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Ethylenediamine Processed Cu_2SnS_3 Nano Particles via Mild Solution Route

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Abstract: *Copper tin sulphide nanoparticles have been prepared by solution growth technique at various ethylenediamine concentrations. Prepared samples have been characterized using x-ray diffraction, fourier transform infrared, Raman and scanning electron microscopy techniques. x-ray diffraction results revealed that the prepared samples are nanocrystalline in nature with tetragonal structure. Fourier transform infrared spectroscopy analysis results showed the presence of Cu-O, Sn-O and Sn-S vibrations in the wavenumber range between 450 and 620 cm^{-1}. Vibrational symmetry of prepared samples have been analyzed using Raman spectroscopy. Scanning electron microscopy analysis indicated the formation of flower like nanocrystals for samples prepared at various Ethylenediamine concentrations.*

Keywords: Cu_2SnS_3, Nanoparticles, Solvothermal method, Ethylenediamine

1.INTRODUCTION

In recent years, there is a world wide interest to develop low cost solar cells to generate electricity from solar energy. Nowadays, research is focussed on naturally abundant, sustainable and non-toxic new materials for the production of low cost solar cells [1]. I-IV-VI group ternary chalcogenides have attracted many researchers due to their promising solid lubricant, outstanding thermal, mechanical and non linear optical properties [2]. Copper Tin Sulphide (Cu_2SnS_3**)** is an important p type semiconducting material found to exhibit the above mentioned properties which is utilized for the fabrication of solar cells. Cu_2SnS_3 is in compound form with interlayer, tunnelling in crystal structures and could be fascinatingly introduced into Li battery applications [3]. Cu_2SnS_3 is found to exists in a number of polymorphic structures, such as monoclinic at higher temperature greater than 775ºC, monoclinic, triclinic and tetragonal structures at lower temperature less than 775ºC [4-6]. Cu_2SnS_3 is found to be a p-type semiconductor with an energy gap value in the range between 0.93 and 1.51 eV which make them quite interesting for photovoltaic applications [7]. Cu_2SnS_3 nanoparticles have been prepared by a number of techniques such as solid state reaction method using different sulphur sources [1], polyol route [8] and solvothermal method with different organic solvents such as ethanol, ethylene glycol, benzene and ethylenediamine (en) [9-11]. Moreover, ethylenediamine ($H_2NCH_2CH_2NH_2$) is an excellent solvent due to its specific properties such as strong polarity, relatively low critical pressure and strong chelating ability. Ethylenediamine acts as practically a solvent for a number of inorganic species. Solvothermal process offers so many advantages such as solubility, diffusion and crystallizsation which are augmented easily thus leading to the formation of phase. Their particle size, shape could be controlled and the contamination of toxic substance is prevented effectively [9]. The data obtained in previous reports show different types of crystal structure and surface morphology which mainly depend upon temperature and synthesis time [9-11].

In the present work, we have prepared Cu_2SnS_3 nanoparticles with different ethylenediamine concentrations using solvothermal

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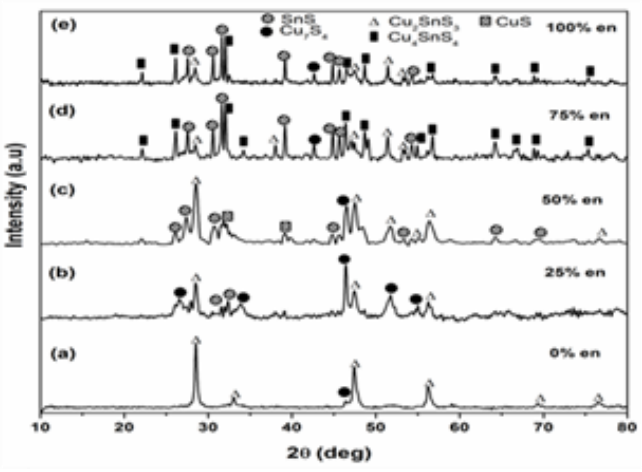

Figure 1. X-ray diffraction pattern for Cu_2SnS_3 nanoparticles obtained for various ethylenediamine concentrations: (a) 0, (b) 25, (c) 50, (d) 75, (e) 100 %.

technique. Prepared samples have been subjected to x-ray diffraction, scanning electron microscopy, fourier transform infrared and Raman spectroscopy techniques. The effect of ethylenediamine concentration on structural, morphological and vibrational properties of the prepared samples are investigated. The observed experimental results are discussed in detail.

