Share Your Innovations through JACS Directory

Journal of Nanoscience and Technology

Visit Journal at https://www.jacsdirectory.com/jnst

ISSN: 2455-0191

Preparation and Characterization of Nano Structured Cu_2ZnSnS_2 (CZTS) Thin Film by Spray Pyrolysis Method for Photovoltaic Application

Mahendra M. Bagul[1,*], Ajay A. Nikam[1], Mohsin Y. Shaha[1], Priyanka J. Gare[1], Gotan H. Jain[2], Anil B. Gite[2]

[1]*Department of Physics, Arts Commerce and Science College, Dindori, Affiliated to Savitribai Phule Pune University, Nashik – 422 002, Maharashtra, India.*
[2]*Department of Physics, S.N.J.B's K.K.H.A. Arts, S.M.G.L. Commerce and S.P.H.J. Science College, Affiliated to Savitribai Phule Pune Univ., Chandwad – 422 002, Maharashtra, India.*

A R T I C L E D E T A I L S

Article history:
Received 24 February 2026
Accepted 11 March 2026
Available online 15 April 2026

Keywords:
CZTS
Ultrasonication
Raman Spectra
Spray Pyrolysis

A B S T R A C T

The nano structured Cu_2ZnSnS_4 (CZTS) were synthesised by ultra-sonication technique using the precursor solution at constant temperature. The precursor solution used to contain copper chloride [$CuCl_2.2H_2O$], zinc chloride [$ZnCl_2.2H_2O$], tin chloride [$SnCl_4.5H_2O$], and thiourea [$SC(NH_2)_2$]. The precursor solution contains 50% of double distilled water and 50% of methanol as solvents then it kept under ultra-sonication for 3 hrs, then the required precursor material CZTS were synthesised by using spray pyrolysis technique. The physical and optical properties of CZTS material have been investigated by different techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy, UV-visible spectroscopy and transmission electron microscopy (TEM). The formation of CZTS has been confirmed by XRD and formation of tetragonal phase with orientation along (112) direction with crystallite size varies from 15 nm to 45 nm. The band gap values of CZTS thin film were found about 1.43 eV by analysis of UV-visible Spectroscopy. Raman spectra are characterized by the main CZTS peaks at 332.01 cm^{-1}, and weaker CZTS modes at 121.16 cm^{-1} and 179.11 cm^{-1}. The SEM image shows formation of nano scale particulate clusters with size vary in the range of 16 nm to 35 nm. Energy dispersive spectrum (EDS) spectra were recorded in order to determine the elemental composition of the CZTS nano particles. A TEM image of the CZTS shows inter planar spacing (*d*-spacing) measured in the HRTEM is 0.31 nm corresponds to (112) family plane. The CZTS solar cell has conversion efficiency (η) is 15.5 %.

1. Introduction

The Cu_2ZnSnS_4 (CZTS) is a direct band gap semiconductor high absorption coefficient in the visible light region (> 104 cm^{-1}) and band gap in the range of 1.4–1.6 eV which is very close to the optimal value of the absorber thin film solar cell layer [1, 2]. In the past few years as a promising cheap green product, after in-depth research photovoltaic material because it contains the rich earth and non-toxic elements [3]. So far, CZTS film has prepared by various experimental techniques as atomic beam sputtering [4], its thermal evaporation ingredients [5], spray pyrolysis [6] and sol-gel [7].recent, Preparation of CZTS colloidal nano crystals by thermal injection method attracts much attention in process able solutions solar cell technology, because of its chemical properties and viscosity can tailored to be used as raw material in film use ink printing, spray coating, dip coating or roll coating deposition roll coating under ambient conditions [8]. CZTS display polymorphism of the crystal structure of potash feldspar or stannous. At the nano meter level, CZTS will also crystallize in diatomaceous earth or cassiterite phase, similar to tetragonal unit Cell [9-13].

