Structural and Optical Properties of Pure and Copper Doped NiS Nanoparticles

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Abstract

In this paper we report tuning of band gap of NiS nanoparticles by doping these with Cu. The pure and Cu doped NiS nanoparticles were prepared following chemical route. These nanoparticles were characterized by XRD, and UV-VIS spectroscopy. The XRD records show well-formed nanocrystalline particles. The particle size of NiS nanoparticles as determined using Scherrer formula is found to be about 43 nm. The particle size is found to decrease in Cu doped NiS nanoparticles. UV-VIS spectroscopy was used to determine the band gap of these nanoparticles. The band gap of NiS nanoparticles is found to be 3.63eV. The effect of doping Cu on the structural and optical properties of NiS nanoparticles is described

Introduction

Transition metal sulfide nanostructures have been the focus of considerable interest due to their unique optical and electrical properties and wide variety of potential applications in devices such as nonlinear optical devices, semiconductor, electroluminescence devices, industrial catalysts, solar energy conversion devices, fluorescence devices and even light emitting diodes for flat-panel displays, superconductor etc[1-5].

Transition metal (TM) sulfides exhibit interesting optical, electronic, thermoelectric and photoelectric properties[6-9]. Nickel sulfide (NiS) an important member of this large family of TM sulfides, finds use as a potential cathode material for the rechargeable lithium battery, as a catalyst in the degradation of organic dyes and in magnetic devices[10,11].

Owing to the tremendous technological importance, different synthesis routes have been tried for the synthesis of nanoparticles of NiS. Some of the techniques, which have being used for the preparation of nanoparticles include solvothermal process, UV irradiation, sol-gel method, laser ablation within copolymer and colloidal microemulsion etc. The chemical precipitation method is one of the important methods for the synthesis of nanoparticles. According to the best of our knowledge, only limited work have been reported on the preparation of NiS nanoparticles by this method.

In this paper, we report synthesis of pure NiS nanoparticles and copper doped NiS nanoparticles by chemical route. The structural and optical properties of pure as well as Cu doped NiS nanoparticles is reported and the effect of doping Cu on the properties of NiS nanoparticles is described.

Methodology

In the preparation of nickel sulfide nanoparticles we have followed chemical route. 1.31g of nickel sulphate ($NiSO_4.6H_2O$) was dissolved in 100 ml distilled water. To the aqueous solution of $NiSO_4$, a few drops of ammonium hydroxide (NH_4OH) were added to obtain appropriate pH value. Then hydrogen sulfide gas was bubbled through this solution and black percipitate of NiS appeared. The black precipitate so produced was filtered , washed several times with distilled water and dried to obtain NiS nanoparticles. For preparing Cu doped NiS nanoparticles appropriate amount of hydrated copper sulphate was added to initial $NiSO_4$ solution and the process was repeated as for the preparation of pure NiS nanoparticles.

The XRD patterns were recorded using D8 Advanced X-ray diffractometer from Bruker. UV-Vis absorption spectra were recorded using Shimadzu 2450 double beams spectrophotometer.

All the experiments were performed at room temperature.

Result and Discussion

3.1 XRD studies: XRD studies of pure and Cu doped NiS nanoparticles: Figure 1a shows the XRD pattern of NiS nanoparticles. The diffraction pattern reveals that the NiS nanoparticles prepared under the aforesaid conditions is polycrystalline in nature. The main peaks appear at 2θ values of approximately $29.31^0, 31.79^0, 48.03^0, 52.74^0$ and 59.43^0 which

match well with the rhombohedral phase of NiS and correspond to (416), (300), (131), (421) and (012) planes. These match well with the values reported[12] in JCPDS card No 65-3686. The interplanar distance d were calculated using Bragg's law

$n\lambda = 2d \sin\theta$

where n is the order of diffraction, λ is the wavelength of the incident x-ray, d is the interplanar distance, θ is the Bragg angle

