

Review

Multiple phases of nanocrystalline materials: Preparation with phase purity by a facile method and characterization

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Abstract: There are many solid materials existing as different structural and other phases (polymorphs), when prepared with different conditions; they exhibit different physicochemical properties. It is important to consider the preparation of all these crystalline phases (along with amorphous phase), at nanoscale, in their pure form by using facile and cost-effective methods. Our study with nickel sulphide is considered here to illustrate this. Nickel sulphide exhibits three prominent phases which are: α -NiS, β -NiS and NiS_{1.03}. These crystalline (and amorphous NiS_{1.03}) nanophases along with doped α -NiS nanocrystals (doped with Cd²⁺, Fe²⁺ and O²⁻) have been successfully prepared in high purity using a facile solvothermal route (with the use of commercially available microwave oven); and they were characterized physicochemically (chemically, structurally, optically, magnetically and electrically) using available standard methods. Obtained results indicate that the facile method adopted for the preparation is found to be an effective and cost-effective one. The role of XRD and TG/DTA measurements is found to be important in this preparation. A brief review is made in this direction.

Keywords: polymorphs; nanocrystalline materials; X-ray diffraction analysis; thermogravimetric analysis; microwave-assisted solvothermal method; physicochemical properties

1. Introduction

Polymorphism (in Solid State Materials Science) describes that some solid materials exist in multiple phases (form or crystal structure); Fe₂O₃, NiS, Bi₂O₃, TiO₂, ZrO₂, CrO₂, Mn_xO_y and Cu_xS_y are examples. Allotropy refers to polymorphism for chemical elements (e.g., carbon has graphite and diamond structures). The prominent phases for the above materials are:

- Ferric oxide (Fe₂O₃) with α -Fe₂O₃-Rhombohedral (Corundum-type); β -Fe₂O₃-BCC (Bixbyite-type); γ -Fe₂O₃-Cubic spinel; ϵ -Fe₂O₃-Orthorhombic; etc.
- Nickel sulphide (NiS) with α -NiS-Hexagonal; β -NiS-Rhombohedral; NiS_{1.03}-Hexagonal; etc.
- Bismuth oxide (Bi₂O₃) with α -Bi₂O₃-Monoclinic; β -Bi₂O₃-Tetragonal; γ -Bi₂O₃-BCC; δ -Bi₂O₃-FCC; etc.
- Titanium oxide (TiO₂) with Tetragonal (Rutile-type); Tetragonal (Anatase); Orthorhombic (Brookite); etc.
- Zirconium oxide (ZrO₂) with Monoclinic; Tetragonal; Cubic (Fluorite-type); etc.
- Chromium oxide (Cr_xO_y) with α -CrO₂-Orthorhombic; Cr₂O₃-Rhombohedral; etc.
- Manganese oxide (Mn_xO_y) with MnO (Birnessite); Mn₂O (Manganosite); Mn₃O₄ (Hausmannite); MnO₂ (Pyrolusite); etc.
- Copper sulphide (Cu_xS_y) with CuS (Covellite); Cu₂S (Chalcocite); Cu_{1.96}S (Djurleite); Cu₇S₄ (Anilite); Cu₉S₅ (Digenite); etc.

It is important to consider the preparation of all prominent nanostructured phases of the above important solid materials with high purity using a facile and cost-effective method. Several researchers have synthesized different phases but ended with one or, at a maximum, two only.

We have attempted (as an illustration) the preparation of all the prominent nanophases (both crystalline and amorphous) of nickel sulphide ($\text{NiS}_{1.03}$, β -NiS, α -NiS and amorphous) in their pure form by adopting a facile microwave-assisted solvothermal route (using domestic microwave oven); the prepared nanophases were characterized physicochemically (chemically, structurally, optically, magnetically and electrically) by using the standard methods available for the purpose. Also, the effect of doping with Cd/Fe/O was investigated on the characteristics (structural, optical, magnetic and electrical) of α -NiS nanocrystals.

Hereby, as it is required, we briefly discuss (in the beginning) on nanostructured materials, and microwave-assisted solvothermal method. Next, presented here (briefly as an illustration) is our study made on the synthesis and physicochemical characterization of pure and Cd/Fe/O doped nanostructured nickel sulphides.

