Synthesis of Nickel Sulfides in Aqueous Solutions Using Sodium Dithionite

Y. U. Jeong and A. Manthiram*

Texas Materials Institute, ETC 9.104, The University of Texas at Austin, Austin, Texas 78712

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Reaction of nickel chloride with sodium dithionite in aqueous solutions at ambient temperature has been investigated systematically to obtain nickel sulfides. The products are characterized by X-ray diffraction, thermogravimetric analysis, and electrical resistivity and magnetic susceptibility measurements. It is found that the compositions and structures of the products are controlled by the reaction pH and the amount of the reactants. While reactions under highly acidic (pH ≤ 2) and basic (pH ≥ 7) conditions yield crystalline sulfur and amorphous or poorly crystalline Ni_yS_x, respectively, those at intermediate 3 ≤ pH ≤ 6 give crystalline Ni_yS_x. Both crystalline Ni_3S_2 (heazlewoodite structure) and Ni_3S_4 (spinel structure) have been obtained at room temperature. Additionally, NiS (millerite structure) is obtained by carefully heating Ni_3S_4 at 200 °C in a mixture of 90% Ar and 10% H_2. Ni_3S_4 is found to be metastable, and it begins to disproportionate above 100 °C. Both Ni_3S_2 and Ni_3S_4 show metallic behavior. While Ni_3S_2 exhibits temperature-independent magnetic susceptibility, Ni_3S_4 shows ferrimagnetic ordering below 20 K.

Introduction

Metal sulfides exhibit interesting electronic properties and find several technological applications. For example, cadmium sulfide can be used for photoresists and solar cells, zinc sulfide is an attractive IR optical material, and silver sulfide is a good photoelectric and thermoelectric material.[1−4] Additionally, some sulfides such as nickel sulfide, cobalt sulfide, and molybdenum sulfide find applications as hydrodesulfurization and hydrogenation catalysts in petrochemical industries.[5]

Metal sulfides are traditionally made by high-temperature reactions between the component metal powders and sulfur in evacuated sealed tubes. The low melting point and volatilization of sulfur in some cases may make the control of composition difficult with such reactions. Additionally, such high-temperature procedures invariably lead to the formation of thermodynamically more stable phases, and it is difficult to access metastable phases by such procedures. These difficulties have created much interest in the low-temperature synthesis of transition metal sulfides. Several low-temperature procedures listed below have been investigated over the years: (i) metathetical reaction between anhydrous transition metal chlorides and alkali metal or ammonium sulfides at room temperature in nonaqueous media,[5,6] (ii) reaction between hexahalometalates and hydrogen sulfide or sodium sulfide,[7,8] (iii) reaction between metal halides and organic sulfur compounds such as hexamethyldisilthane, di-*tert*-butyl disulfide, di-*tert*-butyl sulfide, and *tert*-butylmercaptan,[9−12] (iv) solvothermal disproportionation reaction between metal salts and sulfur in organic medium in an autoclave,[13] (v) homogeneous precipitation reactions between metal salts and ammonium sulfide followed by heat treatment in a mixture of H_2 and H_2S at low temperatures,[14] (vi) reaction of metal disks in contact with sulfur-containing liquids under the conditions of pulsed laser,[15] (vii) mechanochemical reaction between metal powder and sulfur,[16,17] (viii) decomposition of diethyldithiocarbamate complexes, dithiolato complexes, and dithiooxamide complexes,[18−20] (ix) thermal decomposition of thiometalates,[21] and (x) decomposition of metal sulfates in a controlled mixture of H_2 and H_2S at moderate temperatures.[22−29]

We present in this paper the synthesis of nickel sulfides by a reaction between nickel chloride and sodium dithionite solutions. Sodium dithionite is known to act as a reducing agent

