

Synthesis and Characterization of NANOCRYSTALLINE NiS NANOPARTICLES

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Abstract: An efficient procedure for the synthesis of Nickel Sulphide (NiS) Nanoparticles from Nickel Chloride and Sodium Sulphide by nanocrystalline Nickel Sulphide (NiS) can be used as catalyst and a variety of elegant techniques have been done to control growth of shape and size of NiS Crystals. The worldwide availability, larger scale synthesis, higher yields and shorter reaction times are the advantages of the present method.

Keywords: Metal Sulphides, NiS nanoparticles, XRD, UV-Spectra, IR- Spectra

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I. Introduction

Metal Sulphides

Metal sulphide nanomaterials have attracted great attentiveness in recent years owing to their unique possessions in Physics and Chemistry that are notably different from those of their bulk counterparts. These nanoscale metal sulphide materials usually show novel optical, electronic and magnetic properties due to their peculiar quantum size effect and large specific surface areas. Because of their excellent optical, electrical and magnetic properties these materials exhibit wide variety of potential applications in Nano devices such as electro luminescence, non-linear optical devices and fabrication of photocatalytic materials [1-7].

Transition metal nickel sulphides represented by NiS-SiO₂ and NiS₂-SiO₂ are important materials to study the physics of a system with strong electron correlation involving, for instance, the metal insulator transition in which elucidation of the mechanism responsible for the magnetism and electric transport has been the subject of great interest [8-10].

Nickel Sulphides

Nickel sulphide, as one of the transition metal sulphides, has attracted considerable attention because of its unique properties such as its unique electromagnetic property involving a first order phase transition from a low temperature antiferromagnetic semiconductor to a high temperature paramagnetic metal, its toughening effect, catalyst for hydronitrogenation and hydrosulphurization, and exhibits a wide variety of potential applications in various fields such as IR detectors, solar storage devices, photoconductive materials, common cathode material for rechargeable lithium ion batteries [11-16].

Nickel sulphide exhibits complicated, compositional, structural and magnetic phase behaviour. Depending on the synthetic process, a variety of compositions can be obtained including Ni₃S₂, Ni_{3+x}S₂, Ni₄S_{3+x}, Ni₆S₅, Ni₇S₆, Ni₉S₈, Ni₃S₄, NiS₂, NiS [17-21]. The prominent phases exhibited by NiS are two stoichiometric phases: the low temperature rhombohedral (β -NiS, millerite) and high temperature hexagonal (α -NiS) crystal structures and one non-stoichiometric phase hexagonal (Ni_{1.03}) crystal structure [22-23]. The high temperature α - NiS phase is antiferromagnetic and exhibits a metal insulator transition with an abrupt change in magnetic susceptibility when it is cooled below a transition temperature, i.e., Neel temperature TN=271K. Below transition temperature α - NiS has a magnetic moment of about 1.7 μ B; however above the transition the magnetic moment appears negligibly small [24,25], and Neel suggested that some small antiferromagnetic particles, due to the uncompensated number of spins on two sub lattices, should exhibit super Para magnetism and weak ferromagnetism [26]. Hexagonal NiAs-type Ni_{1.03} catalyst showed very good catalytic properties, and it was found that the formation of this NiAs-like hexagonal Ni_{1.03} structure could be related to the formation of nickel vacancies [27].

Nickel sulphide is the inorganic compound with the formula NiS. It is a black solid with density 5500 kg/m³. Its melting point is 976°C and boiling point is 1388°C. Its elemental percentage is: Ni =64.67% and S= 35.33% [28-38].

The high temperature phase of nickel sulphide (α - NiS) exhibits hexagonal NiAs structure, whereas the low temperature phase nickel sulphide (β - NiS) rhombohedral mille rite structure. The hexagonal NiAs structure is one of the most important material in transition metal chemistry. The NiAs-type structure showing the linkage of ions in a unit cell. The metal and anions lie respectively on interpenetrating simple hexagonal and close-packed hexagonal sub lattices. The transition metal atoms occupy all the octahedral holes in the closed packed hexagonal array of anions and the anions are surrounded by six transition metal atoms in the trigonal prism. The octahedral mutually share faces along the c axis, and pairs of tetrahedral share faces forming trigonal bipyramidal holes. The NiAs structure has two important features: i) the ability to accommodate additional transition metal atoms in the trigonal bipyramidal holes, and ii) to omit metal atoms, either randomly or on planes perpendicular to the c axis [39-41].

The structure of mille rite NiS projected along the c-axis. In mille rite rhombohedral structure, there are very short metal-metal distances (2.25 Å) indicative of intermetallic bonds. A projection of the structure along the c-axis shows triangles of Sulphur atoms arranged at lattice points of a rhombohedral cell. These forms trigonal prismatic columns along c, and the nickel atoms are coordinated to the square faces which form the sides of these columns and the Sulphur on an adjacent column. Sulphur is in fivefold coordination in mille rite.