The present work introduces the comprehensive preparation and characterization of CZTS nano structured thin film by spray pyrolysis method. The formation of nano crystals has been systematically X-ray diffraction, Raman spectroscopy, scanning studies Electron microscope (SEM), energy dispersive X-ray spectroscopy (EDS), transmission electron microscope (TEM), and ultraviolet visible light (UV).

2. Experimental Methods

In the current work, copper chloride ($CuCl_2$), zinc chloride ($ZnCl_2$), tin chloride ($SnCl_2$) and thiourea [$(NH_2)_2CS$] are used as a precursor material to deposit CZTS film on soda lime by using a self-made spray pyrolysis deposition device glass (SLG) substrate. All chemicals used are of analytical grade. The chemicals were purchased from Sigma Aldrich (purity 99.99%) and used as is with molar concentration of $CuCl_2.2H_2O$ and $ZnCl_2.2H_2O$, ($SnCl_4.5H_2O$) and $(NH_2)_2CS$ at 0.05 M each. The precursor solution contains 50% of double distilled water and 50% of methanol as solvents then it kept under ultrasonication for 3 hrs, then the required precursor material CZTS were synthesised by using spray pyrolysis deposition technique. Use built-in thermocouple to keep substrate temperature constant at 180 °C. The air flow rate and the distance from the nozzle to the substrate are kept fixed at 22 LPM and 26 cm, respectively. To carry out the required deposition time and then cool the sample to room temperature, the temperature is then taken out for characterization.

3. Results and Discussion

3.1 X-Ray Diffraction Analysis

To identify the crystalline and the existence of material phases of SPD films deposited; low-angle X-ray diffraction (XRD) studies were performed. Fig. 1 shows the low-angle XRD pattern. It can be clearly seen from the figure that the XRD graph shows peaks at 28.3661, 30.7992, 33.1363, 51.2406 and 51.7528 which are corresponds to the planes (112), (101), (020), (031) and (103) crystal orientations of CZTS potassium feldspar [14]. The tetragonal phase [JCPDS data card number 26-0575] indicates that this film is polycrystalline. The main peak at (112) is indicating that the crystallites in the film have a preferential orientation in the (112) direction.

The average crystallite size was calculated from XRD spectrum using Scherer's formula [14]. In accordance with the Table 1, it can be observed that the CZTS particle sizes of these films were estimated to be 15 nm to 45 nm.

*Corresponding Author:mahendra05041989@gmail.com(Mahendra M. Bagul)

https://doi.org/10.30799/jnst.S204.26110304

Cite this Article as: Mahendra M. Bagul, Ajay A. Nikam, Mohsin Y. Shaha, Priyanka J. Gare, Gotan H. Jain, Anil B. Gite, Preparation and characterization of nano structured Cu_2ZnSnS_2 (CZTS) thin film by spray pyrolysis method for photovoltaic application, J. Nanosci. Tech. 11(3) (2026) 1090–1092.

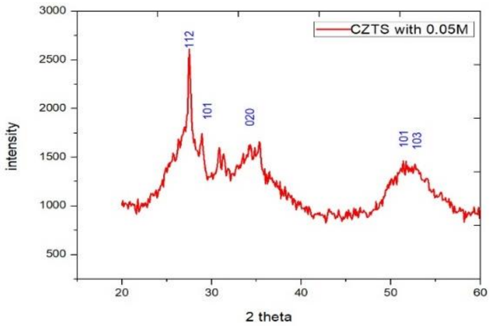

Fig. 1 XRD pattern of CZTS thin film

Table 1 Average crystallite sizes calculated by Scherer's formula

S. No.	2Θ	Intensity	d-spacing	Crystalline size, nm	(hkl)
1	26.9894	3616.077	3.310	15	-
2	28.3661	2374.9274	3.149	27	112
3	30.2709	1991.004	2.945	38	-
4	30.7992	1930.063	2.899	45	101
5	33.1363	2369.8491	2.702	33	020
6	33.7926	2582.1242	2.665	27	-
7	34.7210	2464.3064	2.581	41	-
8	51.2406	1998.1137	1.784	21	031
9	51.7528	2021.4742	1.765	24	103