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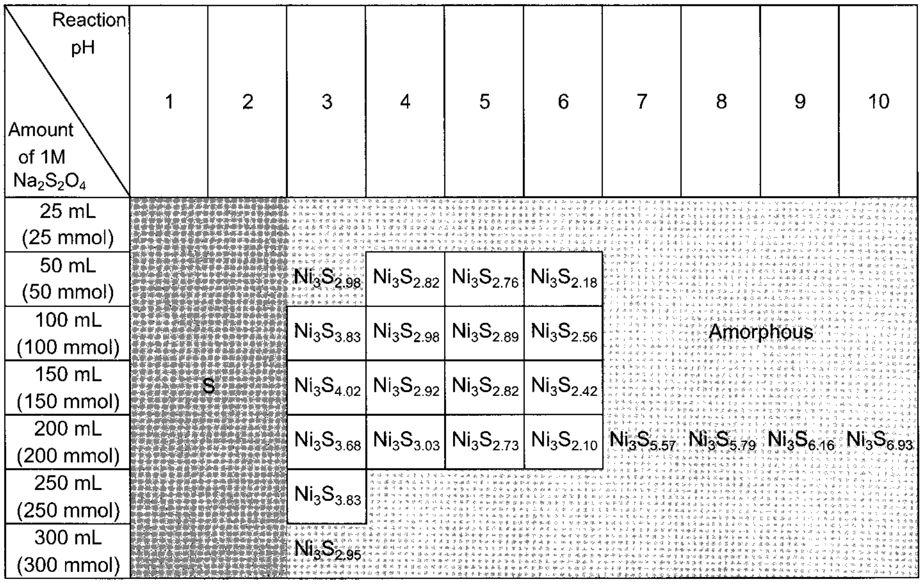

Reaction pH / Amount of 1M $Na_2S_2O_4$	1	2	3	4	5	6	7	8	9	10
25 mL (25 mmol)										
50 mL (50 mmol)			$Ni_3S_{2.98}$	$Ni_3S_{2.82}$	$Ni_3S_{2.76}$	$Ni_3S_{2.18}$				
100 mL (100 mmol)			$Ni_3S_{3.83}$	$Ni_3S_{2.98}$	$Ni_3S_{2.89}$	$Ni_3S_{2.56}$		Amorphous		
150 mL (150 mmol)	S		$Ni_3S_{4.02}$	$Ni_3S_{2.92}$	$Ni_3S_{2.82}$	$Ni_3S_{2.42}$				
200 mL (200 mmol)			$Ni_3S_{3.68}$	$Ni_3S_{3.03}$	$Ni_3S_{2.73}$	$Ni_3S_{2.10}$	$Ni_3S_{5.57}$	$Ni_3S_{5.79}$	$Ni_3S_{6.16}$	$Ni_3S_{6.93}$
250 mL (250 mmol)			$Ni_3S_{3.83}$							
300 mL (300 mmol)			$Ni_3S_{2.95}$							

Figure 1. Diagrammatic representation of the compositions obtained with 50 mL of 0.25 M $NiCl_2{\cdot}6H_2O$ (12.5 mmol) and 25−300 mL of 1 M sodium dithionite (25−300 mmol) at various pH values. The compositions within the rectangular boxes are crystalline Ni_3S_x while those in the shaded area are crystalline sulfur (dark area) and amorphous or poorly crystalline Ni_yS_x (light area).

in their normal reactions and is used in many industrial processes.[30] It can also produce sulfide ion under alkaline conditions and can thus act as a sulfiding agent. We present here a systematic investigation of the influence of reaction conditions on the composition and structure of the products. Additionally, the electrical and magnetic properties of some of the phases are presented.

Experimental Section

Nickel sulfides were prepared by reacting an aqueous solution of $NiCl_2{\cdot}6H_2O$ with various amounts of aqueous sodium dithionite ($Na_2S_2O_4$) solution by two different procedures. In the first procedure, a known volume (25−500 mL) of 0.25−1 M sodium dithionite (6.25−500 mmol) solution was added at once into 50 mL of a 0.25 M $NiCl_2{\cdot}6H_2O$ (12.5 mmol) solution with stirring without controlling the reaction pH. In the second procedure, a known volume (25−300 mL) of 1 M sodium dithionite (25−300 mmol) solution was added slowly from a buret into 50 mL of a 0.25 M $NiCl_2{\cdot}6H_2O$ (12.5 mmol) solution that was stirred constantly with a magnetic stirrer at a predetermined pH value of 1−10. During the slow addition of sodium dithionite in the second procedure, the pH of the reaction mixture was maintained constant at the predetermined value by adding NaOH or HCl. The addition of sodium dithionite resulted in the formation of a black precipitate, which was filtered, washed with deionized water, and allowed to air-dry under suction. The products were then heated in a mixture of 90% Ar and 10% H_2 at various temperatures $100 \leq T \leq 600$ °C for 24 h, where needed.

