Low temperature synthesis of rod shaped IV- VI semiconductor hetrostructured (SnS) nanocrystalline particles in aqueous solution by co-precipitate method

N. Jabammal Raj[1*] and Dr.P.Elangovan[2]

[1*]Research Scholar, PG & Research Dept of Physics, Pachaiyappa's College, Chennai-600 030.

[2]Assistant Professor, PG & Research Dept of Physics, Pachaiyappa's College, Chennai-600 030,

ABSTRACT

The narrow band gap IV-VI semiconductor hetrostructured SnS nanoparticles have been synthesized by co-precipitate method. In which tin chloride di hydrate was used as tin source and thiourea as sulfur source. Structure and phase purity were confirmed by Powder X-ray Diffraction (PXRD) SnS of orthorhombic structure. The direct band gap estimated from UV-Vis NIR absorption spectrum of 1.9eV, blue shift of direct transition. The FTIR spectrum of SnS nano structured particles shows all the predicted shift towards 400- 4000cm^{-1} and the Morphology were identified by FE-SEM as rod shape.

KEYWORDS

Co Precipitate Method, Orthorhombic, Direct Transition, Rod Shape

INTRODUCTION

The metal sulfide semiconductor nanostructures are attracted much attention in recent years due to their physico-chemical properties (1). In the category of semiconductor materials, IV-VI type semiconductors possessed novel physico -chemical properties with orthorhombic structure (2). where in SnS the two bonds are held together names of the bonding are covalent and van der waals forces are present in the layers (3). There are various semiconductor IV-VI nanoparticles are their such as PbS , PbSe, SnTe and SnS (4).Out of which IV-VI semiconductors SnS have an unique optical active property with an optical band gap of indirect and direct band gaps(5) , less toxicity(6) . An narrow band gap semiconductors IV-VI series semiconductor are a research hotspot in nano-science and nano technology. Synthesis of stable SnS colloidal particles still remains a challenge and is crucial for many potential application (7). SnS are that optically active in the near infrared (NIR) and infrared (IR) are of great interest for their applications in photovoltaic's, near infrared detectors . Co-ordinating characteristics of tin and sulfur permit tin sulfide to adopt a various phases. There is a various method to synthesis the SnS such as Co-Precipitated (8), Hydrothermal (9), Solvothermal (10) Aqueous solution (11) and polyol route (12) . In the present study , optical and structural properties of the synthesized SnS nanocrystalline particles were investigated. The SnS nanostructured material performance were highly related to its crystalline nature, morphology size and surface property .which are ultimately depends on the preparation method and optimized condition. In co-precipitate method SnS nanostructured material was synthesized and its exhibits direct band gap and rod shape morphology.

EXPERIMENTAL SECTION

SYNTHESIS OF SnS NANOPARTICLES

All chemicals and other reagent with the highest purity available were purchased from Merck, Tin chloride di-hydrate ($SnCl_2.2H_2O$, 99.9%), Thiourea ($(NH2)_2CS$ 99.9%), Acetic acid (CH_3COOH, 98.2%) and ethanol (CH_3CH_2OH, 99.4%) was used without further purification. The synthesis procedure was carried out as reported in literature (13), complex tin was yield in the way of initially taken an tin chloride di hydrate of 0.2 M in a beaker of 200ml, containing a dionized water of 100ml followed by the adding slowly thiourea of 0.8M in the beaker. The chemical compounds are dissolved in the similar amount of solvent. The solution is vigorous stirring for 800 rpm carried out for 5 hours with maintaining a constant temperature of 80◦C. An instantaneous color change from transparent to pale Yellow takes place and the temperature is kept for 60mins cooling down with an ice bath.The SnS particles are purified by precipitation with a Ethanol mixture, centrifugation (9000 rpm, 5 minutes). The Product is subjected to furnace to 80 degrees for 8 hours and obtained a final product of dark brown color powder

CHARACTERIZATION

UV-Vis-NIR absorption spectrum was recorded using Agilent Cary 5000 spectrophotometer in the range of 200-1100 nm; Powder X-ray Diffraction (PXRD) patterns were recorded in the range of 2Θ = 10 to 80 degree using Rigaku Miniflex X-Ray Diffractometer using Cu Kα (λ=1.54Å) as the radiation source; FT-IR experiment was carried out using (PerkinElmer frontier FI-IR Spectrometer) in the range between 400 and 4000cm^{-1}. scanning electron microscope (TESCAN Co., Czech Republic) and attached with energy dispersive analysis of X-ray spectroscopy (EDAX).

