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Effect of Solvent on the Structural, Morphological and Optical Properties of Cu_2ZnSnS_4 (CZTS) Nanoparticles

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ABSTRACT:

Copper zinc tin sulphide Cu_2ZnSnS_4 (CZTS) nanoparticles were synthesized by using different solvents like deionized water (DW) and ethanol. Selection of suitable solvents will direct the phase and morphology as well. The structural properties of nanoparticles have been characterized by X-Ray Diffraction. XRD pattern confirms the formation of CZTS. SEM reveals the formation of nanoplate like structure with agglomerations. The presence of Cu, Zn, Sn and S are identified by EDAX. The UV-Vis absorption spectra confirm the direct band gap of CZTS nanoparticles and were found to be 1.41eV, 1.45eV for water and ethanol respectively, which is quite close to the optimum value for semiconductor material.

KEYWORDS: CZTS nanoparticles, Solgel, Solvent

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INTRODUCTION:

Quaternary and ternary semiconductor nanomaterials have emerged as the most promising candidates for the current generation photovoltaics. The material with direct - band gap energies ranging between 1-2eV provide maximum absorption in solar spectrum[1]. Copper based ternary nanoparticles are studied in the last few years for solar energy applications[2]. Cu_2ZnSnS_4 (CZTS) is a promising alternative to current photovoltaic materials[3-5], such as Copper Indium Selenium - $CuInSe_2$ (CIS), Copper Indium Gallium Di-Selenide - $Cu(In,Ga)Se_2$ (CIGS). CZTS belongs to the I_2-II-IV-VI_4 group semiconductors. The optical and electronic properties of CZTS are similar to Copper Indium Gallium Selenide (CIGS). Due to its high absorption coefficient ~10^4 cm^{-1} in the visible range and direct band gap energy of 1.4 – 1.5eV, which are beneficial for harvesting maximum photon energy[6-7]. All the constituents in CZTS are highly abundant in earth's crust, non-toxic, economic and non-hazardous[8-11].

The solar cell performance is very sensitive to the electrical and optical properties. These properties are mainly depending upon the crystal structure and composition of the absorber material. In order to achieve the desired stoichiometry, it is highly important to understand and optimize the growth and formation of photovoltaic material. Various synthetic routes have been developed to prepare CZTS thin films and nanoparticles such as electrodeposition[12], thermal evaporation[13], sol–gel[14], sputtering[15], spray-pyrolysis[16], pulsed laser deposition[17], chemical vapor deposition[18], solvothermal method[19], hydrothermal method[20], and so on. The present work reports the synthesis of CZTS nanoparticles by a simple Sol-gel technique using different solvents which can yield very low cost, low power consumption and effective control of the size and shape of nanoparticles. The solvents have drastic influence of crystallographic phase and growth of the nanomaterials[21-22]. In this paper we report the structural, morphological, compositional and optical properties of CZTS nanoparticles.

EXPERIMENTAL DETAILS:

Copper(II)Chloride Dihydrate ($CuCl_2.2H_2O$), Zinc Chloride ($ZnCl_2$), Tin(II)Chloride Dihydrate ($SnCl_2.2H_2O$) and Thiourea (H_2NCSNH_2) are the starting materials. All the chemicals were used without further purification. CZTS nanoparticles have been synthesized through sol-gel technique. To form the sol-gel solution, Copper chloride, Zinc chloride, Tin chloride and Thiourea were dissolved in 40ml of ethanol in the stoichiometric ratio of 2:1:1:4, respectively under magnetic stirring.

Diethnolamine was used as a stabilizer to prevent the formation of precipitates. The solution was stirred at 60°C until a clear transparent sol-gel solution was obtained. The precipitate was filtered out, centrifuged in deionized water followed by ethanol several times to remove the byproducts. Further, it was dried at 70°C in hot air oven for 1 hour. The final products were annealed at 400°C for 3 hour and allowed to cool ambient temperature naturally. Finally black colored nanoparticles were collected by grinding the final product. A similar experiment was carried out in ethanol as a solvent instead of deionized water to see the effect of solvent on the structural, morphological and optical properties of the CZTS nanoparticles. There is no significant variation in the yield of the products with two different solvents.

