Journal of Alloys and Compounds 731 (2018) 318–322

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

# Influence of S content on the structure and ignition time of $CuIn(S,Se)_2$ powders prepared by mechanochemical process

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## ARTICLE INFO

*Article history:*
Received 16 March 2017
Received in revised form
23 August 2017
Accepted 3 October 2017
Available online 7 October 2017

*Keywords:*
$CuIn(S,Se)_2$
Mechanochemical processing
Structural properties
Ignition time
Reaction mechanism

## ABSTRACT

$CuIn(S,Se)_2$ (CISS) powders with varying S/[S + Se] ratios were synthesized by mechanochemical process (MCP) and a self -propagating combustion occurred during milling. Influence of S content on the structure was investigated by X-ray diffraction and Raman spectroscopy. Morphology of CISS powders was investigated by scanning electron microscopy (SEM). Characteristic peaks of the chalcopyrite structure are clearly observed and CISS (112) peaks shifts to higher value as S content was increased. Lattice constants for CISS samples decrease with the S content increased. Moreover, the large size mismatch between S and Se atoms leads to the lattice parameters negative deviate from Vegard's law. The Raman A1 mode of the chalcopyrite CISS has been observed, and $In_xSe_y$ and CuS has been also detected in some samples. The morphology observation of CISS powders shows that the uniformity of particle size distribution decreases with increasing sulfur content. The ignition time of Cu-In-S-Se self-propagating reaction was extended with the increase of sulfur content and the possible reason has been explained. Furthermore, the reaction mechanism of Cu-In-S-Se system has also been discussed.

## 1. Introduction

Recently Cu-based chalcopyrite semiconductors have attracted more and more attention as their exceptional photovoltaic properties. $CuIn(Se,S)_2$ (CISS) solar cell is one of the most potential thin film solar cells. Liu Wei et al. obtained 12% efficiency CISS photovoltaic device by using a hydrazine solution process [1], and the corresponding band gap of CISS material is 1.15 eV.

CISS thin films or nanocrystals have been prepared using a variety of methods such as electrodeposition [2,3], solvothermal route [4,5], heating-up synthesis [6] and mechanochemical process (MCP) [7]. Recently, MCP has also been used to synthesize $CuInSe_2$, $CuInS_2$, $Cu(In,Al)\ Se_2$ and $Cu(In,Ga)Se_2$ [8,9] powders as its advantages of high energy efficiency, high productivity and short processing cycle time. And a mechanically induced self-propagating reaction (MSR) was confirmed to take place in Cu-In-Se [10] and Cu-In-S system [11].

MSR have been observed in numerous systems, especially in metal chalcogenides system. Such as the reactions between Zn, Cd, In, Sn(II), Sn(IV) and Pb and the chalcogen elements S, Se, and Te. The mechanochemistry of chalcogenides, particularly sulfides, is an area of active research, partly due to the importance of sulfide minerals and the application of chalcogenides in technology [12]. Moreover, the formation of metal chalcogenides is also a very convenient model reaction for MSR studies, with superior milling properties, insensitivity to air and impurities, and ignition times from minutes to hours.

In MSR, ignition becomes after a certain activation time, as milling reduces the particle size, thoroughly mixes the components, and increases in the number of chemically active defect sites [12]. Whether a self-propagating process takes place depends on minor differences in composition and milling conditions. There are many factors that can affect the ignition time, such as balls and powder mass, inert additives and off-stoichiometry. Therefore, the study of mechanical activation and ignition is a possible way to obtain information about the mechanism of mechanochemical processes.

In this paper, CISS powders with different sulfur contents have been synthesized by MCP using planetary ball milling, and the structural properties and morphology of the powders have been studied. Then elemental components of Cu-In-S-Se have been milled in an agate mortar to investigate the variation of the ignition time with different sulfur contents as its visibility. Furthermore, the reaction mechanism of Cu-In-S-Se system has been discussed.

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https://doi.org/10.1016/j.jallcom.2017.10.015

## 2. Experimental procedures

CISS powders with different S contents were synthesized by milling copper (<20 μm, 99.99%), indium (<60 μm, 99.999%), sulfur (<5 μm, 99.5%) and selenium (<5 μm, 99.5%) mixture with the molar ratio Cu:In:(S + Se) = 1:1:2. S content $x$, the composition ratio of [S]/[S + Se], was varied from 0 to 1.0 to obtain different CISS powders. That is the molar ratio of Cu:In:S:Se = 1:1:2$x$:2-2$x$ ($x$ = 0, 0.2, 0.4, 0.6, 0.8, 1.0). The experiments were performed in an agate vial loaded on a planetary ball mill (KXM-Y-ISP-L) milled for 120 min. The ball-to-powder weight ratio and rotational speed were 10:1 and 600 rpm, respectively. In addition, copper, indium, sulfur and selenium mixture with different S content were milled in an agate mortar by manual grinding to observe the experimental phenomena and detect the ignition time variation. As it is difficult for manual grinding to maintain a constant speed for long time, we take 15 min for a grinding cycle.

Structures of milled CISS powders and the influence of S content on the structural properties has been investigated by X-ray diffraction (XRD) and Raman spectroscopy. X-ray characterization was done with the Empyrean diffractometer with Cu K$\alpha$ radiation of wavelength 1.5406 Å. A Raman spectroscope (Jobin Yvon HR800) with a He-Ne laser ($\lambda$ = 514.5 nm) was used to measure the Raman scattering and the Raman spectra (150–600 cm$^{-1}$ range) were recorded. Morphology of CISS powders milled for 120 min were observed using a JSM-6360LV scanning electron microscope (SEM).