2. EXPERIMENTAL DETAILS

All the chemicals used in the present work were of AR grade reagents. The chemicals used for the synthesize of Cu_2SnS_3 nanoparticles were copper chloride dihydrate ($CuCl_2\,2H_2O$), tin chloride monohydrate ($SnCl_2\ H_2O$) and thiourea (NH_2-CS-NH_2). 0.6 M $CuCl_2\ 2H_2O$, 0.2M $SnCl_2\ H_2O$ and 0.8M thiourea were dissolved in 100 ml deionized water. To the solution ethylenediamine with different concentrations in the range between 0 and 100 % was added. The solution was kept under magenetic stirrer cum heater untill it dissolved completely. The solution mixture was transferred into a teflon-lined autoclave of 100 ml capacity filled upto to 80% of the volume and maintained at 200ºC for 7.5 hours and cooled to room temperature. The final product was dried in vacuum at 90ºC for 5 hours.

X-ray diffraction data of the prepared samples was carried out using an XPERT PRO PANalytical x-ray diffractometer with CuKα radiation with wavelength (λ=1.5406Å). Fourier transform infrared spectroscopy analysis was done using a Jasco FT-IR/4100 spectrometer. Raman spectroscopy analysyis was carried out using a Jobin Yvon T64000 Raman spectrometer. Surface morphology of the samples was analyzed using a JEOL JSM 5610 Scanning Electron Microscope.

3. RESULTS AND DISCUSSION

3.1. Structural Analysis

X-ray diffraction pattern of Cu_2SnS_3 nanoparticles prepared at various ethylenediamine concentration is shown in Figure 1. It is obvious from the figure that the ethylenediamine has a great effect on the crystallographic structure. The formation of tetragonal Cu_2SnS_3 and orthorhombic Cu_7S_4 is observed for samples obtained at all concentrations. This may be due to multiple local coordination around center of the metallic ion (anion) with ability of the cation (here sulphur) leading to produce tetragonal and orthorhombic phases of Cu_2SnS_3 and Cu_7S_4. The different peaks in the diffractogram are indexed and the corresponding values of interplanar spacing "d" is calculated and compared with standard JCPDS ICDD file for tetragonal and orthorhombic phases of Cu_2SnS_3 and Cu_7S_4 [12-13]. The diffraction peaks of tetragonal phase Cu_2SnS_3 are observed at 2θ values of 28.51, 33.05, 47.36, 56.21, 59.20, 69.25 and 76.56 degree corresponding to the lattice planes (1 1 2), (2 0 0), (2 2 0), (3 1 2), (2 2 4),(4 0 0) and (3 3 2) respectively [12]. The appearance of peak at 2θ value around 46.36 degree may corresponds to an impurity phase Cu_7S_4[13]. The formation of ternary phase tetragonal Cu_2SnS_3 nanocrystallites may be attributed to the following mechanism. Initially, the reactants are mixed with ethylenediamine, there is dissolution reaction of sulphur (S^{2-}) taking place. Thereafter, the chalcogenides undergo disproportionation reaction to form polychalcogen anions S_x^{2}. At the same time, ethylenediamine chelates the metal ions to produce the cations in the form of complex. In the preparation of Cu_2SnS_3, Cu^{2+} is reduced to form Cu^{+} and then there is formation of Cu^{+}- ethylenediamine metal complex taking place. S_x^{2-} oxidize $SnCl_2.H_2O$ to form S^{2-} and Sn^{4+}. By the attack of S^{2-} with the metal complex, it slowly releases metal ions and the chalcogenides are formed from the obtained precipitates. The released fresh binary centers have higher activity and immediately incorporated with the surrounding Sn^{4+} to produce ternary based nanocrystallites in the form of chalcogenides [9]. It is noted that the intensity of XRD peaks are found to decrease when one compares figure 1a with 1b which may be due to presence of some additional impurities in the form of binary phase such as SnS and Cu_7S_4 at 2θ value of 31.50, 31.99 degrees and 27.95, 33.95, 46.38, 51.69 and 54.98 degrees respectively. The formation of more number of planes of binary phases such as Cu_7S_4, SnS may be due to the chealting ability of ethylenediamine. It is not easy to avoid the formation of Cu_7S_4 due to binary–center mechanism. The newly produced Cu_4S_7 nuclei is easy to grow larger, and it is difficult to transfer Sn^4 into the lattice of binary center completely to form ternary products [9]. Further increase in the ethylenediamine concentration to 50% the tetragonal peaks of Cu_2SnS_3 becomes sharp and broadened when compare the peaks obtained for films obtained at 25 % concentration. Braodening of the peaks is reltated to reduction in the size of the particles. On the other hand, the formation of impurities cannot be ruled out due to increase in the quantity of ethylenediamine concentration. The appearance of binary alloy phases observed at 2θ values of 32.00, 39.10 degrees for CuS, 26.00, 27.48, 31.63, 44.85, 54.27, 64.21 and 71.42 degrees for SnS and 46.38 degrees for Cu_7S_4 are in terms of impurities. It is also observed that the intensity of tetragonal peaks are found to decrease and not broadened when one compares figure 1c with figure 1d. Hence, we have concluded that there is formation of multi phases such as Cu_2SnS_3, Cu_4SnS_4, Cu_7S_4 and SnS for films obtained at ethylenediamine concentrations above 50%. Cu_4SnS_4 is appeared as the dominant secondary phase and the formation of SnS may be due to the presence of excess amount of Sn as impurity in the deposited films. On the other hand, the formation of Cu_4SnS_4 takes place which may due to the presence of excess amount of Cu, because of chelating nature of ehtylenediamine concentration above 50 percentage [14]. Crystallite size is defined as