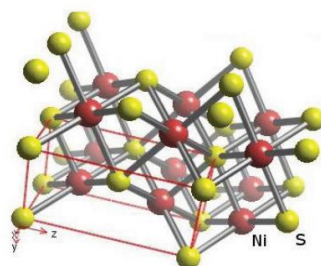


Figure 2.1: Solid state structure of nickel sulphide

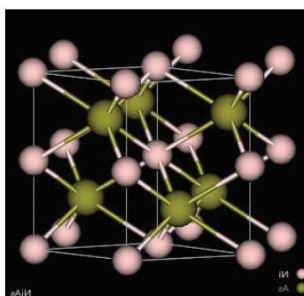


Figure 2.2: NiAs type structure of nickel sulphide

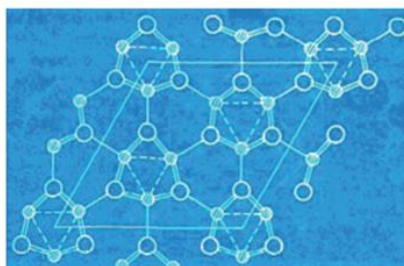


Figure 2.3: Structure of mille rite NiS projected along the c-axis.

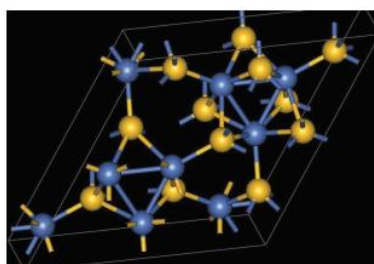


Figure 2.4: The crystal structure of mille rite NiS

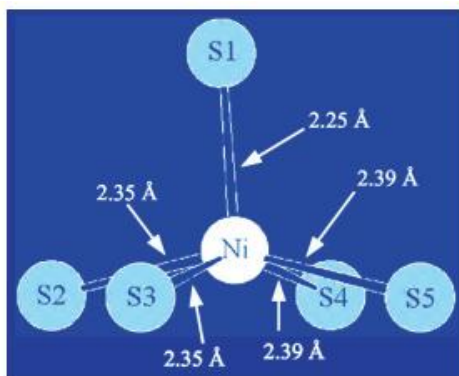


Figure 2.5: The local structural environment of the Ni atom which is penta coordinated with S atoms in the mille rite NiS

The crystal structure of mille rite NiS is shown in Figure 2.4. Here, the Ni atoms have five nearest neighbour S atoms occupying the corners of the square pyramid. Figure 2.5 shows the local structural environment of the Ni atom which is penta coordinated with S atoms in the mille rite NiS. In this pyramid geometry (Figure 2.5) the Ni atoms are displaced slightly out of the basal plane, toward the apical Sulphur atom.

PRESENT WORK:

Different synthesis routes have been tried for the synthesis of Nanoparticles of NiS-SiO₂. The chemical precipitation method is one of the important method for the synthesis of Nanoparticles

In this work NiS-SiO₂ nanoparticles have prepared by Co-Precipitation Method. The Structure average grain size of as-prepared sample is characterized by XRD and its optical properties is studied by UV Spectroscopy and FT-IR Spectrometry.

Experimental:

All chemicals used in our experiments were reagent grade and used without further purification. The morphology and structure of the NiS-SiO₂ nanoparticles and products were determined by the X-ray diffraction (XRD), FT-IR and UV-Visible spectrophotometer.

II. Materials and Methods

Preparation of NiS-SiO₂ nanoparticles

Nickel Chloride was used as a precursor to prepare pure NiS-SiO₂ nanoparticles. For This 0.5M Of NiS was taken and was dissolved in 100ml Methanol and stirred it for half an hour. To this solution, 0.5M of Silicon dioxide was added slowly. NiS-SiO₂ precipitate was washed with water three times to remove the unwanted residues. It was also washed with Methanol two times to remove the impurities. At 200⁰C, the solid was heated in hot air oven for 24 hours. NiS- SiO₂ Nano crystalline compound thus formed was Black-Grey in color.

III. Results And Discussion

XRD ANALYSIS:

A typical XRD pattern of the NiS-SiO₂ sample. The XRD pattern reveals the sample is highly crystalline. The four diffraction peaks at $2\theta = 31.8^{\circ}$, 45.4° , 56.4° and 67.0° can be indexed to the (100), (101), (102), and (110) planes, respectively, of the hexagonal NiS-SiO₂ structure.

The average crystalline size has estimated from Scherrer's formula

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

was found to be 22.43 nm for NiS and, 32.48 nm, for NiS-SiO₂ respectively. Where, β is the FWHM of most intense peak.