The interplanar distances of important planes of the prepared NiS nanoparticles and those reported in JCPDS card No. 65-3686 are reproduced in table 1 and show good agreement between the two values. Figure 1b shows the XRD pattern of Cu doped NiS nanoparticles. The Cu doped NiS nanoparticles also exhibit rhombohedral phase. However, the peaks are broader indicating that the particle size has reduced as a result of doping.
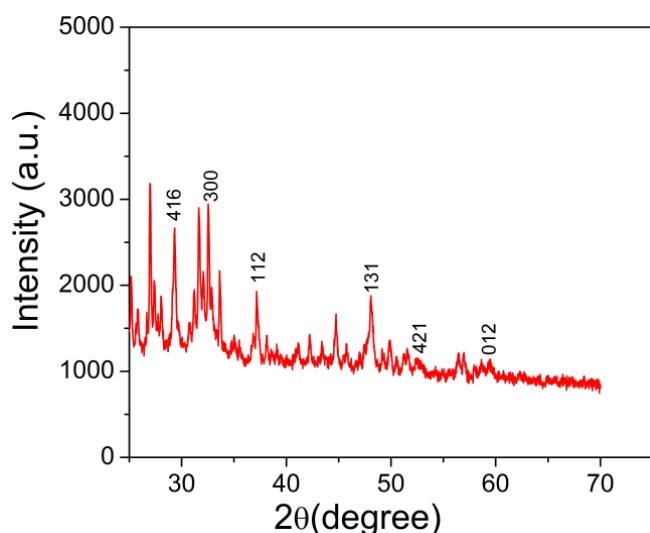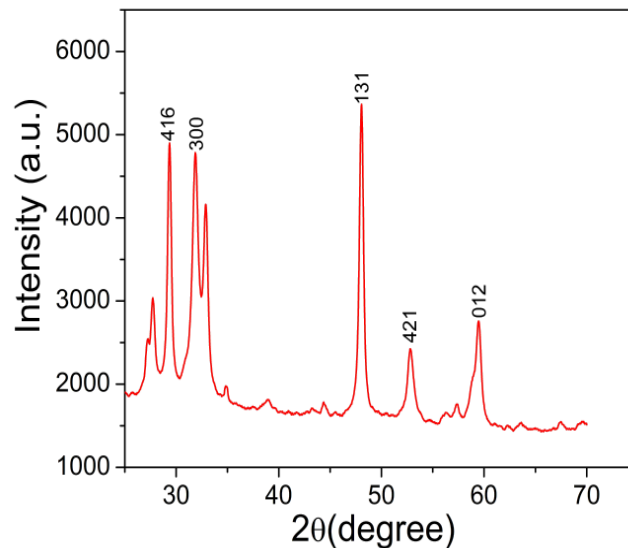

Figure-1(b)
XRD pattern of Cu doped NiS Nanoparticles

The crystallite size D of the nanoparticles is estimated by using Schererr's formula[13]

$D = k\lambda / \beta \cos\theta$

Where k is constant, its value is 0.94, λ is the wavelength of X-Ray, θ is the Bragg angle of the peak under consideration and β is the full width at half maximum (FWHM) of the diffraction peak.

Table 1 also displays the values of interplanar spacing and particle size at room temperature for pure and Cu doped NiS nanoparticles. The particle size for NiS nanoparticles is found to be about 43.09 nm and particle size for Cu doped NiS nanoparticles is found to be 15.31 nm.

Figure-1(a)
XRD pattern of NiS Nanoparticles

Table-1
XRD data and crystallite size of pure and Cu doped NiS Nanoparticles

Sample	2θ (Degree)	Interplanar spacing (nm)		D(nm)
		Observed	Reported [13]	
NiS	29.31	0.304	0.294	43.09
	31.79	0.282	0.277	
	48.03	0.189	0.182	
	52.74	0.173	0.173	
	59.43	0.155	0.154	
Cu doped NiS	29.33	0.304		15.31
	32.54	0.281		
	48.08	0.189		
	52.53	0.173		
	59.48	0.155		

Strain and dislocation studies: The origin of strain is related to lattice "misfit" which depends upon the growing condition of nanoparticles The strain ε have been calculated by the following formula [14].