Crystal-chemical characterizations of the samples were carried out with X-ray powder diffraction. The X-ray patterns were generally recorded with a counting time of 2 s/0.05°. Sulfur contents were determined by oxidizing the samples into NiO in a Perkin-Elmer series 7 thermogravimetric analyzer (TGA) and monitoring the weight loss. The TGA experiments were typically carried out with approximately 70 mg of sample from room temperature to 900 °C with a heating rate of 2 °C/min in a flowing mixture of 75% N_2 and 25% O_2. The completion of oxidation was indicated by the formation of well-crystalline NiO. Electrical resistivity was measured with a four-probe technique from 5 to 300 K. Magnetic properties were evaluated with a SQUID magnetometer from 5 to 300 K.

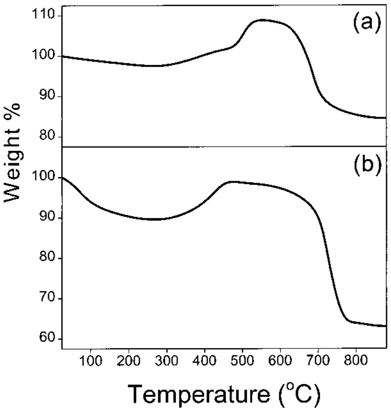

Figure 2. TGA plots of the samples obtained with 200 mL of sodium dithionite at (a) pH = 5 (crystalline $Ni_3S_{2.73}$) and (b) pH = 7 (amorphous $Ni_3S_{5.57}$).

Results and Discussion

Synthesis and Characterization. It was found from X-ray diffraction that the samples prepared without controlling the reaction pH generally consist of mixtures of phases. These samples on heating in a mixture of 90% Ar and 10% H_2 gave generally Ni_3S_2 first and finally metallic Ni at higher temperatures $T > 500$ °C. Since it was difficult to control the composition of the products in these reactions, further sample preparations were carried out by controlling the reaction pH.

Figure 1 gives the compositions of the products obtained at various pH values by reacting 50 mL of 0.25 M $NiCl_2{\cdot}6H_2O$ with various volumes of 1 M sodium dithionite solution. The compositions are expressed as Ni_3S_x in Figure 1 since Ni_3S_2 and Ni_3S_4 were found to be the predominant crystalline reaction products (see later). The compositions given in Figure 1 were obtained from the TGA data. Figure 2 gives the TGA plots for two representative samples. All the samples show first an increase in weight above 300 °C due to a partial conversion of the nickel sulfides Ni_3S_x to $NiSO_4$ followed by a large decrease in weight above about 600 °C due to the decomposition of the sulfate and the oxidation of the remaining Ni_3S_x into NiO. The completion of the formation of NiO is indicated by a plateau at higher temperatures $T > 800$ °C. The samples with high sulfur

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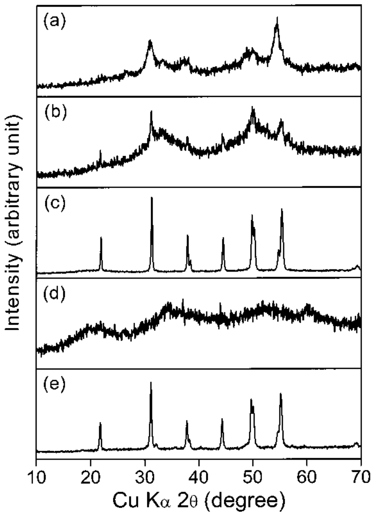

Figure 3. X-ray powder diffraction patterns of the samples obtained with a constant volume (200 mL) of 1 M sodium dithionite at various pH values: (a) pH = 3 (spinel Ni_3S_4-like phase), (b) pH = 5 (Ni_3S_2-like phase), (c) pH = 6 (Ni_3S_2 phase), (d) pH = 8 (amorphous or poorly crystalline), and (e) after heating sample d at 300 °C in a flowing mixture of 90% Ar and 10% H_2 (Ni_3S_2 phase).

contents ($x > 4$) also show an initial weight loss below 300 °C due to the loss of sulfur (Figure 2b).