3.2 Optical Properties of CZTS Thin Film

The absorption spectrum of CZTS thin film. It is clearly reveals that the CZTS sample holds higher absorption in the wavelength range of 300-650 nm. Absorption beyond this wavelength range the coefficient is reduced. Use the relationship $(\alpha h\upsilon)^2 = A\,(h\upsilon - E_g)$, optical band gap energy was derived, here α is the absorption coefficient, hυ is the photon energy in electron volts, A is a constant, and Eg is the band gap energy. Fig. 2 shows the relationship between $(\alpha h\upsilon)^2$ and hυ. The Tauc plot of CZTS gives an optical band gap value of thin film is 1.43 eV. The value is in the range of 1.4-1.6 eV reported earlier, and is also the best band gap of the absorber solar cells [15].

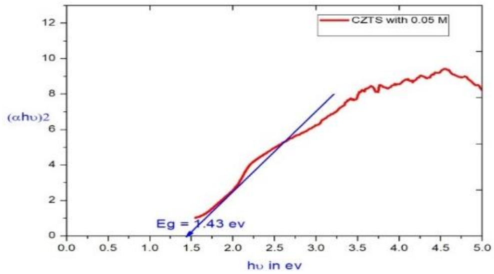

Fig. 2 Tauc plot of CZTS thin film

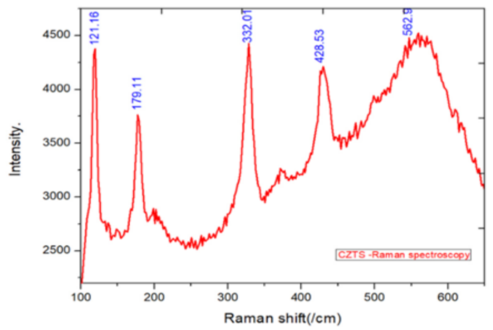

Fig. 3 Raman spectrum of the CZTS thin film

3.3 Raman Spectroscopic Analysis

Recently, many researchers have used Raman technology to study the phase purity of CZTS. Fig. 3 shows the Raman spectrum of the CZTS thin film prepared by spray pyrolysis deposition. Raman peaks are observed at 121.16, 179.11, 332.01, 428.53 and 562.9 cm^{-1} in thin films, which is close to the reported overall value CZTS [16, 17]. The Raman spectral peaks are interpreted as the main CZTS peaks at 332.01 cm^{-1}, and weaker CZTS modes at 121.16 cm^{-1} and 179.11 cm^{-1}. Interestingly, due to the characteristic mode of SnS and the other peaks like 428.53 and 562.9 are observed. These results indicate the formation of secondary-phase CZTS by chemical spray pyrolysis method [16].

3.4 FE-SEM Surface Study

Fig. 4 shows a field emission scanning electron microscope (FE-SEM) image of a CZTS thin film prepared at prepared by spray pyrolysis deposition. The FESEM images show formation of nano scale particulate clusters which constitute the films. It shows a large number of micro grains exist on the glass. In addition to this there are grains covered with clusters. The sizes of the islands vary in the range of 17 to 40 nm. Due to volume contraction arising from the evaporation of volatile products [18].

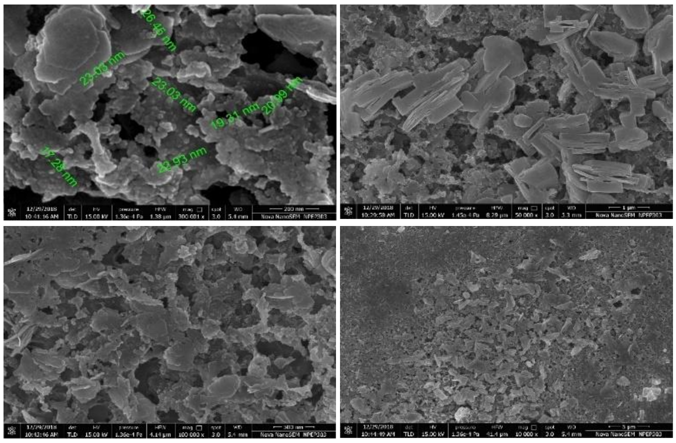

Fig. 4 FE-SEM images of CZTS thin film

3.5 Energy Dispersive Spectrum (EDS) Study

Energy dispersive spectrum (EDS) spectra (Fig. 5) were recorded in order to determine the elemental composition of the CZTS nanoparticles [19]. Table 2 shows EDS of CZTS material confirms the presence of Cu, Zn, Sn and S, typically showing a copper-poor and zinc-rich composition for optical solar cell performance.

