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Characterization of CZTS Nanoparticles Synthesized by Solvothermal Method for Solar Cell Application

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Abstract: The Copper zinc tin sulfide, a quaternary chalcogenide semiconductor with a direct band gap of ~1.5 eV and high absorption coefficient (10^4 cm^{-1}) is considered as the best absorber layer for next generation solar photovoltaics. In the present work, structural and optical properties of CZTS nanoparticles synthesized using solvothermalroute (Water, Ethylene diamine) are presented. CZTS nanoparticles exhibit Kesterite structure with preferential orientation along the (112) direction as observed from XRD and Raman spectra. The crystallite sizes of the nanoparticles are found to vary from 14 nm (water) to 10 nm (EDN). Morphological analysis using SEM shows that the growth of the particles are controlled using EDN as a solvent. Composition of the nanoparticles from EDAX spectra reveals that the EDN grown particles are found to be nearly stoichiometric. Optical measurements using spectrophotometer shows that the absorption edge of the nanoparticles prepared in EDN is shifted towards shorter wavelength when compared to nanoparticles prepared in water exhibiting quantum confinement effect. The calculated optical band gap of CZTS nanoparticles are 1.29 eV and 1.37 eV for water and EDN respectively, in which the later one is optimum band gap value for the absorber layer in the fabrication of photovoltaic cells.
Keywords: CZTS nanoparticles, Solvothermal, Raman spectroscopy, Optical properties.

Introduction

In recent years, Copper zinc tin sulfide (Cu_2ZnSnS_4 or CZTS)are widely used as an alternative absorber layer to $Cu(In,Ga)(S,Se)_2$ (CIGS) due to its earth abundant and environmentally benign constituents.CZTS has a direct band gap of 1.4 - 1.5 eV which is the optimum band gap for high efficiency solar cells, with p-type conductivity and high absorption coefficient(10^4 cm^{-1})[1,2]. Though there has been significant progress and evolution in cell performance of these materials during last few years, further improvement is necessary to make CZTS a viable material in industrial terms.

Various synthetic routes have been developed to prepare CZTS thin films and nanoparticles such as sputtering[3], spray-pyrolysis[4],sol–gel[5],electrodeposition[6],pulsed laser deposition[7], thermal evaporation[8], chemical vapor deposition[9], hydrothermal method[10] and so on. In the present work, CZTS nanoparticles were synthesized by simple solvothermal method using different solvents. Two reaction media, water (H_2O) and ethylene diamine (EDN), are used as solvents. The influence of water and ethylene diamine as solvents for the preparation of CZTS semiconducting nanoparticles on the structural, compositional and optical properties are analyzed and discussed.

Experimental

All chemicals used in this work are analytical grade reagents and used without any further purification. In a typical procedure, 0.5 mole of copper acetate ($Cu(CH_3COO)_2$), 0.25 mole of zinc acetatedihydrate ($Zn(CH_3COO)_2.2H_2O$), 0.25 mole of tin chloride pentahydrate ($SnCl_4.5H_2O$), and 1 mole of thiourea (CH_4N_2S) solutions are prepared in deionized water. The solution was stirred continuously until a clear solution is obtained. The solution is then transferred to a Teflon lined autoclave and it was maintained at 180^{o}C for about 6 hours and then air cooled at room temperature. The precipitates were filtered out, washed with distilled water and absolute ethanol. The final products were dried in vacuo at 60^{o}C for three hours. A similar experiment was carried out in ethylene diamine instead of deionized water to see the effect of solvent on the structural and optical properties of the CZTS nanoparticles.

The synthesized CZTS powders were characterized by X-ray diffraction (XRD) method using Schimadzu XRD-6000 X-ray diffractometer with a CuKα radiation λ =1.5406Å. Raman scattering measurements were performed using Horiba JobinYvon HR800 spectrometer. The morphological and compositional analysis of the nanoparticles were carried out using JEOL mode JSM 6390 SEM with EDX and optical studies of the samples were done using spectrophotometer Jasco corp. V-570spectrophotometer.

