



# Synthesis and characterisation of magnetic iron sulfide nanocrystals

John H.L. Beal\*, Pablo G. Etchegoin, Richard D. Tilley

School of Chemical and Physical Sciences and The MacDiarmid Institute of Advanced Materials and Nanotechnology, Victoria University of Wellington, P.O. Box 600, Wellington, New Zealand

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## ABSTRACT

Fe<sub>1-x</sub>S and Fe<sub>3</sub>S<sub>4</sub> nanocrystals with a variety of morphologies and average sizes were synthesised by the reaction of iron(II) acetylacetonate (Fe(acac)<sub>2</sub>) and elemental sulfur in oleylamine. Reaction at 200 °C for 240 min produced extremely thin Fe<sub>3</sub>S<sub>4</sub> sheets, which displayed low coercivities (14 kA m<sup>-1</sup>) suggestive of pseudosingle-domain or multidomain particles. Reaction temperatures ≥ 300 °C for 30 min produced 70 nm Fe<sub>1-x</sub>S nanocrystals with hexagonal plate and hexagonal prism morphologies, which displayed high magnetic coercivities (110 kA m<sup>-1</sup>) characteristic of single magnetic domain particles. Rapid injection of sulfur solution at 280 °C followed by immediate cooling produced a mixture of Fe<sub>1-x</sub>S nanocrystals and spherical, polydisperse ~5 nm Fe<sub>3</sub>S<sub>4</sub> nanocrystals, which displayed superparamagnetism above an average blocking temperature of 55 K.

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## 1. Introduction

Magnetic nanocrystals have been investigated extensively for potential use in applications ranging from magnetic data storage [1] to MRI (Magnetic Resonance Imaging) contrast agents [2,3]; while the contribution of submicrometer-sized magnetic inclusions in mineral deposits to paleomagnetism is increasingly recognised [4,5]. Hence the study of the variation of magnetic behaviour with particle size and morphology in the nanometre size regime is of continued interest in the field of materials science.

The iron sulfide system contains a number of magnetic phases encountered as minerals, including hexagonal and monoclinic Fe<sub>1-x</sub>S, derived from the NiAs-type substructure [6] (hexagonal and monoclinic pyrrhotite, respectively); the cubic inverse spinel Fe<sub>3</sub>S<sub>4</sub> [7] (greigite); and tetragonal FeS [8] (mackinawite). The mineralogical role of these iron sulfides, along with their complex variations in crystal structure and magnetic behaviour have lead to frequent investigations, including numerous synthetic studies [6,8–10].

However, relatively little work has been directed towards synthetically controlling the crystal size of magnetic iron sulfides and examining the consequences on their physical properties. Fe<sub>1-x</sub>S has traditionally been prepared either via standard solid state techniques [6], or the hydrothermal method [9], with the deliberate aim of obtaining the thermodynamically favoured phase with crystals of sufficient size for single-crystal X-ray

diffraction. More recently 10–15 nm nanocrystalline Fe<sub>1-x</sub>S has been prepared by high-energy mechanochemical processing of mixtures of elemental iron and sulfur, or elemental iron and FeS<sub>2</sub> for 24 h [11]. Rao et al. synthesised an iron sulfide–ethylene diamine composite, which was subsequently fired at 200–300 °C to produce Fe<sub>1-x</sub>S nanowires [12]. More recently, the solution-based synthesis of Fe<sub>1-x</sub>S nanocrystals from single source precursors was reported by O'Brien [13] and also by ourselves [14].