RESULTS AND DISCUSSION

OPTICAL PROPERTY

UV–vis-NIR absorption spectra were measured in the spectral range of 200-800 nm of the sns synthesized nanoparticles by Co-Precipitated method. The SnS nanoparticles exhibited high absorbance in the visible region (below800nm)(14) **. Figure1** shows the absorbance spectra of SnS synthesized nanoparticles (similar absorbance was reported by Zhang *et al*. [15].

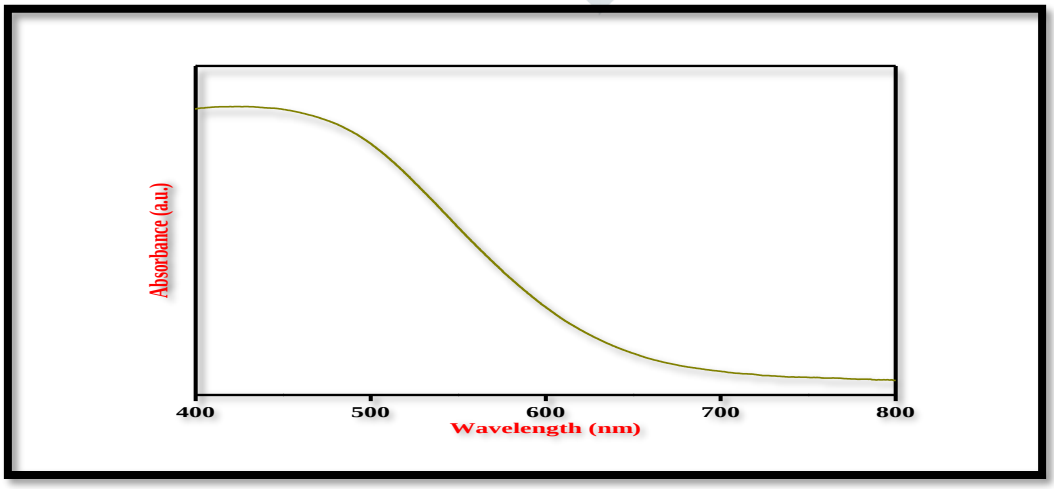

Figure 1: Absorption Spectra Of SnS Nanoparticles

To get the type of transition responsible the optical absorption and optical band gap in both the regions (16).The absorbance data was fitted to the following relation,

$$(\alpha h\nu)^{n} = (\nu - Eg)$$

Where ν is the frequency, h is the Planks's constant, A is a constant while n carries the value of either 2 for direct transition, or ½ for indirect transition. The dependence of α^2 on the photon energy $\nu$and $(\alpha)^{0.5}$on the photon energy (ν) for direct band gap are shown in **Figure 2**.

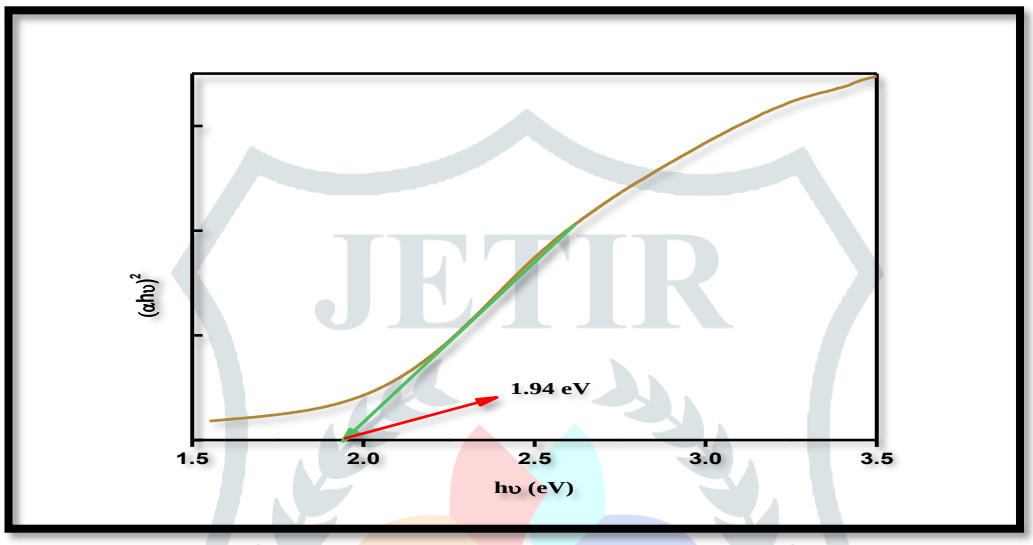

Figure 2: Tauc plot of the SnS nanoparticles

From the intercepts of plot the direct band gap of SnS nanoparticle synthesized has the value of 1.94 eV. There were many reports with different values of sns nanostructure materials , optical spectrum of direct band gap of 1.92eV SnS nanostructure was reported (17). The band gap of semiconductor nanomaterial increased as the size reduced .

