

Study of Structural and Optical Properties of FeS₂ Nanoparticles Prepared by Polyol Method

G.S. Chandrawat^{1,2,*}, J. Tripathi^{1,†}, A. Sharma², J. Singh¹, S. Tripathi³, Jyotsna Chouhan⁴

¹ Department of Physics, ISLE, IPS Academy, Indore, Madhya Pradesh, India

² Department of Physics, Manipal University Jaipur, Jaipur, Rajasthan, India

³ Atomic & Molecular Physics Division, Bhabha Atomic Research Centre, Mumbai, 400085, India

⁴ RGPV, Bhopal, Madhya Pradesh, India

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FeS₂ nanoparticles were prepared using a simple and cost-effective Polyol method with ethylene glycol and precursor thiourea as capping reagents. The crystalline structure of FeS₂ nanoparticles were confirmed by X-ray diffraction. Dimensions of the unit cell and Pa-3 space group were determined by Rietveld refinement. The average crystallite size was found to be ~ 42.1 nm. The stoichiometry of these nanoparticles were also confirmed by, Raman and Fourier Transform Infrared Spectroscopy. Further, Raman spectroscopy revealed the chemical bonding and symmetry of molecules. FTIR spectroscopy exhibited the presence of functional groups of Fe=S, Fe-S and S-S in the samples. Advanced measurements and analysis towards the applicability of surfactant coated pyrite FeS₂ nanoparticles for solar cell etc. applications are in progress.

Keywords: Nanoparticles, Polyol Method, XRD, FTIR, Raman.

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1. INTRODUCTION

FeS₂ is well profusion in nature and has reasonably priced [1, 2]. In the midst of various metal sulfides such as cadmium sulfide (CdS), nickel sulfide (NiS₂), copper sulfide (CuS₂), the FeS₂ (iron sulfide) has drained momentous interest because of its high storage capacity (~ 894 Ah kg⁻¹) and green impact [3-5].

It is found as a practical material for conservation of energy [6, 7] and in fussy for photovoltaic's (PV) [8]. FeS₂ exhibits the bandgap energy of 0.95 eV in the bulk form. It is an attractive optoelectronic semiconductor due to its exceptionally large optical absorption coefficient of the order of 10⁵ cm⁻¹ in the visible region for bandgap larger than 1.3 eV [9] with a tolerable minority carrier diffusion length (100-1000 nm) [10, 11]. FeS₂ has created to possess various devices such as in photoelectric devices [12], photodetectors [13], and dye-sensitized solar cells [14], etc.

2. METHODS AND MATERIALS

2.1 Materials and Synthesis of FeS₂ Nanoparticles

The analytic reagent grade chemicals were used in this experiment. FeCl₃·6H₂O, NH₂CSNH₂ were purchased from Thomas baker and C₂H₆O₂ from Merck, India.

In general, the synthesis of FeS₂ nanoparticles (NPs) is not simple, but we have simplified the synthesis by using a relatively less complicated Polyol synthesis method for preparing the FeS₂ NPs [18].

In this experiment, the mixture of 0.25 g (3.2842 mmol) of thiourea (NH₂CSNH₂) and 1.0 g (3.699 mmol) of ferric chloride (FeCl₃·6H₂O) were placed in a round bottom flask fitted with a thermometer. After that 50 ml of ethylene glycol (EG) was added into the mixture. Further, the whole mixture was heated at

180 °C for 3 h. The black precipitate was obtained and then cooled up to room temperature; precipitate was washed by adding 20 ml of ethanol. Washing was done 4 times to extract FeS₂ NPs. The particles were dried at 60 °C and used directly for characterizations.

2.2 Characterizations

The as-prepared FeS₂ were characterized by X-ray diffraction (XRD) and Raman spectroscopy. The Bruker D8 Advance X-ray diffractometer is used to XRD measurement in the 2θ range of 10°-70° with a step size 0.02°. For this a wavelength 1.54 Å (Cu Kα radiation) is taken. The X-rays were detected using Bruker Lynx Eye detector based on silicon strip technology. Further, the Full-Prof 2000 software was used to the refinement through the profile matching routine of software package.

