

SYNTHESIS Cu_2SnS_3 AND Cu_3SnS_4 NANOPOWDER AND STUDYING THE COMPOSITION, STRUCTURAL AND MORPHOLOGICAL PROPERTIES

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Nanopowders of Cu_2SnS_3 and Cu_3SnS_4 were prepared from their solutions by chemical bath deposition (CBD) technique. The composition, structural and morphological properties of the nanopowder was characterized by energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and scanning electron microscope (SEM), respectively. The compositional results showed that the Cu and S content are poor and rich Sn content for both Cu_2SnS_3 and Cu_3SnS_4 nanopowder, with real phase of 75% and 72%, respectively. XRD results showed the predominant peaks associated to Cu_2SnS_3 with cubic structure and the crystallite size value was calculated to be 3 to 5.1 nm, whereas for Cu_3SnS_4 nanopowder characterized with a mixed phase of orthorhombic and tetragonal structure with some binary phases. The value of crystallite size was calculated with 6 and 50 nm. SEM images showed the surface of Cu_2SnS_3 nanopowder denser, less voids and vacancies compared with Cu_3SnS_4 nanopowder.

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1. Introduction

It may be noted that copper tin sulfide (CTS) is composed of three elements has band gap similar to that of CZTSSe. Further, synthesis of ternary CTS is expected to be much easier than quaternary CZTS and CZTSe or pentanary CZTSSe [1]. About 25 years ago, Kuku and Fakalajo demonstrated for the first time the use of CTS thin films in solar photovoltaic devices [2]. The research and development of present solar cell technologies are driven by practical requirements of sustainability and eco-friendliness [3]. The sustainability of solar cell is primarily dependent on two factors, i.e. materials utilized and their processing for solar cells [3]. Conventional thin film solar cell (TFSC) based on CIGS or CdTe require much less material, but still the costs are high. CIGS or $\text{CuIn}(\text{S},\text{Se})_2$ (CIS) absorber based solar cells uses indium, which is a rare metal and hence costly. CdTe absorber layer solar cells involve cadmium and tellurium, where Cd is toxic and Te is scarce [3-5].

With ever increasing demand of electricity and exhausting fossil fuels, sustainable and low-cost PV technologies are thus required. The basic factors governing the sustainability and cost of PV technology are material and deposition process [5]. It is apparent from the preceding discussions that direct liquid coated CTS can lead to fabrication of sustainable and low cost solar cells. Thus for large scale low cost deposition of CTS via direct liquid coating methods, facile synthesis of nanoparticles or powder are required. The literature show scanty reports on the synthesis of CTS nanoparticles, crystals and powder [5].

The present study is concentrated on prepare nanopowder for Cu_2SnS_3 and Cu_3SnS_4 compounds from their prepared films by chemical bath depositions then characterized the compositional, structural and morphological properties for both prepared powders.

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2. Experimental details

The nanopowder for Cu_2SnS_3 and Cu_3SnS_4 compounds was prepared from their solutions which have been prepared by CBD technique at the best prepared conditions as described earlier [6-8]. The chemical solution were candidate, followed by wished the precipitated powder with distilled water and acetone for several times, after that the nanopowder were heated by placed in oven at 373 K for 120 min. The nanopowder was then cooled to room temperature with approximately the same rate as the heating rate. The compositions were obtained by energy dispersive spectroscopy (EDS) model (Inspect S50). The crystalline structures of the nanopowder of Cu_2SnS_3 and Cu_3SnS_4 were characterized using X-ray diffractometer (XRD) with Cu K_α radiation ($\lambda = 1.54060 \text{ \AA}$), where operated in the range of 2θ degree from 20° to 60° using step size of 0.05° and step time of 0.60 s. The morphological features were measured by scanning electron microscope (SEM) model (Inspect S50) with accelerating voltage 200V to 30 kV, probe current 1pA to 2 μA utilized high resolution mode.

3. Results and discussion

The compositions ratio of elements as percentage ratio of nanopowder of Cu_2SnS_3 and Cu_3SnS_4 was recorded by EDS data, which were shown in figure 1. Standard formula of compound and real and secondary phases were tabulated in the Table 1. The results indicated the composition ratio of real phase of nanopowder of both Cu_2SnS_3 and Cu_3SnS_4 are good ratio compared with that found by Pengyi and Shuying [9], and indicated that nanopowder of both Cu_2SnS_3 and Cu_3SnS_4 have poor Cu and S content, and rich Sn. This may be as a result of CBD prepared technique which was used to obtain the nanopowder at different conditions of interaction materials such as a substrate temperature (T_s), pH value, concentration of compounds, and deposition time.