POWDER X-ray DIFFRACTION

The structures of the synthesized nanostructured material were examinated by using Powder X-ray Diffraction (PXRD). XRD analysis verified the formation of highly crystalline SnS shown in the **Figure3** (18). The reflections were indexed and assigned to SnS of orthorhombic structure (19) with the lattice parameter a=1/4 4.329A0 nm, b=1/4 11.192A0 nm and C=1/4 3.983A0 (JCPDS 39.35A Herzenbergile are given in the paper of Hu, X.,et al., (20). There are some small additional peaks from trace impurities were observed as well, due to the low temperature synthesis. The reflection peaks can be assigned to different crystal plane, Viz, (120), (111), (140), (211) and (231) of crystalline SnS. Our results were accordance with shujaat (21). Which is in agreement with the literature value (JCPDS (38 – 354) of (Devika et al., (22)). According to Scherrer formula the calculated crystallite size of sample is 46 nm .

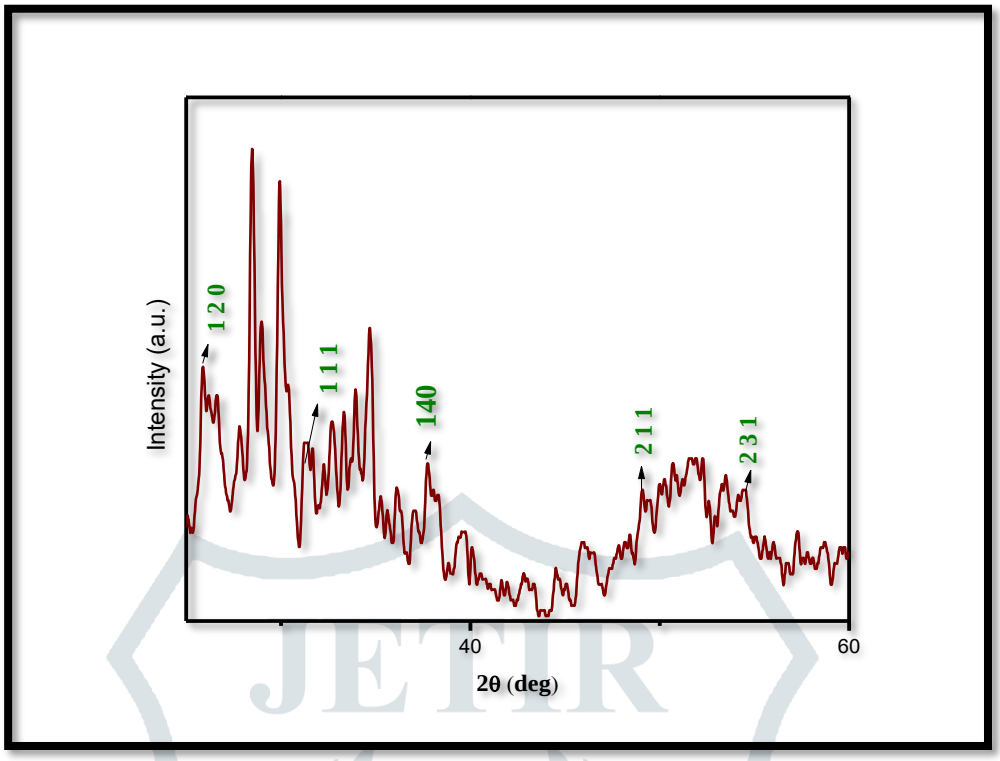

Figure 3: XRD Pattern of the prepared SnS nanoparticles

FT-IR ANALYSIS

The FT- IR measurements were carried out for the sample SnS nanostructered particles . FT-IR spectra were recorded in the range of 400cm^{-1} to 4000cm^{-1}which is shown in the **Figure5**. The spectra in a region 600-660cm^{-1} indicate the formation of Sn-S Bond (23). In this paper the spectrum of SnS bond are formed in the regions 611cm^{-1} and 736 cm^{-1} (24). The band observed at 1084 cm^{-1}-1184 