## 3. Results and discussion

### 3.1. Structural properties

Fig. 1 shows the structure of Cu-In-S-Se powders with different S content milled for 120 min. From these patterns, it is observed that copper, indium, sulfur and selenium mixture has transformed to CISS after milled for 120 min. While some weak peaks from unreacted indium have been detected by XRD. A significant shift of all peaks to higher 2$\theta$ positions is noted with increasing S due to a decrease in d-spacing and unit cell dimensions. Detailed examples of this shift are presented in Fig. 2, where the normalized (112) reflections are shown.

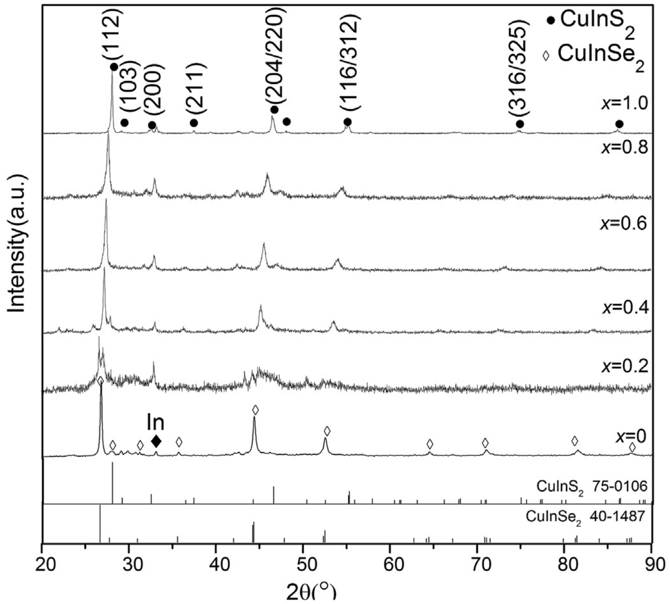

**Fig. 1.** Diffraction patterns of Cu-In-S-Se samples with a molar ratio Cu:In:S:Se = 1:1:2$x$:2-2$x$ milled for 120 min.

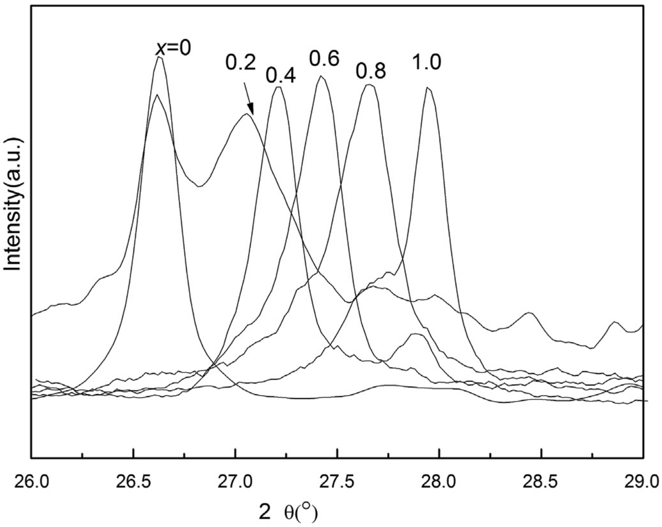

**Fig. 2.** XRD spectra of CuIn(S,Se)$_2$ powders showing shift in (112) peak with increasing S content.

It is clearly seen that (112) peaks shift from 26.62° to 27.96° when S content varied from 0 to 1. (112) peak splits into two peaks (2$\theta$ equal to 26.62°and 27.06°) when S content increased to 0.2. Similar doublet peaks appeared in (112) have been observed in CIAS powders synthesized by MCP in our previous work [13]. The peak appeared at 26.62° is CuInSe$_2$ and another peak appeared at 27.06° is CISS, as its value is greater than that of CuInSe$_2$ (26.60°) and less than that of CuInS$_2$ (27.97°) according to the standard PDF card (40-1487, 75-0106) respectively. This situation may attribute to the aggregation of S. S aggregation will lead to the formation of S-poor and S-rich region and CuInSe$_2$ and CISS generate in corresponding areas.

The lattice parameters $a$ and $c$, which are presented in Fig. 3, were calculated from peak positions corresponding to reflections (112), (204) and (312). Their values varied in the range from 5.793 Å to 5.526 Å for $a$ and from 11.582 Å to 11.131 Å for $c$, with a $c/a$ ratio $\eta \cong 2$. And their dependence on S content is nonlinear with negative deviations from Vegard's law.

Both $a$ and $c$ values decrease with increasing S content, since the effective ionic radius of S$^{2-}$ (0.170 nm) is smaller than that of Se$^{2-}$

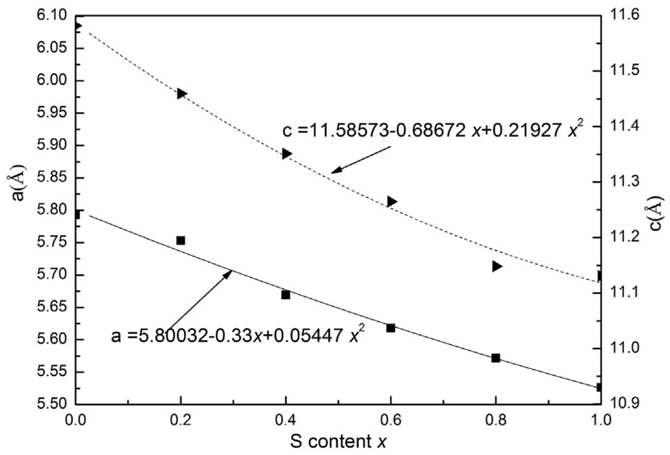

**Fig. 3.** Lattice constants of $a$ and $c$ for CuIn(S,Se)$_2$ samples with increasing S content.