Synthesis, Characterization and Performance of Cu_2SnS_3 for Solar Cell Application

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Abstract— Cu_2SnS_3 (CTS) powders were prepared by hydrothermal (HR) and solid state reactions (SSR) using low cost starting materials. Using HR, single triclinic (mohite) Cu_2SnS_3 phase was obtained. Otherwise, for SSR cubic Cu_2SnS_3 was obtained with two other compounds, Cu_4SnS_4 and SnS having orthorhombic crystal structure for both of them. UV-Vis spectra for HR and SSR preparations showed maximum absorbencies at about 290 and 240 nm with band gap values of 2.25 and 2.5 eV, respectively. The calculated conductivities were equal to $2.5x10^{-2}$ and $6.12x10^{-3}$ S/cm for samples that prepared by HR and SSM reactions, respectively. Also the charge transfer resistance (Rct) were 3.5 and 24 Ω for photo electrochemical cells (PEC) prepared by HR and SSR, respectively. A good electrochemical photovoltaic cell was accomplished power conversion efficiency per unit area (PCE) of about 1.58 and 0.93 % for cells prepared by HR and SSR, respectively.

Indexed Terms— Hydrothermal and Solid State Reaction; Optical and electrical properties; photovoltaic properties.

1 INTRODUCTION

Solar cell energy applications took a great importance in the last few decades. This is because of the energy crisis and pollution caused by the traditional energy sources like fossil fuels. So it's important to develop newer low cost light absorber materials for thin film solar cell energy applications. Recently, relatively high efficient materials were discovered and investigated for example copper indium gallium diselenide (CIGS) and CdTe [1], [2], [3]. Such materials have the problems of being expensive and lower availability, especially indium tellurium and gallium. Also the toxicity of elements like cadmium makes these materials lower applicable.

Copper-containing calcogenides, especially compounds of groups [1-4-6] have been reported to have wide applications in photovoltaic (thin film solar cell) devices, light emitting diodes, non linear optical materials [4]. These materials have a suitable range of band gap, 0.96-1.35 eV. Meanwhile, they have a relatively high absorption coefficient ≥ 10^4 cm^{-1} [5], [6]. These advantages make them a promising candidate for thin film solar cell absorbing materials.

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Copper tin sulfide compounds were prepared with different elemental ratios such as Cu_2SnS_3 [7], [8], [9], [10], [11], [12], [13] Cu_4SnS_4 [14] Cu_3SnS_4 [15], [16], [17] $Cu_4Sn_7S_{16}$ [18], [19]. Recently, Cu_2SnS_3 (CTS) gained a great attention in many applications specially the field of thin film solar cell application. CTS material is suitable for solar cell energy application because it is environmentally friendly, cheap in preparation, non-toxic, inexpensive and earth-abundant.

CTS was prepared with different methods such as solid state reaction, solvothermal route, spray pyrolysis technique and mechanochemical ball milling process [4], [7], [9], [13], [14], [16], [18], [19], [20], [21], [22], [23]. It was prepared with different crystal structures e.g cubic, tetragonal, Monoclinic and Triclinic [4], [7], [8], [10], [13], [18], [20], [24], [25], [26], [27]. The crystallite size range was 5-200 nm [4], [7], [20], [24], [28] and particle size range 35-600 nm [20], [22], [23], [24], [28]. The particle shapes morphologies are flower like, Spherical [7], [9], and band gap values range of (1.1-2.5 eV) [7], [9], [28], [29]. These all parameters affected the efficiency of a definite prepared phase. CTS was reported to have power conversion efficiencies values of 0.54 %, 1.10-1.92 %, 2.10 %, and 2.54 % [10], [12], [27], [30]. This makes CTS a promising candidate for potential applications in photovoltaics.

This work was done to study the effect of HR reaction using hydrazine as reducing agent on the

electric and electrochemical properties in comparison with the traditional SSR. Furthermore, using hydrazine with samples prepared by HR does not need further thermal treatment after the preparation like annealing and sintering. Moreover, in our humble believe there are few articles reported about using hydrazine as a reducing agent in HR. Besides that, there are only a little data available about the electrochemical properties CTS such as impedance, resistivity and conductivity.