cm^{-1} in the sample which terms as the presence of inorganic compound in them (25).The IR bands at around 1383 cm^{-1} and 1590 cm^{-1} are described to be the presence of bending of C-H group (26) , OH stretching and bending mode which may be surface hydroxyls and due to absorbed water (27) .the peak at the 2059 cm^{-1}, 2803 cm^{-1} and 3258 cm^{-1} is formed due to the presence of the sulfur oxygen stretching, symmetric stretching and N-H stretching (28).

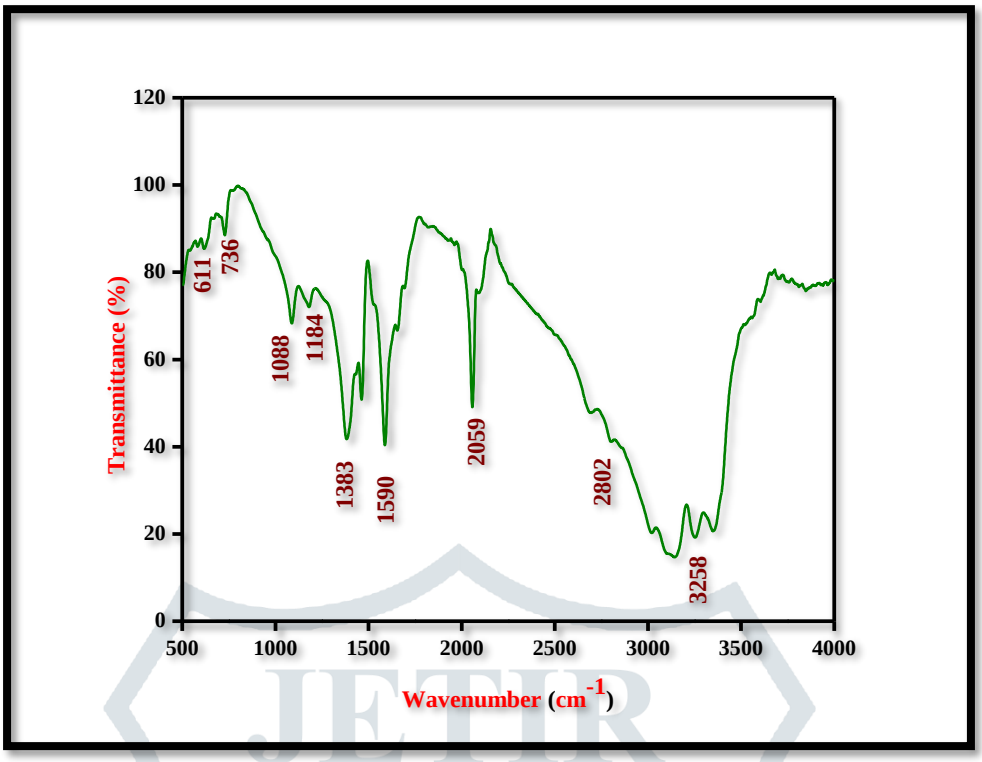

Figure 4: FTIR Spectrum of the synthesized SnS nanoparticles

FE-SEM

The morphological behavior from Field Effect Scanning Electron Microscope, we have obtained rod like morphology of synthesized SnS nanocrystalline particles, which is also reported by Ren, et al., (29). Because of high surface energy due to high surface area of contact aggregations in nanoparticles have been observed **Figure 5** (about the aggregations are discussed by Panda, et al., (30)). EDAX Quantitatively gives elemental confirmation of SnS phase in the **Figure 6** .The SEM Image of the prepared sample the metallic core of Sn is not present resulting of microstructure converted with nanostructure. The hierarchically nanostructure has been formed in the metallic layer followed by a SnS outer layer, and nanorods on the top . The SnS layer and nanostructure consumed the metallic core which may significantly influence the evaporation process at low temperature in metallic part.

