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Studies on copper zinc tin sulphide nanoparticles synthesised by a simple co-precipitation technique

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Abstract: The I_2-II-IV-VI_4 quarternary compound copper zinc tin sulphide (CZTS), due to its manifold merits such as near optimum direct band gap energy of 1.4 to 1.6 eV, large absorption coefficient (>10^4 cm^{-1}), non toxic and earth abundant constituents, has become an promising material for photovoltaic applications. Investigations on the structural, morphological and optical properties of CZTS nanoparticles synthesized by a simple co-precipitation technique with copper chloride dihydrate, zinc chloride, tin (IV) chloride pentahydrate and thiourea were carried out in the present work using powder x-ray diffraction (XRD), uv-visible spectroscopy (uv-vis), photoluminescence spectroscopy (PL) and scanning electron microscopy (SEM) analysis. The crystalline nature and purity of the sample was confirmed by XRD. All the diffraction peaks were indexed to kesterite CZTS nanoparticles and the average grain size was estimated using the Sherrer formula. SEM observations demonstrate the morphology of the nanoparticles. The Uv-vis and PL measurements divulge the optical properties which confirm that the prepared CZTS nanoparticles will be an fitting entrant for photovoltaic applications and other light emitting applications.

1. Introduction

The quaternary semiconductor Cu2ZnSnS4 (CZTS) has of late gathered enormous attention of researchers due to its promising merits such as its optimal band gap(1.4 to 1.6 eV), high absorption coefficient(>10^4 cm^{-1}), low toxicity, high availability of raw materials and much more.[1-3] The CZTS is a kesterite semiconductor compound which can be utilized for various applications like in solar cell device fabrication, as gas sensors, as optical devices, thin film solar cells, etc., can be prepared by various techniques such as co-precipitation, hydrothermal method, sol-gel process, ball milling, and much more.[4-6] In the present work CZTS nanoparticles were synthesized by co-precipitation technique and the manuscript elucidates the structural, morphological and optical properties of the as-prepared nanoparticles.

2. Experimental

2.1 Materials used

Analytically pure Merck chemicals copper chloride dihydrate, zinc chloride, tin (II) chloride dihydrate and thiourea were used without further purification for the synthesis of CZTS nanoparticles with the aid of double distilled water as the solvent.

2.2 Experimental procedure

The synthesis of CZTS nanoparticles were carried out using co-precipitation technique wherein appropriate amount of copper chloride dihydrate, zinc chloride, tin (II) chloride dihydrate and thiourea were taken in the molar ratio 2:1:1:4 and dissolved separately in 40 ml of double distilled water. The solutions were then mixed together with the help of rigorous magnetic stirring inorder to obtain a homogenous mixture. Required amount of sodium hydroxide was introduced into the mixture to adjust the pH value of the solution to 8 which assisted the formation of black coloured precipitate. The turbid solution was stirred with a magnetic stirrer for 3 hours at 60° C and subsequently washed with double distilled water and ethanol. The product obtained was dried in a hot air oven at 80° C for 24 hours whereby black solids were attained. The solids were subsequently ground well using a mortar and pestle, annealed at 300° C for 5 h and collected for storage.