Cubic Fe<sub>3</sub>S<sub>4</sub> is identified increasingly frequently as a diagenetic mineral in marine and lacustrine sediments, and is metastable, but has been found to be long-lived under appropriate storage conditions [7]. Synthesis of Fe<sub>3</sub>S<sub>4</sub> has traditionally been by the hydrothermal method [10]. The fact that this methodology typically resulted in a low average particle diameter (9–14 nm), resulting in at least a portion of the sample being superparamagnetic at room temperature, was first recognised by Spender et al. [15]. More recent attempts at deliberately synthesising Fe<sub>3</sub>S<sub>4</sub> with small crystallite size include modifications of hydrothermal methodology by Chen et al. [16], and a solvothermal method by Qian et al. [17]. We have also previously demonstrated the synthesis of Fe<sub>3</sub>S<sub>4</sub> nanocrystals either by the in situ sulfidation of the decomposition product of Fe(acac)<sub>2</sub> [18], or the decomposition of a single source precursor [14]. In addition, a physical approach to the synthesis of nanocrystalline Fe<sub>3</sub>S<sub>4</sub> and Fe<sub>7</sub>S<sub>8</sub> by magnetron sputtering of iron sulfide material onto silicon substrates, followed by annealing, was reported recently by Liu et al. [19].

Tetragonal FeS has been frequently observed to be the first iron sulfide phase to precipitate from aqueous solution and frequently to have a disordered [20] or nanocrystalline nature [21], which has lead to it sometimes being mislabelled “amorphous” FeS. Tetragonal FeS has been found to be produced in nature by the action of sulfate

\* Corresponding author. Present address: Industrial Research Ltd., 69 Gracefield Road, P.O. Box 31310, Lower Hutt 5040, New Zealand.  
E-mail address: [j.beal@irl.cri.nz](mailto:j.beal@irl.cri.nz) (J.H.L. Beal).

reducing bacteria in iron-rich environments [22]; and has produced in the laboratory by hydrothermal methods [8].

In this work we used a simple, one-pot procedure to synthesise  $\text{Fe}_{1-x}\text{S}$  and  $\text{Fe}_3\text{S}_4$  nanocrystals from the iron-precursor, iron acetylacetonate ( $\text{Fe}(\text{acac})_2$ ), and elemental sulfur in the coordinating, high-boiling point solvent oleylamine (OAm). The magnetic behaviour of the iron sulfide nanocrystals was then examined by SQUID magnetometry.

## 2. Materials and methods

### 2.1. Preparation of iron sulfide nanocrystals

Iron(II) acetylacetonate ( $\text{Fe}(\text{acac})_2$ ) (99.95%) was obtained from Aldrich and stored over a silica bead desiccant. Sulfur (sublimed) was from BDH. Oleylamine (OAm) ( $\geq 70\%$ , tech.) was from Fluka. All chemicals were used as received. A 0.5 M stock solution of sulfur in OAm was prepared by dissolving sulfur (0.17 g) in OAm (10 cm<sup>3</sup>) assisted by mild heating. The resulting deep red solution was degassed by bubbling nitrogen through rapidly for 30 min, and stored under nitrogen.

Reactions were carried out in a three-necked flask equipped with a condenser, temperature probe and magnetic stirbar. OAm was degassed by bubbling nitrogen through vigorously for 30 min before use, and reactions were kept under a nitrogen atmosphere.

In a typical experiment using the so-called heating-up method [23],  $\text{Fe}(\text{acac})_2$  (0.385 g, 1.5 mmol) and sulfur (0.049 g, 1.5 mmol) were placed in a flask, and flushed with nitrogen. Degassed OAm (30 cm<sup>3</sup>) was added and stirred to produce a dark red suspension. The suspension was heated rapidly to the reaction temperature, and held for 10–240 min before being cooled to room temperature.

In an alternative procedure using rapid injection, a flask containing  $\text{Fe}(\text{acac})_2$  (0.397 g, 1.6 mmol) in degassed OAm (27 cm<sup>3</sup>) was heated to 280 °C and sulfur solution (3 cm<sup>3</sup> containing 1.6 mmol sulfur in OAm) was injected rapidly. The reaction mixture was then allowed to cool immediately to room temperature. In both cases blackening of the reaction mixture and gentle evolution of gas were observed above 90 °C.

Samples were purified by addition of acetone (20 cm<sup>3</sup>), followed by centrifugation to precipitate the nanocrystals. The viscous brown supernatant was removed and discarded; the dark black iron sulfide precipitate was resuspended in toluene with the aid of sonification. This process was repeated twice or three times as necessary, until the supernatant was clear and colourless. The samples were then either resuspended in toluene, or dried in vacuo at room temperature and stored as a powder.