Table 2 EDS results of chemical composition of CZTS thin film

El AN Series	unn.C [wt.%]	norm.C [wt.%]	Atom.C [at.%]	Error (1 Sigma) [wt.%]
Sn 50 L-series	19.86	43.16	26.88	0.65
Zn 30 K-series	16.29	35.39	40.00	0.71
Cu 29 K-series	6.57	14.28	16.61	0.34
S 16 K-series	3.30	7.16	16.51	0.15
Total:	46.02	100.00	100.00	

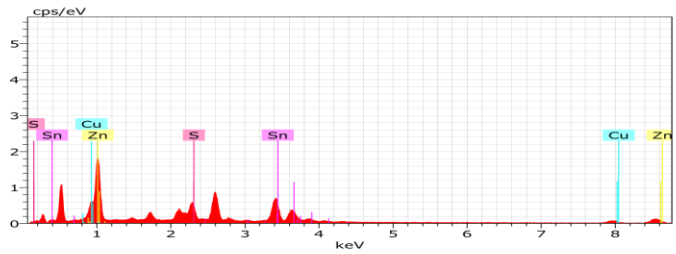

Fig. 5 EDS spectral chemical composition of CZTS thin film

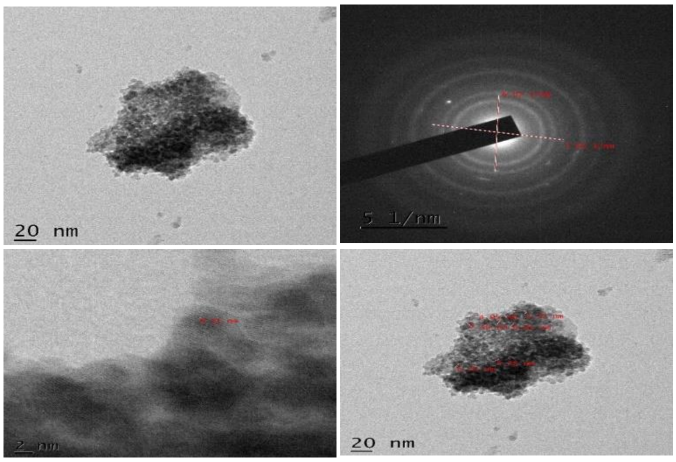

Fig. 6 (a) TEM images of as-synthesized CZTS nano particles, (b) selected area electron diffraction (SAED) image of a synthesized CZTS nanoparticles, (c) high resolution transmission electron microscopy (HRTEM) image of a synthesized CZTS and d) variation of crystal size from 3.23 nm to 7.5 nm

https://doi.org/10.30799/jnst.S204.26110304

Cite this Article as: Mahendra M. Bagul, Ajay A. Nikam, Mohsin Y. Shaha, Priyanka J. Gare, Gotan H. Jain, Anil B. Gite, Preparation and characterization of nano structured Cu_2ZnSnS_2 (CZTS) thin film by spray pyrolysis method for photovoltaic application, J. Nanosci. Tech. 11(3) (2026) 1090–1092.

3.6 Transmission Electron Microscopy (TEM) Study

Transmission electron microscopy (TEM) images of the CZTS nanocrystals produced by 3 hours ultrasonication are shown in Fig. 6. The inter planar spacing (*d*-spacing) measured in the HRTEM is 0.31 nm corresponds to (112) family plane [19].