3. Results and Discussions

3.1 Structural analysis

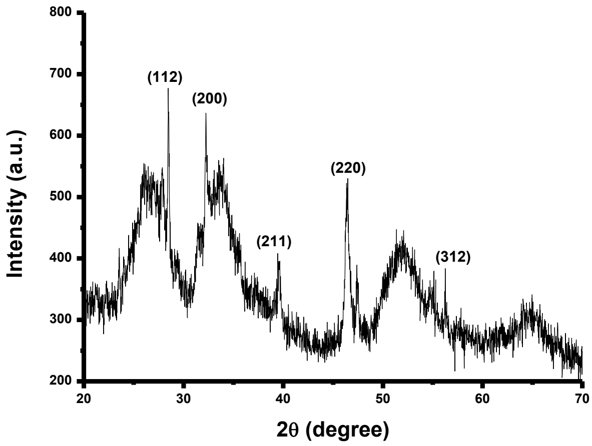


Fig. 1: XRD pattern of the CZTS nanoparticles

Figure 1 shows the XRD pattern of CZTS nanoparticles synthesized by co-precipitation. The XRD examination was performed on a GE Inspection technology 3003 TT X-ray diffractometer with CuKα radiation (λ=1.540598 Å) wherein the X-ray tube was operated at 40 kV and 30 mA in the 2θ range 20-70°. The attained major diffraction peaks were attributed to hkl values (112), (200), (211), (220) and (312). The obtained peaks matched well with the standard JCPDS card no. 26-0575 and shows that the formed CZTS nanoparticles exhibit the kesterite structure. The average grain size was estimated to be 2.52 nm using the Sherrer's formula

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad (1)$$

where D is the grain size in nm, k = 0.89, λ = 1.5406 Å which is the wavelength of CuK_{α}, β is the full width half maximum (FWHM in radians) and θ is the Bragg's angle in degrees.

3.2 Morphological analysis

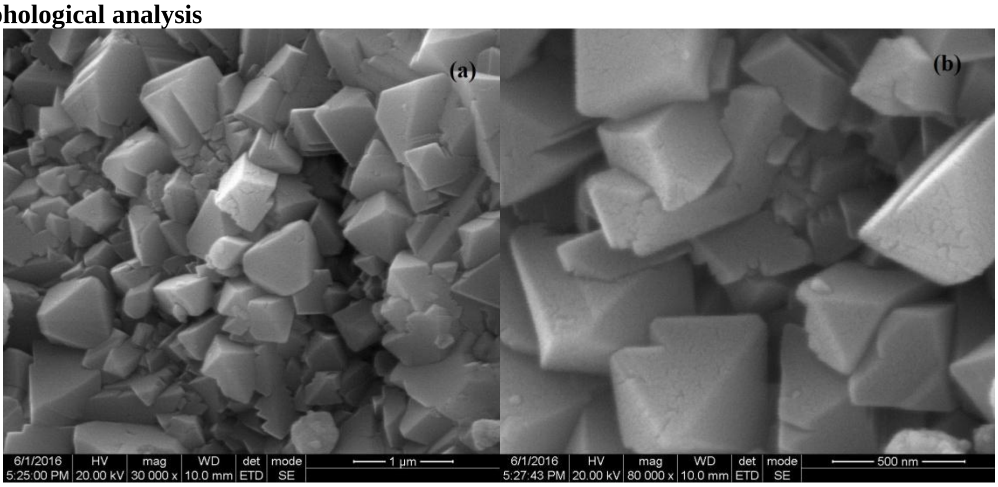


Fig. 2: SEM images of the CZTS nanoparticles at two different magnifications

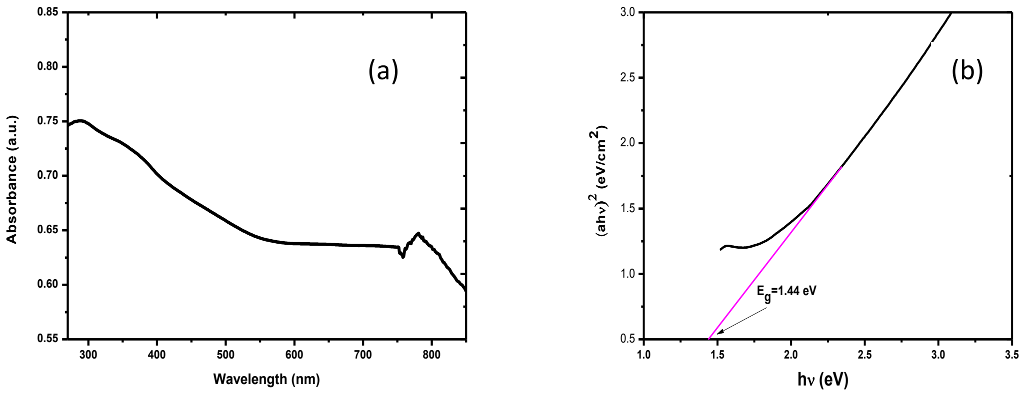
Surface morphology of the synthesized nanostructured CZTS sample has been studied using Scanning Electron Microscope. Figure 2 a and b show the SEM images of the CZTS synthesized sample obtained at different magnification by TESCAN. The figure shows a compact arrangement of small size homogeneous nanoparticles. the exact shape and size of the particles could not be estimated as most of the particles are aggregated. The high surface energies possessed by the nanoparticles may be the reason for the agglomeration.