Results and Discussion

X-ray diffraction pattern

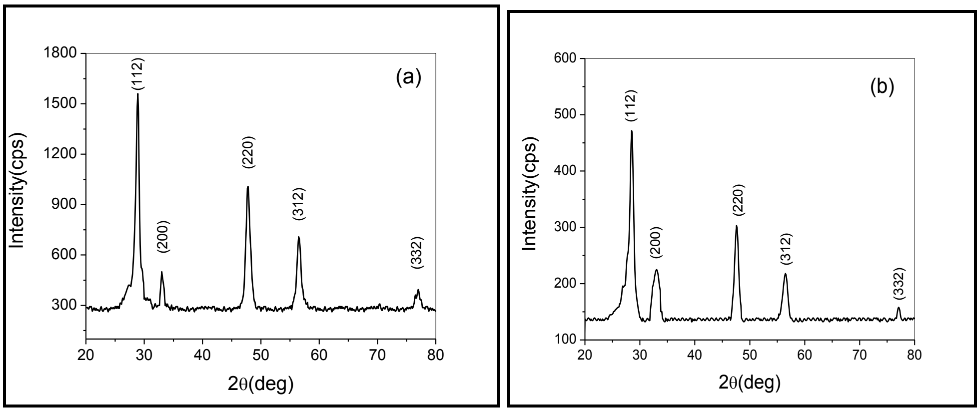

Fig. 1. XRD spectra of CZTS nanoparticles prepared in (a) water and (b) EDN

Fig.1a and 1b shows the XRD pattern of CZTS nanoparrticles using water and ethylene diamine as a solvent. Both the samples exhibit diffraction peaks corresponding to the (112), (200), (220), (312) and (332) reflection planes of kesterite structure, which is confirmed using standard JCPDS (Card No. 26-0575) and matches well with that of the earlier reports[11,12,13]. The broadening of the XRD peaks indicates the nanocrystalline nature of the samples. Clearly, the peak in Fig. 1b are a little broader than that of Fig. 1a indicating that the particles prepared in presence of ethylene diamine are smaller when compared to those prepared in water. The mean crystallite size D is determined according to the Scherer equation $D = 0.9\lambda/\beta\cos\theta$, where λ is the X-ray wavelength (for Cukα radiation λ= 1.5406 Å), β is the full width half maximum (FWHM) and θ is the diffraction angle. The calculated mean crystallite size is 14 nm for CZTS nanoparticles prepared in water and 10 nm for CZTS nanoparticles prepared in ethylene diamine. It is worth mentioning that the calculated lattice constant of CZTS nanoparticles by using water (a = 0.5405 nm and c= 1.0871 nm), and ethylene diamine as a solvent (a = 0.5414 nm and c= 1.0859 nm), are the same as the value from the standard card (a = 0.5427 nm and c= 1.0848 nm) confirming the kesterite structure.

Raman Analysis

In order to find out the existence of the secondary phase, Raman spectroscopy was performed. Fig. 2 shows the Raman Spectra of CZTS nanoparticles prepared in (a) water and (b) EDN. It indicates the presence of the two major peaks at 338 cm^{-1} and 289 cm^{-1} and is similar to that reported by earlier researchers[14,15]. Both these peaks correspond to the CZTS phase. The stronger peaks at 338 cm^{-1} is due to the A_1 symmetry and it is related with the vibration of the S atoms in CZTS. Moreover, it is obvious that there are no extra peaks related to the presence of other compounds, which means that the single phase CZTS nanoparticles were obtained on both solvents.

