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Liquid phase synthesis of iron sulfide particles

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Abstract Iron sulfide particles were prepared using a polyol method; a mixture of ferrocene, 1,2-hexadecanediol (HD), and 1-octadecanethiol in oleylamine were heated to obtain particles. The particles were investigated using Mössbauer spectroscopy, scanning electron microscopy, and powder X-ray diffraction. Hexagonal plate shaped $Fe_{1-x}S$ particles with sizes of 2–3 μm were obtained in the solvent without HD, whereas 100–200 nm Fe_2S_3 particles were obtained in the presence of HD. The Fe_2S_3 particles were transformed to Fe_3S_4 (greigite) by heating at 100 °C.

Keywords Iron sulfide · Trivalent iron · Particles · Mössbauer spectroscopy · Polyol method

Introduction

The phase diagram of iron sulfide is complicated and each phase has different magnetic characteristics [1]. Most of the stable iron sulfides are sulfides of Fe(II), while very few iron sulfides with trivalent iron Fe(III) have been reported. Boehm et al. reported the X-ray diffraction (XRD) pattern of Fe_2S_3; however, the product was heavily contaminated and Mössbauer parameters were not reported [2]. Stiller et al. reported Mössbauer spectra for amorphous Fe_2S_3 measured at 78 and 4.2 K [3]. Thus, XRD patterns and Mössbauer spectra of well-defined Fe_2S_3 particles have yet to be reported. The polyol process, which uses a polyhydric alcohol, is a useful method to synthesize particles in solution, where the polyhydric alcohol acts as both a stabilizer and reducing agent [4]. Recently, spinel type γ-Fe_2S_3 nanoparticles have been synthesized by the polyol process [5]. In this study, iron sulfide particles are synthesized using a polyol method with 1-octadecanethiol (OT) employed as the sulfur source and Mössbauer spectra and XRD patterns are measured.

Experimental

A mixture of ferrocene (2 mmol), oleylamine (30 mL), 1,2-hexadecanediol (HD), and OT was introduced into a three-necked flask. The amounts of ferrocene and oleylamine were kept constant and the amounts of HD and OT were varied (Table 1). The mixture was stirred for 1 h at room temperature and then refluxed for 2 h at 320 °C under an Ar flow. Precipitated particles were washed three times with ethanol and hexane, followed by centrifugation after air-cooling. The resultant particles were investigated using Mössbauer spectroscopy (^{57}Co/Rh source), XRD (Rigaku, RINT2500, Cu Kα), and scanning electron microscopy (SEM; Jeol, JSM7001F).

Results and discussion

Figure 1 shows selected SEM images of iron sulfide particles (S1, S4, and S7). The particles produced without HD

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Table 1 HD/OT ratios for the production of iron sulfide particles and room-temperature Mössbauer parameters for the corresponding products

Sample names	HD/OT (mmol)	Components	δ (mm/s)	$\Delta E_q(2\varepsilon)$ (mm/s)	H (kOe)	Γ (mm/s)	Area int (%)
S1	0/8	$Fe_{1-x}S$ (A)	0.71 (1)	0.06 (1)	282 (1)	0.47 (4)	54.0
		$Fe_{1-x}S$ (B)	0.69 (1)	0.16 (3)	265 (1)	0.39 (6)	23.9
		$Fe_{1-x}S$ (C)	0.69 (1)	0.10 (2)	303 (1)	0.34 (5)	18.5
		$Fe_{1-x}S$ (D)	0.66 (3)	1.40 (6)		0.30 (6)	3.6
S2	8/16	$Fe_{1-x}S$[a]	–	–	–	–	40.2
		Fe_2S_3 (A)	0.39 (1)	0.77 (2)		0.37 (1)	42.1
		Fe_2S_3 (B)	0.44 (1)	0.48 (2)		0.29 (2)	17.7
S3	8/8	$Fe_{1-x}S$	0.71 (1)	0.04 (3)	283 (1)	0.74 (4)	27.6
		Fe_2S_3 (A)	0.38 (1)	0.73 (2)		0.37 (1)	48.9
		Fe_2S_3 (B)	0.44 (2)	0.47 (4)		0.36 (3)	23.5
S4	8/4	$Fe_{1-x}S$[a]	–	–	–	–	41.6
		Fe_2S_3 (A)	0.35 (1)	0.72 (2)		0.36 (1)	39.8
		Fe_2S_3 (B)	0.46 (2)	0.62 (4)		0.37 (3)	18.6
S5	8/2	FeS	0.75 (1)	−0.17 (1)	312 (1)	0.34 (1)	25.7
		Fe_2S_3 (A)	0.42 (2)	0.72 (4)		0.48 (2)	23.1
		Fe_2S_3 (B)	0.50 (1)	0.51 (2)		0.23 (3)	9.2
		α-Fe	−0.005 (2)	0.001 (2)	329 (1)	0.27 (1)	42.0
S6	8/0.5	FeS	0.71 (3)	−0.08 (6)	308 (2)	0.59 (8)	12.7
		Fe_2S_3 (A)	0.41 (2)	0.86 (3)		0.41 (2)	22.6
		Fe_2S_3 (B)	0.46 (3)	0.50 (5)		0.34 (7)	10.9
		α-Fe	0.000 (2)	0.009 (5)	329 (1)	0.30 (1)	53.8
S7	8/0.1	α-Fe	0.00 (1)	0.01 (1)	338 (1)	0.35 (1)	34.9
		Fe_3O_4 (A)	0.32 (2)	0.02 (3)	503 (1)	0.36 (1)	4.1
		Fe_3O_4 (B)	0.67 (1)	−0.01 (4)	465 (1)	0.42 (3)	8.7
		Fe(III)	0.43 (1)	0.95 (1)		0.90 (1)	19.3
		Relaxation	0.50 (3)				33.0

