Synthesis and Characterization of Fe Doped Copper Sulphide Nanoparticles

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***Abstract*— Fe doped Copper Sulfide nanoparticles were synthesized via chemical co-precipitation method from cupric nitrate, sodium sulphide and ferric chloride. The formed nano particle is characterized by powder x-ray diffraction, scanning electron microscopy, Energy Dispersive X-ray Spectroscopy, Ultra-Violet Spectroscopy and Fourier transform infrared spectroscopy, XRD confirmed the preferential growth of copper sulfide nanoparticles that width is 19 nm. The SEM image shows the synthesized Fe doped copper sulphide show nanoparticles with spherical morphology. The EDAX spectra show the elements present in the sample. The FTIR spectrum is used to study the stretching and bending frequencies of molecular functional groups in the sample. From UV spectrum, the band gap of Fe doped copper sulfide nanoparticles is found to be 3.7 eV.**

***Keywords*— XRD, SEM, FTIR, UV, EDAX.**

I. INTRODUCTION

Among the semiconducting materials, the metal sulphides are studied in abundance because of their characteristic band gap, high extinction coefficient which makes them an ideal candidate for solar cells applications as light absorbers [1]. Simplest among the semiconductor metal chalcogenides are copper sulphides which fall in the binary semiconductor category. Copper sulfide (CuS), a p-type semiconductor, has attracted tremendous interest due to its excellent optical and electronic properties [2]. Several methods have been used to synthesize metal sulphide nanoparticles [3]. In present study, copper sulphide nanoparticles were synthesized by chemical co-precipitation method and it is doped with Fe by adding ferric chloride The Fe doped copper sulphide nanoparticles were characterized by Power X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Energy Dispersive X-ray Analysis (EDAX), Fourier Transform Infrared Spectroscopy (FTIR) and UV-Visible Spectroscopy (UV-Vis).

II. MATERIALS AND METHODS

Nanoparticles of Copper sulfide were prepared by chemical co precipitation method by adding Cupric Nitrate and sodium Sulfide. Precise amounts of reagents taking into account their purity were weighed and dissolved separately in distilled water into 0.1M concentration. After obtaining a homogeneous solution, the reagents were mixed using magnetic stirring. The solution is mixed with ferric chloride to prepare Fe doped copper sulfide nanoparticle. The precipitate was separated from the reaction mixture and washed several times with distilled water and ethanol. The wet precipitate was dried and thoroughly ground using agate mortar to obtain the samples in the form of fine powder [3].

III. TESTS CONDUCTED

X-ray diffraction is an ideal technique for the determination of crystallite size of the powder samples. The basic principle for such a determination involves precise quantification of the broadening of the peaks. XRD line broadening method of particle size estimation was chosen in this investigation for determining the crystallite size of the powder sample. The morphology of the powder samples was studied by the scanning electron microscope (SEM) analysis. The elemental analysis of the sample was studied from EDAX analysis. The infra red spectroscopic (IR) studies of copper sulphide nanoparticles were made by using 'SHIMADZU' FTIR 8400S model spectrometer through KBr method. The UV spectrum was taken in the absorbance mode in the wavelength range from 200 to 800 nm.

IV. RESULTS AND DISCUSSION

A. XRD Studies

XRD – Particle Size Calculation

The XRD patterns of the prepared samples of Fe doped Copper Sulfide nanoparticles are shown in figure.1. XRD studies reveal that the samples are nano sized and crystalline. The fine particle nature of the samples is reflected in the X-ray line broadening. The size of the synthesized Fe doped Copper Sulfide nanoparticles is calculated using Scherer equation

$$\mathbf{D = 0.9\ \lambda / \beta \cos\theta} \qquad (1)$$

where λ represents wavelength of X rays, β represents half width at full maximum and θ is the diffraction angle [4]. The average grain size of the particles is found to be 19 nm. The XRD pattern of Fe doped Copper sulfide nanoparticles is shown in fig 1.