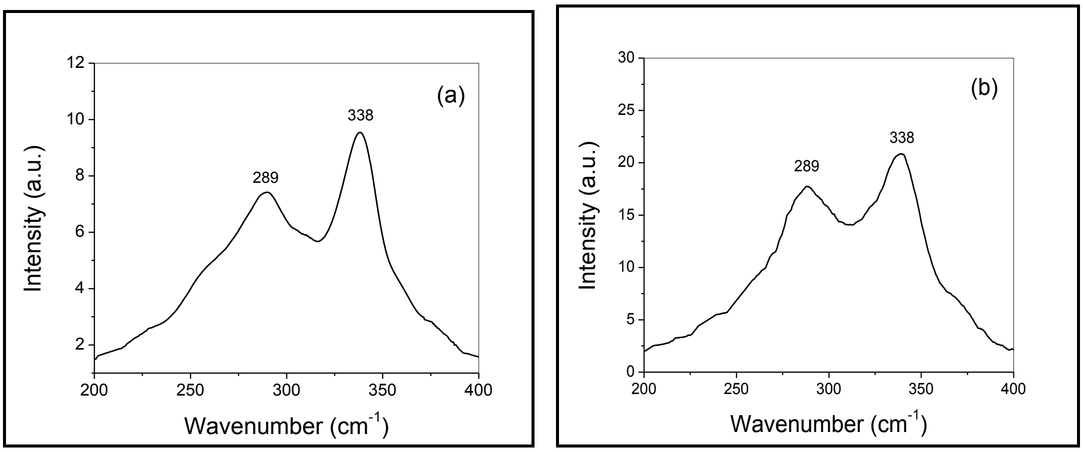

Fig. 2. Raman Spectra of CZTS nanoparticles prepared in (a) water and (b) EDN

SEM analysis

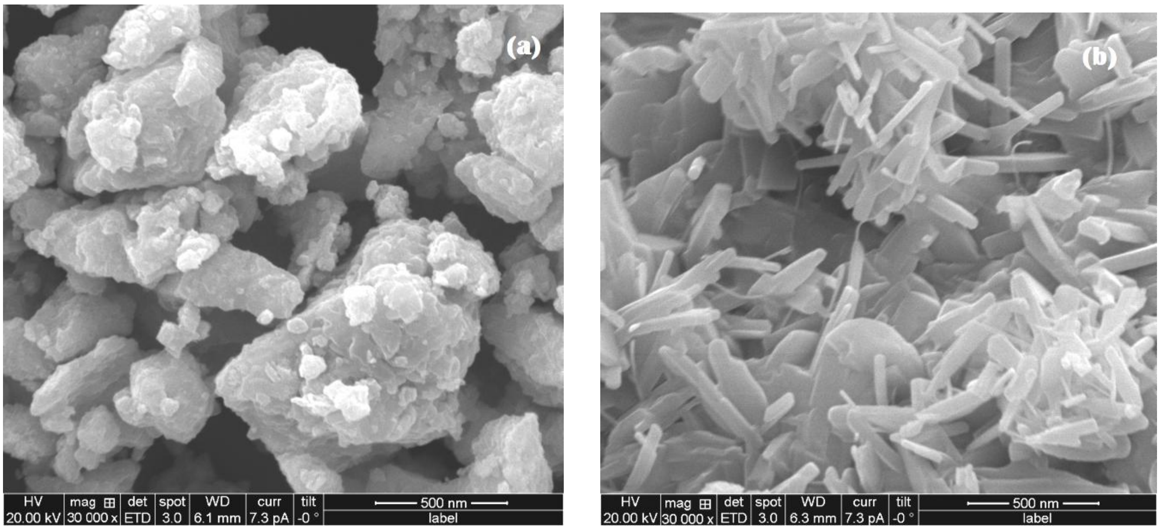

Fig. 3. SEM Micrographs of CZTS nanoparticles prepared in (a) water and (b) EDN

Fig. 3a and 3b shows the SEM images of CZTS nanoparticles using (a) water and (b) ethylene diamine as a solvent. It is observed (Fig. 3a) that the CZTS nanoparticles prepared in water are inhomogeneous in nature consisting of agglomerated particles. Fig. 3b shows that the CZTS particles prepared in ethylene diamine has nanorod structures. These nanorods are typically few hundred nm in diameter and several micro meters in length and appeared in bunches owing to a high surface energy[16]. The morphology of the fig 2b shows that the size of CZTS nanoparticles prepared using ethylene diamine is smaller than that by water which is consistent with the result of the XRD.

Compositional analysis

The elemental analysis of CZTS nanoparticles prepared in water and EDN are carried out by energy dispersive X-ray analysis (EDX) technique. The respective EDX spectra are shown in Fig. (4 a &b). EDX analysis indicates the presence of copper, zinc, tin and sulfur for both the samples. The stoichiometric ratio of Cu, Zn, Sn and S were computed by integrating the area under each Cu, Zn, Sn and S peak. The EDX spectra of nanoparticles exhibits nearly the stoichiometric composition with atomic percentage of Cu, Zn, Sn and S ratio in the range 23.13 : 15.26 : 13.80: 47.81 for water and 24.81 : 14.13 : 13.05: 48.01 for ethylene diamine, respectively and theoretically expected stoichiometric composition of CZTS (in terms of at %) is Cu : Zn : Sn : S equal to 25.00 : 12.50 : 12.50 : 50.00. Therefore the particle prepared using ethylene diamine is very near to stoichiometric and theprepared particles are free from impurities.