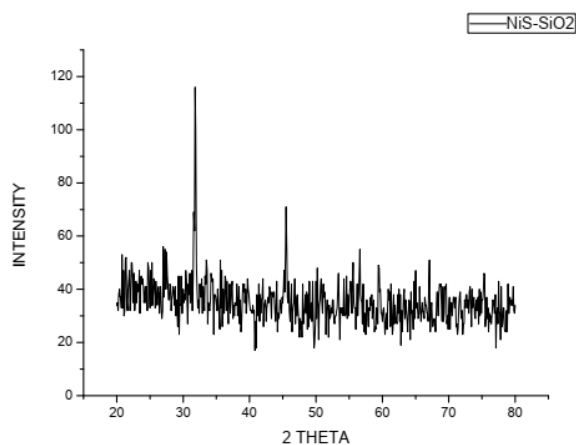


Figure 1: XRD patterns of hierarchical flower-like NiS-SiO₂. Vertical lines (bottom) represent the typical pattern of the hexagonal NiS phase.

U.V SPECTRAL ANALYSIS:

U.V-VISSIBLE spectra of the samples was taken in the wavelength between 200 nm to 800 nm. The absorbance spectra of the NiS-SiO₂ nanoparticles calcined at 200 °C are shown in Fig.2

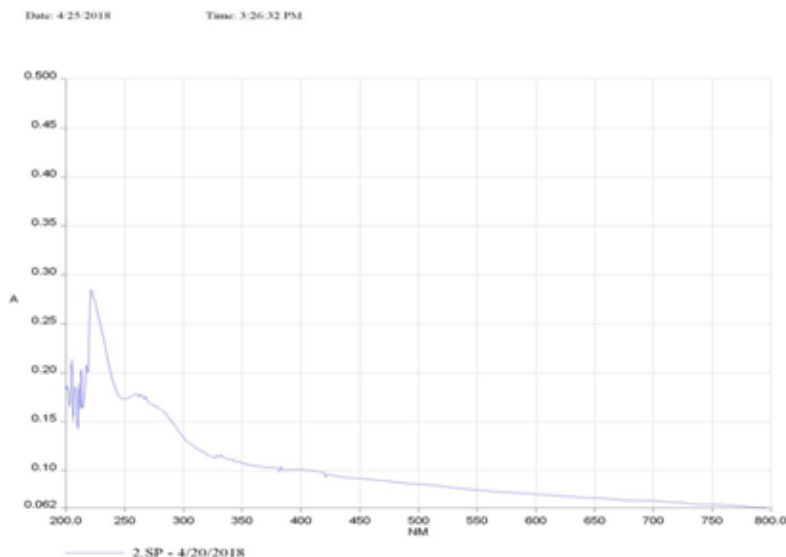


Figure 2: UV Spectra of NiS-SiO₂

The optical band gap of NiS-SiO₂ nanoparticles for calcined at 200 °C is 4.24 eV. Both the samples show good transmittance.

Also it is evident that for NiS-SiO₂ nanoparticles, the relation between the mean size and the onset absorption wavelength is related by Henglein’s empirical formula (Ref).

$$2R = \frac{0.1}{0.1338 - 0.0002345\lambda e}$$

Where λe is the wavelength of absorption onset and R is the size of the nanoparticles. The calculated size of the NiS-SiO₂ nanoparticles by Henglein’s formula is also closely agreed with the size of the nanoparticles calculated from XRD pattern using Scherrer’s formula.

FT-IR ANALYSIS

The figures exhibit the FT-IR spectrum for the prepared NiS nanoparticles NiS-SiO₂ shown broad peak bands obtained at 3406 cm⁻¹ can be attributed to water adsorbed to the surface of the sample while bands at 1635, 1160, 1099, 793, 638, 609 cm⁻¹.

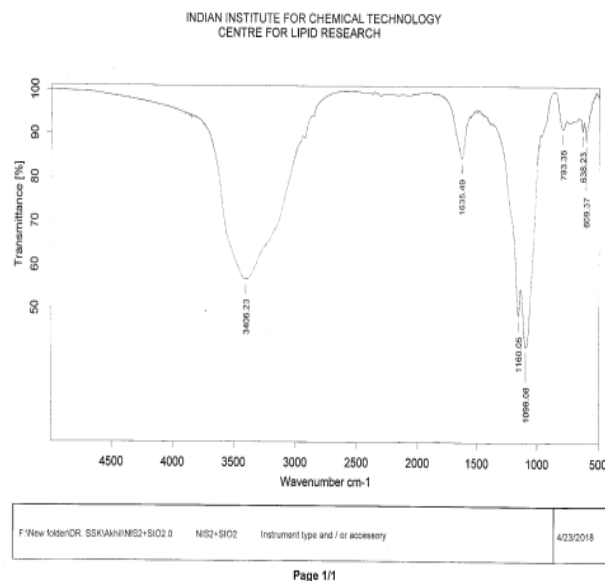


Figure 3: IR Spectra of NiS-SiO₂

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