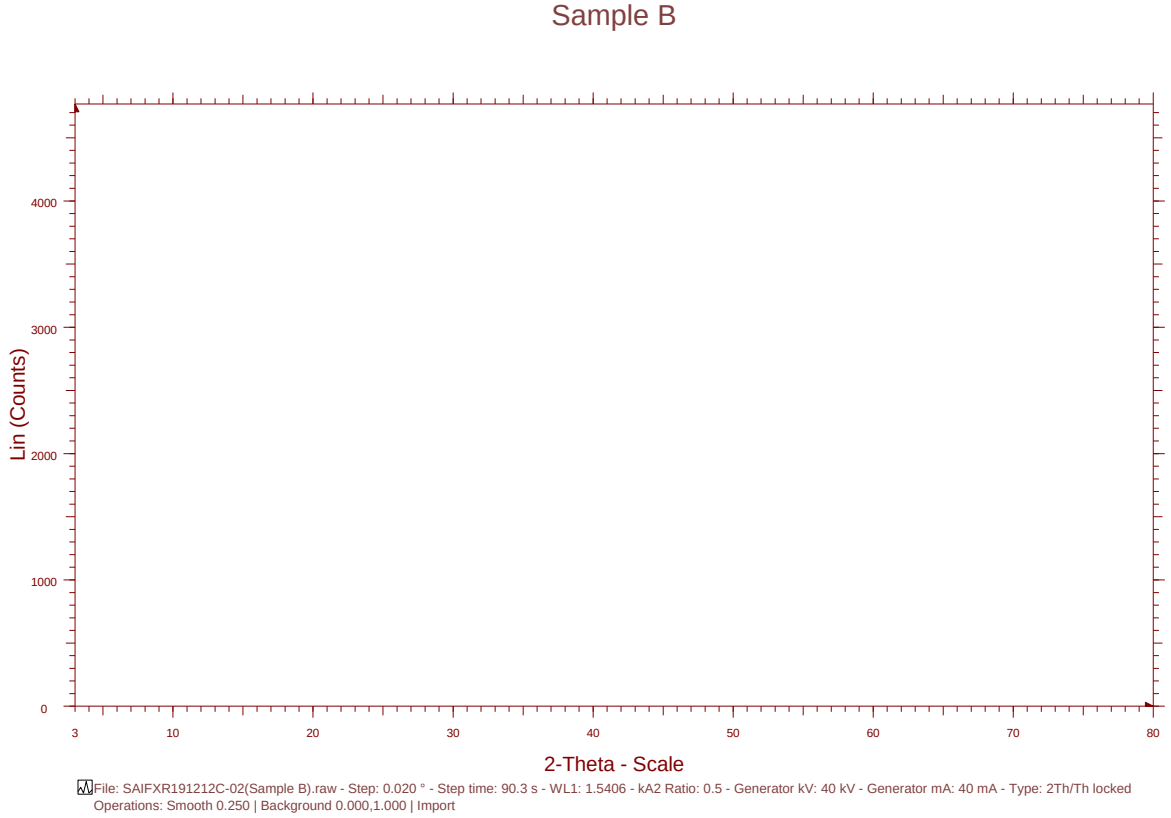

Fig .1. XRD Pattern of Fe doped Copper Sulfide Nanoparticles.

A good agreement between the Experimental diffraction angle [2θ] and Standard diffraction angle [2θ] of specimen is confirming standard of the specimen. Many peaks at 2θ values of Copper Sulfide is observed and tabulated in table.1 and compared with the standard powder diffraction card of Joint Committee on Powder Diffraction Standards (JCPDS), Copper Sulfide file No. 78-2121. The d-spacing values of experimental is also confirming to the standard values.

Experimental		Standard – JCPDS 78-2121	
Diffraction angle (2θ in degrees)	D spacing (Å)	Diffraction angle (2θ in degrees)	D spacing (Å)
29.223	3.06372	29.289	3.0468
31.79	2.81268	31.794	2.8122
35.411	2.53303	35.031	2.5594
47.87	1.89855	47.763	1.9027
52.686	1.73585	52.732	1.7345

Table.1. Experimental and Standard Diffraction Angles of Fe Doped Copper Sulfide Nanoparticles.

XRD – Dislocation Density

The dislocation density is defined as the length of dislocation lines per unit volume of the crystal. In materials science, a dislocation is a crystallographic defect, or irregularity, within a crystal structure. The presence of dislocations strongly influences many of the properties of materials. The movement of a dislocation is impeded by other dislocations present in the sample. Thus, a larger dislocation density implies a larger hardness.

The X-ray line profile analysis has been used to determine the dislocation density.

