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Synthesis, Characterization and Performance of Cu_2SnSe_3 for Solar Cell Application

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***Abstract* -** Cu_2SnSe_3 (CTSe) powders were prepared by solvothermal (SR) and solid state reactions (SSR) using low cost starting materials. The crystal structure, morphology, UV-Vis absorbance, electrochemical and solar energy properties were investigated using X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Electrochemical Impedance Spectroscopy (EIS) and solar energy applications using I-V characteristics measurements. A single cubic Cu_2SnSe_3 was obtained for the two methods of preparations. The calculated crystallite size (L) values for CTSe prepared by SR and SSR are 24.1 and 30.3 nm, respectively. UV-Vis. spectra for SR and SSR preparations showed maximum absorbencies at 240 nm with band gap (E_g) values of 0.9 and 1.4 eV, respectively. The charge transfer resistances (R_{ct}) were equal to 3.5 and 24 Ω for photoelectrochemical cells (PEC) and the calculated conductivities were equal to $3x10^{-2}$ and $2x10^{-2}$ $S.cm^{-1}$ for samples that prepared by SR and SSR methods, respectively. A good photoelectrochemical cell (PCE) has accomplished power conversion efficiency per unit area of about 0.84 and 0.64 % for cells prepared by SR and SSR, respectively.

***Keywords* -** CTSe; Solvothermal; Solid State Reaction; Optical properties; Photoelcetrochemical cell (PEC).

I. INTRODUCTION

Solar cell energy applications have become widely important 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 is 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]-[3]. Such materials encounter the problems of being expensive and unavailable, especially indium, tellurium and gallium. Also, the toxicity of elements like cadmium makes these materials less applicable. Copper-containing calcogenides, especially compounds of groups (I–IV–VI) 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 band gap range: 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. Copper tin selenide compounds were prepared mainly in the 2:1:3 elemental ratio i.e Cu2SnSe3[7]-[8] and 2:1:4 ratioi.eCu_2SnSe_4 [9].

Recently, Cu_2SnSe_3 (CTSe) have gained a great attention in many applications, especially the field of thin film solar cell application. CTSe material is suitable for solar cell energy application because it is environmentally friendly, cheap in preparation, non-toxic, inexpensive and earth-abundant. CTSe was prepared with different methods such as Vertical Bridgman–Stockbarger technique [10],[11], Direct current sputtering technique [12]-[14], Coevaporation process[15]-[17], Colloidal synthetic process[18]-[19], and Solvothermal process[7],[9],[20]. It was prepared with different crystal structures, e.g Cubic[7],[9],[15],[17]-[20] and Monoclinic [10],[11]. The crystallite size range is 12-30 nm [7],[18]. The band gap values range is (0.84-2.1 eV) [7],[12],[15]. All these previous parameters affect the efficiency of a definite prepared phase.

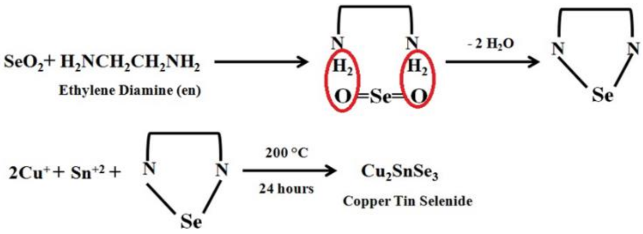
This work was done to study the preparation of Cu_2SnSe_3 (CTSe) using solvothermal reaction (SR) in comparison with the traditional solid-state reaction (SSR). Furthermore, there are only a are not enough data available about the electrochemical and photovoltaic properties of CTSe such as impedance, resistivity and conductivity, and solar power conversion efficiency so that this work was conducted to study these properties. In addition to that, a photoelectrochemical cell will be fabricated for the current-voltage measurements.