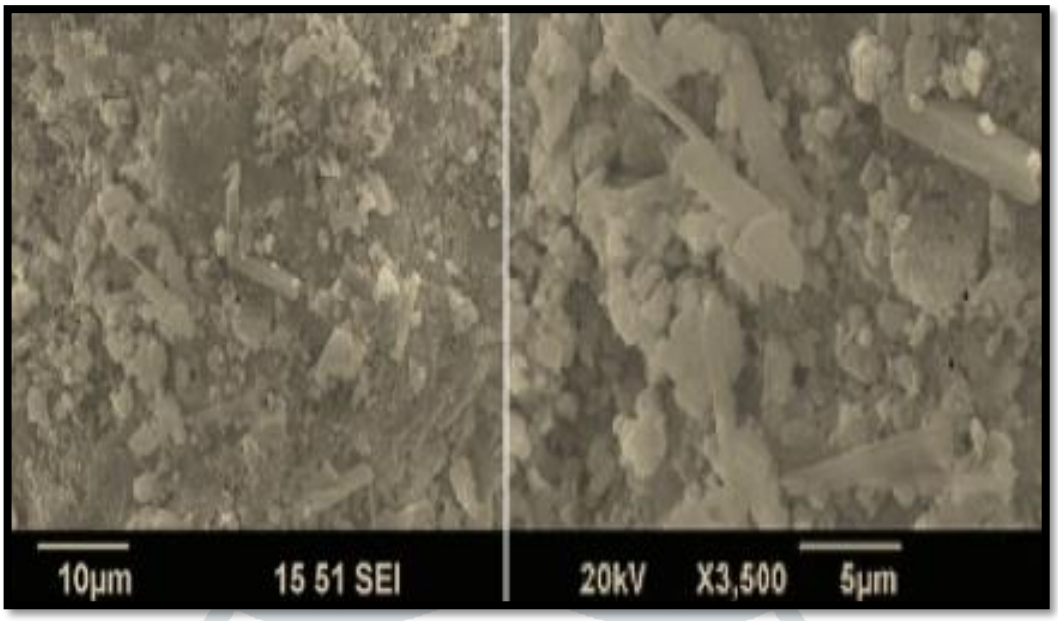

Figure 5: SEM Image of synthesized rod shape SnS nanoparticles

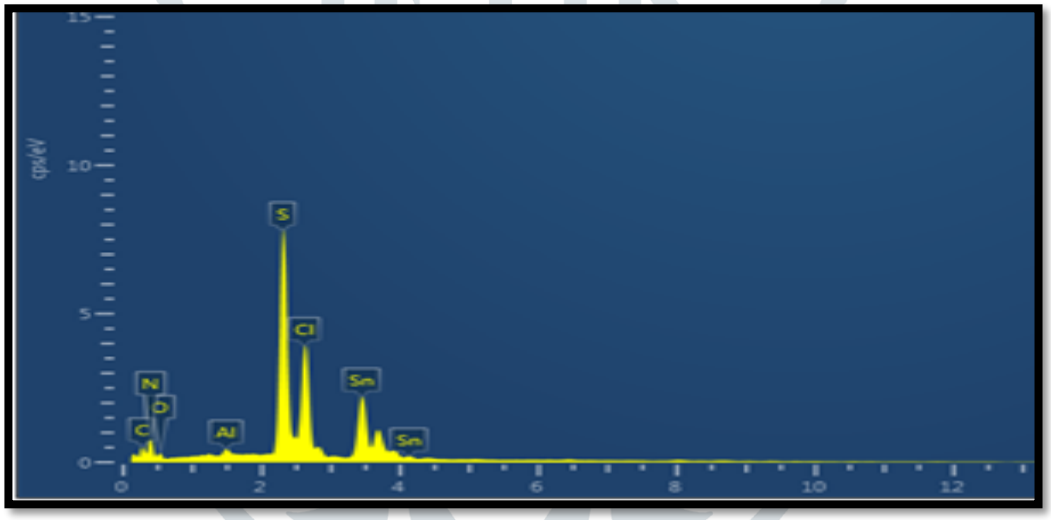

Figure 6: EDAX Image of synthesized SnS nanoparticles

CONCLUSION

An facile IV-VI SnS nanostructured particles were synthesized by co-precipitated method with using tin chloride di hydrate, thiourea and capping agent Acetic acid. The main advantage of this method cost efficiency and simple process. The synthesized nanocrystallined SnS with the structure of orthorhombic crystal lattice with the band gap energy of 1.9eV of direct band gap with the blue shift , which reveals the size reduction with the increase of band gap energy in this paper. The morphology of the synthesized SnS are in rod like structure were studied in the present investigation.

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