hence, it can be concluded that, ball milling can be considered in place of initial melting of solid state synthesis

route to synthesize $CuSbSe_2$ with equivalent material properties.

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Conflict of interest

The authors declare that there is no conflict of interests regarding the publication of this article.

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