II. EXPERIMENTAL

1. Synthesis of Cu2SnSe3 by Solvothermal (SR) and Solid-State (SSR) Reactions

Cu_2SnSe_3 was prepared by solvothermal reaction as follows:- a mixture of 3.03 gm $Cu(NO_3)_2$.$_3H_2O$, 2.1 gm of SeO_2,1.2 gm of SnCl2 was added to 250 ml autoclave then about 200 ml ethylenediamine (ED) was added to the mixture then put in the oven at about 205 °C for about 24 hours (overnight). A black precipitate was obtained which was filtered and washed with distilled water and ethanol three times then put in the dryer at about 60 °C for about 4 hours; a black Cu_2SnSe_3 powder was obtained and kept for characterization and further investigation

The role of ethylene diamine (en) in the preparation of Cu2SnSe3 by SR can be illustrated by the following equations:



Cu_2SnSe_3 was also synthesized by solid-state process using stoichiometric ratios of Cu, Sn and Se powders that were mixed and ground well in a mortar. Then, the mixture was put in a boat crucible in a tube furnace at 600 °C for three hours under argon with 5 % H2 atmosphere. It was cooled to the room temperature under the argon atmosphere. A black powder was obtained, which was ground and kept for further investigations.

2. Samples Characterization

Samples compositions were identified by an X-ray diffractometer (XRD), model: Brukur advanced D8 Kristalloflex (Ni-filtered Cu K_α 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.

3. PhotoElectrochemical 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/cm^2. The cell configuration was: ITO/Cu_2SnSe_3/0.5 M KI + 0.5 M I_2/C. It was fabricated and characterized through current–voltage (I–V) measurements [21].Xenon arc lamp 150 W was used as a light source with solar simulator SciencetechSS150W- AAA. The cell was exposed to light intensity 1 Sun (100 mW cm^{-2}) 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 wereopen circuit voltage (V_{oc}), short circuit current (I_{sc}), maximum power (P_{max}), and filling factor (FF).

III. RESULTS AND DISCUSSION

1. Cu_2SnSe_3 Samples Characterization

The Cu_2SnSe_3 compound prepared by SR and SSM is characterized by XRD as shown in Fig. 1. The pattern of the XRD shows main three peaks at 2θ equal to 27°, 45°, and 53°. The crystal structure of this compound is cubic phase for both samples prepared by SR and SSR methods with miller indices of (111), (220) and (311) planes. The obtained results are in agreement with JCPDS data (01-089-2879) [7],[9],[15],[17]. Furthermore, the crystallite size was calculated from Scherer equation:

$$\mathbf{L} = \frac{\mathbf{0.94}}{\boldsymbol{\beta}\ \mathbf{cos}} \qquad (1)$$

Where; **(L)** is the crystallite size (nm), **(λ)** is wave length of the target (1.5406 Å for Cu), **(β)** is full width half maximum (FWHM) in radians, and **(θ)** is the chosen diffraction angle [22]. The calculated crystallite size values for CTSe prepared by SR and SSR are 24.1 and 30.3 nm, respectively

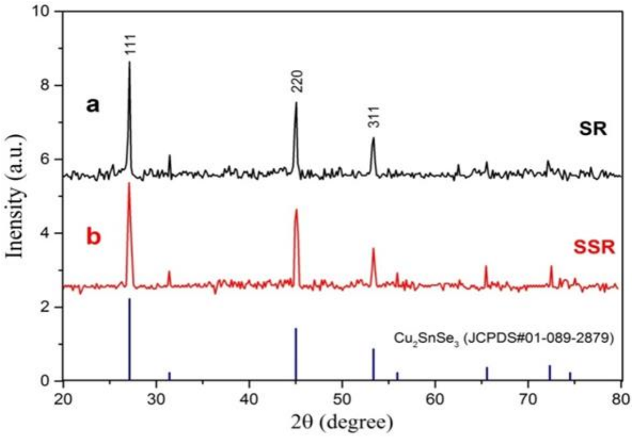
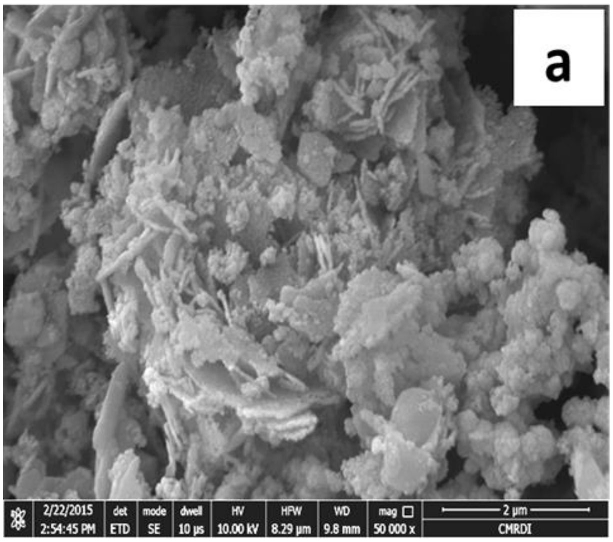


Fig .1. XRD pattern of Cu2SnSe3 prepared by (a) SR and (b) SSR

The morphology of the prepared samples is characterized by SEM inspection as shown in Fig. 2.The sample prepared by SR has homogenous spherical particles with a particle size of about 40 nm. On the other hand, the sample prepared by SSR shows agglomerate bulked shape. The particle size of the sample prepared by SSR is about 100 nm.