CHARACTERIZATION TECHNIQUES:

The crystal structure of CZTS was examined by using XPERT-PRO X-ray diffractometer operated at 40 kV and 30 mA, using CuKα radiation source of λ=1.5406A°. The morphological and compositional analysis of the nanoparticles was carried out using JEOL mode JSM 6390 SEM with EDAX. Optical studies of the sample were done by using JASCO Corp., V-570 spectrophotometer.

RESULT AND DISCUSSION:

XRD Analysis:

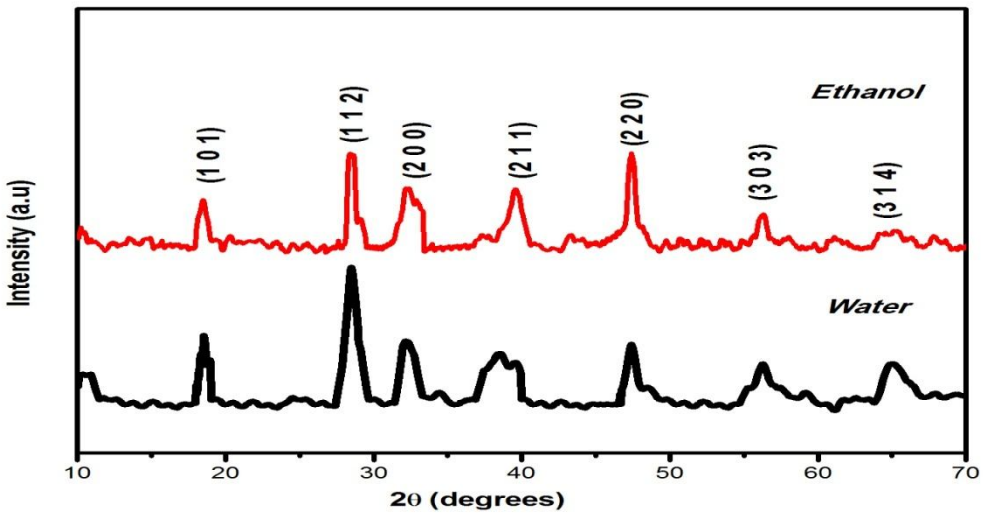

Fig.1: X-ray Diffraction pattern of CZTS nanoparticles with different solvents

X-ray Diffraction was used as the major tool for identification of the phases of CZTS nanoparticles. Also the crystallinity and particle size of the prepared nanoparticles was examined by using X-ray diffractometer. Fig.1 shows the XRD pattern of CZTS nanoparticles prepared using water and ethanol as solvent. It was scanned at 2θ angels starting from 10° to 70° with a step of 0.05 and counting time of 10s per step. The diffraction peaks at 2θ values 18.43°, 28.50°, 32.46°, 38.30°, 47.43°, 56.37° and 64.7° corresponds to (101), (112), (200), (211), (220), (303) and (314) reflection planes. The peaks are in good agreement with the structure of kesterite CZTS which is conformed using standard JCPDS data: (26-0575)[23]. The lattice parameters were calculated as a=0.54nm and c=1.08nm which are in good agreement with the previous reported data[24-26].

Crystalline size of the nanoparticles was estimated from XRD pattern according to full width half maximum (FWHM) of diffraction peaks using the Debye Scherer's formula[27],

$$\mathbf{D=\frac{0.9\lambda}{\beta Cos\theta}\ (nm)}$$

where, λ is the wavelength of CuKα1 radiation source =1.5406°A, β is the full width half maximum (FWHM) and θ is the diffraction angle. The calculated mean crystallite sizes for CZTS nanoparticles prepared in water and ethanol are 45 nm, 43 nm respectively.

SEM Analysis:

Scanning electron microscopic images depict the surface morphology of CZTS nanoparticles. Fig 2 shows the SEM image of CZTS nanoparticles for different solvents. Both the samples exhibited nanoplate like structure with agglomeration. By comparing this SEM images the grain size is almost same for both the sample.