2. Nanostructured materials

Ultrafine microstructured solid materials are considered to be nanostructured materials (or simply nanomaterials) when they have their average particle size at nanoscale (< 100 nm); nanocrystals are nanoparticles with mostly crystalline nature. On the nanoscale: nanostructured surfaces having their surface thickness between 0.1 (after achieving graphene) and 100 nm are considered to be one dimensional; nanotubes having their tube diameter between 1 and 100 nm are considered to be two dimensional (tube length can be much greater); and spherical nanoparticles having their particle size within 1 and 100 nm (in all three dimensions) are considered as three dimensional.

Nanomaterials exhibit unique physical properties due to their small particle size; when the nanomaterial reduces to a point (called as quantum dot) quantum size effect prevails and the physical properties get modified very significantly from a three dimensional bulk material (micro and macro). In general, nanostructured materials are prepared either by reducing in size a bulk material to nanoscale pattern (top-down approach) or by building (molecule by molecule) a larger structure (bottom-up approach) [1–4].

3. Microwave-assisted solvothermal method

A large number of nanostructured materials have been prepared and characterized for about four decades. Among several methods available for the preparation, microwave-assisted solvothermal method (with an involvement of dielectric heating) is considered to be an efficient one for the preparation of several nanomaterials [5–22]. 918 MHz and 2.45 GHz are the frequencies normally allotted for this microwave-assisted heating; 2.45 GHz is more frequently used, and also in commercially available domestic microwave ovens. Dielectric heating is possible with both pulsed microwave and continuous microwave; pulsed microwave heating is preferred for preparing high quality nanoparticles [23].

Precursor(s) should have higher dielectric constant(s) and should decompose on microwave absorption. Solvent(s) should not decompose before boiling temperature, and the product(s) should not get dissolved in that. The product particles growing larger can be avoided using a capping agent; also, the solvent boiling violently can be avoided by controlling the microwave power. Water (with high dipole moment) is considered to be a good solvent; however, solvents have an important influence on the morphology and size of the final product material particles when they are formed under microwave irradiation.

The actual method using a domestic microwave oven

The above microwave-assisted solvothermal technique can be followed with a domestic microwave (normally pulsed) oven also. For the first time, we proposed this facile and cost-effective method, and successfully prepared several high quality nanostructured materials and reported in the literature [24–33]; the actual method is given below.

The precursor(s) in required amount(s) should be dissolved in a suitable solvent, placed in a domestic microwave oven (frequency 2.45 GHz; power 800/840 W) and microwave irradiated up to complete solvent evaporation. Precipitate obtained (normally colloidal) after microwave irradiation should be cooled, washed with distilled water (several times), and then with acetone for removing the organic impurities (present if any). Thus obtained precipitate should then be dried in atmospheric air, and collected as the product. In order to get the product in the required condition, if required, it should be annealed for the particular (required) duration at the particular (required) temperature. The crystallinity and phase purity can be identified by making XRD analysis [34]; the annealing temperature can be fixed by making thermogravimetric (TG) analysis [35].

4. Nanostructured nickel sulphides

Nickel sulphide (NiS) exhibits three prominent phases: two stoichiometric phases, viz. Rhombohedral β -NiS (millerite) (see **Figure 1** for its crystal structure) and Hexagonal α -NiS (see **Figure 2** for its crystal structure); and one non-stoichiometric hexagonal NiS_{1.03} phase. Amorphous phase can be considered as the fourth.

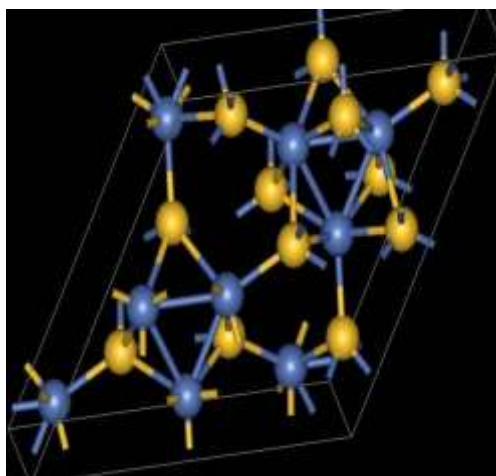


Figure 1. The β -NiS structure.