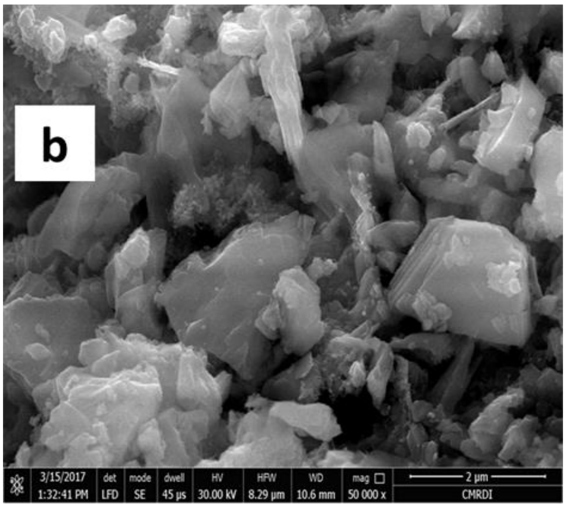


Fig .2. SEM photo for (a) CTSe prepared by SR (b) CTSe prepared by SSR

2. Optical Measurements

UV–Vis. absorbance measurements are used to reveal the energy structure and optical properties of the as-prepared Cu_2SnSe_3 architecture as shown in Fig. 3. Cu_2SnSe_3 crystal gives maximum absorbance wavelength of 240 nm that is somewhat near the visible region for both samples prepared with SR and SSR. The absorbance characteristics of the samples obey the model equation $\alpha h\nu = A\,(h\nu\text{-}E_g)^{0.5}$ 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 $(E_g)$is the energy gap [23].The energy band gap of Cu_2SnSe_3 is obtained from the plot of $(\alpha h\nu)^2$ vs. $h\nu$ (photon energy) by extrapolation as shownalso in Fig. 3. The energy gab of SR sample equals 0.9 eV that is smaller than the SSR one, 1.4 eV and this is attributed to the small particle and crystallite sizes of the CTSe prepared by SR. Also, the obtained value agrees with the previously reported values [7], [24]. It has been reported that CTSe thin films have a wide range of band gap energies, 0.7–1.38 eV [25], [26].

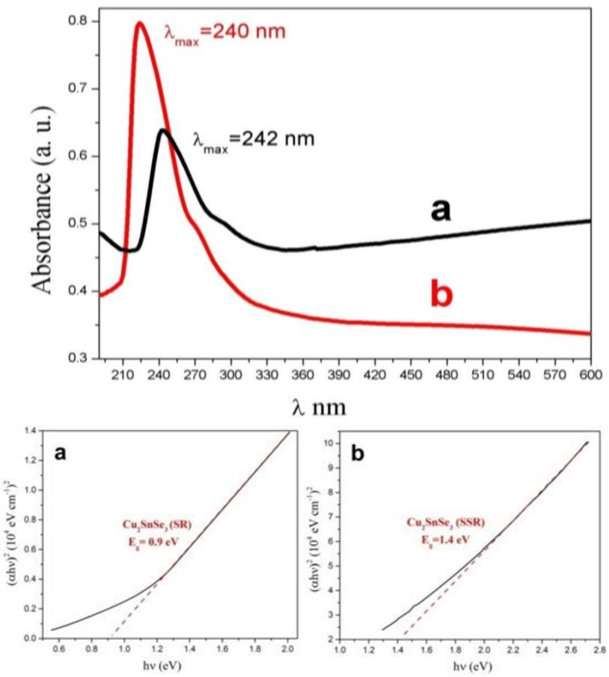


Fig .3. UV-Vis. Absorbance and band gap diagrams for CTSe prepared by (a) SR and (b) SSR ATSe

3. Electrochemical Impedance Spectroscopy (EIS) Measurements

EIS is applied for pellets of dimensions: radius (r) 0.675 cm and thickness (t) 0.35 cm of the prepared CTSe powder to measure the resistance of the material itself. Nyquist plot for CTSe pellets prepared by SSR and SR is shown in Fig. 4. The conductivities of CTSe powders materials prepared by SR and SSR are $3x10^{-2}$ and $2x10^{-2}$ $S.cm^{-1}$, respectively.