The dislocation density can be calculated from equation

$$\delta = \frac{1}{D^2}$$

Where δ is dislocation density and D is the crystallite size. Results of the dislocation density calculated from the formula is given in table.2. The number of unit cell is calculated from equation

$$n = \pi\,(4/3) \times (D/2)^3 \times (1/V)$$

Where D is the crystallite size and V is the cell volume of the sample.

2θ (deg)	**Particle Size D (nm)**	**Dislocation Density (m^2) x10^{15} $\delta = 1 / D^2$**	**Number of Unit Cell X10^5**
18.238	28.73864777	0.001210786	0.610487817
25.695	25.86992064	0.001494204	0.445310876
29.223	21.21574795	0.002221689	0.245613964
31.79	18.86016655	0.002811311	0.172549849
35.411	26.14378064	0.001463064	0.45960335
47.87	18.49346238	0.002923907	0.162679451
52.686	11.54282939	0.007505428	0.039556225

Table .2. Dislocation Density and Number of Unit Cell from XRD of Fe doped Copper Sulfide Nanoparticles.

It is observed from these tabulated details, and from fig.2, fig.3 and fig.4, dislocation density is indirectly proportional to particle size and number of unit cells. Dislocation density increases while both particle size and number of unit cell decreases.

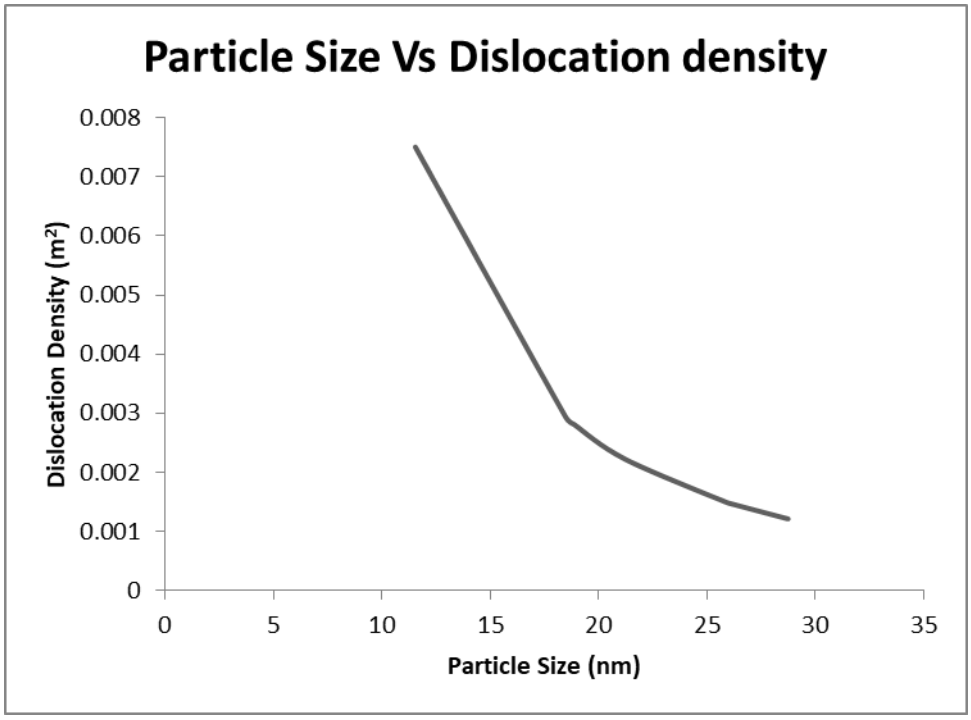

Fig.2. Particle Size Vs Dislocation Density Curve of Fe Doped Copper Sulfide Nanoparticles.