For reactions at pH $\leq$ 2, sulfur is formed predominantly as the reaction product (Figure 1) as indicated by X-ray diffraction and the yellow color of the samples. On the other hand, reactions at pH $\geq$ 3 give nickel sulfides Ni_3S_x. The hydrolysis of dithionite ion is known to produce sulfide ion under alkaline conditions,[30] which can act as a sulfiding agent. Under acidic conditions, the hydrolysis involves the formation of sulfoxylate intermediate, which decomposes to give H_2S. Further reaction of dithionite with H_2S results in the formation of thiosulfate and sulfur.[30] For a given volume of dithionite (for example, 200 mL), the sulfur content in Ni_3S_x decreases initially with increasing pH up to pH = 6 and then increases thereafter. For a given reaction pH (for example, pH = 3), the sulfur content in Ni_3S_x increases initially with increasing volume of dithionite up to 150 mL and then decreases thereafter. Thus both the reaction pH and the amount of reactants play a role in controlling the composition of the products.

Figure 3 shows the X-ray diffraction patterns of the samples obtained at various pH values with 200 mL of dithionite. While the samples obtained at pH = 3 (Figure 3a) and 5 (Figure 3b) show broad reflections corresponding to Ni_3S_4 (spinel structure) and Ni_3S_2 (heazlewoodite structure), respectively, that obtained at pH = 6 (Figure 3c) shows sharp reflections corresponding to Ni_3S_2. The poor crystallinity of the sample obtained at pH = 5 compared to that obtained at pH = 6 is due to a large deviation of the sulfur content from the ideal stoichiometry of Ni_3S_2. Additionally, the sample obtained at pH = 5 may also contain a small amount of spinel Ni_3S_4. On the other hand, the samples obtained at pH $\geq$ 7 were found to be poorly crystalline or amorphous due to a high sulfur content (Figure 3d). In Figure 1, the crystalline Ni_3S_x compositions are enclosed with rectangular boxes and the shaded regions refer to crystalline sulfur (dark region) and amorphous or poorly crystalline Ni_3S_x (light region). All the Ni_3S_x samples lose sulfur on heating in reducing atmospheres (mixture of 90% Ar and 10% H_2) to give Ni_3S_2 first (Figure 3e) and finally metallic Ni.

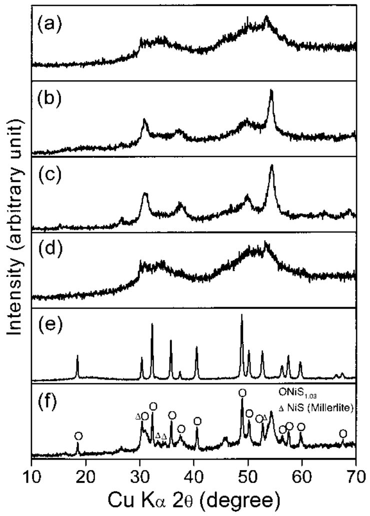

Figure 4. X-ray powder diffraction patterns of the samples obtained at a constant pH of 3 with various volumes of sodium dithionite: (a) 50 mL (amorphous or poorly crystalline), (b) 100 mL (spinel Ni_3S_4-like phase), (c) 150 mL (spinel Ni_3S_4-like phase), (d) 300 mL (amorphous or poorly crystalline), (e) after heating sample b at 200 °C in a flowing mixture of 90% Ar and 10% H_2 (millerite NiS), and (f) after heating sample c at 150 °C in an evacuated sealed glass tube (spinel Ni_3S_4, $NiS_{1.03}$, and millerite NiS). The unmarked reflections in f correspond to spinel Ni_3S_4.

Figure 4 shows the X-ray diffraction patterns of the samples obtained with various volumes of dithionite at a constant pH = 3. While the samples formed with low ($\leq$50 mL) or high ($\geq$300 mL) volumes of dithionite are poorly crystalline or amorphous, those obtained with 100−250 mL show broad reflections corresponding to spinel Ni_3S_4. The reflection corresponding to the spinel Ni_3S_4 becomes broader and poorly defined as the sulfur content deviates from the ideal stoichiometry of Ni_3S_4. Although Ni_3S_4 with a possible substitution of a small amount of Fe or Ni is known to occur in nature as a mineral (polydymite) crystallizing in the spinel structure, it is rather difficult to synthesize it in the laboratory as a single-phase material. This is because of the instability of Ni_3S_4 at higher temperatures.[31] Conventional solid state reactions for 6−8 months at low temperatures (200−300 °C) as well as other low-temperature procedures have invariably resulted in the formation of impurity phases.[15,16,32,33] Interestingly, the ambient temperature procedure described in this study is able to access single-phase Ni_3S_4. However, it disproportionates on heating at higher temperatures $T > 100$ °C (Figure 4) to give other phases. For example, it loses sulfur and gives single-phase NiS (millerite) on heating carefully at 200 °C in a flowing mixture of 90% Ar and 10% H_2 (Figure 4e). On the other hand, heating in an evacuated sealed glass tube at 150 °C leads to the formation of NiS (millerite) and $NiS_{1.03}$ (Figure 4f), which is consistent with that found recently by Olivas et al.[14]

