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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:

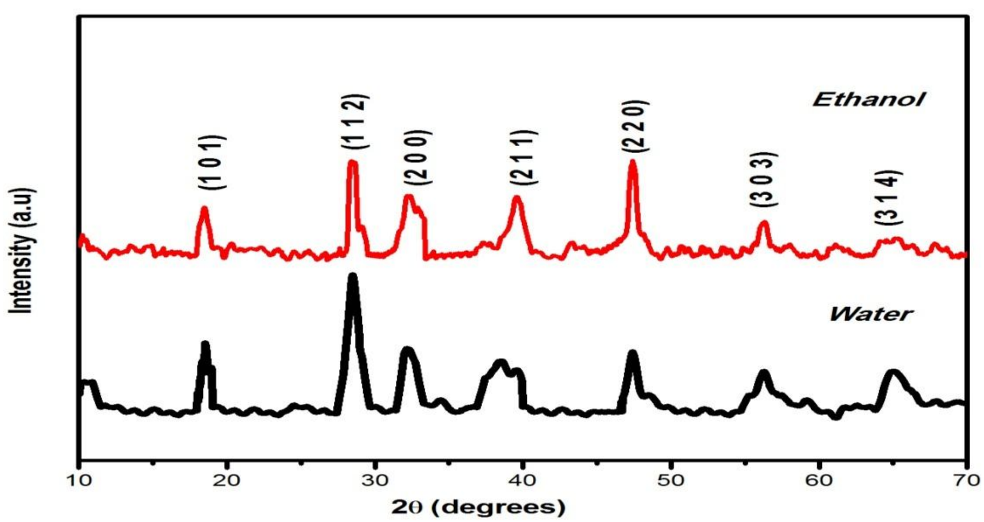

Fig.1: X-ray Diffraction pattern of CZTS nanoparticles with different solvents

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],

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

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.

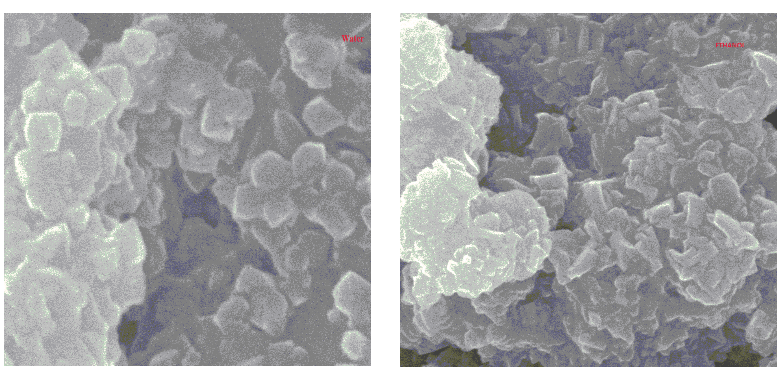

Fig.2: SEM morphology of CZTS nanoparticles with different solvents

Compositional Analysis:

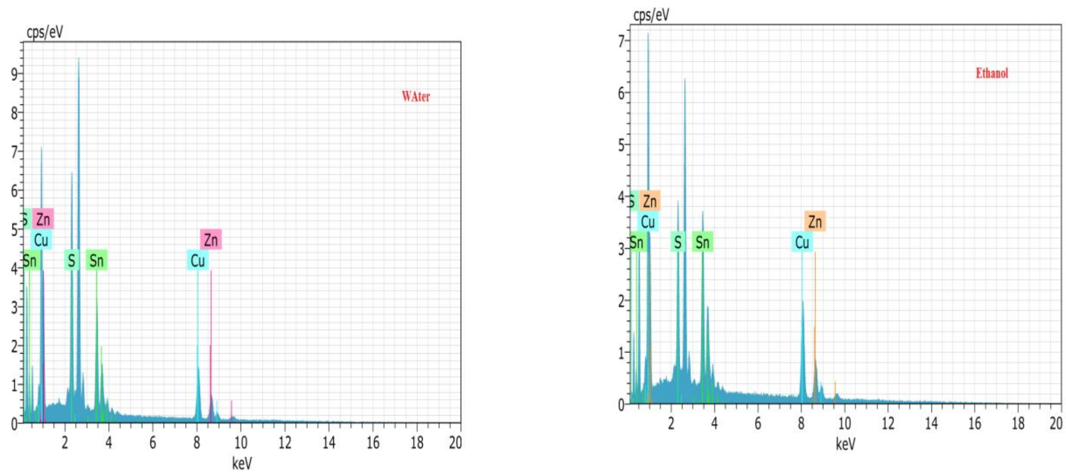

Fig.3: EDAX Spectra of CZTS nanoparticles with different Solvents

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].