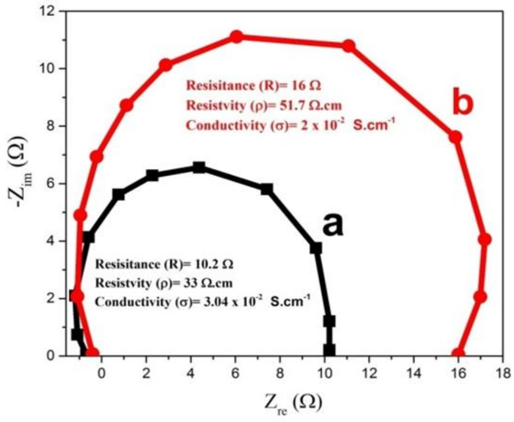


Fig .4. Nyquist plot for CTSe pellets prepared by (a) SR and (b) SSR

The EIS is also applied for photoelectrochemical cell (PEC) containing the sample plated on ITO glass as working electrode against glassy carbon counter electrode in electrolyte of iodine in potassium iodide. Cell configuration is: ITO/CTSe/ 0.5 M KI + 0.5 M I2 /C. The double layer capacitance (Cdl) is calculated using equations:

$$\mathbf{C_{dl} = 1/\,\omega R_{ct}} \qquad (2)$$

$$\boldsymbol{\omega = 2\pi f} \qquad (3)$$

Where; **(C_{dl})** is the double layer capacitance (Farad), **(ω)** is the radial frequency (radians/second), **(f)** is the frequency (hertz) and (R_{ct}) is the charge transfer resistance (Ω).

Nyquist plots for CTSe photo electrochemical cell (PEC) are shown in Fig. 5. For the CTSe sample prepared by SR two semicircles are presented with two values of charge transfer resistances R_{ct} and two values of double layer capacitance (C_{dl}). The charge transfer resistances (R_{ct}) are equal to 32.2 and 6 Ω for the sample prepared by SR. and While, R_{ct} of CTSe prepared by SSR is 40.1 Ω. The two semicircles can be attributed to the bulk and grain boundary resistances of CTSe [27],[28]. Double layer capacitances (C_{dl}) for photo electrochemical cells (PEC) and for the sample prepared by SR are equal to $7.8x10^{-9}$ and $6.67x10^{-5}$ F and for the sample prepared by SSR C_{dl} is equal to $2.51x10^{-8}$F. EIS results show higher conductivity of CTSe prepared by SR than that prepared by SSR with higher double layer capacitances (C_{dl}) for photo electrochemical cells (PEC) because electron transfer through double layer interface for cell prepared by SR is higher than that prepared by SSR which may be attributed to the fine structure of the samples obtained from SR as explained previously[29].

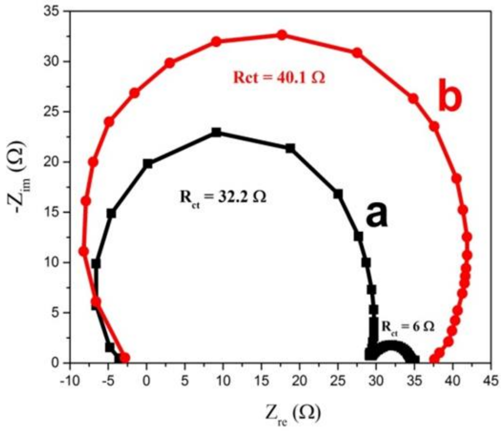
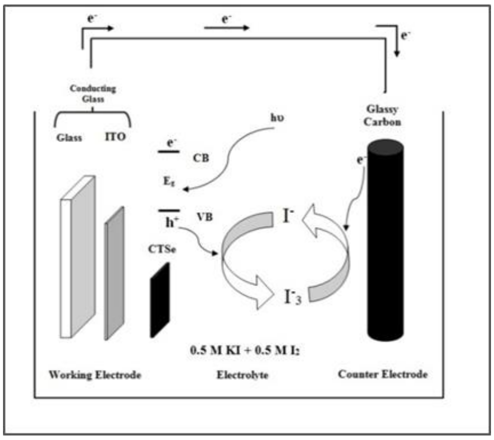