Table 1. Elemental compositions, ratio of real and secondary phases of formed nanopowder of Cu_2SnS_3 and Cu_3SnS_4 .

| Sample | Ratio at. % of EDS | | | Percentage Ratio % of EDS | | | Formula standard of moles | Real phase of formed compound% | Secondary phase% |
|---------------------------|--------------------|-------|-------|---------------------------|----|----|---|--------------------------------|------------------|
| | Cu | Sn | S | Cu | Sn | S | | | |
| Cu_2SnS_3 | 11.86 | 22.97 | 21.01 | 21 | 42 | 37 | $\text{Cu}_{1.27}\text{Sn}_{2.46}\text{S}_{2.25}$ | 75 | 15 |
| Cu_3SnS_4 | 16.59 | 18.17 | 10.13 | 27 | 30 | 43 | $\text{Cu}_{2.18}\text{Sn}_{2.39}\text{S}_{3.41}$ | 72 | 18 |

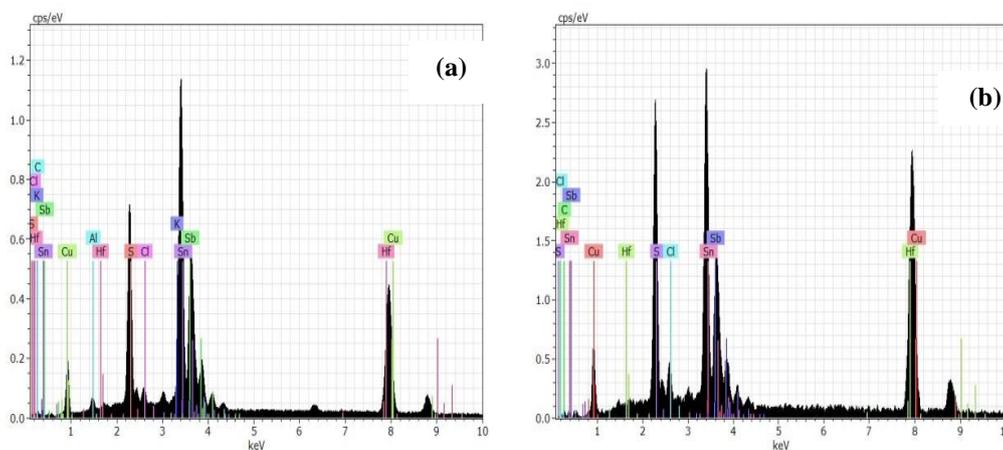


Fig.1. Composition results from EDS measurements for nanopowder of (a) Cu_2SnS_3 (b) Cu_3SnS_4 .

The structure properties of nanopowder of Cu_2SnS_3 and Cu_3SnS_4 were characterized using X-ray diffraction. The assignment of the phases was done using the International Center for Diffraction Data (ICDD) database [10].

Fig. 2(a & b) illustrated XRD spectra of nanopowder (precipitated powder) of Cu_2SnS_3 and Cu_3SnS_4 respectively. The x-ray pattern of Cu_2SnS_3 as shown in Fig. 2a showed that the predominant peaks associated to Cu_2SnS_3 with a cubic structure and traces of Cu_3SnS_4 with the orthorhombic structure, in addition to traces of Sn_2S_3 . The shift of 2θ of the peaks toward smaller angles because the powder has Sn-rich and this clear from the composition analysis, which causes extended of the lattice due to the larger atom radius [11]. Also, the deviation of these peaks from ICDD database value may be related to presence of strain in nanopowder [12]. The crystallite size of nanopowder was calculated to be (3 to 5.1 nm) using Scherrer formula [13]:

$$C.S = \frac{B'\lambda}{\beta \cos \theta} \dots (1)$$

where $C.S$ is the crystallites size in nm unit, λ is the X-ray wavelength in nm unit, β is the full width at half maximum intensity of the peak in radians, θ is the diffraction angle in degrees, and B' is a constant ,and its value vary between 0.89 and 1.39, but is usually taken as close to unity[13]. The 2θ , inter planner spacing d_{hkl} , compound phase, miller indices, and card number of ICDD database [10] were illustrated in Table 2.