Experiments were performed varying the reaction temperature between 100 and 330 °C and the heating period between 0 and 240 min (see Table 1 for selected experimental parameters).

**Table 1**  
Experimental parameters.

Sample	Rxn. Temperature (°C)	Inject. Temperature (°C)	Rxn. Time (min)	Morphology	Product(s)	Particle size <sup>a</sup> /nm
I	140	n/a	60	Layered structures	Amorphous iron sulfide	n.a
II	200	n/a	240	Sheets	Major: $\text{Fe}_3\text{S}_4$ Minor: $\text{Fe}_{1-x}\text{S}$	12 55
III	310	n/a	30	Hexagonal plates Hexagonal prisms	$\text{Fe}_{1-x}\text{S}$	70
IV	280	280	0	Hexagonal plates Hexagonal prisms Spherical	Major: $\text{Fe}_{1-x}\text{S}$ Minor: $\text{Fe}_3\text{S}_4$	25 5.0

<sup>a</sup> Particle size as determined from p-XRD patterns by use of the Scherrer equation [22]. The 1 0 1 reflection was used for  $\text{Fe}_{1-x}\text{S}$ , and the 4 0 0 reflection for  $\text{Fe}_3\text{S}_4$ ; as these represent the lowest-index peak for each phase with appreciable relative intensity, and no overlap with reflections of the other phase.

### 2.2. Characterisation procedure

Transmission Electron Microscopy (TEM), Selected-Area Electron Diffraction (SAED), and Energy Dispersive X-ray Spectroscopy (EDS) were performed on a JEOL 2010 transmission electron microscope (200 kV accelerating voltage) fitted with an EDS detector. Samples were prepared by suspending the sample in toluene and placing a drop on a TEM grid (carbon film copper 200 mesh, ProSciTech).

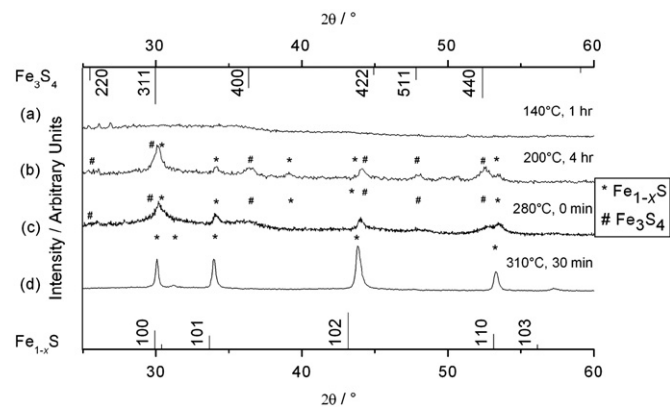
Powder X-ray Diffraction (XRD) was performed on approximately 60 mg of powdered sample using a Philips PW1050 diffractometer with secondary graphite monochromator and  $\text{Cu K}_\alpha$  radiation.

Magnetic measurements were performed using a Quantum Design Ltd. MPMS 2 SQUID magnetometer, and approximately 15 mg of powdered sample, which was dried overnight in a vacuum desiccator, weighed, then sealed in a gelatin capsule.

## 3. Results

### 3.1. Heating-up method

With the heating-up methodology, particles of an iron sulfide material with a stacked layer structure were the major product formed for all reaction temperatures below 200 °C. For example, Sample I was produced by reaction at 140 °C for 1 h, and both XRD (Fig. 1(a)) and SAED (not shown) indicated that the sample was amorphous or poorly crystalline, with SAED displaying only diffuse rings. EDS spectra (Figure S1a in Supplementary Information) indicated an atomic iron:sulfur ratio of 56:44, and contained a strong oxygen signal, suggesting a partially oxidised iron sulfide.



**Fig. 1.** XRD patterns of (a) Sample I (b) Sample II (c) Sample III (d) Sample IV. Reference patterns for  $\text{Fe}_3\text{S}_4$  and  $\text{Fe}_{1-x}\text{S}$  shown on upper and lower axis, respectively.

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