Fig .5. Nyquist plot for CTSe Photo Electrochemical Cell (PEC) prepared by (a) SR and (b) SSR

4. PhotovoltaicProperties

To obtain the power output characteristics of the photo electrochemical cell (PEC), V_{oc} and I_{sc} are recorded for the prepared CTS samples. The semiconductor | liquid junction proposed operating mechanism is illustrated in Fig. 6 diagram.



$$ITO/CTSe + h\upsilon \longrightarrow ITO/CTSe^{*}$$

$$ITO/CTSe^{*} \longrightarrow ITO/CTSe + (e^{-}/h^{+})$$

$$1/2\, I_3^{-} + e^{-}_{(C.E)} \longrightarrow 3/2\, I^{-}$$

$$3/2\, I^{-} + h^{+} \longrightarrow 1/2\, I_3^{-}$$

$$1/2\, I_3^{-} + e^{-}_{(CB)} \longrightarrow 3/2\, I^{-}$$

$$(ITO/CTSe)\, h^{+} + e^{-} \longrightarrow ITO/CTSe \quad \text{Recombination Process}$$

Fig .6. Representation of photoelectrochemical cell proposed operating mechanism

Table 1. I-V characteristics results of Cu_2SnSe_3 which was prepared with the two methods

Preparation Method	Voc (V)	Isc (mA.cm-2)	FF %	η %
Solvothermal Reaction (SR)	0.47	7.2	25	0.85
Solid State Reaction (SSR)	0.42	4.6	24	0.64

I–V curves are shown in Fig. 7. The power conversion efficiency (η %) and fill factor (FF %) are given by the following equations:

$$FF = \frac{V_{max}\, I_{max}}{V_{oc}\, I_{sc}} \; 100 \qquad (4)$$

$$\eta = \frac{FF\, V_{oc}\, I_{sc}}{P_{in}\, A} \; 100 \qquad (5)$$

Where: V_{oc}: open circuit potential for working electrode, I_{sc}: short circuit current measured at zero voltage, V_{max}, and I_{max} are the optimum maximum voltage and current, respectively of the I-V characteristic relation, A: area of the working electrode, 1 cm^2 and P_{in} is the incident intensity of the light (1Sun = 100 mW cm^{-2}). Photovoltaic I-V characteristics results are summarized in Table I. This study is considered one of the priority researches reported about the solar efficiency for Cu_2SnSe_3[30].

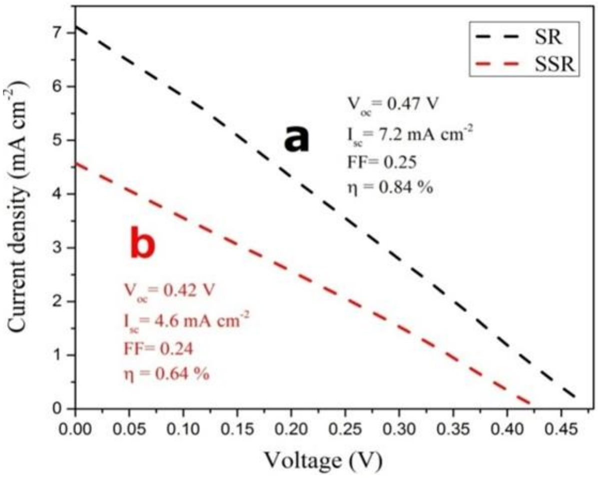


Fig .7. I-V characteristics curve for CTS prepared by (a) SR (b) SSR under 1 sun and AM 1.5

IV. CONCLUSIONS

Cu_2SnSe_3(CTSe) compound has been prepared with two different ways, Solvothermal (SR) and solid state reactions (SSR). Single cubic Cu_2SnSe_3 phase was obtained. CTSe sample papered with SR present better morphological, optical, electrochemical and photoelectrochemical measurements in comparison with the sample prepared with SSR. The crystallite size (L), E_g,R_{ct}, conductivities and power conversion efficiency per unit area values for CTSe prepared by SR and SSR are 24.1 & 30.3 nm, 0.9 & 1.4 eV, $3x10^{-2}$ & $2x10^{-2}$ $S.cm^{-1}$ and 0.84 & 0.64 %, respectively.This demonstrates the advantage of the SR method for the preparation of such compounds over the SSR method. The results also show the ability for the development of such compound for the application in solar cell fabrication.

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