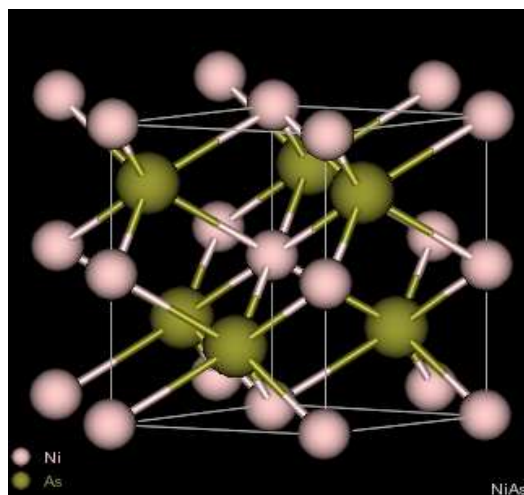
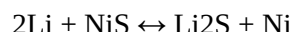


Figure 2. The α -NiS structure.

NiS has stimulated great research interest due to its importance in technological applications: in magnetic storage media, hydrogenation catalysis, window glass (as possible transformation toughener), etc [36–38]. It is a very promising cathode material for lithium ion batteries (the most promising renewable clean energy source); the theoretical capacity of it is 590 mAhg^{-1} which is high with good electronic conduction [39]. The mechanism of total charge-discharge can be denoted as [40]:



In earlier days, vapour phase and high temperature solid state reaction methods were used to synthesize (prepare) the NiS nanoparticles [41]. In later days, molecular precursor method, elemental reaction in liquid ammonia and homogeneous sulphide precipitation followed by sulphur addition were used to prepare them [42–45].

Synthesis of α -NiS and β -NiS (but not the amorphous and $\text{NiS}_{1.03}$) nanophases could be achieved by Meng et al. [46] using two different solvents (ethanol and pyridine) by a solvothermal-reduction route. Synthesis of α -NiS and $\text{NiS}_{1.03}$ mixed nanocrystals (with hexagonal layered structure) could be achieved by Sun [47] using a hydrothermal route; however, individual nanophases (with purity) of α -NiS and $\text{NiS}_{1.03}$ could not be achieved. Idris et al. [48] synthesized α -NiS- β -NiS mixed nanocrystalline powder (but not the individual α -NiS and β -NiS nanocrystals) using a hydrothermal microwave autoclave. While preparing $(\text{NiS})_x(\text{CdS})_{1-x}$ thin films, Ubale and Bargal [49] have got β -NiS nanophase as the NiS component. There was found no report available earlier on the preparation of all the four individual nanophases of NiS using a single procedure.

Earlier we [26] investigated the effect of calcination at four different temperatures (400, 500, 600 and 700 °C) on the ferric oxide (Fe_2O_3) nanoparticles prepared in a similar way as described below (for the preparation of NiS nanophases), using ferric chloride and urea as the precursors and ethylene glycol as the solvent; the as-prepared nanophase was found to be mostly amorphous (or poor crystalline γ - Fe_2O_3 nanophase). The calcined (annealed) and cooled nanophases were found to be: crystalline ε - Fe_2O_3 (calcined at 400 °C), $\varepsilon + \beta$ - Fe_2O_3 (calcined at 500 °C), $\beta + \alpha$ (small)- Fe_2O_3 (calcined at 600 °C) and α - Fe_2O_3 (calcined at 700 °C) [26]. This earlier work prompted us to make

an investigation systematically on the preparation of all the four prominent nanophases of nickel sulphide.

4.1. Preparation of NiS nanophases

AR grade chemicals were used in our study. To prepare the pure NiS phases, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and NH_2CSNH_2 (thiourea) (mixed in 1:3 molar ratio) were dissolved in 100 mL ethylene glycol [27]. To prepare Fe/Cd/O doped α -NiS nanoparticles, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ / $\text{CdCl}_2 \cdot 6\text{H}_2\text{O}$ / NH_2CONH_2 (urea) were the precursors considered for the Fe/Cd/O dopants (in two concentrations for each viz. 2.5 and 5.0 mol% with respect to the host precursor) [33]. The greenish black homogeneous solution got after stirring was placed in a domestic microwave oven (frequency 2.45 GHz; power 800 W) and microwave irradiated up to complete solvent evaporation. Precipitate obtained (colloidal) after microwave irradiation was cooled (naturally), washed with double distilled water (several times), and then with acetone to wash out the organic impurities (present if any). Thus obtained precipitate was then filtered, dried in atmospheric air, and collected as the product.