2 EXPERIMENTAL

2.1 Synthesis of cu_2snse_3 by hydrothermal method

Cu_2SnS_3 powder was synthesized by HR as follow: 0.14 M solutions for each of $Na_2S.9H_2O$, Cu $(NO_3)_2.3H_2O$ and $SnCl_2$ compounds were prepared, separately. At first, Cu $(NO_3)_2.3H_2O$ solution was added to $SnCl_2$ solution. Then, sodium sulfide solution was introduced to the mixture slowly with gentle heating at about (353 K = 80°C) with stirring. Ammonia solution was added slowly until the pH of the solution reached to about 9 with heating and stirring for 4 hours. The obtained black precipitate was subjected to hydrothermal treatment in an oven at (473 K = 200°C) for 24 hours using an autoclave made from vessel covered with stainless steel closed case. Then the precipitate was filtered, washed with distilled water and ethyl alcohol several times to remove any impurities or byproducts. After that, it was put in a dryer at (333 K = 60°C) for 6 hours. The obtained Cu_2SnS_3 was kept for further investigations. HR steps are illustrated in the Flow sheet as shown in Fig. 1.

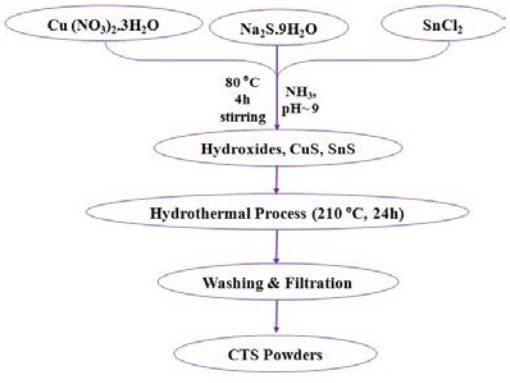

Fig. 1 Flow sheet of hydrothermal process for Cu_2SnS_3 preparation.

2.2 Synthesis of Cu_2SnS_3 by solid state reaction

Cu_2SnS_3 was synthesized by solid state process using stoichiometric ratio of Cu, Sn and S powders that mixed and grinded well in a mortar. Then, it was put in a boat crucible in a tube furnace at (873 K = 600°C) for two hours under argon with 5 % H_2 atmosphere. It was cooled to the room under the argon. A black powder was obtained, which was grinded and kept for further investigations.

2.3 Characterization techniques

Samples compositions were identified by an X-ray diffractometer (XRD), model: Brukur advanced D8 Kristalloflex (Ni-filtered Cu Ka radiation; 1.5406 Å). The microstructure was examined by backscattered electron (BSE) in the field emission scanning electron microscopy (FESEM QUANTAFEG 250). The optical measurements were performed using UV–vis–NIR scanning spectrophotometer (PerkinElmer lambda 1050 Spectrophotometer, USA) using 1 cm path length quartz cell. EIS measurements were done using potentiostat (Parastat 4000 Princeton, USA). The impedance measurements amplitude was 20 mV and the frequency range was 1MHz-10 mHz.

2.4 Photo electrochemical cell fabrication and measurements

The prepared samples were coated on indium tin oxide (ITO) conducting glass as working electrode the resistivity of the ITO is 30 Ω/cm². The cell configuration was: ITO/Cu_2SnS_3/0.5 M KI + 0.5 M I_2/C. It was fabricated and characterized through current–voltage (I–V) measurements 31. Xenon arc lamp 150 W is used as a light source with solar simulator Sciencetech SS150W- AAA. The cell was exposed to light intensity 1 Sun (100 mW/cm) using Air Mass 1.5 Global Filter. I-V tester is 2400 Keithley Source Meter SSIVT-60WC. The calibrated reference cell consists of a 20 x 20 mm monocrystalline silicon (model SC-LT) photovoltaic cell encased in a 92 x 70 x 16 mm metal enclosure with a protective quartz window. The reference detector (SSIVT-refl) is effective in sensing wavelengths between 190 nm and 1100 nm and is calibrated with the 1 Sun. Parameters measured by I-V Software were open circuit voltage (Voc), short circuit current (Isc), maximum power (Pmax) and filling factor (FF).

3 RESULTS AND DISCUSSION

3.1 Cu_2SnS_3 samples characterization

The Cu_2SnS_3 compound prepared by HR and SSM was characterized by XRD as shown in Fig. 2. According to XRD interpretations the prepared Cu_2SnS_3 compound by HR has the main peaks within the recorded miller indices that corresponding to triclinic (Mohite) structure. The obtained data are in agreement with reported previous works and JCPDS data (35-0684) [9], [10], [25]. On the other hand SSR gives Cu_2SnS_3 of cubic crystal structure, matching JCPDS data (89-2877) beside Cu_4SnS_4 and SnS of orthorhombic structures for both of them as explained by data JCPDS data (71-0129) and (75-0925), respectively [22], [32].