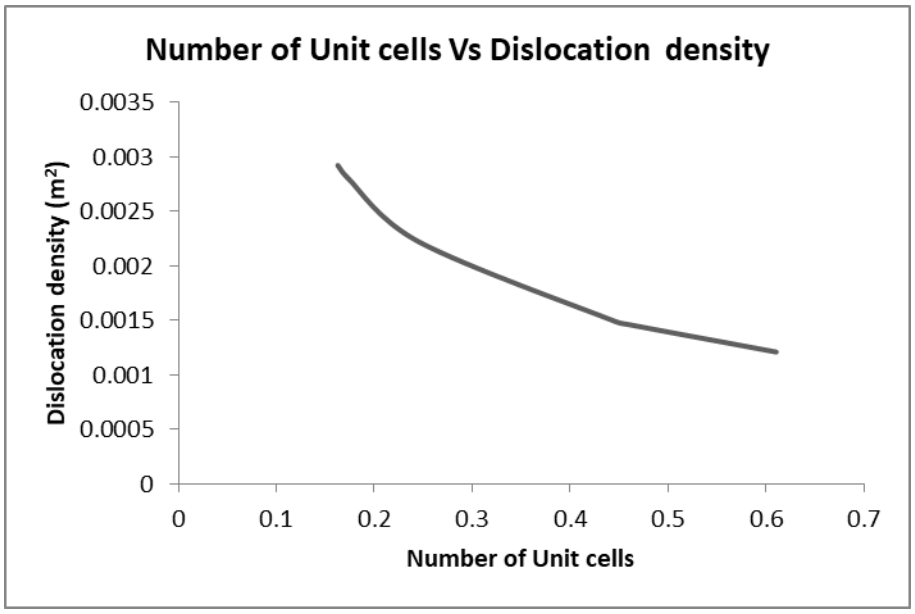

Fig.3. Number of Unit Cells Vs Dislocation Density Curve of Fe Doped Copper Sulfide Nanoparticles.

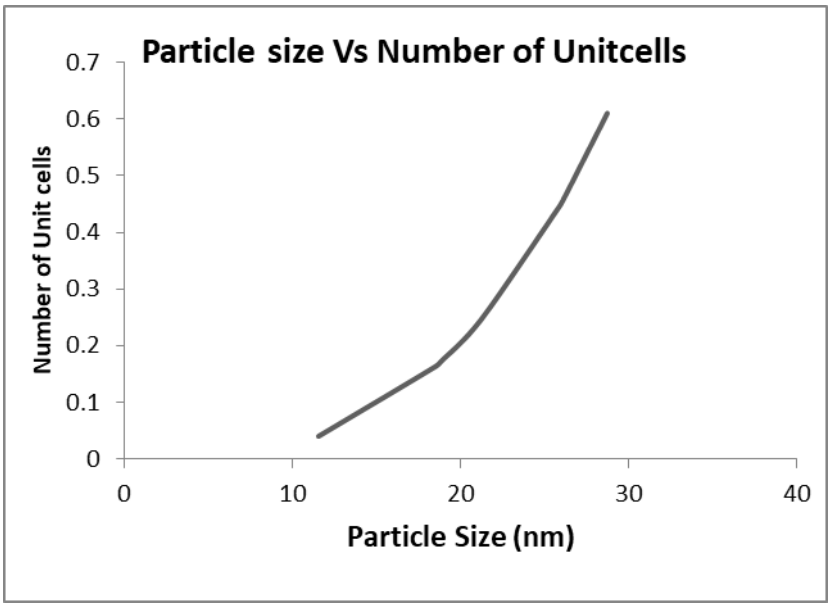

Fig.4. Particle Size Vs Number of Unit Cells Curve of Fe Doped Copper Sulfide Nanoparticles.

XRD – Morphology Index

A XRD morphology index (MI) is calculated from FWHM of XRD data using the relation

$$M.I = \frac{FWHM_h}{FWHM_h + FWHM_p}$$

Where M.I. is morphology index, $FWHM_h$ is highest FWHM value obtained from peaks and $FWHM_p$ is value of particular peak's FWHM for which M.I. is to be calculated. The relation between morphology index and particle size is shown in table .3.

FWHM in rad	Particle Size in nm	Morphology Index
0.004884444	28.73864777	0.610038233
0.005564778	26.14378064	0.578610373
0.005495	25.86992064	0.581683922
0.006751	21.21574795	0.530919956
0.007640667	18.86016655	0.500010906
0.008198889	18.49346238	0.482389747
0.013397333	11.54282939	0.363194169

Table .3. Relation Between Morphology Index and Particle Size for Fe Doped Copper Sulfide Nanoparticles