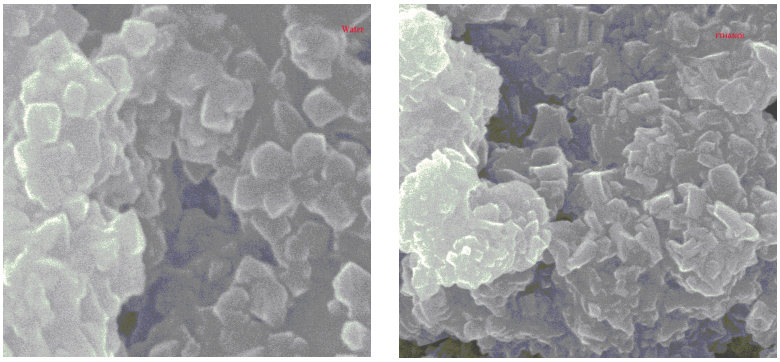

Fig.2: SEM morphology of CZTS nanoparticles with different solvents

Compositional Analysis:

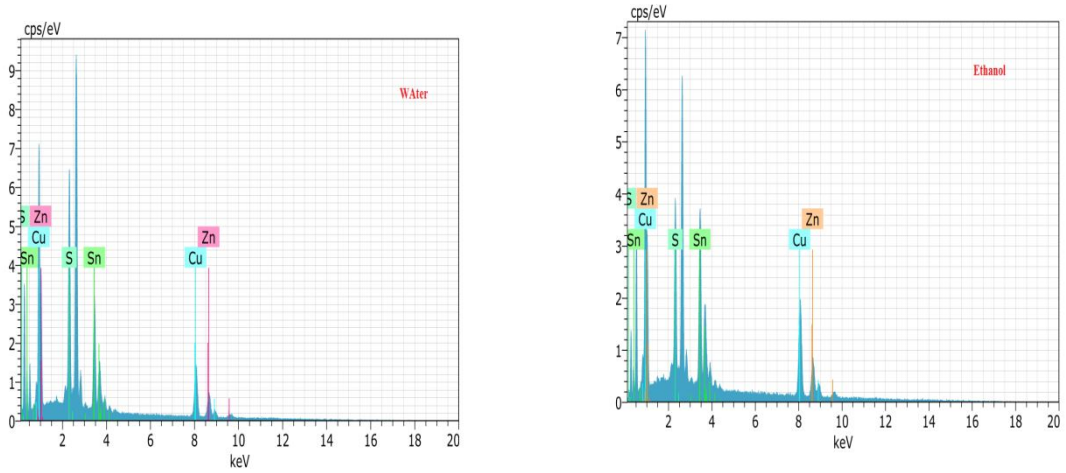

Fig.3: EDAX Spectra of CZTS nanoparticles with different Solvents

The energy dispersive analysis using X-rays (EDAX) is the most commonly used method for elemental analysis of materials. In this investigation, nanoparticles prepared by water and ethanol were subjected to EDAX analysis to confirm the existence of Cu, Zn, Sn and S. Fig. 3. Shows respective EDAX spectrum of CZTS nanoparticles. It shows the presence of Copper, Zinc, Tin and Sulphur in both the samples. The atomic percentages of the samples are shown in the table.1. The expected stoichiometric ratio of CZTS nanoparticles in terms of atomic percentage of Cu:Zn:Sn:S is 25.0 : 12.5 : 12.5 : 50.0. It is observed that both the samples are almost near to stoichiometric.

Table.1: Atomic % of Cu,Zn,Sn,S in CZTS nanoparticles with different solvents

Elements	**Atomic Percentage**	
	Water	**Ethanol**
Copper (Cu)	24.88	24.75
Zinc (Zn)	12.97	12.59
Tin (Sn)	12.32	12.91
Sulphur (S)	49.83	49.75

Optical Absorption and Band Gap:

The optical absorption spectra for the CZTS nanoparticles are recorded in the wavelength range of 250nm to 1000nm at room temperature. Optical band gap energy E_g can be determined from the experimental values of absorption coefficient as a function of photon energy hγ, using the relation[28],

$$\alpha = A(h\gamma - E_g)^2/h\gamma,$$

where the symbols have their usual meaning. The value of absorption coefficient in the present case is of the order of 10^4 cm^{-1}, which supports the band gap nature of the earlier reportsl. Fig.4 shows the absorption spectra of CZTS nanoparticles with different solvents. The optical band gap of nanoparticles was determined by the Tauc plot method[29]. The optical band gap energy was calculated by extrapolating the linear region of the plot of $(\alpha h\gamma)^2$ versus hγ and taking the intercept on the hγ axis where y=0. Fig.5 shows the plot of $(\alpha h\gamma)^2$ versus hγ for CZTS nanoparticles. In the present study, the calculated band gap for water and ethanol was 1.41eV,1.45eV respectively, which is consistent with the earlier reports[30-33].

