Synthesis and Chraracterization of Tin Sulfide Nanoparticles

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Abstract—In my present paper, Tin sulfide nanoparticles were successfully synthesized using wet chemical process and studied their structural properties. The prepared nanoparticles were characterized by X-Ray diffraction (XRD) and Raman spectroscopy. The XRD confirms the Tin Sulfide nanoparticles possessing orthorhombic structure having particle size is approx. 12.72 nm. The Raman spectrum shows the frequency of the phonon in these nanoparticles and the Raman modes of Tin Sulfide nanoparticles were found to shifts towards lower wave number side.

Keywords: *Synthesis, Characterization, Nanoparticles, Tin Sulfide, Wet Chemical Process.*

INTRODUCTION

Nanomaterial's as well as nanotechnologies attracts attention in researches. The physical properties and technologies in sample preparation as well as device fabrication evoke on accounts of the development of Nano science. Physical and chemical properties of a given material are derived from its crystalline structure. Tin Sulfide has a narrow band gap and lies IV-VI group layered semiconductor (An C *et al*., 2003, Andres *et al*., 1998). Tin Sulfide was first reported by the German mineralogist Herzenberg. Single crystal of Tin Sulfide has been prepared by reacting stoichiometric mixture of Sn and S elements over the temperature range of 600 - 750 °C. Tin Sulfide has orthorhombic structure (Chaki *et al*., 2014, Esumi *et al*., 1998) and is stoichiometric under Sn rich conditions and it will form $Sn_{1-x}S_x$ in Sulfur rich conditions. It has both indirect (1.09 eV) and direct (1.3 eV) band gaps along with a high absorption coefficient of 104 cm^{-1}. It has both p-type and n-type conductivity depending on the departure of Sn stoichiometry from ideal (Jiang *et al*., 1998). Optical properties of Tin Sulfide can be studied by a variety of experimental techniques such as optical absorption, transmission, reflection, photoluminescence spectroscopy etc. (Suresh 2014, Tanusevski *et al*., 2003).

In recent years, considerable efforts have been made in the synthesis of SnS nanostructures. The authors (Xu *et al*., 2009) have reported the synthesis of SnS quantum dots. Where, $SnBr_2$ is reacted with sodium sulfide in ethylene glycol (EG) at room temperature in the presence of various stabilizing ethanolamine as ligands. The ethanolamine is tri-ethanolamine (TEA), N- methyl-di-ethanolamine (MDEA). Among these ethanolamine's small size and dispersed SnS nanoparticles with average particles size 3.2 nm are found in the presence of TEA. This could be attributed two regions: (i) During nucleation, the strong binding of multiple hydroxyl groups on the surface of SnS nanoparticles and (ii) reaction of TEA with Sn^{2+} forms $[Sn(TEA)n]^{2+}$ complex. Biswas *et al*., reported the synthesis of Tin Sulfide nanorods and nanosheets through thioglycolic acid (TGA) assisted hydrothermal process (Biswas *et al*., 2007). The diameter of the SnS nano-rods varied within 30-100 nm and the crystal size and shape depends on the amount of TGA and sulfur source.

Salavati-Niasari *et al*. (2010) reported the synthesis of different morphologies of nanostructured Tin Sulfide including nanoparticles, nanosheets and nanoflowers by a simple hydrothermal process in the presence of TGA. The authors (Zhu *et al*., 2006) reported the synthesis of SnS nano-flowers using TGA assisted hydrothermal method. The nanoflowers assembled from more than ten needle - like tin Sulfide nanorods which are 70 nm in width and ~1μm in length. Tin Sulfide nanoflower shows direct and indirect band gap transition at 1.53 eV and 1.43 eV respectively. The Structural, optical and electrical characterization of Tin Sulfide nanomaterial's grown at different temperatures were studied by Rana Chandan and Saha Satyajit (2019).

https://doi.org/10.22232/stj.2019.07.02.13

SYNTHESIS OF TIN SULFIDE NANOPARTICLES

Wet chemical process has been followed to synthesized Tin Sulfide nanoparticles. Tin chloride and sodium sulfide were taken as sources of Tin and Sulfide respectively. 6 grams of Tin chloride was dissolved with 100 ml of distilled water in a beaker of 250 ml under magnetic stirrer for 40 min. During this moment sodium sulfide solution is prepared by dissolving 2.07 grams of sodium sulfide in 100 ml of distilled water. Now sodium sulfide solution was added drop wise, such that 100 ml of sodium sulfide solution is completely added to the tin chloride solution within 90 min. under the continues vigorous stirring of tin chloride solution. Afterwards the mixed solution was constantly stirred for 2 hours. The reaction is carried out at room temperature. At some moments during adding the sodium sulfide solution to the tin chloride solution the colorless tin chloride solution was turned into dark and brown color this confirms the formation of tin sulfide nanoparticles. After 2 hrs. vigorous stirring of the mixed solution, the solution kept 40 min. at room temperature without stirring. Now filtered and washed the prepared solution with deionized water or distilled water and ethanol several times. The filtered SnS nanoparticles were kept for 1 hr. at room temperature and then 1 hr. in oven at 40 ^{0}C. Keeping the sample for 24 hrs. at room temperature, the synthesized SnS nanoparticles | were obtained.

CHARACTERIZATION

The crystallinity and phases of the precursor and SnS nanoparticles were characterized by X-ray diffractometer, XRD-rigaku ultima-iv with Cu-kα radiation (λ = 1.5412 Å), 40 Kv, 40 mA in the 2θ range of 10-80° with 3°/min scanning rate. Also the Raman imaging of the sample (SnS) nanoparticles was done using Xplora one 785 nm Raman microscope.