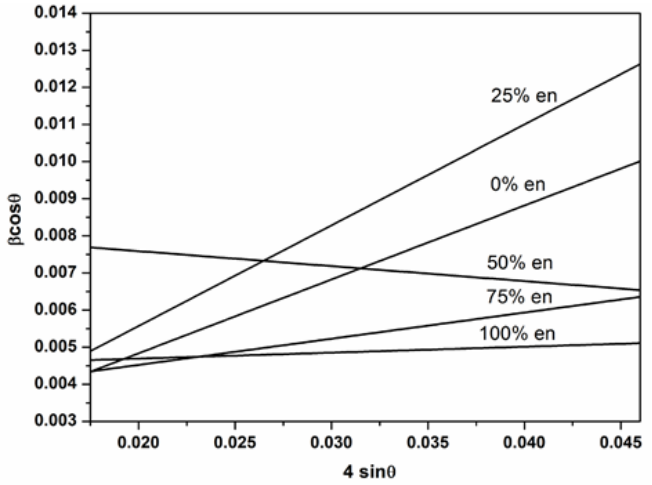

Figure 2. Williamson Hall plot for Cu_2SnS_3 nanoparticles obtained for various ethylenediamine concentrations: 0 to 100 %.

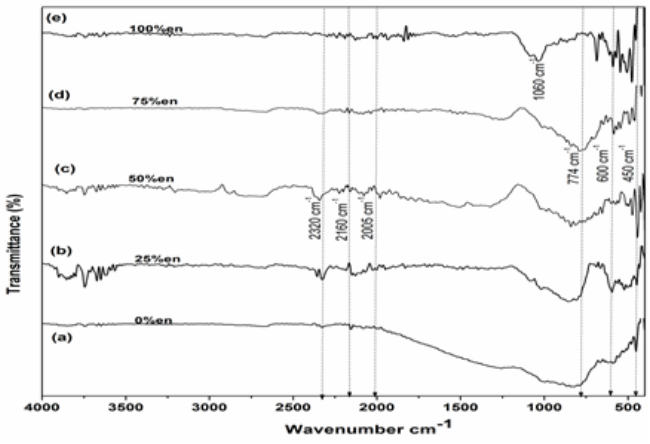

Figure 3. FTIR spectra for Cu_2SnS_3 nanoparticles obtained for various ethylenediamine concentrations: (a) 0, (b) 25, (c) 50, (d) 75, (e) 100%.

the number of crystallites formed along the surface of the substrate.The crystallite size of the deposited films is calculated using FWHM data and Debye-Scherrer formula.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where λ is wavelength of CuK_α radiation (λ =1.54060 Å), β is the full width at half maximum (FWHM) of the peak position in radians and θ is Bragg's diffraction angle at peak position in degrees. Williamson Hall plot for Cu_2SnS_3 nanoparticles prepared at various ehtylenediamine concentrations is shown in Figure 2. Williamson Hall plot exhibited straight line indicating homogeneous distribution of crystallite size and strain. The graph is fitted by linear function which provides the strain value from the value of slope and crystallite size value from its intercept with Y-axis. The positive slope of the line indicated lattice expanision, whereas negative slope denoted lattice compressions [15]. It is also observed that Cu_2SnS_3 films prepared at 50 % ethylenediamine concentration is found to exhibit positive slope, indicating lower value strain. Hence films prepared at 50 % concentration has strain free nano particles with narrow size. The value of crystallite size and strain calculated for Cu_2SnS_3 nanoparticles prepared at various ehtylenediamine concentration is given in Table 1.

