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Effect of thermal annealing on the properties of nickel sulfide nanostructures: Structural phase transition

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ABSTRACT

This work covers the effects of annealing temperature on crystalline size, surface morphology, optical, structural and paramagnetic properties of NiS and Ni_3S_4 nanostructures grown through SILAR technique into FNBR matrix. Annealing at low temperature was performed in air and vacuum for 8 h. X-ray diffraction results confirm structural phase transitions (like NiS→Ni_7S_6 and Ni_3S_4→Ni_9S_8) and oxidation processes (by the formation of NiO-SO_4-H_2O) after thermal annealing of nanocomposites (NCs) in a vacuum and in air, respectively. By EDX spectrum the average Ni:S atomic ratio is approximately 1:1 for as-prepared NiS, 1:0.89 for NiS annealed in a vacuum and 1:0.91 for NiS annealed in air.

1. Introduction

Nanostructured nickel sulfides have stimulated great interest because of their technological utilization such as hydrogenation catalysis, magnetic storage media, as possible transformation toughen in window glass, due to their extremely small size, large surface area, large anisotropy and perfect crystallinity [1–4].

Niasari et al. presented a convenient and green hydrothermal route to synthesize nickel sulfide nanostructures from $Ni(NO_3)_2{\cdot}6H_2O$ and thioglycolic acid (TGA), in which water was used as the environmentally benign solvent throughout the preparation [5]. Ni_3S_4 crystallizing in the cubic spinel structure has been synthesized by an ambient temperature reaction between aqueous nickel chloride and sodium dithionite solutions [6]. Manthiram et al. demonstrated that Ni_3S_4 is metastable and it begins to decompose above 100 °C [6].

Homogeneous precipitation by a reaction between nickel nitrate and ammonium sulfide solutions at 80 °C followed by heat treatment at 100 °C in a mixture of 20% H_2S-80% H_2 has shown a few broad reflections corresponding to Ni_3S_4 [7]. However, the product produced by such a procedure decomposes to well-crystalline $NiS_{1.03}$ and NiS (millerite) on heat treating at 200 °C in a mixture of 20% H_2S-80% H_2. These results clearly reveal that it is difficult to synthesize single phase Ni_3S_4 [6,7].

Muhammed Shajudheen et al. were reported that, synthesis of nanoparticles of nickel oxide by thermal oxidation of nickel sulfide is scarcely reported [8]. In their work the nickel sulfide nanoparticles (Ni_9S_8) synthesized by chemical precipitation method were annealed at 700 °C to synthesize nanoparticles of NiO. The thermo gravimetric (TG) and differential thermal curves of the samples were recorded and the phase transformation temperature of nickel sulfide (Ni_9S_8) to NiO was found to be at 600 °C [8].

In tempered glasses, the inclusions quenched from high temperature display the hexagonal α-NiS structure [9]. The α-NiS phase is metastable at room temperature and will subsequently transform into its stable form at low temperature, known as the β-phase, which has a rhombohedral structure [9]. Yousfi reported that observations allow to investigate the morphological evolution during transformation, the phase orientation relationships and the first stages of the transformation were investigated by optical microscopy, electron backscatter diffraction, and scanning and transmission electron microscopy [9]. The transformation mechanisms change significantly with the change in sulfur content of the α-NiS phase. From the typical morphologies, further confirmed by composition analysis, they have been able to identify the existence of partitioned and partitionless phase transformation depending on the temperature and the initial α-NiS composition, i.e. the domain in the NiS phase diagram [9].

The mineralogy and phase equilibria of the binary Ni-S system seem to be relatively well understood. A summary of minerals and phases in the Ni-S system is given in Table 1 [10].

In the work, we describe the affect of low temperature annealing on

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Table 1
Summary of studies by different investigators on the maximum thermal stabilities of Ni-S system [10].

Composition	Mineral name	Thermal stability (°C)		Structure type (cell edges in Å)	Remarks
		Maximum	Minimum		
Ni_3S_2	Heazlewoodite	556	–	Hexagonal *R*32	
$Ni_{3+x}S_2$	–	806	524		Lower
α-Ni_7S_6	Godlevskite	400	–	Orthorhombic	
Ni_7S_6	–	573	400		
NiS	Millerite	379	–	Hexagonal *R*3*m*	
α-$Ni_{1-x}S$	–	999	282	Hexagonal	Lower
Ni_3S_4	Polydymite	356	–	Cubic *Fd*3*m*	
NiS_2	Vaesite	1007	–	Cubic *Pa*3	

crystalline size, morphology, optical, structural and paramagnetic properties of NiS and Ni_3S_4 nanostructures grown through SILAR technique into FNBR matrix. The annealing processes were performed in air and vacuum at different temperatures during 8 h. Factors affecting the properties of the air dried and annealed NiS/FNBR NCs are studied by XRD, UV–Vis, FT-IR, EPR, EDX spectroscopy and SEM.