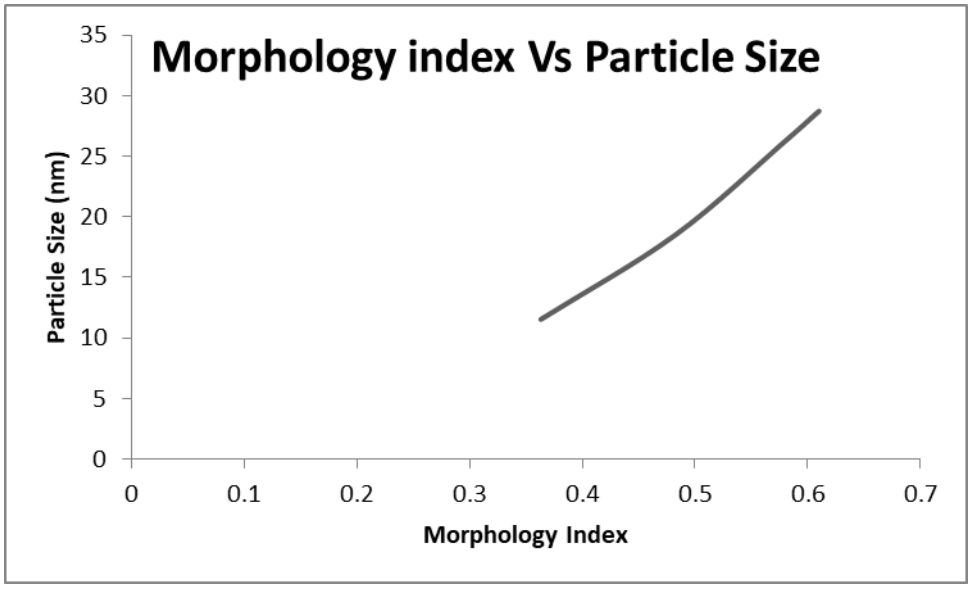

Fig .5. Morphology Index of Fe doped Copper Sulfide Nanoparticles.

It is observed that MI has direct relationship with particle size and the results are shown in Fig .5.

XRD – Unit Cell Parameters

Unit cell parameters values calculated from XRD are enumerated in table .4.

Parameters	Values
Structure	Hexagonal
Space group	P63/mmc [194]
Symmetry of lattice	Primitive
Particle size	28 nm
Lattice parameters	a=3.791; c=16.342
Vol.unit cell(V)	203.47
Density (ρ)	4.681
Dislocation Density	$1.252x10^{15}$
Mass	95.61amu

Table .4. XRD Parameters of Fe Doped Copper Sulphide Nanoparticles.

B. SEM Studies

Scanning electron microscopy was used to analyze the morphology and size of the synthesized Fe doped copper sulphide nanoparticles. Fig.6 shows the SEM images of the Fe doped copper sulphide nanoparticles at various magnifications. The SEM images of Fe doped copper sulphide nanoparticles show nanoparticles with spherical morphology. In this case the particles sizes are slightly increased and is also observed that the particles are distributed with agglomeration.

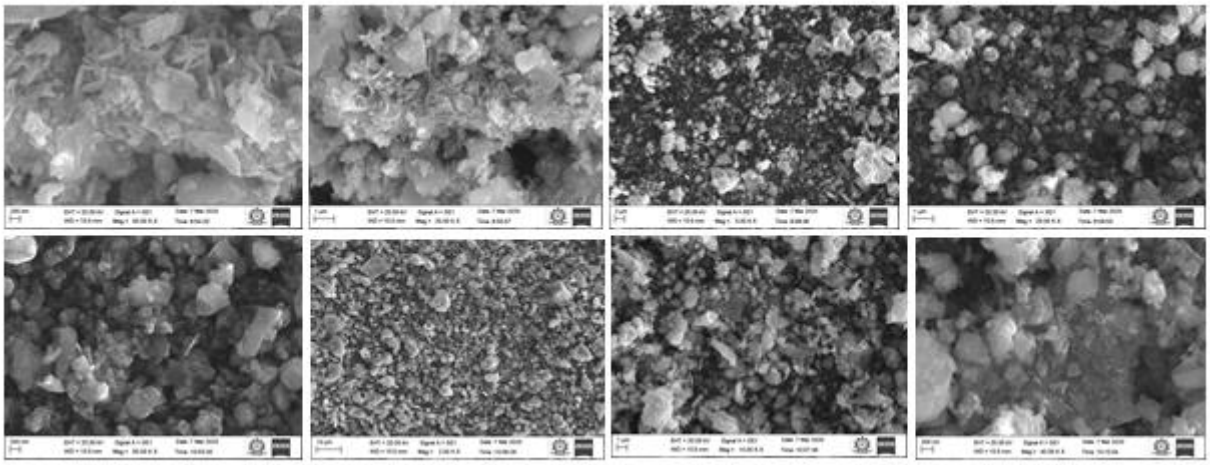

Fig.6. SEM Images of Fe Doped Copper Sulphide Nanoparticles at Various Magnifications.