[a] This component was fitted into the combination of three sets of sextets and a doublet

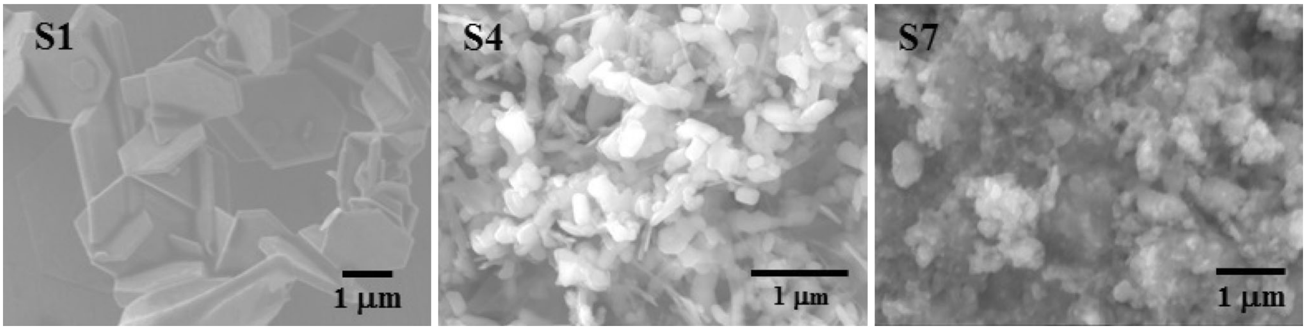

Fig. 1 SEM images of iron sulfide particles

(S1) were hexagonal plate shaped with sizes of 2–3 µm. In contrast, the particles produced with HD were 100–200 nm in size (S4 and S7) and had various rough shapes, rather than the unique plate-like shape. The shape and size of the particles was significantly changed by the presence of HD, whereas the particle size was only slightly changed with varying the amount of OT in the range of 0.5–16 mmol (S2–S6).

Figure 2 shows Mössbauer spectra of the particles (S1–S7) measured at room temperature and the Mössbauer parameters are summarized in Table 1. The Mössbauer spectrum of the S1 particles had three sets of sextets and a small intensity doublet, and was thus assigned to $Fe_{1-x}S$. The assignment was confirmed by XRD of the S1 sample, as described later. The peak intensity ratio of the sextet was 3:3.4:1:1:3.4:3 due to the