$\varepsilon = (\beta_{2\theta} \cot\theta) / 4$

Where θ is the Bragg angle, $\beta_{2\theta}$ = full width at half maximum (FWHM) of the diffraction peak

The calculated strain has been reproduced in table 2. From this table we can see that the strain values increases with the doping of copper, such type of change in the strain may be due to the predominant recrystallization process in the nanoparticles

Table-2
Values of crystallite size, strain and dislocation density Of pure and Cu doped NiS Nanoparticles

System	Crystallite size(D)(nm)	strain(ε)	Dislocation density (δ) (nm⁻²)
NiS	43.09	0.00259	0.00060
Cu doped NiS	15.31	0.00511	0.01701

A dislocation is linear defect in a crystal. The dislocation density is defined as the length of dislocation line per unit volume of the crystal. The dislocation density δ have been calculated by the following relationship[15]

$\delta = n / D^2$

Where D = crystallite size and n=1

The calculated data have been reproduced in table 2. From this table it is clear that the dislocation density increases with the doping of copper. The increase in the dislocation density suggests that the NiS nanoparticles become less orderly on doping.

Optical studies: In this work, the influence of copper doping on the optical properties of NiS nanoparticles prepared by chemically route has been studied. The optical absorption spectra of NiS nanoparticles and Cu doped NiS nanoparticles is reproduced in Figure 2a and 3a respectively. Each shows well defined absorption edge.

The energy band gap estimated by Tauc[16] relation

$\alpha = k (h\nu - E_g)^n / h\nu$

where υ is the frequency , h is the Planck's constant. K and n are constants. For NiS, the value of n is 2. The plots of $(\alpha h\nu)^{1/2}$ vs. hυ for NiS nanoparticles and Cu doped NiS nanoparticles are shown in Figure.2b and 3b respectively. The optical band gap energy can be determined by extrapolating the linear portion of the curve to the energy axis. The energy band gap of NiS nanoparticles is found to be 3.63 eV. We can see that the band gap energy of the resultant nanoparticles showed marked increment as compared with that of bulk 0.4eV [17] of the bulk NiS. The increase of band gap energy with the decrease of particle size of the nanoparticles clearly shows the effect of

quantum confinement, which is consistent with the previous theoretical argument by Brus[18]. The bandgap of Cu doped NiS is found to be 4.94 eV. This is greater than the bandgap of pure NiS nanoparticles and can be attributed to the smaller particle size of Cu doped NiS nanoparticles and/or to the doping of copper.
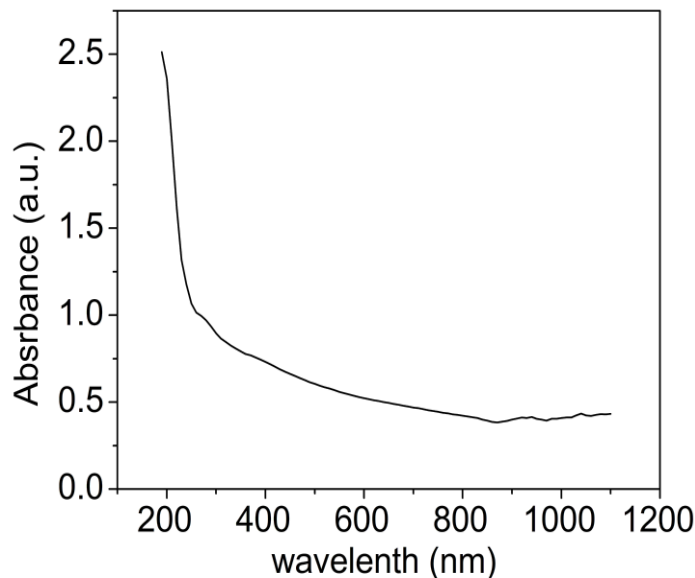