In the above microwave synthetic procedure, the pulsed microwave irradiation and solvent ethylene glycol played the important role in preparing the NiS nanoparticles; the solvent acted effectively both as the reaction and dispersion media (by absorbing and stabilizing the particle surfaces) and produced (with smaller size) the NiS nanoparticles. Pure NiS phase (the product) obtained (represented as As-prepared) was subjected to XRD and TG measurements. The observed XRD pattern (shown in **Figure 3** [27]) indicates the amorphous nature of the sample prepared with a higher level of disorder. The TG and DTA (differential thermal analysis) patterns observed (shown in **Figure 4** [27]) indicate the thermal stability of the sample beyond 295 °C; the major mass loss (26.15%) observed below this temperature could be associated to desorption of water molecules (physically adsorbed). Further, these TG and DTA patterns indicate structural phase transitions which can be in correspondence with the different NiS prominent phases. So, at three temperatures viz. 300, 500, and 700 °C, the As-prepared was annealed (in air) for 1 h (in each case) and the annealed samples were cooled naturally to the room temperature.

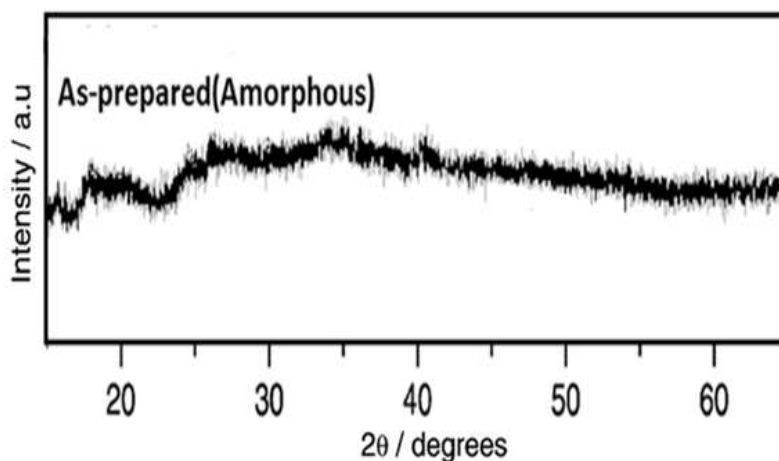


Figure 3. XRD pattern observed for the As-prepared (amorphous nanophase) [27].

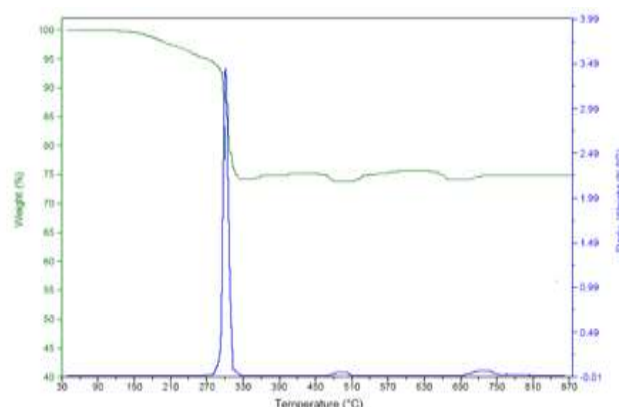


Figure 4. TG-DTA curves observed for the As-prepared (amorphous nanophase) [27].

The annealed samples were subjected to XRD analysis and determination of lattice parameters [27]. The lattice parameters observed for the As-prepared annealed at 300, 500 and 700 °C correspond to $\text{NiS}_{1.03}$, β -NiS and α -NiS phases, respectively. So, to get Fe/Cd/O doped α -NiS nanocrystals, the as-prepared Fe/Cd/O doped samples were calcined at 700 °C for 1 h and cooled naturally to the room temperature. Photographs of all the ten prepared samples (nanopowders) along with corresponding pellets are shown in **Figures 5 and 6**.