XRD ANALYSIS OF SNS NANOPARTICLES

Using X-ray diffractometer the crystallinity and phases of the precursor and SnS nanoparticles were characterized.

The XRD pattern of Tin Sulfide nanoparticle is shown in fig 1. Diffraction angle 2θ value 31.560 shows the dominant plane (111). The other planes (221), (131), and (002) are corresponding to the 2θ values of 27.470, 51.460, and 60.240 respectively. The full width half maxima value was obtained from the dominant plane. The crystalline size of the formation of the nanoparticle is depend on the value of full width half maxima. It was clearly known from the Scherrer equation, that the larger the value of FWHM smaller the crystalline size of the nanoparticles. So crystalline size directly depends on FWHM value. The crystalline size of the nanoparticle depends on diffraction angle or the Bragg's angle also, but at a diffraction angle, a particular XRD peak is observed. In the other words the dominant peak or the peak having highest height occurs at a diffraction angle. So, for same nanoparticle having same crystalline size, the diffraction angle is same for dominant plane of the XRD pattern. The crystalline size of the SnS nanoparticles were calculated from the Scherrer equation.

$$D = \frac{K\lambda}{\beta \cos\theta}$$

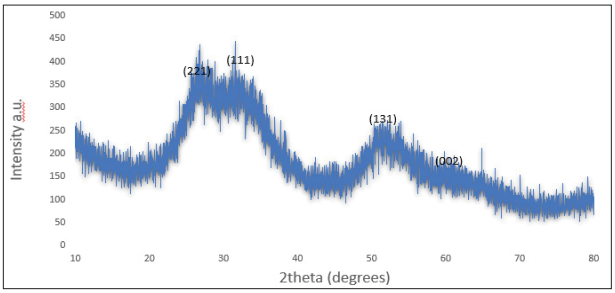

Fig. 1: XRD Pattern of Tin Sulfide (SnS) Nanoparticles

Where,

D = crystalline size

λ = wavelength of the incidence radiation

K= a constant and is equal to 0.9

θ = diffraction angle

B = full width half maxima (FWHM)

Using FWHM and diffraction angle from the XRD pattern, the crystalline size was found 12.72nm. It is a good agreement of synthesis of SnS nanoparticles using wet chemical process.

All peaks are attributed to Tin Sulfide (JCPDS: 39-0354) with the Herzenbergite orthorhombic structure with lattice parameters a = 4.3137 Å, b = 11.2853 Å and c = 3.9958 Å. These values of the lattice parameters are in good agreement with JCPDS card no. (JCPDS: 39-0354) and the result reported by Ariswan *et a*l (2017).

RAMAN SPECTROSCOPY OF SNS NANOPARICLES

Raman spectroscopy of SnS nanoparticles were performed at the room temperature. Fig. 2 shows Raman spectroscopy of SnS nanoparticle. The Raman modes for SnS nanoparticles

were observed at 409.80 cm^{-1}, 736.64 cm^{-1}, and 1275.71cm^{-1} with some weak intensity modes. Raman modes of SnS nanoparticles are found and due to phonon confinement which shifted towards lower wave number side, because size of the nanoparticles compared to the bulk one is huge difference. The phonon confinement give rise to energy band gap of nanoparticles.

Spectra having three distinguishable peaks at 409.80 cm^{-1}, 736.64 cm^{-1} and 1275.71 cm^{-1}. The 409.80$cm^{-1}$and 736.64cm^{-1} peaks are the characteristic Ag mode of Tin Sulfide, which arises due to inter atomic vibration between metal (Sn) and chalcogen (S). The 736.64 cm^{-1} peak is associated with secondary Tin Sulfide phase Sn_2S_3, may be arising from the intra-layer vibration of chalcogen–chalcogen.

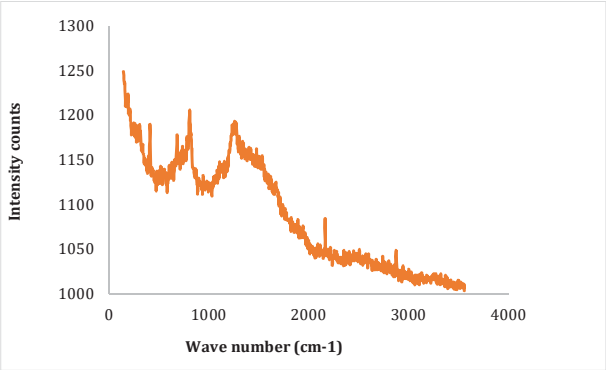

Fig. 2: Raman Spectrum of SnS Nanoparticles

CONCLUSION

Tin Sulfide nanoparticles were successfully synthesized by wet chemical method. The characterization was performed by X-ray diffractometer and Raman spectroscopy. XRD pattern of Tin Sulfide nanoparticles revealed the at dominant plane (111) was found at the diffraction angle of 31.50^0 and this result is good agreement with JCPDS curd no. (JCPDS: 39-0354) and confirms the orthorhombic structure of Tin Sulfide nanoparticles with lattice parameters a = 4.3137 Å, b = 11.2853 Å and c = 3.9958 Å. The Raman modes for SnS nanoparticles were observed at 409.80 cm^{-1}, 736.64 cm^{-1}, and 1275.71cm^{-1} with some weak intensity modes. Due to phonon confinement, Raman modes of Tin Sulfide nanoparticles were found to shifts towards lower wave number side.

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