C. EDAX Studies

The EDAX elemental analysis of Fe doped copper sulphide nanoparticles shows that the Fe copper sulphide nanoparticles was mainly composed of Cu, S and O elements. The O element may be due to the water molecule. The EDAX spectrum of Fe doped copper sulphide nanoparticles is shown in Fig.7. The weight percentage of the elements are given in the table.5

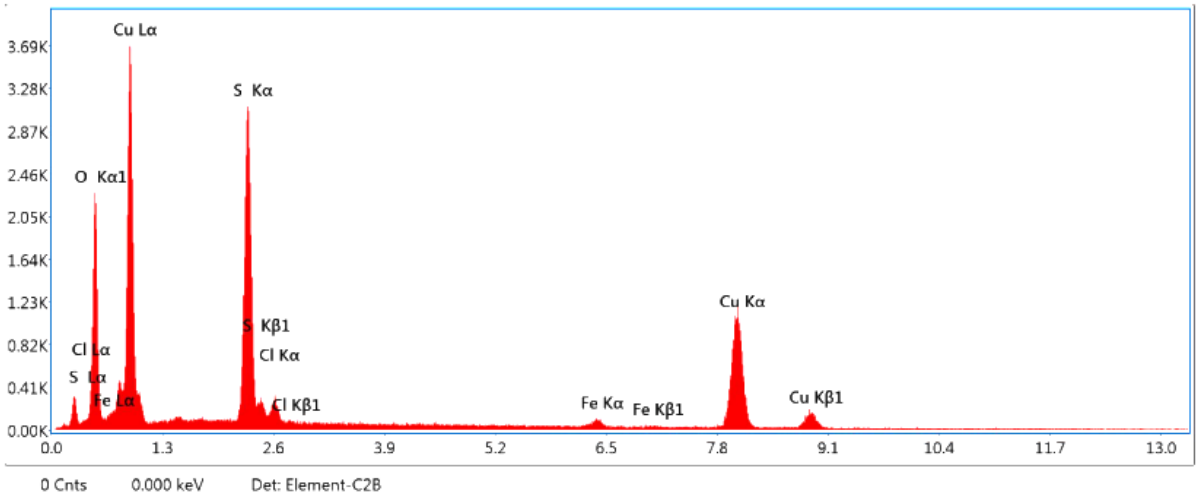

Fig.7. EDAX Spectrum of Fe Doped Copper Sulphide Nanoparticles

Element	Wt%	Atomic %	Error %	K ratio
O	24.4	49.3	9.1	0.0837
S	22.5	22.7	4.3	0.1750
Cl	2.1	1.9	11.7	0.0146
Fe	2.1	1.2	11.4	0.0212
Cu	49.0	25.0	2.7	0.4330

Table.5. The Weight Percentage of The Elements of Fe Doped Copper Sulphide Nanoparticles

D. FTIR Studies

The FTIR spectrum of the Fe doped copper sulfide sample is shown in the fig.8.The FTIR spectrum for Fe doped copper sulfide nanoparticles show peak at 3730.33 cm^{-1}, 3442.92 cm^{-1},3334.92 cm^{-1} are due to free O-H group [6] and

1610.56 cm^{-1} corresponds to the bending mode of hydroxyl group of water [7]. The peak at 611.43 cm^{-1} is due to Cu-O stretching bond [8] and the peak at 459.06 cm^{-1} is due to the Fe – O vibrations [7].