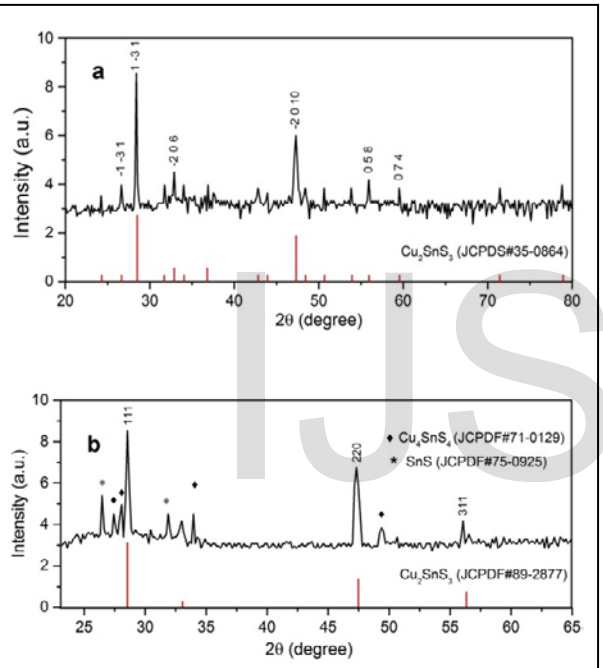

Fig. 2 XRD pattern of CTS prepared by (a) HR (b) SSR.

Furthermore, the crystallite size was calculated from Scherer equation:

$$L = \frac{0.94\,\lambda}{\beta\,\cos\theta} \qquad (1)$$

Where; L is the crystallite size, λ is wave length of the target (1.5406 Å for Cu), β is full width half maximum (FWHM) and θ is the chosen diffraction angle [33]. The calculated crystallite size values for CTS, which was prepared by HR and SSR, were 35 and 70 nm, respectively.

The morphology of the prepared samples was characterized by SEM inspection as shown in Fig. 3. The shape of CTS, which was prepared with HR, was like rock morphology with dense structure. The grains were agglomerated with average particle size of about 100 nm. On the other hand, CTS that prepared with SSR has spherical particles shape and less agglomerated with particle size of about 130 nm. The calculations of the crystallite size from XRD and crystal size from SEM for CTS compound prepared by HR were less in values than the one prepared by SSM.

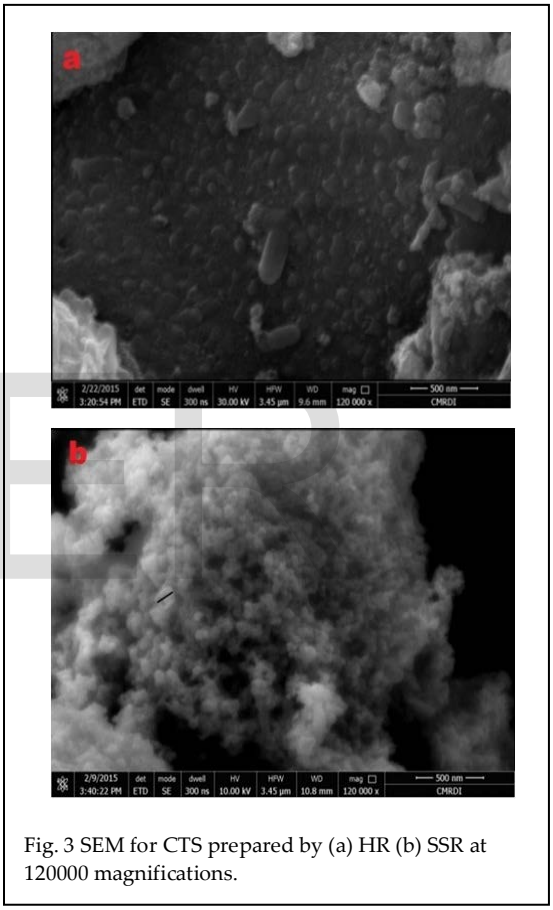

Fig. 3 SEM for CTS prepared by (a) HR (b) SSR at 120000 magnifications.

3.2 Optical measurements

UV–vis absorbance measurements are used to reveal the energy structure and optical properties of the as-prepared Cu_2SnS_3 architecture as shown in Fig. 4. Cu_2SnS_3 crystal gave maximum absorbance at wavelength of 290 nm that some near the visible region for the sample prepared with HR. While the maximum absorbance wave length was 240 nm for the sample prepared with SSR, which was relative far from the visible region relative to HR process. This confirms that the transition of electrons between the

valence band (VB) and the conduction band (CB) occurs easily with HR rather than SSR for CTS preparation.