3.2. Fourier Transform Infra Red Spectroscopy Results

Fourier Transform Infrared spectroscopy of prepared films has been done using an FTIR spectrophotometer. FTIR spectra of Cu_2SnS_3 samples prepared at various ethylenediamine concentrations is shown in Figure 3. It is observed that the appearance of a narrow band at 450 cm^{-1} may be assigned to Cu-O bond vibrations in copper oxides such as Cu_2O and CuO. The vibarations reflected in the range between 500 and 750 cm^{-1} corresponds to Cu-S, Sn-S, Sn (IV)-O and Sn(II)-O bonds present in the deposited films. The appearance of weak bands in the range between 2000 and 2300 cm^{-1} may be assigned to C ≡ S and nitrile bond C ≡ N in thiourea [19].

The presence of the broad band at 774 cm^{-1} represents the symmetric stretching of C = S vibrational band in thiourea. The peaks observed in the range between 680 and 720 cm^{-1}, 800 and 850 cm^{-1} corresponds to the presence of ligands such as –S–C ≡ N and –N=C=S in the compound Cu_2SnS_3 [20]. At 100 percentage ethylenediamine concentration C – N stretching band appeared at 1060 cm^{-1}, indicated that the concentration of ethylenediamine plays a significant role upon complexation process if the concentration of ethylenediamine varied in the range between 0 and 100 %. For lower concentration of ethylenediamine, C-N band shifted towards lower frequency in the complexes formed with thiourea and metal ions which confirms the polydentate chelating nature of ethylenediamine in these complexes [21].

Table 1. Variation of crystallite size and strain for Cu_2SnS_3 nanoparticles obtained for various ethylenediamine concentrations.

Ethylendiamine concentration (vol %)	Crystallite Size (nm)		Strain ($line^{-2}$ $metre^{-4}$)	
	Debye Scherrer's Formula	Williamson Hall Plot	ε= β/4tanθ	Williamson Hall Plot
0	22.50	16.65	0.194	0.199
25	16.01	17.16	0.344	0.315
50	19.86	16.50	0.197	-0.040
75	30.49	32.61	0.192	0.035
100	33.13	33.64	0.670	0030

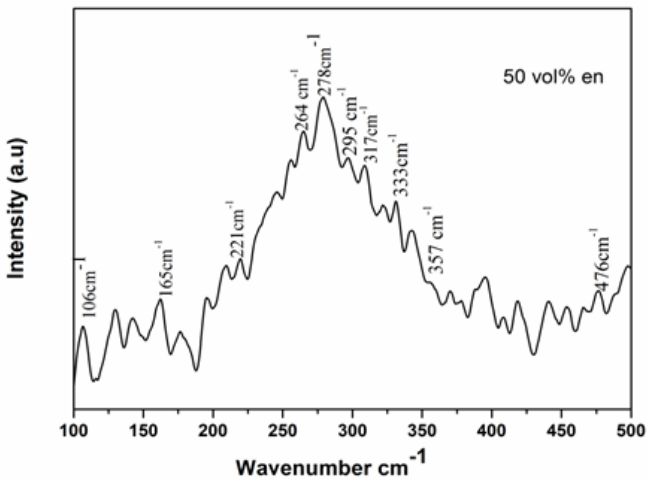

Figure 4. Raman spectra for Cu_2SnS_3 nanoparticles prepared at 50 % of ethylenediamine concentration.

3.3. Raman Spectroscopy Results

Raman spectrum of prepared samples has been taken out using a Raman spectrometer. Raman spectrum of Cu_2SnS_3 nanoparticles prepared at 50 percentage of ethylenediamine concentration is shown in Figure 4. The observation of peaks at 295, 333, 357 cm^{-1} correspond to tetragonal phase of Cu_2SnS_3. It is also observed that the appearance of peaks at 106, 165, 221, 264 and 278 cm^{-1} correspond to the presence of impurities like CuO and CuS respectively [21,22]. The results observed in the present work is quite closer to the value reported earlier [23,24].