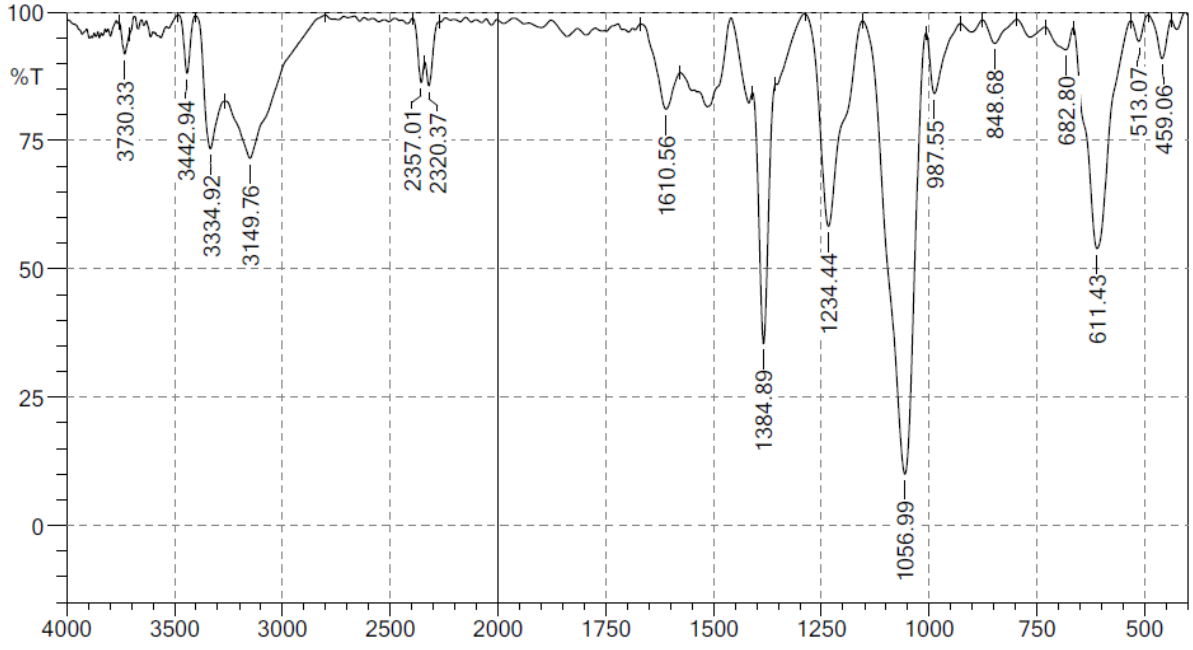

Fig.8. FTIR Spectra of Fe Doped Copper Sulfide Nanoparticles.

E. UV Studies

The band gap of the prepared sample Fe doped copper sulfide was determined by using UV visible studies. Fig.9 shows the UV-Visible absorption spectra for Fe doped copper sulfide nanoparticles and the maximum absorption is at 300 nm wavelength. Fig.10 shows the graph to find the band gap of Fe doped copper sulfide nanoparticles. From the graph, the optical band gap of copper sulfide is 3.7 eV. The optical transmittance of Fe doped copper sulfide nanoparticles is shown in Fig11 and the transmittance is 37% .

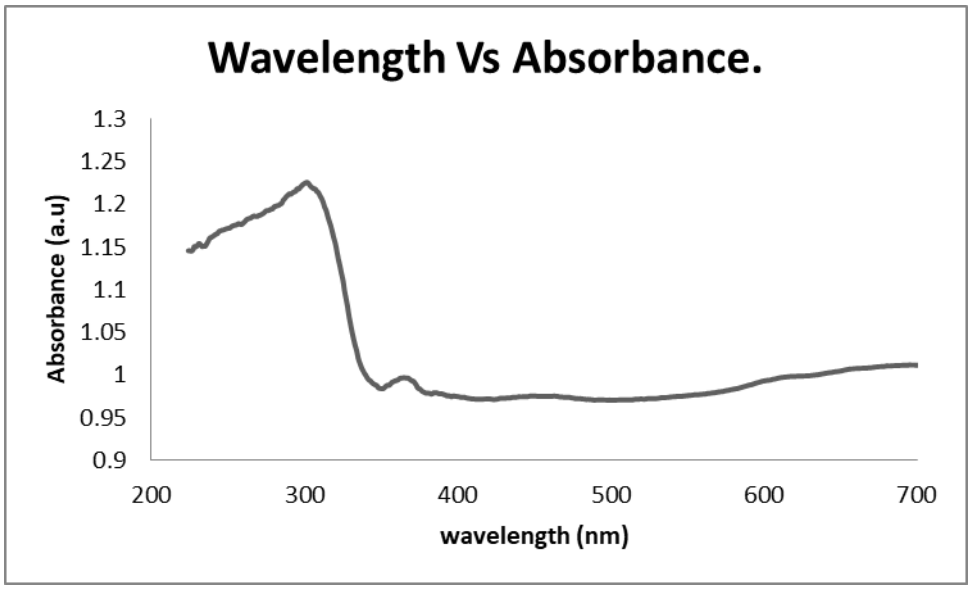

Fig.9. UV-Visible Absorption Spectra of Fe Doped Copper Sulphide Nanoparticles.