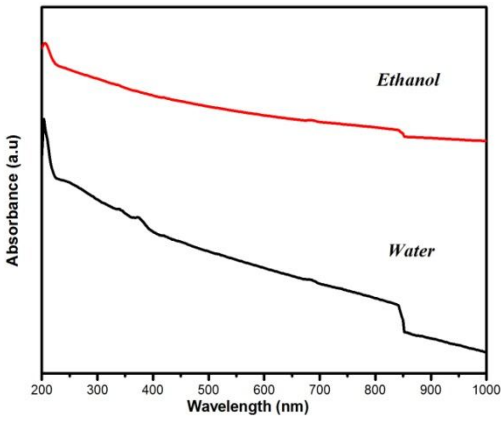

Fig.4:Absorption spectra of CZTS nanoparticles with different solvents

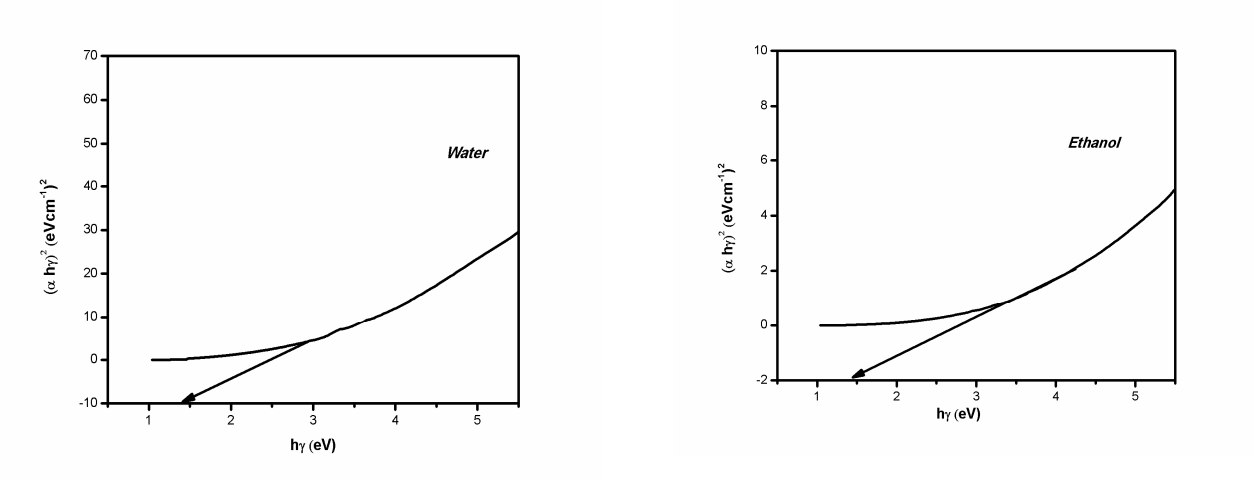

Fig.5:Tauc plot of CZTS nanoparticles with different solvents

CONCLUSION:

CZTS nanoparticles were synthesized using water and ethanol as solvent by simple sol-gel method. The crystal lattice parameters of nanoparticles extracted from XRD result strongly support the kesterite crystal structure. The SEM micrograph shows the CZTS particles of both the samples are same structure with agglomeration. The EDAX confirms the presence of all four constituents Cu, Zn, Sn and S with good stiochiometry. The band gap of the CZTS nanoparticles for water and ethanol was calculated as 1.41eV and 1.45eV, which is in the range of optimal band gap value for absorber layer in the photovoltaic cells. Cu_2ZnSnS_4 nanoparticles prepared here demonstrate the kesterite structure with desired composition, ideal band gap and superior photo response. Hence both the solvents are suitable for further sol-gel synthesizing of CZTS nanoparticles for the photovoltaic application.

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