2. Experimental

2.1. Materials and instrumentation

All reagents ($NiSO_4{\cdot}7H_2O$, $Na_2S{\cdot}9H_2O$, $SC(NH_2)_2$, KOH and FNBR) were of analytical grade and used without further purification. XRD patterns were recorded on a Bruker D2 Phaser X-ray diffractometer (λ = 1.54060 Å) using Ni-filtered Cu Ka radiation. Varian 3600 FTIR spectrometer was used to record of fourier transform infrared (FTIR) spectra by using the KBr pellet. Optical absorption study was conducted using a UV–Vis spectrometer (Specord 250). The morphology of NCs was noticed by a JEOL JSM- 7600F scanning electron microscope (SEM). The elemental analysis was studied using X-max 50 energy-dispersive X-ray spectroscopy (XRD). X-band coupled EMX spectrometer (Bruker) was used to record of EPR spectra. For the measurement of paramagnetic property cylindrical quartz sample tubes with 3.5 mm o.d. (3.0 mm i.d.) have been used. “g” factor evaluations were corrected using the internal reference standard marker (gM = 2.0052). The EPR spectra were simulated on an IBM compatible computer PC using the QPOW program.

2.2. Preparation of nickel sulfide/FNBR NCs

For synthesis of nickel sulfide nanoparticles (NPs), the functionalized nitrile-butadiene rubber (FNBR) was used as a stabilizer [11]. The formation of nickel sulfide NPs was carried out by a successive ionic layer adsorption and reaction (SILAR) method. Analytical reagent (AR) grade nickel sulfate ($NiSO_4{\cdot}7H_2O$) and thiourea- $(NH_2)_2CS$ taken in 1:2 M ratio were used for the formation of NiS nanoparticles. AR grade nickel sulfate ($NiSO_4{\cdot}7H_2O$) and sodium sulfide ($Na_2S{\cdot}9H_2O$) taken in 5:1 M ratio were used for formation of Ni_3S_4 nanoparticles. 0.2 g of FNBR powders were added to each solution and stirred for 24 h at room temperature. Samples were washed with distilled water to remove unexchanged ions. 25 ml of 1 M KOH solution was used in hydrolysis of thiourea to release S^{-2} ions. This process was repeated several times and air-dried [11]. All samples were annealed at 100 °C, 150 °C and 180 °C for 8 h in air and in vacuum.

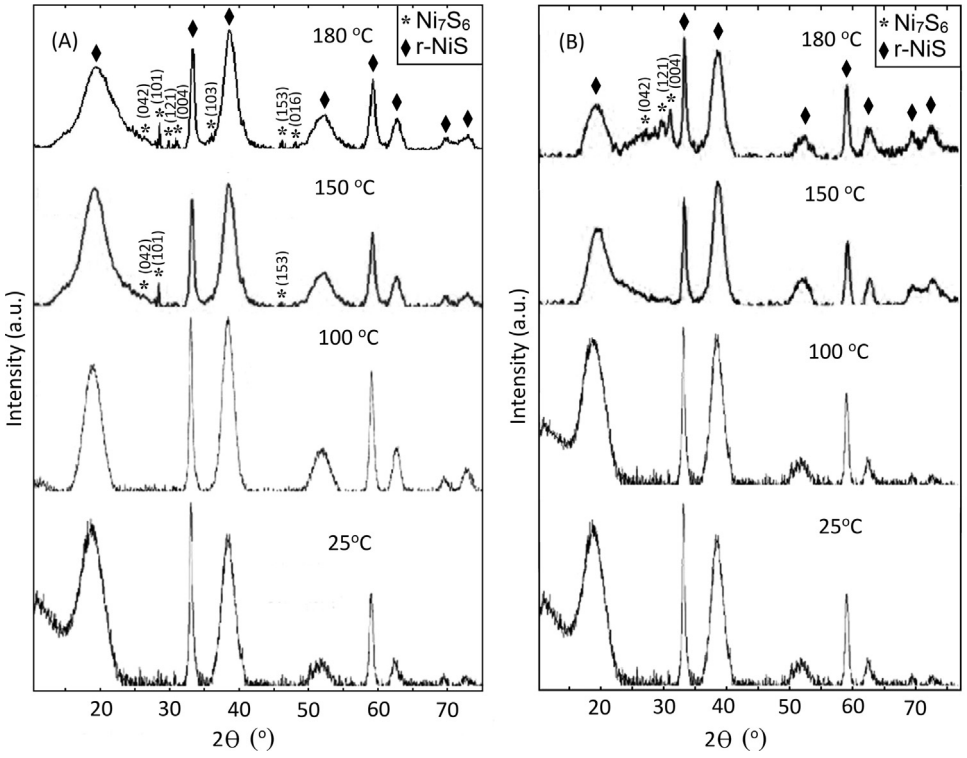

Fig. 1. XRD patterns of NiS/FNBR NCs: (A) annealing in a vacuum and (B) annealing in air for 8 h.