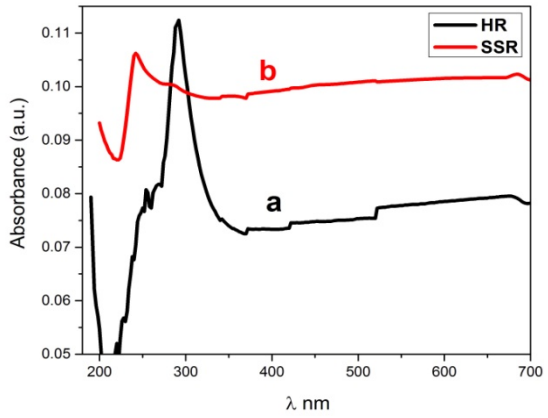

Fig. 4 UV-vis-NIR absorbance spectra of CTS prepared by (a) HR (b) SSR.

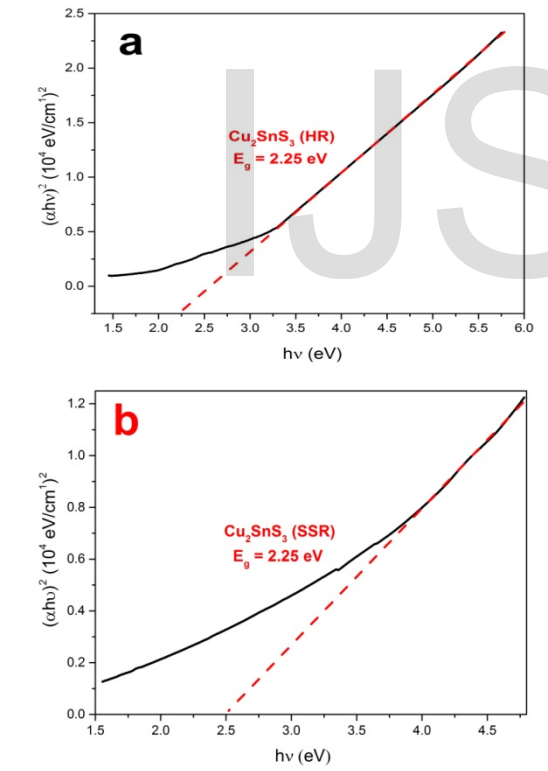

Fig. 5 Band gap values for CTS prepared by (a) HR (b) SSR by extrapolation.

The absorbance characteristics of the samples obey the model equation $\alpha h\nu = A (h\nu - Eg)^{0.5}$ for the direct transition, where α is the optical absorption coefficient, h is Planck's constant, ν is the photon frequency, A is a constant and Eg is the energy gap [34]. The energy band gap of Cu_2SnS_3 is obtained from the plot of $(\alpha h\nu)^2$ vs. $h\nu$ (photon energy) by extrapolation as shown in Fig. 5. The energy gab of HR sample was small than SSR one and this is attributed to the small particle and crystallite sizes of the CTS prepared by HR as explained in Section 3.1. Also, the obtained value was slightly small in comparison with the reported value [9].

3.3 Electrochemical Impedance Spectroscopy (EIS) measurements

EIS was done for pellets of dimensions: radius (r) ~0.675 cm and thickness (t) ~0.35 cm of the CTS powders to measure the resistance of the material itself. The characterization was also done for photo electrochemical cell (PEC) containing the CTS plated on ITO glass as working electrode against glassy carbon counter electrode in electrolyte of iodine in potassium iodide. Cell diagram was: ITO/Cu_2SnS_3 / 0.5 M KI + 0.5 M I_2 /C.

Nyquist plot for CTS pellets prepared by SSR and HR is shown in Fig. 6. The conductivities of CTS powders materials prepared by HR and SSR are 2.5×10^{-2} and 6.12×10^{-3} S/cm, respectively.

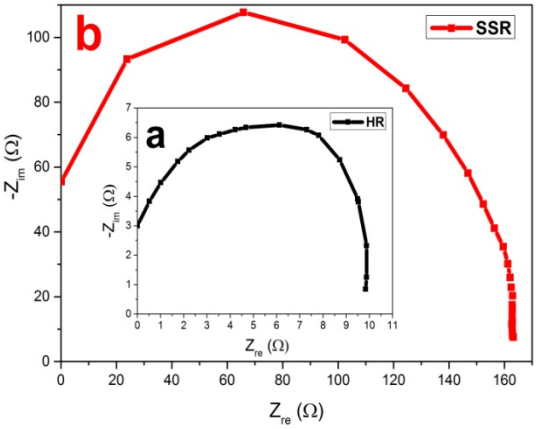

Fig. 6 Nyquist plot for CTS pellets prepared by (a) HR and (b) SSR.