3.7 I-V Characterization of CZTS Solar Cell

The CZTS solar cell exhibit typical p-n junction diode I-V characteristics (Fig. 7), featuring a forward bias voltage, increased current under illumination and a characteristic diode behaviour. They have optimal direct bandgap 1.43 eV and high absorption coefficients (>10^4 cm^{-1}). The conversion efficiency (η) of the spray deposited CZTS solar cell is 15.5 %with short circuit current density 3.5 mA/cm^2, open circuit voltage 990 mV and fill factor 44.76%.

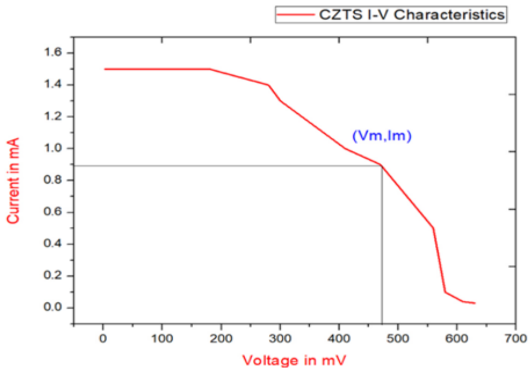

Fig. 7 I-V characteristics of CZTS solar cell

4. Conclusion

CZTS absorber thin films were successfully fabricated through a simple and cost-effective spray pyrolysis technique. An organic solvent CZTS was used for preparing the solution for the spray pyrolysis. X-ray diffraction, Raman spectroscopy, FESEM, UV-visible spectroscopy, TEM and efficiency measurements were carried out to characterize the spray pyrolyzed film. Formation of phase pure CZTS was confirmed from the XRD patterns and Raman spectra.

The absorption co-efficient calculated from the UV-visible spectra was found that the optical band gap value of thin film is 1.43 eV. The SEM micrographs reveal that the particles consist of similar morphology with average size in the range of 17-40 nm. The inter planar spacing (*d*-spacing) measured in the HRTEM is 0.31 nm corresponds to (112) family plane. The conversion efficiency (η) of the spray deposited CZTS solar cell is 15.5%. The experimental results showed that the current-voltage (I-V) characteristic properties of the cell have a strong dependence on the photovoltaic parameters of the thin films.

Based on the results of the analysis, it concluded that CZTS with suitable physical properties could fabricate for solar cell by spray pyrolysis technique.

Acknowledgement

Authors are grateful to acknowledge to The Principal, MVP Samaj's Arts Commerce and Science College, Dindori, Nashik, Maharashtra, India.

References

[1] S.Y. Gezgin, A. Houimi, B. Mercimek, H.S. Kılıç, The effect of Cu_2ZnSnS_4 ultrathin film thickness on the electrical characteristic of Cu_2ZnSnS_4/Si heterojunction solar cells in the darkness and under illumination conditions, Silicon 13 (2021) 3555–3567.

[2] A. Haddout, A. Raidou, M. Fahoume, A review on the numerical modeling of CdS/Cu_2ZnSnS_4-based solar cells, Appl. Phys. A 125 (2019) 124.

[3] P. Jackson, D. Hariskos, E. Lotter, S. Paetel, R. Wuerz, et al., New world record efficiency for Cu(In,Ga)Se_2 thin-film solar cells beyond 20%, Prog. Photovolt. 19 (2011) 894–897.

[4] T.M. Razykov, C.S. Ferekides, D. Morel, E. Stefanakos, H.S. Ullal, H.M. Upadhyaya, Solar photovoltaic electricity: Current status and future prospects, Sol. Energy 85 (2011) 1580–1608.

[5] A. Rios-Flores, O. Arés, J.M. Camacho, J.L. Peña, Procedure to obtain higher than 14% efficient thin film CdS/CdTe solar cells activated with HCF_2Cl gas, Sol. Energy 86 (2012) 780–785.

[6] H. Katagiri, N. Sasaguchi, S. Hando, S. Hoshino, J. Ohashi, T. Yokota, Preparation and evaluation of Cu_2ZnSnS_4 thin films by sulfurization of stacked metallic layers, Sol. Energy Mater. Sol. Cells 49 (1997) 407–414.