At room temperature Lab RAM HR Visible instrument (Horiba Jobin Yvon) were used for Raman spectroscopy measurements which have an Ar ion laser with a wavelength of 488 nm. Fourier transform infrared spectroscopy (FTIR) measurements were done by using vertex 70 is used in the range between 400-4000 cm⁻¹.

3. RESULTS AND DISCUSSION

3.1 Structural Characterization

X-ray diffraction Fig. 1a represents the structural Rietveld refinement of the XRD pattern of the prepared FeS₂ sample.

The peaks in the XRD spectra arising from corresponding Bragg's (*hkl*) planes for various diffraction positions were recorded at 2θ values ~ 28.53°, 32.96°, 36.94°, 40.69°, 47.23°, 56.11°, 58.92°, 61.38°, and 64.18° which is shown in Fig. 1a. This is related to FeS₂ pyrite (cubic structure) with phase purity [15]. The well-known

* govind.chandrawat1@gmail.com

† jtripathi00@gmail.com

standard Scherrer relation was used for the determination of average particle size (L)

$$L = \frac{0.9\lambda}{B \cos \theta}. \quad (1)$$

Here, λ is the incident X-ray wavelength (1.54 Å), B is the Full width at half maxima of the peak and θ is the Bragg angle.

The average crystallite size determined from this formula was ~ 42.1 nm. The dimensions of the unit cell, hkl values, and space group of FeS₂ NPs were obtained using the profile matching routine of FullProf 2000 software package after the refinement. The Bragg peaks were modeled with pseudo-Voigt function and the background was estimated by linear interpolation between selected background points. The crystal system was found the fcc with space group Pa-3(205) and cell parameters 5.4349 Å.

Corresponding fit values are R_p (Profile Factor) 63, R_{wp} (Weighted Profile Factor) 46.4, R_{exp} (Expected Weighted Profile Factor) 36.1, R_B (Bragg Factor) 26.8, R_F (Crystallographic R_F Factor) 19 and χ^2 1.647, respectively, were calculated from Rietveld Refinement. Description of parameters is given in Table 1.

The results show the crystal structure of FeS₂ is closely matching with that of pure FeS₂ phase exhibiting the capability of this method to produce stoichiometric and pure nanoparticles.

The sharp well-defined nature of the peaks indicates good crystallinity of the samples. The lattice constant was calculated from different planes using the equation

$$a = d\sqrt{(h^2 + k^2 + l^2)}, \quad (2)$$

where d is the interplanar distance and (hkl) are the Miller indices. The values of lattice constant a (Å) are found to be slightly different for each plane.

The value of lattice constants is estimated from the Nelson-Riley plots. For this, the lattice parameters (a) calculated from the different planes are plotted against

$$f(\theta) = \frac{1}{2} \left[\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right]. \quad (3)$$

The corrected value of ' a ' is obtained by Fig. 1b. The estimated value is 5.4353 Å which is close to the reported value of the bulk sample (JCPDS file No. 710053, $a = 5.432$ Å).