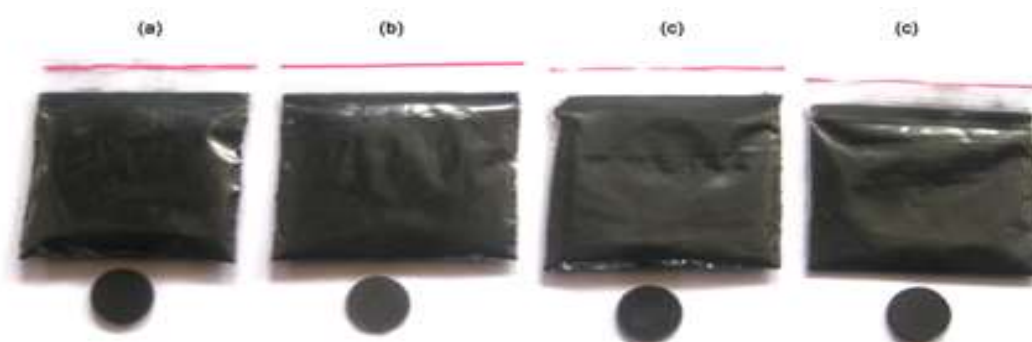


Figure 5. Photograph showing the pure samples prepared along with the corresponding pellets: **(a)** Amorphous $\text{NiS}_{1.03}$; **(b)** $\text{NiS}_{1.03}$ nanocrystals; **(c)** β -NiS nanocrystals; **(d)** α -NiS nanocrystals.

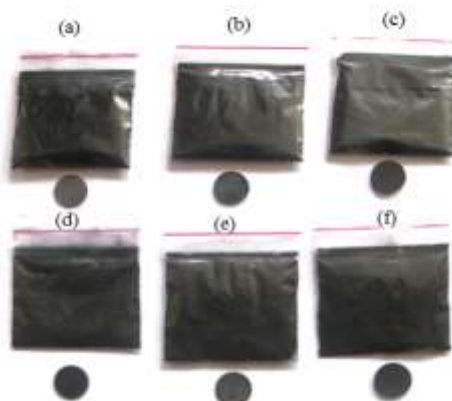


Figure 6. Photograph showing the doped α -NiS samples prepared along with the corresponding pellets: **(a)** 2.5 mol% Cd^{2+} doped; **(b)** 5.0 mol% Cd^{2+} doped; **(c)** 2.5 mol% Fe^{3+} doped; **(d)** 5.0 mol% Fe^{3+} doped; **(e)** 2.5 mol% O^{2-} doped; **(f)** 5.0 mol% O^{2-} doped.

4.2. Structure, morphology and chemical composition

All the samples prepared (four pure NiS nanophases and six doped α -NiS nanoparticles) were subjected to XRD, Fourier transform infrared (FTIR) spectral, atomic force microscopic (AFM), scanning electron microscopic (SEM) and energy dispersive X-ray absorption (EDX) spectral analyses by using the standard available techniques to understand the structure, morphology, chemical composition and quality of them. Also the four pure NiS nanophases were subjected to transmission electron microscopic (TEM) analysis, using a HITACHI H-800 TEM instrument. XRD data were obtained (in 10° – 70° 2θ range with monochromated $\text{CuK}\alpha$ radiation) using an XPERT PRO PANalytical instrument; average crystallite (particle) sizes were determined from peak widths using the Scherrer formula [34]. FTIR spectra were recorded in the wavenumber range 4000 – 400 cm^{-1} , using a Perkin Elmer SPECTRUM RSI spectrophotometer; SEM and EDX spectral analyses were made, using a JEOL-JSM 5600LV SEM instrument.

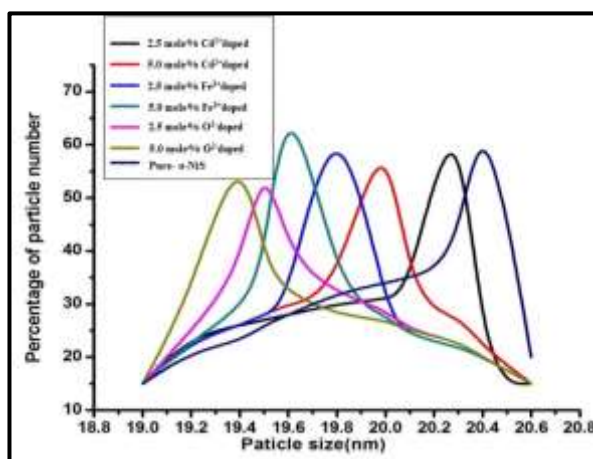


Figure 7. Particle size distributions determined by AFM analysis for pure and doped α -NiS nanoparticles [33].