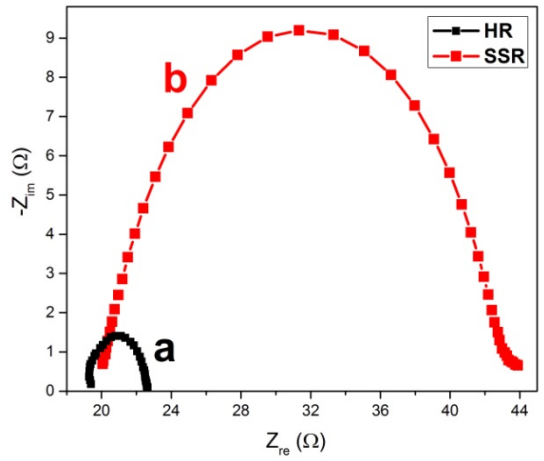

Fig. 7 Nyquist plot for CTS Photo Electrochemical Cell (PEC) prepared by (a) HR and (b) SSR

3.4 Photovoltaic properties

To obtain the power output characteristics of the photo electrochemical cell (PEC), Voc and Isc are recorded for the prepared CTS samples. I–V curves are shown in Fig. 8.

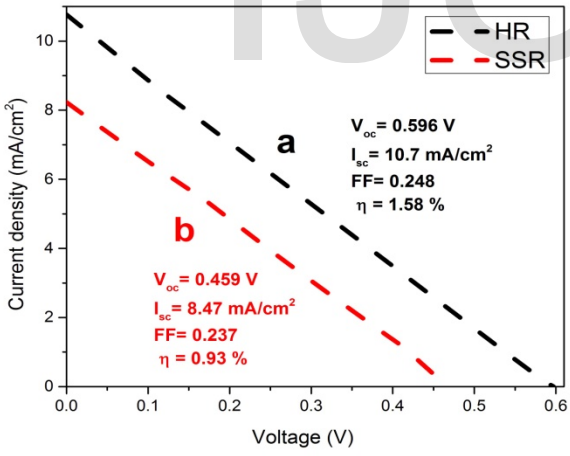

Fig. 8 I-V characteristics curve for CTS prepared by (a) HR (b) SSR under AM 1.5 and 1 sun

The power conversion efficiency (η %) and fill factor (FF %) are given by the following equations:

$$FF = \frac{V_{max}\, I_{max}}{V_{oc}\, I_{sc}} \quad 100 \qquad (2)$$

$$\eta = \frac{FF\, V_{oc}\, I_{sc}}{P_{in}\, A} \quad 100 \qquad (3)$$

Where: Voc: open circuit potential for working electrode, Isc: short circuit current measured at zero voltage, Vmax, and Imax are the optimum maximum voltage and current, respectively of the I-V characteristic relation, A: area of the working electrode, 1 cm^2 and Pin is the incident intensity of the light (100 mW/cm = 1Sun). Photovoltaic I-V characteristics results are summarized in Table I.

TABLE I. I-V characteristics results of Cu_2SnS_3 prepared by HR and SSR methods

Preparation method	Voc (V)	Isc (mA/cm^2)	FF %	η %
Hydrothermal method (HR)	0.596	10.7	24.8	1.58
Solid state reaction (SSR)	0.459	8.47	24	0.92

4 CONCLUSIONS

Cu_2SnS_3 (CTS) compound has been prepared with two different ways, hydrothermal (HR) and solid state reactions (SSR) methods. Single triclinic Cu_2SnS_3 phase is obtained through HR. While, cubic Cu_2SnS_3 is obtained beside orthorhombic phases of Cu_4SnS_4 and SnS. CTS powders give a maximum absorbances of light at wavelength of 290 and 240 nm for HR and SSR, respectively. The Calculated band gaps equal 2.25 and 2.5 eV for CTS samples prepared by HR and SSR, respectively. The conductivities of CTS powders synthesized by HR and SSR are $2.5x10^{-2}$ and $6.12x10^{-3}$ S/cm, respectively. Also the charge transfer resistance (Rct) are 3.5, 24 Ω for PEC prepared by HR and SSR, respectively.

The solar power conversion efficiencies are 1.58 and 0.93 % for CTS samples synthesized by HR and SSR, respectively. The formed (CTS) materials have suitable band gap and efficiencies values suggesting the application potential for this thin film in solar cells. Moreover, HR was found to be better than SSR for the preparation of (CTS).

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