3.4. Morphological Analysis

Surface morphology of Cu_2SnS_3 nanoparticles has been analyzed using a scanning electron microscope. Scanning electron microscopy image of Cu_2SnS_3 obtained at 50 % value is shown in Figure 5. It is observed that there is appearance of flower like grains which is indicated in figure 5. The sizes of the grains are found to be in the range between 750 and 1000 nm. It is obvious that the size calculated from XRD results is much smaller than those observed from SEM images. The exact reason is that the XRD method measures the property of the crystallite and not the size of the aggregated particles [23]. Cu_2SnS_3 flowers are constructed by aggregation of large-scale thinner nano-flakes. The result observed in the present work which is similar to the results reported earlier for Cu_2SnS_3 nanostructures obtained through solvothermal route [9,10].

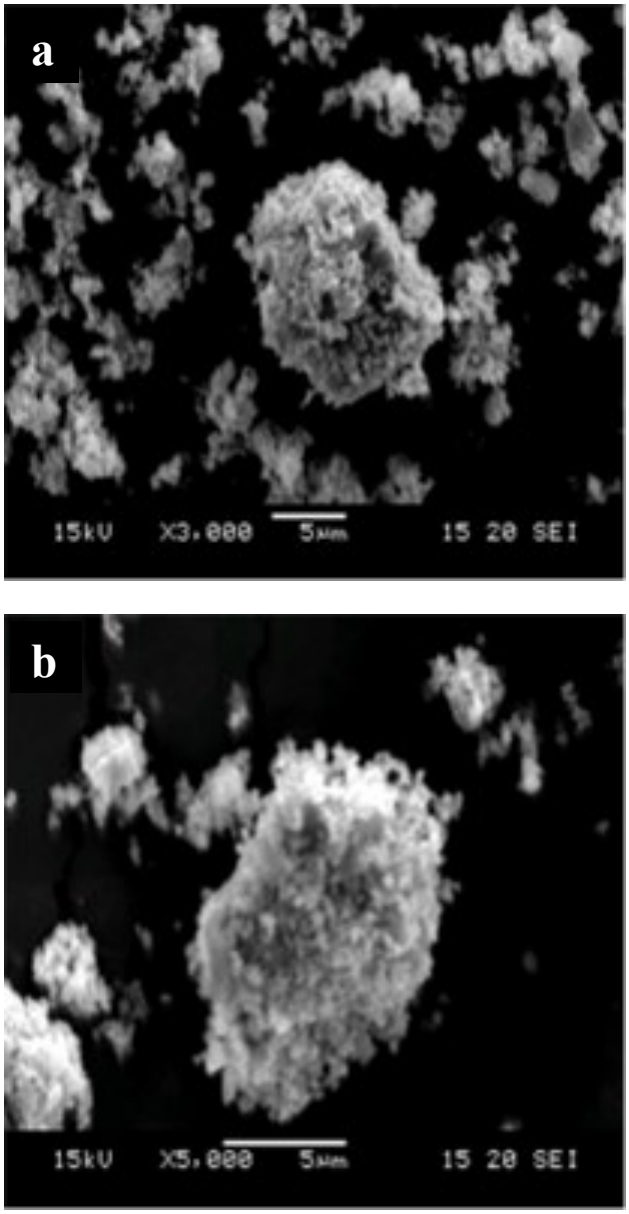

Figure 5. SEM image for Cu_2SnS_3 nanoparticles prepared at 50 % of Ethylenediamine concentration.

4. CONCLUSIONS

Cu_2SnS_3 nanoparticles were prepared through an environmental friendly solvothermal technique. XRD pattern showed that Cu_2SnS_3 nanoparticles were found to exhibit tetragonal structure. The concentration of ethylenediamine is found to be 50 percentage to obtain particles with higher crystallinity with less amount of impurities. SEM observation showed the formation of flower like nanocrystals. FTIR analysis showed the presence of functional groups such as Cu-O, Sn-O, Cu-S and Sn-S vibrations in the corresponding wavenumber region between 450 and 620 cm^{-1}. Raman spectroscopy analysis confirmed the symmetric vibration of formed nanoparticles. It may be concluded that Ethylenediamine plays a significant role in the formation of shape and crystallinity of the formed Cu_2SnS_3 nanocrystallites.

5. ACKNOWLEDGMENT

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