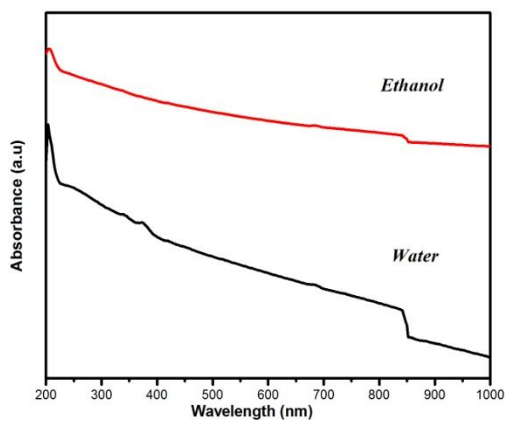

Fig.4:Absorption spectra of CZTS nanoparticles with different solvents

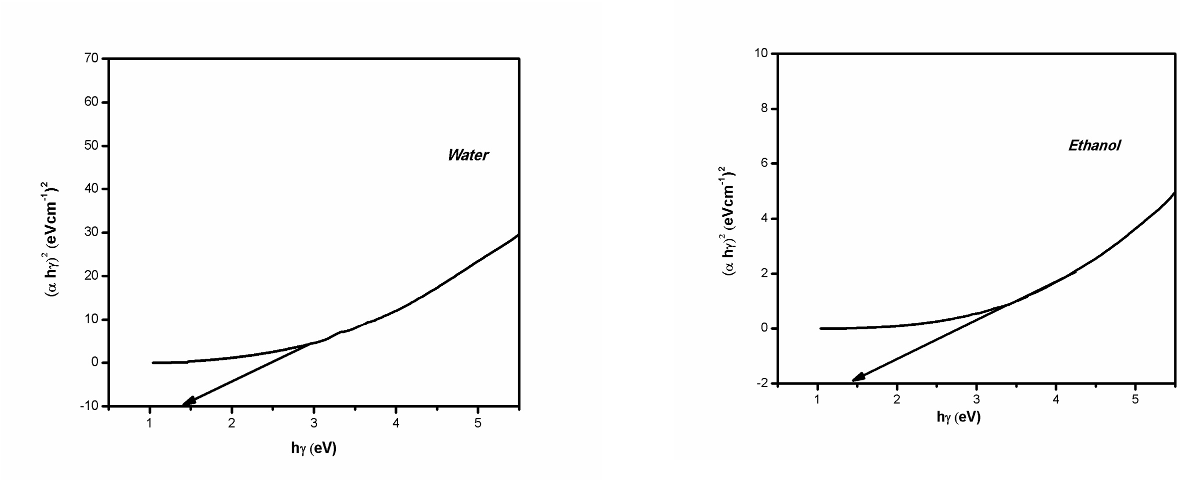

Fig.5:Tauc plot of CZTS nanoparticles with different solvents

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.

REFERENCES:

1. Inamdar AI, Ki-Young Jeon, et al. Controlled Growth of Cu_2ZnSnS_4 (CZTS) Thin Films for Heterojunction Solar-cell Applications, Journal of the Korean Physical Society. 2012; 60(10):1730-1734.
2. Ananthakumar S Ram Kumar J, Moorthy Babu S, Influence of co-ordinating and non-coordinating solvents in structural and morphological properties of Cu_2ZnSnS_4 (CZTS) nanopar ticles, Optik - International Journal for Light and Electron Optics. 2016;130.

3. Kwang-Soo Lim, Seong-Man Yu, Arun R.Khalkar, et al. Comparison of Cu_2ZnSnS_4 thin films and solar cell performance using Zn target with ZnS target, Journal of Alloys and Compounds. 2015;650:641-646.
4. Jiahua Tao, Junfeng Liu, Jun He, et al. Synthesis and characterization of Cu_2ZnSnS_4 thin films by the sulfuriation of co-electrodeposited Cu-Zn-Sn-S precursor layers for solar cell applications, Royal Society of Chemistry. 2014; 4: 23977.
5. Muska K, Kauk M, Altosaar M, et al. Synthesis of Cu_2ZnSnS_4 Monograin powders with different compositions, Energy Procedia. 2010;10:203-207.
6. Shinde NM, Dubal DP, Dhawale DS, et al. Room temperature novel chemical synthesis of Cu_2ZnSnS_4 (CZTS) absorbing layer for photovoltaic application, Material Research Bulletin. 2012;47:302-307.
7. Hossain MI, Prospects of CZTS solar cells from the perspective of material properties, fabrication methods and current research challenges, Chalcogenide letters. 2010;9:231-242.
8. Cheng ZHANG, Jie ZHONG and Jiang Tang, $Cu_2ZnSn(S,Se)_4$ thin film solar cells fabricated with benign solvents, Frontiers of Optoelectronics.2015;8(3): 252-268.
9. Duy-Cuong Nguyen, Seigo Ito, Dang Viet Anh Dung, Effects of annealing conditions on crystallization of the CZTS absorber and photovoltaic properties of $Cu(Zn,Sn)(S,Se)_2$ Solar Cells, Journal of Alloys and Compounds. 2015;1:258.
10. Kask E, Raadik T, Grossberg M, et al. Deep defects in Cu_2ZnSnS_4 monograin solar cells, Energy Procedia.2011;10:261–265.
11. Jeon M, Tanaka Y, Shimizu T, Shingubara S, Formation and characterization of single-step electrodeposited Cu_2ZnSnS_4 thin films: Effect of complexing agent volume, Energy Procedia. 2011;10:255-260.
12. Scragg JJ, Dale PJ, Peter LM, Synthesis and characterization of Cu_2ZnSnS_4 absorber layers by an electrodeposition-annealing route, Thin Solid Films. 2009; 517:2481–2484.
13. Schubert BA, Marsen B, Cinque S, et al. Cu_2ZnSnS_4 thin film solar cells by fast coevaporation, Progrss in Photovoltaics Research and. Applications. 2011;19:93-96.
14. Tanaka K, Moritake N, Uchiki H, Preparation of Cu_2ZnSnS_4 thin films by sulfurizition sol-gel deposited precursors, Solar Energy Materials and Solar Cell.2007;91: 1199–1201.
15. Jimbo K, Kimura R, Kamimura T, Yamada S, Cu_2ZnSnS_4-type thin film solar cells using abundant materials, Thin Solid Films.2007;515:5997–5999.