Particle size distributions resulted through AFM analysis (using a PARK SYSTEM XE70 AFM instrument) for the pure and doped α -NiS nanoparticles are shown (illustrated) in **Figure 7** [33]. XRD patterns and FTIR spectra observed (not shown here as these appear elsewhere [27,33]) indicate that the pure nickel sulphide nanophases and the doped α -NiS nanoparticles prepared in our study are with high phase purity. SEM, TEM and AFM analyses (the pictures obtained are not shown here as these appear elsewhere [27,33]) indicate that the formed nanoparticles are agglomerative, and spherical in shape; all the systems studied are found to exhibit homogeneous morphology. The obtained particle sizes are within 15 – 20 nm ; and the average particle sizes (obtained through XRD, AFM and TEM analyses) are found to compare well. The EDX spectra observed for the doped α -NiS nanoparticles indicate the incorporation of Cd/Fe/O impurities in the host matrix. The Ni:S ratios obtained are $1:1.030$, $1:1.028$, $1:1.006$ and $1:1.002$ respectively for the amorphous NiS, $\text{NiS}_{1.03}$, β -NiS and α -NiS nanophases.

The above results indicate that all the four pure nickel sulphide nanophases and six doped α -NiS nanoparticles prepared are of high quality; that is, the prepared

samples exhibit chemical purity, homogeneous spherical morphology, reduced particle size, and narrow size distribution. The above indicates that the method followed in our study for preparing the proposed nanophases (the prominent nickel sulphide nanophases and doped α -NiS nanoparticles) with high quality is found as an effective, economical (cost-effective) and scalable one.

4.3. Optical properties

All the ten prepared samples were characterized optically. A Perkin Elmer λ 35 spectrophotometer was used to record the optical (UV-Vis-NIR) absorption spectra (in the wavelength range 200–1150 nm); and a Perkin Elmer LS55 luminescence spectrometer (with a pulsed xenon lamp excitation source) was used to record the photoluminescence (PL) spectra (in the wavelength range 270–800 nm). The full optical absorption and PL spectra observed are not shown here as these appear elsewhere [27,33]; only the PL spectra recorded for pure and Fe/Cd/O doped α -NiS nanocrystals [33] are shown in **Figure 8**, as an illustration. The optical bandgap energies (the E_g values) obtained are: 4.52, 4.35, 4.01 and 3.81 eV respectively for the pure nanophases viz. amorphous NiS, NiS_{1.03}, β -NiS and α -NiS; the E_g values obtained for the doped α -NiS nanoparticles are: 4.30 and 4.73 eV respectively for 2.5 and 5.0 mol% Cd-doped, 3.77 and 3.72 eV respectively for 2.5 and 5.0 mol% Fe-doped, and 3.66 and 3.62 eV respectively for 2.5 and 5.0 mol% O-doped.

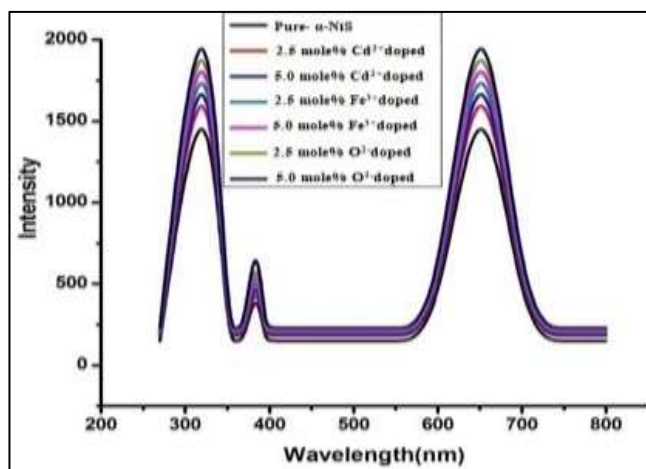


Figure 8. PL spectra recorded for pure and doped α -NiS nanocrystals [33].