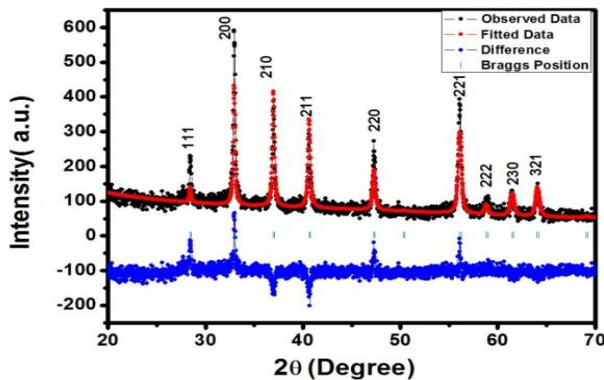


Fig. 1a – Structural Rietveld refinement of XRD patterns of FeS₂ NPs

Table 1 – Description of Rietveld refinement parameters

R_p (Profile Factor) = $100[\sum \omega_i y_{io} - y_{ic} / \sum y_{io}]$, where y_{io} is the observed intensity and y_{ic} is the calculated intensity at the i th step.
R_{wp} (Weighted Profile Factor) = $100[\sum \omega_i y_{io} - y_{ic} ^2 / \sum \omega_i (y_{io})^2]^{1/2}$, where $\omega_i = 1/\sigma_i^2$ and σ_i^2 is the variance of observation.
R_{exp} (Expected Weighted Profile Factor) = $100[(n-p)/\sum \omega_i (y_{io})^2]^{1/2}$, where n and p are the numbers of profile points and refined parameters, respectively.
R_B (Bragg Factor) = $100[\sum I_{obs} - I_{calc} / \sum I_{obs}]$, where I_{obs} is the observed integrated intensity and I_{calc} is the calculated integrated intensity.
R_F (Crystallographic R_F Factor) = $100[\sum F_{obs} - F_{calc} / \sum F_{obs}]$, where F is the structure factor, $F = \sqrt{(I/L)}$, L is Lorentz polarization factor.
$\chi^2 = \sum \omega_i (y_{io} - y_{ic})^2$

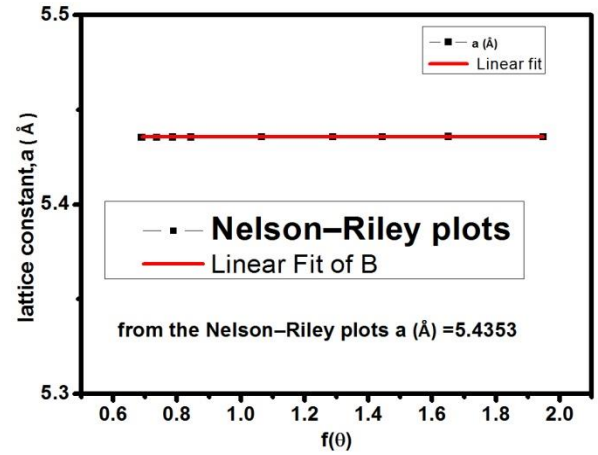


Fig. 1b – Nelson-Riley plots of FeS₂

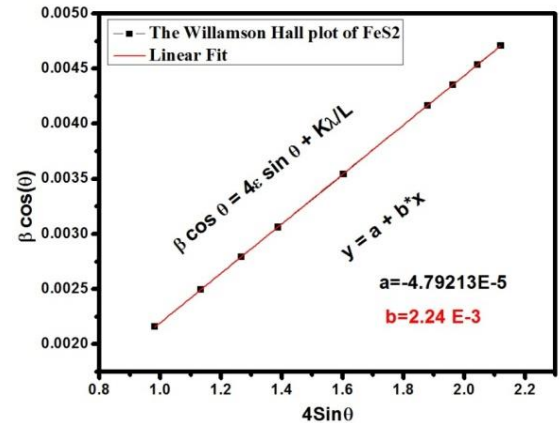


Fig. 1c – Williamson-Hall plot of FeS₂ NPs

The strain (shown in Fig. 1c) was estimated by Williamson-Hall method which relates the crystallite size and strain-induced broadening by the equation

$$B \cos \theta = 4\epsilon \sin \theta + \frac{K\lambda}{L}, \quad (4)$$

where B is FWHM in radians, L is the crystallite size in nm, λ is the wavelength of X-ray (1.54 Å), ϵ is the strain.

The slope of this plot of the $B \cos \theta$ versus the $4 \sin \theta$ curve gives the strain (ϵ). From Fig. 1c, the tangential

strain (ϵ) due to the spherical shape of the particle was found to be 2.24×10^{-3} .