Electrical and Magnetic Properties. Figure 5 shows the variation of electrical resistivity with temperature for two crystalline samples: Ni_3S_2 and Ni_3S_4. Both samples show metallic behavior. The larger difference in the resistivity values between the two Ni_3S_2 specimens in panels a and b of Figure 5 is due to a larger grain boundary in the sample heated at 100 °C compared to that in the sample heated at 500 °C. The observed metallic properties of Ni_3S_2 are in agreement with the literature data.[34] The crystal structure of Ni_3S_2 consists of a series of interconnected Ni_3S_2 bipyramids composed of Ni_3 tri-

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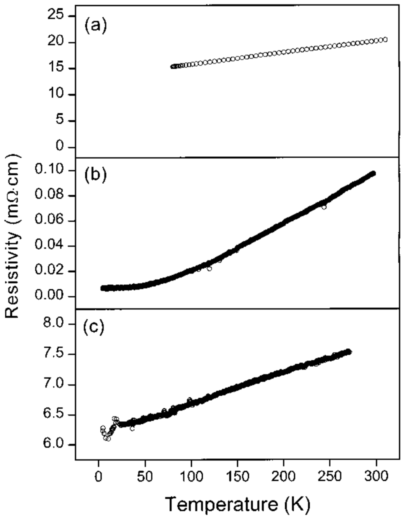

Figure 5. Variation of electrical resistivity with temperature: (a) after heating at 100 °C in 90% Ar and 10% H_2 the $Ni_3S_{2.1}$ sample obtained at pH = 6 with 200 mL of sodium dithionite, (b) after heating sample a at 500 °C in 90% Ar and 10% H_2, and (c) compacted $Ni_3S_{4.02}$ sample obtained at pH = 3 with 150 mL of sodium dithionite.

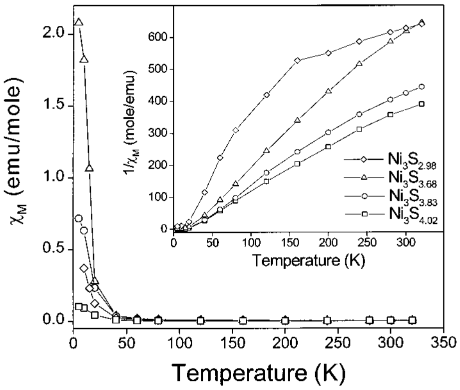

Figure 6. Variation of molar magnetic susceptibility and inverse molar magnetic susceptibility (inset) with temperature for samples obtained at pH = 3 with various volumes of sodium dithionite. The compositions refer to those given in Figure 1.

angles,[35,36] and the metallic behavior is due to a delocalization of the electrons among the Ni_3 triangular clusters. However, the electrical properties of the spinel Ni_3S_4 were not known before in the literature. The good metallic behavior observed even with the just compacted (unsintered due to the instability at higher temperatures) pellets evidences a strong covalent mixing between the Ni:3d and S:3p orbitals leading to good delocalization of the electrons. Ni_3S_4 shows a room temperature Seebeck coefficient value of $-10\ \mu$V/K indicating that electrons are the predominant carriers and they are delocalized.[31]

Figure 6 shows the variation of magnetic susceptibility with temperature for the Ni_3S_x samples that were synthesized with various volumes of dithionite at a constant pH value of 3. All the samples in Figure 6 have the spinel structure except the one ($Ni_3S_{2.98}$) synthesized with 50 mL of dithionite, which is amorphous. The spinel samples show a ferrimagnetic ordering at low temperatures ($T < 20$ K) as indicated by the hysteresis loop in Figure 7 and a downward curvature before T_c in the plots of inverse molar susceptibility versus temperature in Figure 6. The occurrence of ferromagnetic behavior is due to a spontaneous alignment of the octahedral and tetrahedral site moments of the spinel lattice in the opposite directions. The electrical and magnetic properties of Ni_3S_4 reveal that it is an itinerant electron ferrimagnet.[31] A comparison of the various spinel samples in Figure 6 reveals that the magnetic susceptibility value at a given temperature and the effective magnetic moment in the paramagnetic region increase with increasing sulfur content x. Also, the ferrimagnetic ordering becomes more pronounced as the sulfur content increases toward the stoichiometric value of 4.