[7] J. Zhang, L. Shao, Y. Fu, E. Xie, Cu_2ZnSnS_4 thin films prepared by sulfurization of ion beam sputtered precursor and their electrical and optical properties, Rare Met. 25 (2006) 315–319.

[8] S.M. Bhosale, M.P. Suryawanshi, J.H. Kim, A.V. Moholkar, Preparation and characterization of Cu_2ZnSnS_4 thin films for photovoltaic applications, Ceram. Int. 41 (2015) 8299–8305.

[9] L. Choubrac, A. Lafond, C. Guillot-Deudon, Y. Moëlo, S. Jobic, Structure flexibility of the Cu_2ZnSnS_4 absorber in low-cost photovoltaic cells: From stoichiometric to copper-poor compounds, Inorg. Chem. 51 (2012) 3346–3348.

[10] J.B. Li, V. Chawla, B.M. Clemens, Investigating the role of grain boundaries in Cu_2ZnSnS_4 and $Cu_2ZnSn(S,Se)_4$ thin-film solar cells with scanning probe microscopy, Adv. Mater. 24 (2012) 720–723.

[11] J. Tao, J. Liu, J. He, G. Chen, S. Chen, Y. Wang, Synthesis and characterization of Cu_2ZnSnS_4 thin films by sulfurization of co-electrodeposited Cu–Zn–Sn–S precursor layers for solar cell applications, RSC Adv. 4 (2014) 23977–23984.

[12] G.K. Williamson, W.H. Hall, X-ray line broadening from filed aluminium and wolfram, Acta Metall. 1 (1953) 22–31.

[13] O. Zaberca, A. Gillorin, B. Durand, J.Y. Chane-Ching, A general route to the synthesis of surfactant-free solvent-dispersible ternary and quaternary chalcogenide nanocrystals, J. Mater. Chem. 21 (2011) 6483–6486.

[14] N.M. Shinde, C.D. Lokhande, J.H. Kim, J.H. Moon, Low-cost and large-area chemical synthesis of Cu_2ZnSnS_4 thin films, J. Photochem. Photobiol. A 235 (2012) 14–20.

[15] K. Tanaka, N. Moritake, H. Uchiki, Preparation of Cu_2ZnSnS_4 thin films by sulfurizing sol–gel deposited precursors, Sol. Energy Mater. Sol. Cells 91 (2007) 1199–1201.

[16] X. Fontané, V. Izquierdo-Roca, E. Saucedo, S. Schorr, V.O. Yukhymchuk, M.Ya. Valakh, A. Pérez-Rodríguez, J.R. Morante, Structural and vibrational properties of kesterite-type Cu_2ZnSnS_4 thin films, J. Alloys Compd. 539 (2012) 190–194.

[17] C.P. Chan, H. Lam, C. Surya, Preparation of Cu_2ZnSnS_4 films by electrodeposition using ionic liquids, Sol. Energy Mater. Sol. Cells 94 (2010) 207–211.

[18] M. Jeon, Y. Tanaka, T. Shimizu, S. Shingubara, Formation and characterization of single-step electrodeposited Cu_2ZnSnS_4 thin films: Effect of complexing agent volume, Energy Procedia 10 (2011) 255–260.

[19] S.M. Pawar, B.S. Pawar, A.V. Moholkar, Single-step electrosynthesis of Cu_2ZnSnS_4 thin films for solar cell application, Electrochim. Acta 55 (2010) 4057–4061.

https://doi.org/10.30799/jnst.S204.26110304

Cite this Article as: Mahendra M. Bagul, Ajay A. Nikam, Mohsin Y. Shaha, Priyanka J. Gare, Gotan H. Jain, Anil B. Gite, Preparation and characterization of nano structured Cu_2ZnSnS_2 (CZTS) thin film by spray pyrolysis method for photovoltaic application, J. Nanosci. Tech. 11(3) (2026) 1090–1092.