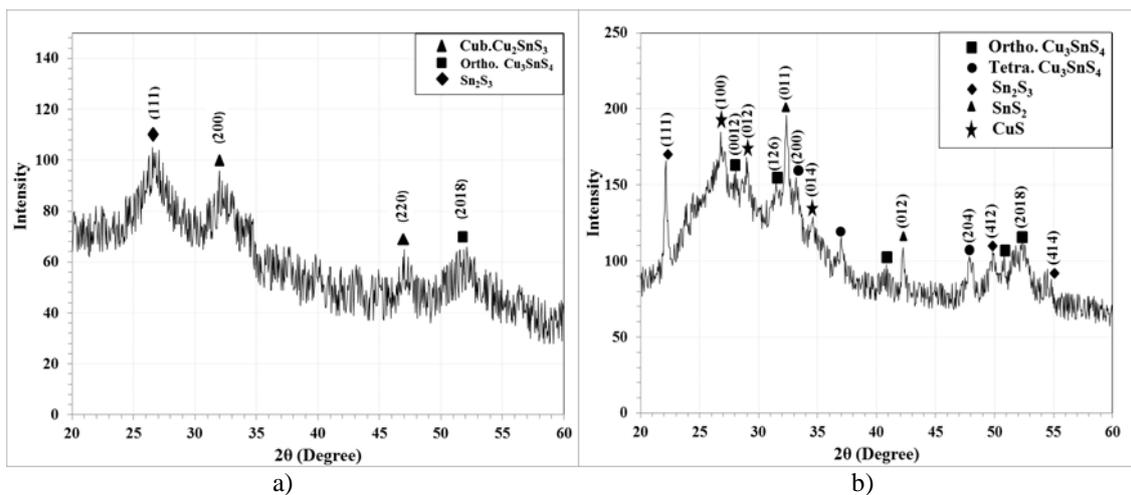


Fig.2. XRD spectra of nanopowder for (a) Cu_2SnS_3 (b) Cu_3SnS_4 .

Table 2. XRD analysis and ICDD references for nanopowder of Cu_2SnS_3 [10].

| $2\theta_{\text{Exp.}}$ (Deg.) | $d_{hkl \text{ Exp.}}$ (Å) | $d_{hkl \text{ Theor.}}$ (Å) | Phase | (hkl) | ICDD ref. |
|-----------------------------------|----------------------------|---------------------------------|----------------------------------|--------|-------------|
| 26.650 | 3.3422 | 3.3549 | Sn_2S_3 | (111) | 96-901-1237 |
| 31.950 | 2.7989 | 2.7151 | Cub. Cu_2SnS_3 | (200) | 01-089-2077 |
| 46.950 | 1.9337 | 1.9198 | Cub. Cu_2SnS_3 | (220) | 01-089-2077 |
| 52.150 | 1.7525 | 1.7620 | Ortho. Cu_3SnS_4 | (2018) | 00-036-0217 |

Figure 2b showed XRD spectrum of nanopowder Cu_3SnS_4 . There are two phases appeared for Cu_3SnS_4 , orthorhombic as a base phase and tetragonal phase as a secondary phase. Also there are some secondary binary phases such as SnS_2 , CuS and traces of Sn_2S_3 were observed and this agree with that found by Becerra et al.[14]. The deviation of these peaks from ICDD database value [10] was less than in Cu_2SnS_3 because, the ratio of Sn atoms of Cu_3SnS_4 nanopowder in

composition analysis less than in Cu_2SnS_3 . Also, presence many secondary phases and presence CuS phase due to higher Cu content in nanopowder which tend to formation of Cu_3SnS_4 with a orthorhombic structure and losses of Sn in sulphide form SnS were relevant [12]. The presence these secondary phases may be related to the phase diagram of two compound, where the compound Cu_3SnS_4 was not lie on the stoichiometric line and that represented pseudo-binary system compare with the compound Cu_2SnS_3 which

lie on it. The crystallite size of nanopowder was calculated to be within range (6 - 50 nm). The Cu_3SnS_4 crystallite size was greater than of nanopowder of Cu_2SnS_3 . This may be due to the presence many secondary phases which causes increasing in crystallite size. The 2θ , inter planner spacing d_{hkl} , compound phase, miller indices, and card number of ICDD database [10] were illustrated in Table 3.