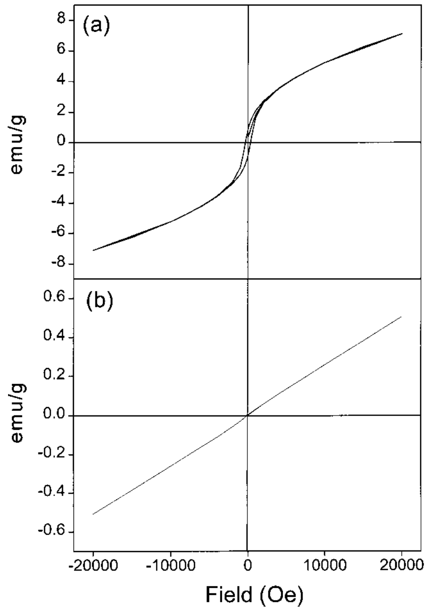

Figure 7. Variation of magnetization with field for the $Ni_3S_{4.02}$ sample obtained at pH = 3 with 150 mL of sodium dithionite: (a) 4 K and (b) 100 K.

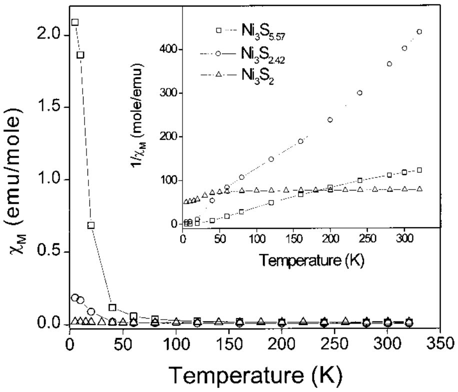

Figure 8. Variation of molar magnetic susceptibility and inverse molar magnetic susceptibility (inset) with temperature for various samples: $Ni_3S_{5.57}$ (amorphous or poorly crystalline) obtained with 200 mL of sodium dithionite at pH = 7, $Ni_3S_{2.42}$ (Ni_3S_2-like phase) obtained with 150 mL of sodium dithionite at pH = 6, and Ni_3S_2 phase obtained by heating at 300 °C in 90% Ar and 10% H_2 the $Ni_3S_{2.1}$ sample that was obtained with 200 mL of sodium dithionite at pH = 6.

Figure 8 shows the variation of magnetic susceptibility with temperature for an amorphous (or poorly crystalline) sample having high sulfur content ($Ni_3S_{5.57}$) and crystalline samples showing diffraction patterns characteristic of Ni_3S_2. The amorphous $Ni_3S_{5.57}$ composition shows ferrimagnetic ordering similar to the spinel Ni_3S_4 composition possibly due to the presence of poorly crystalline spinel Ni_3S_4 or a trace amount of metallic Ni in this sample. While the nonstoichiometric $Ni_3S_{2.47}$ sample shows a temperature-dependent susceptibility, the stoichiometric

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Ni_3S_2 sample obtained after heating at 300 °C shows nearly temperature-independent susceptibility characteristic of Pauli paramagnetic behavior, which is in agreement with the literature data for Ni_3S_2.[34] However, the room temperature magnetic susceptibility (0.5×10^{-4} emu/g) of our sample is 2 orders of magnitude higher than that reported (0.6×10^{-6} emu/g) in the literature for polycrystalline samples.[28] The higher value observed in our sample could be due to a possible contamination by Ni_3S_4 or ferromagnetic Ni impurities.

Conclusions

Crystalline Ni_3S_2 and Ni_3S_4 as well as several amorphous or poorly crystalline Ni_yS_x compositions have been synthesized by reacting aqueous nickel chloride and sodium dithionite solutions at room temperature under controlled pH conditions. This solution-based synthesis procedure has accessed successfully the metastable spinel Ni_3S_4, which is otherwise difficult to obtain as a single-phase product by conventional high-temperature procedures. Ni_3S_4 is found to be an itinerant electron ferrimagnet. The solution-based approach used here offers nanocrystalline products with small particle size, which may be attractive for catalytic applications. Sodium dithionite is a potential reagent to synthesize other transition metal sulfides as well, and such experiments are currently in progress in our laboratory.

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