3.3 Optical analysis

The optical analysis of the synthesized CZTS nanoparticles were carried out using uv-visible absorption spectroscopy and photoluminescence spectroscopy. The UV-visible absorption spectra were determined using VARIAN in the wavelength span of 270 – 1000 nm. The dielectric studies were carried out using HIOKI 3532-50 LCR HITESTER meter in the frequency region 50 Hz to 50 MHz. Figure 3a shows the absorption spectrum of the CZTS nanoparticles. The uv measurements show that the obtained CZTS nanoparticles have a broad absorption in the visible light region. The optimal band gap of the synthesized nanoparticles was estimated using the Tauc plot and calculated by Tauc's law

$$(\alpha h\nu)^n = C(h\nu - E_g) \tag{2}$$

where E_g is the direct band gap and n depends on the type of transition, α is the absorption coefficient, $h\nu$ is the photon energy and C is a constant.[6] Figure 3.b shows the comparison plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of the synthesized CZTS nanoparticles. The obtained band gap value of 1.44 eV suggests that the primed CZTS nanoparticles can be used for solar cell applications since the band gap value is in the optimal region for such applications.



. (a) UV-vis Absorption spectra of CZTS nanoparticles (b) Comparison plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of the CZTS nanoparticles

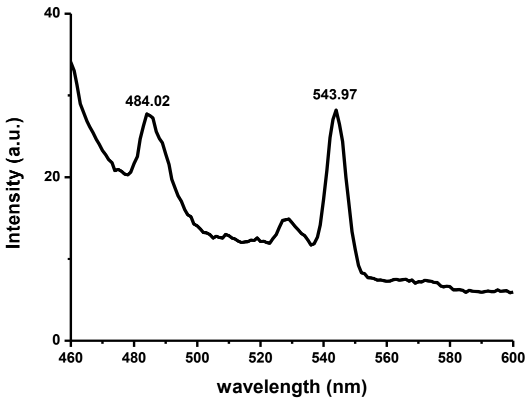


Fig. 4: PL spectrum of the CZTS nanoparticles

The photoluminescence spectrum of the CZTS nanoparticles prepared by co-precipitation technique is revealed in figure 4. The spectrum shows two emission peaks at 484.02 an 543.97 nm. The emissions can be attributed to a high level transition in the semiconductor crystallites. The blue emission at 484.02 nm represents that the tailored CZTS nanoparticles can be used as blue light emitter and for various other optical applications.

4. Conclusions

Copper zinc tin sulphide (CZTS) nanoparticles were effectively synthesized by a facile co-precipitation technique by maintaining the pH of the solution at 8. The obtained nanoparticles were subjected to various structural, morphological and optical investigations. The XRD pattern revealed that the synthesized nanoparticles exhibit kesterite phase of pure CZTS with an average grain size of 2.52 nm. The SEM micrographs reveal a homogeneous growth of the CZTS nanocrystallites. The optical absorption and emission data reveal that the obtained CZTS nanoparticles can be used for optical applications especially for solar applications as the obtained band gap of 1.44 eV is in the optimal range for solar cell device fabrication.

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