Table 3. XRD analysis and ICDD references for nanopowder of Cu_3SnS_4 [10].

| 2θ (Deg.) | d_{hkl} Exp. (Å) | d_{hkl} Theor. (Å) | phase | (hkl) | card No. of ICDD |
|---------------------|-----------------------|-------------------------|----------------------------------|--------|------------------|
| 22.1951 | 4.0020 | 4.1354 | Sn_2S_3 | (111) | 96-901-1237 |
| 26.8293 | 3.3203 | 3.2926 | CuS | (100) | 96-101-0921 |
| 28.0488 | 3.1787 | 3.1370 | Ortho. Cu_3SnS_4 | (0012) | 00-036-0217 |
| 28.9634 | 3.0803 | 3.0563 | CuS | (012) | 96-101-0921 |
| 31.5244 | 2.8357 | 2.8920 | Ortho. Cu_3SnS_4 | (126) | 00-036-0217 |
| 32.3780 | 2.7628 | 2.7632 | SnS_2 | (011) | 96-101-1331 |
| 33.1707 | 2.6986 | 2.7063 | Tetra. Cu_3SnS_4 | (200) | 01-089-4714 |
| 34.6341 | 2.5879 | 2.5691 | CuS | (014) | 96-101-0921 |
| 42.2561 | 2.1370 | 2.1387 | SnS_2 | (012) | 96-101-1331 |
| 47.8659 | 1.8988 | 1.9137 | Tetra. Cu_3SnS_4 | (204) | 01-089-4714 |
| 49.8171 | 1.8289 | 1.8430 | Sn_2S_3 | (412) | 96-901-1237 |
| 52.3171 | 1.7473 | 1.7620 | Ortho. Cu_3SnS_4 | (2018) | 00-036-0217 |
| 54.4512 | 1.6837 | 1.6773 | Sn_2S_3 | (414) | 96-901-1237 |

Morphological properties of nanopowder of Cu_2SnS_3 and Cu_3SnS_4 were measured by scanning electron microscope (SEM). Figure 3 illustrated the SEM images of nanopowder of Cu_2SnS_3 and Cu_3SnS_4 .

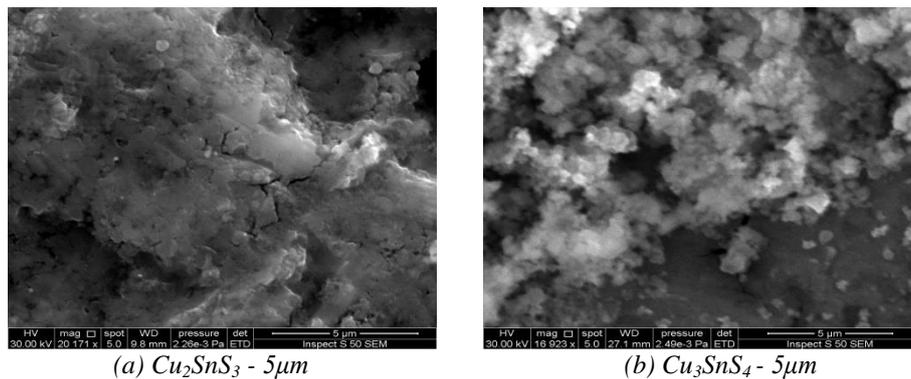


Fig.3. SEM pictures of nanopowder of (a) Cu_2SnS_3 and (b) Cu_3SnS_4 .

These images showed the surface of Cu_2SnS_3 denser, less voids and vacancies compared with Cu_3SnS_4 which contain tiny particles. This may be due to the different in number of total moles of compound, which effect on the bonded between anions and cations, where octet number rule was agreed for Cu_2SnS_3 compared with Cu_3SnS_4 , which different on the stoichiometric. Both Cu_2SnS_3 and Cu_3SnS_4 were obtained from their precipitated nanopowder using CBD technique.

4. Conclusions

Nanopowder of Cu_2SnS_3 and Cu_3SnS_4 were prepared from their solutions using CBD technique. Compositional, structural and morphological characterizations were investigated. The outcome of these investigations can be summarized as follows:

The composition ratio of real phase of nanopowder of both Cu_2SnS_3 and Cu_3SnS_4 were 75 and 72 %, respectively.

The EDS analysis showed that nanopowder of Cu_2SnS_3 and Cu_3SnS_4 had poor Cu and S, while Sn was rich.

The predominant peaks for Cu_2SnS_3 was associated with cubic structure and traces of Cu_3SnS_4 with orthorhombic structure, also traces of Sn_2S_3 , while Cu_3SnS_4 had mixed phases orthorhombic and tetragonal structure, also some binary phases such as SnS_2 , CuS, and traces of Sn_2S_3 .

The crystallite size of Cu_3SnS_4 nanopowder was greater than Cu_2SnS_3 .

The surface of Cu_2SnS_3 nanopowder was denser, less voids and vacancies compared with Cu_3SnS_4 nanopowder.

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