16. Kamoun N, Bouzouita H, Rezig B, Fabrication and characterization of Cu_2ZnSnS_4 thin films deposited by spray pyrolysis technique, Thin Solid Films. 2007;515:5949–5952.
17. Sun L, He J, Kong H, et al. Structure, composition and optical properties of Cu_2ZnSnS_4 thin films deposited by pulsed Laser deposition method, Solar Energy Materials and Solar Cells. 2011;517:2907-2948.
18. Washio T, Shinji T, Tajima S, et al. Efficiency of Cu_2ZnSnS_4-based thin film solar cells using oxide precursors by open atmosphere type CVD, Journal of Material Chemistry. 2012;22: 4021-4024.
19. Tian Q, Xu X, Han L, et al. Hydrophilic Cu_2ZnSnS_4 nanorystals for printing flexible, low cost and environmentally friendly solar cells, Crystal Engineering Communication. 2012;14: 3847-3850.
20. Wang C.R, Cheng C, Caoet Y, et al. Synthesis of Cu_2ZnSnS_4 nanocrystallines by a hydrothermal route, Japanese Journal of Applied Physics. 2011;50:065003-(1-3).
21. Dalmaschio CJ, Ribeiro C, Leite ER, Impact of the colloidal state on the oriented attachment growth mechanism, Nanoscale. 2010;2:2336-2345.
22. Jun YW, Seo JW, Oh SJ, Cheon J, Recent advances in the shape control of inorganic nano-building blocks, Coordination Chemistry Review. 2005;249:1766-1775.
23. Krishnaiah Mokuralaa, Anvita Kamblea, Chaitanya Bathinab, et al. Effect of solvent, reaction time on morphology of Cu_2ZnSnS_4 (CZTS) nanoparticles and its application in Dye Sensitized Solar Cells, Materials Today: Proceedings. 2016;3:1778–1784.
24. Prabhakar T, Jampana N, Effect of sodium diffusion on the structural and electrical properties of Cu_2ZnSnS_4 thin films, Solar Energy Materials and Solar Cells. 2011;95:1001-1004.
25. Kishore Kumar YB, Suresh Babu G, Uday Bhaskar P, Sundara Raja V, Preparation and characterization of spray-deposited Cu_2ZnSnS_4 thin films, Solar Energy Materials and Solar Cells.2009;93:1230-1237.
26. Mali SS, Shinde PS, Betty CA, et al. Synthesis and characterization of Cu_2ZnSnS_4 thin films by SILAR method, Journal of physics and chemistry of solids. 2012;73:735-740.
27. Kannan AG Manjulavalli TE, Characterization of CZTS nanoparticles synthesized by solvothermal method for solar cell application, International Journal of Chem Tech Research. 2015;7(3):1167-1171.
28 .Deokate RJ, Adsool AD, Shinde NS, et al. Structural and optical properties of Spray-Deposited Cu_2ZnSnS_4 thin films, Energy Procedia. 2014;54:627-633.

29. Chinnaiyah Sripan, Vinod E Madnavan, Annamraju Kasi Viswanath and Ganesan R. Sulfurization and annealing effects on thermally evaporated CZTS films, Materials letter. 2017;189:110-113.
30. Guo BL, Chen YH, .Liu XJ, et al. Optical and electrical properties study of sol-gel derived Cu_2ZnSnS_4 thin films for solar cells, AIP Advances. 2014;4:97155.
31. Todorov T, Kita M, Carda J, Escribano P, Cu_2ZnSnS_4 films deposited by a soft-chemistry method, Thin Solid Films. 2009;517:2541–2544.
32. Wangperawong A, King JS, Herron SM, et al. Aqueous bath process for deposition of Cu_2ZnSnS_4 photovoltaic absorbers, Thin Solid Films. 2011;519:2488–2492.
33. Sarkar S, Bhattacharjee K, Dasb GC, Chattopadhyay KK, Self-sacrificial template directed hydrothermal route to kesterite- Cu_2ZnSnS_4 microspheres and study of their photo response properties, Crystal Engineering Communication. 2014;16:2634-2644.