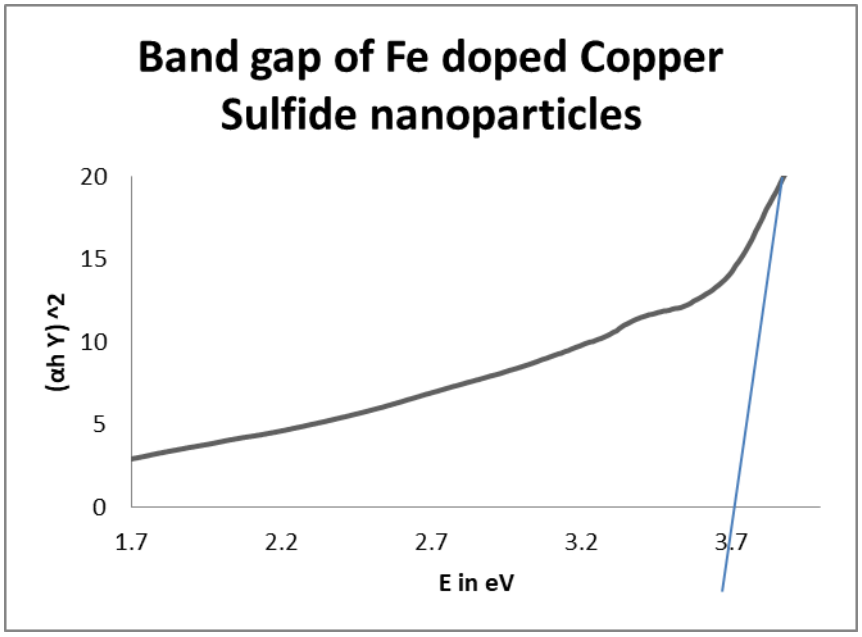

Fig.10. Graph to Find The Band Gap of Fe Doped Copper Sulphide Nanoparticles.

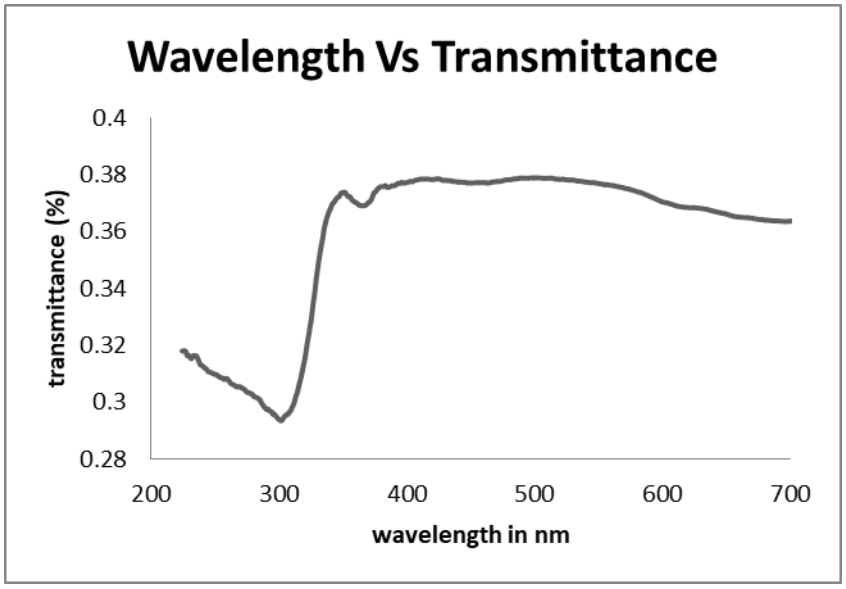

Fig.11. Optical Transmittance of Fe Doped Copper Sulphide Nanoparticles

V. CONCLUSION

The Fe doped copper sulpide nanoparticles have been prepared by chemical co-precipitation method. XRD analysis suggests that the average particle size is in the nano range (19nm). The SEM picture reveals the nanoparticles with spherical morphology. The EDAX spectra show the elements present in the sample. From the FTIR spectrum, the stretching and bending frequencies of the molecular functional groups in the sample are studied. From the UV spectra, the band gap was found.

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