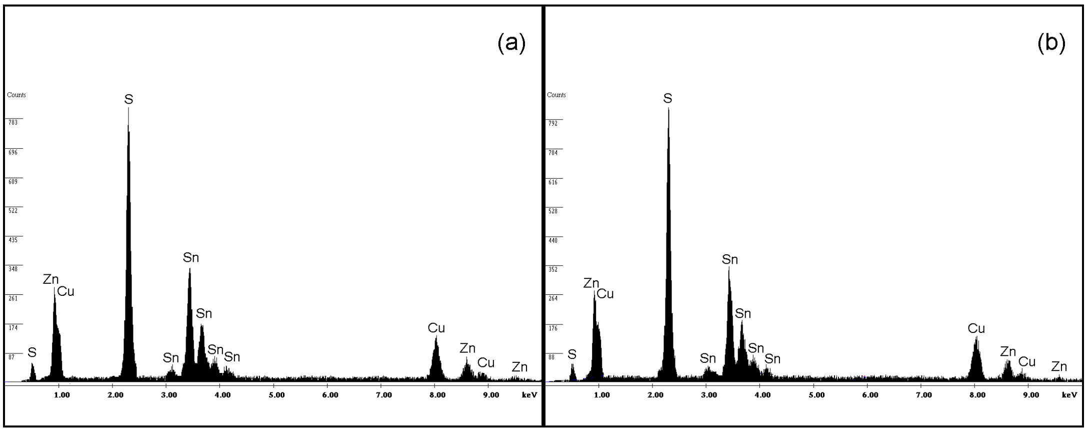

Fig. 4. EDX spectra of CZTS nanoparticles prepared in (a) water and (b) EDN

Optical absorption and band gap

The room temperature UV–vis absorption spectra of CZTS samples prepared using (a) water (b) ethylene diamine as a solvent are shown in Fig. 5. Absorption edge of CZTS nanoparticles prepared in water is 890 nm and that prepared in EDN is 825 nm. The absorption edge of CZTS prepared using water as a solvent shifts towards the longer wavelength when compared to CZTS prepared using ethylene diamine as a solvent.

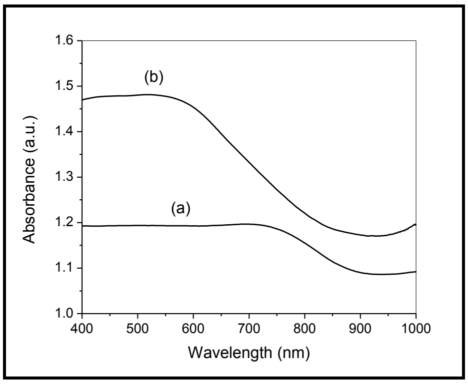

Fig. 5. Absorbance spectra of CZTS nanoparticles prepared in (a) water and (b) EDN

The band gap was calculated by plotting energy (E) versus $(\alpha h\nu)^2$(Fig. 6) for CZTS nanoparticles prepared using water and ethylene diamine as a solvent. It is found that the band gaps of the CZTS samples prepared using water and ethylene diamine as a solvent are 1.29 and 1.37 eV respectively, in which the later one is optimum band gap value for the absorber layer in the fabrication of photovoltaic cells.This increase in the band gap with decrease in the crystallite size is attributed to size confinement effects[11].

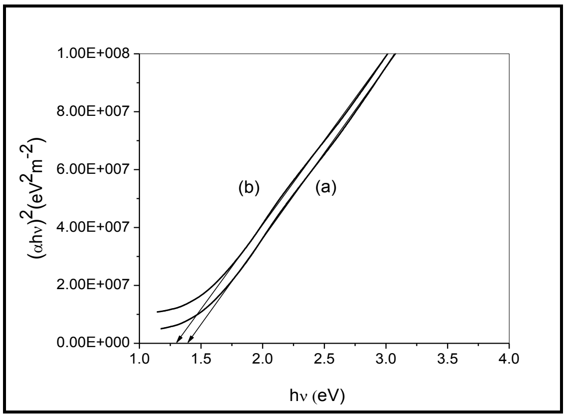

Fig. 6. Plot of $(\alpha h\nu)^2$ versus (hν) of CZTS nanoparticles prepared in (a) water and (b) EDN

Conclusion

CZTS nanoparticles were synthesized using different solvent by a simple solvothermal method. The XRD results reveal that the CZTS nanoparticles are kesterite crystalline in nature, which is confirmed by Raman spectrum analysis. The SEM micrograph shows that the CZTS particles prepared in water areinhomogeneous in nature and that prepared in ethylene diaminepossess nanorod structures. The EDXanalysis confirms the presence of all four constituents Cu, Zn, Sn and S. Optical analysis shows that the band gap value (1.37 eV) of CZTS nanoparticles prepared in EDN is optimal for photovoltaic application.From these results, the CZTS nanoparticles prepared in EDN have good morphology, near stoichiometric ratio and optimum band gap value for the absorber layer in the fabrication of photovoltaic cells.

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