UV-Vis-NIR peaks observed are blue-shifted on comparison with bulk NiS (E_g = 2.1 eV); also, the grain size dependence is exhibited. Moreover, decrease in nanoparticle size increasing the E_g value shows presence of quantum confined states; the observed steep absorption edges show good crystallinity along with uniformity in morphology and size of nanoparticles. Doping with Fe/O is found to decrease the E_g value with the increase in concentration; however, Cd doping is found to increase the E_g value. The absorption edges of Cd-doped α -NiS nanocrystals show blue-shifting on comparison with pure α -NiS nanocrystals; however, the absorption edges of Fe- and O-doped α -NiS nanocrystals are found to be red-shifted. This indicates doping with Fe/O creating more surface defects or surface crystalline defects than done by Cd

doping. Further, it is found that absorbance is increased due to O (anionic) doping and decreased due to Fe/Cd (metal/cationic) doping.

The observed PL spectra (excited at 280 nm) show two major emission peaks (at 324 nm, UV and 652 nm, red) and one minor emission peak (at 384 nm, UV). The peaks are similarly positioned for the pure NiS nanophases but the peak intensity (considered as yield) is found to increase with the increase in calcination temperature; the yield is minimum for amorphous and maximum for α -NiS nanophases. Doping leads the PL peaks similarly positioned but with intensity difference; doping (in general) increases the PL yield, and it is done in a better way for the α -NiS nanoparticles when doped with oxygen than with Fe/Cd.

4.4. Magnetic properties

All the ten prepared samples were magnetically characterized by making magnetization measurement (with magnetic fields up to 20 kOe) using a vibrating sample magnetometer (VSM VT-7410, Lakeshore). All the M-H plots (magnetization curves) observed are not shown here as these appear elsewhere [27,33]; only the magnetization curves observed for the pure and doped α -NiS nanocrystals [33] are shown in **Figure 9**, as an illustration.

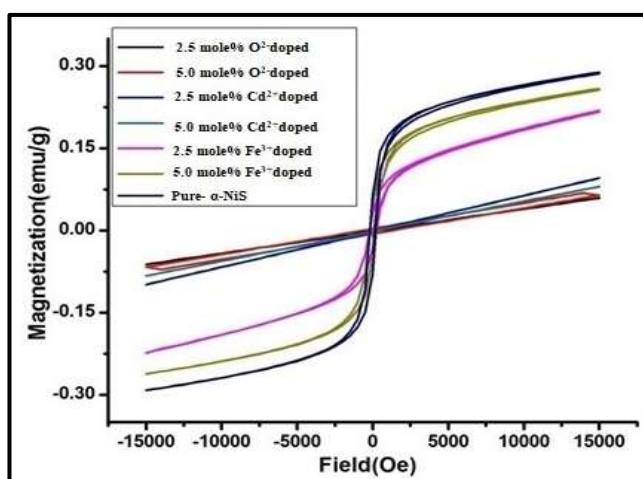


Figure 9. Magnetization curves recorded for pure and doped α -NiS nanocrystals [33].

In the case of pure NiS nanophases, increase in calcination temperature is found to increase coercivity (H_c), retentivity (M_r), and saturation magnetization (M_s), which are the magnetic parameters considered. The observed M - H plots show ferromagnetic behaviour with significant hysteretic parameters. Increase in coercivity observed could be due to: Ni vacancies creation (evidenced by EDX spectra), magneto-crystalline anisotropy creation (by some grain boundaries) and uncompensated moments at the nanocrystal surface created from reduced coordination of the surface spins [27]. Doping with Fe/Cd/O is found to reduce the ferromagnetic order, which can be understood as due to improvement in the coordination of surface spins caused by doping; doping with Fe is found to retain ferromagnetic order in a better way than with Cd/O [33].

4.5. Electrical properties

All the ten prepared (and pelletized) samples were electrically characterized by making DC and AC electrical measurements at different temperatures (within 40–150 °C) and with five frequencies viz. 100 Hz, 1 kHz, 10 kHz, 100 kHz and 1 MHz. All the electrical parameters observed viz. DC electrical conductivity (σ_{dc}), real part of dielectric constant (ϵ'), imaginary part of dielectric constant (ϵ''), dielectric loss factor ($\tan\delta$) and AC electrical conductivity (σ_{ac}) are not shown here as these appear elsewhere [27,33]; only the σ_{dc} values obtained for the pure and Fe/Cd/O doped α -NiS nanocrystals [33] are shown in **Figure 10**, as an illustration.