3.2 Raman Spectra

Fig. 2 depicts the Raman spectrum of FeS₂ NPs. As clearly seen from XRD, the particles do not have very large crystallites, thus the Raman signals are also not very intense. However, all the observed peaks are in well agreement with the earlier reported results which confirms the purity of FeS₂ NPs. Weak Raman peaks are seen around ~ 222 cm⁻¹ and 276 cm⁻¹ which are assigned to the asymmetric and symmetric stretching vibration modes respectively. The peak at 391 cm⁻¹ also corresponds to coupled vibration and stretching mode (T_{g2}), in agreement with the FeS₂ previously observed report [16].

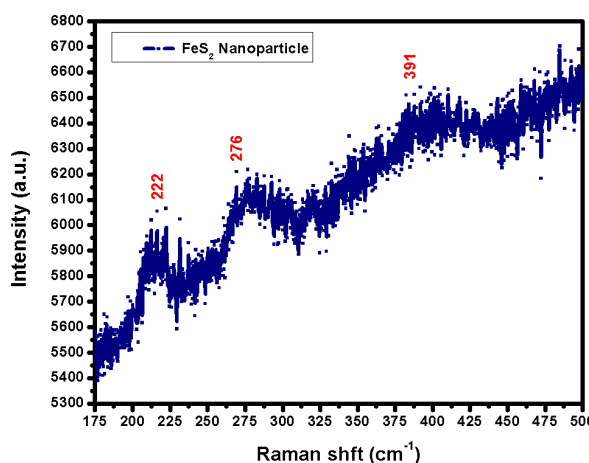


Fig. 2 – Raman spectrum of prepared FeS₂ NPs

3.3 Fourier Transform Infrared Spectroscopy

Fig. 3 depicts the FTIR Spectrum. FTIR spectra proved functional groups of Fe=S, Fe-S and S-S in the samples. Vibration mode of FeS₂, Fe=S lies between 1050-1156 cm⁻¹, disulfide stretching (S-S) and (Fe-S), 607-625 cm⁻¹ is found [17].

Other peaks are attributed to adsorbed moisture,

Symmetrical stretching adsorption of C-H at 2945 cm⁻¹, and C=O at 1656 cm⁻¹. The peaks at 1452 cm⁻¹ correspond to the deformation mode of C-H.

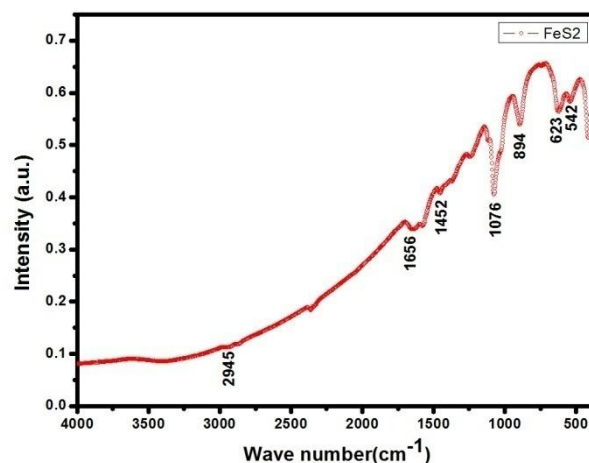


Fig. 3 – The transmission FTIR spectrum of prepared FeS₂ NPs

4. CONCLUSIONS

In conclusion, we find out the average crystallite size is ~ 42.1 nm. However, in all these applications, only a certain range of properties is useful and any deviation in these may result in drastic alteration of the important features thereby affecting the overall performance to a great extent. So, the understanding of the properties and their correlation is very important at the basic level. For this, the Polyol method was selected to yield FeS₂ nanoparticles in powder form and XRD, as well as Raman spectroscopy, were utilized to understand their basic properties. From FTIR we found the functional groups of Fe=S, Fe-S and S-S in the samples.

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