Figure-2(a)
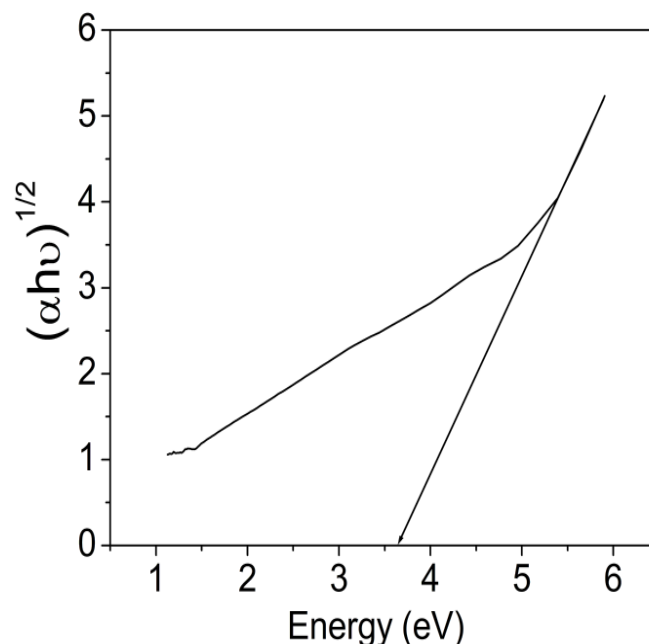**Absorption spectrum of NiS Nanoparticles**

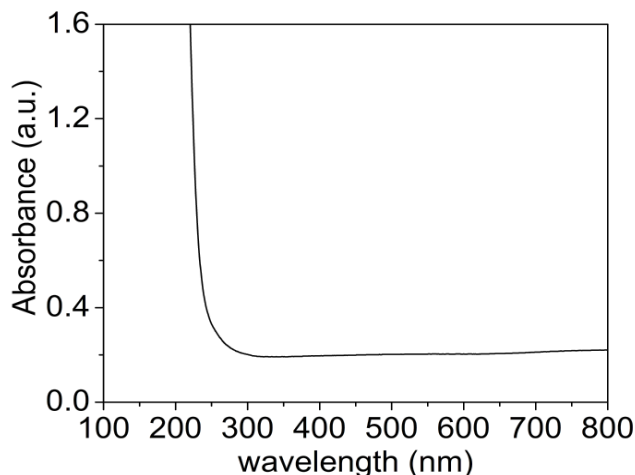**Figure-2(b)**
$(\alpha h\nu)^{1/2}$ vs. hυ for NiS Nanoparticles

Figure-3(a)
Absorption spectrum of Cu doped NiS Nanoparticles
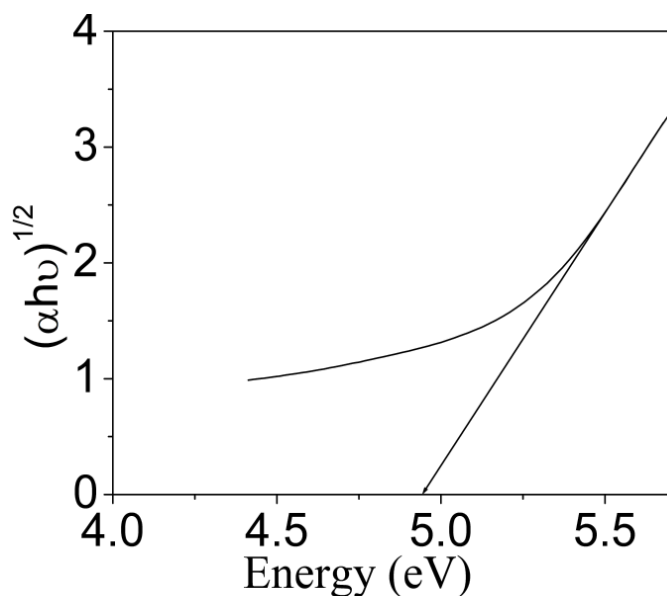

Figure-3(b)
$(\alpha h\upsilon)^{1/2}$ vs. $h\upsilon$ for Cu doped NiS Nanoparticles

Conclusion

In conclusion, pure and copper doped nanoparticles have been prepared by simple chemical route. The XRD results show that the nanoparticles are nanocrystalline with rhombohedral phase. The crystallite size of NiS nanoparticles was found to be 43.09 nm. The strain, dislocation density and particle size were found to change significantly with the doping of copper. The band gap of NiS nanoparticles was found to be 3.63 eV, which is higher than the bandgap of bulk NiS which is 0.4 eV. We can also see the band gap NiS nanoparticles increases with the doping of copper The experimental characterizations indicate that copper doping plays an important role in modifying the structural and optical properties of NiS nanoparticles.

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