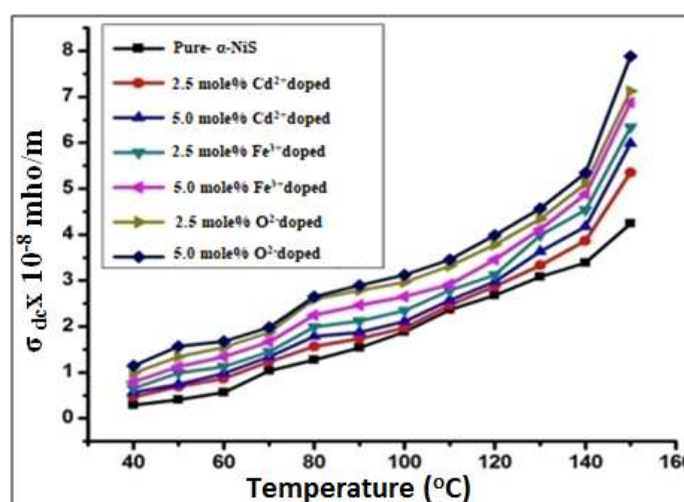


Figure 10. DC electrical conductivities ($\sigma_{dc} \times 10^{-8}$ mho/m) observed for pure and doped α -NiS nanocrystals [33].

Electrical parameters considered (σ_{dc} , ϵ' , ϵ'' , $\tan\delta$ and σ_{ac}) have been observed to increase with the temperature increase; and, as normally expected, it was observed that $\sigma_{ac} > \sigma_{dc}$. Increase in frequency leads to decrease of ϵ' , ϵ'' , and $\tan\delta$ values and increase of σ_{ac} value. Also, increase in the calcination temperature leads to increase of all the electrical parameters considered [27]. Moreover, increase in doping concentration leads to increase of all the electrical parameters (at all frequencies and temperatures) for the dopants considered; in addition, the parameters ($X = \sigma_{dc}/\epsilon'/\epsilon''/\tan\delta/\sigma_{ac}$) are found to vary in the order [33]:

$$X (\text{Pure}) < X (\text{Cd-doped}) < X (\text{Fe-doped}) < X (\text{O-doped})$$

When grain size becomes smaller than the electron mean free path, the grain boundary scattering dominates and thereby the electrical resistivity increases. The electrical resistivity observed is higher; this indicates that, in the charge transport process, grain boundary scattering may play an important role. The low dielectric constant values observed (for the nanocrystals considered) indicate that the polarization mechanism is mainly due to the space charge polarization.

Normally it is considered that higher the lattice defects when smaller the particle size; also, the lattice defects are expected to form acceptor/donor like levels in the forbidden energy gap, and they act as trapping centers for charge carriers, which affect

considerably the electrical behaviour [27,50]. It is expected that the S vacancies and interstitial Ni act as donors while interstitial S and Ni vacancies act as acceptors.

It is possible that the electrochemical sensing performance of α -NiS nanoparticles can be enhanced by: increasing the specific surface area, decreasing the optical bandgap energy, improving the electronic conductivity, improving the optical absorption and decreasing the electron-hole recombination rate. Results of our study [33] indicates that doping with O leads to increasing the specific surface area, decreasing the optical bandgap energy, improving the optical absorption and improving the electronic conductivity, in a better way. The above result indicates that doping α -NiS nanoparticles with oxygen (anionic doping) is found to improve the electrochemical sensing performance in a better way than doping it with Fe/Cd (metal/cationic doping).

5. Major conclusions

In effect, our illustrative study made with NiS nanophases indicates that the facile method adopted can be considered as an effective, scalable and cost-effective one for preparing the prominent nickel sulphide nanophases ($\text{NiS}_{1.03}$, β -NiS, α -NiS and amorphous) and Cd/Fe/O doped α -NiS nanoparticles with high quality (high chemical purity, reduced particle size, and homogeneous spherical morphology) and useful physicochemical properties. Moreover, this method of preparation can be considered as a suitable one for preparing the prominent nanophases of other such materials (in pure form at a cheaper cost). In addition, our study indicates that doping with oxygen (anionic) makes α -NiS nanocrystals a better electrochemical sensing performer than doping with Fe/Cd (metal/cationic).

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Conflict of interest: The author declares no conflict of interest.

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