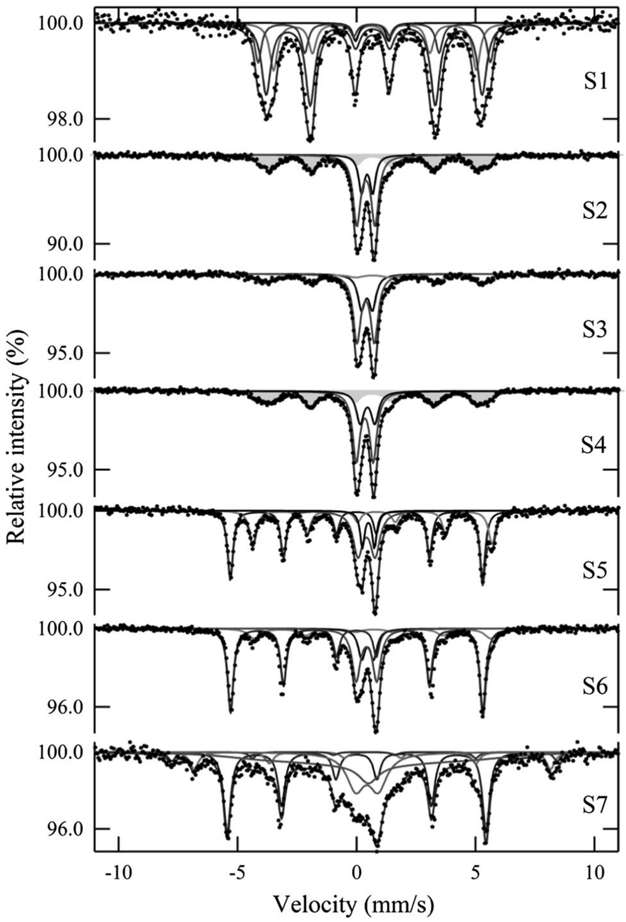

Fig. 2 Room-temperature Mössbauer spectra for iron sulfide particles produced with various HD/OT ratios. The mixture ratios and the Mössbauer parameters were summarized in Table 1

shape anisotropy, similar to Mössbauer spectra reported in the literature [6].

The Mössbauer spectra of samples S2–S4 had very similar features. The spectra had a magnetic component and two sets of doublet. The magnetic component was fitted by three sets of sextets, the parameters of which were similar to those of $Fe_{1-x}S$ in S1. Low-spin iron(II) sulfide FeS_2 (pyrite, marcasite) has been reported with similar Mössbauer parameters [7], but the XRD patterns of these particles did not correspond with the pattern reported for FeS_2 (pyrite: PDF #42-1340, marcasite: PDF #37-0475). The two sets of doublets had small δ values, which may be due to the presence of trivalent iron Fe(III). The intensity ratio of the two sets of doublets in the spectra was always approximately 2:1 and the Mössbauer parameters of the doublets had similar values to those reported for Fe_2S_3 [3], although the ΔE_q value of one of the doublets was smaller than that reported in the literature.

The Mössbauer spectra of the particles produced in solutions containing less than 2 mmol of OT (S5–S7) had a sextet that was assigned to α-Fe, in addition to the two sets of doublets indicative of Fe(III) sulfides. Therefore, it was presumed that the sulfurization reaction did not progress sufficiently fast compared with formation of α-Fe which remains unreacted further. The S5 and S6 particles contained FeS, which was indicated by the presence of divalent Fe(II) species with small ΔE_q.

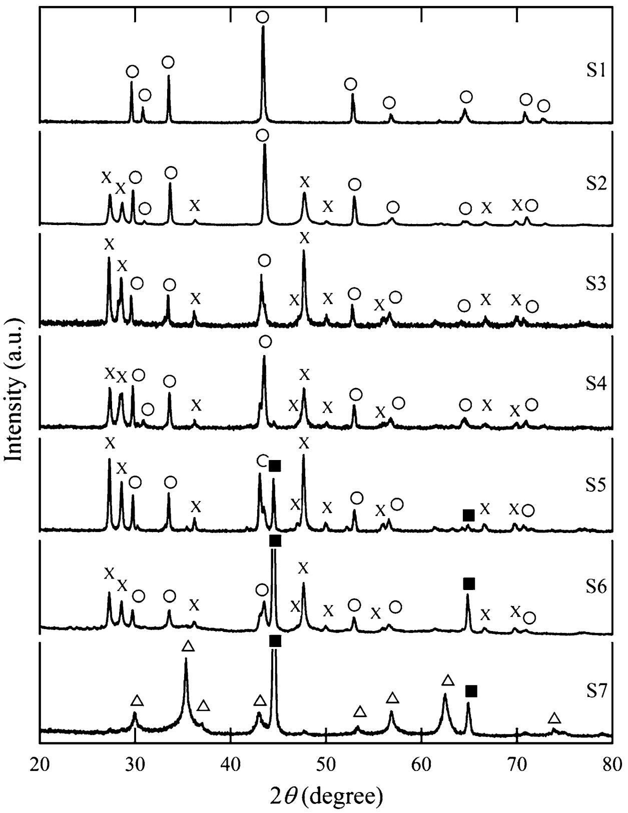

Fig. 3 XRD patterns for iron sulfide particles obtained by reaction with various HD/OT ratios. *Open circles* $Fe_{1-x}S$ (PDF #29-0724), *filled squares* α-Fe (PDF #87-0721), *open triangles* Fe_3O_4 (PDF #19-0629), *times* unidentified peaks

Particle S7 was produced with a very low concentration of OT. The Mössbauer spectrum of S7 had two sets of sextets, which were assigned to Fe_3O_4 (magnetite). In addition, a component with a broad absorption due to magnetic relaxation and a doublet with a large half-width were observed. The broad absorption may be due to the superparamagnetism of small γ-Fe_2O_3 (maghemite) particles.

The Mössbauer spectrum of S3 measured at 6 K gave a sextet of $Fe_{1-x}S$ ($\delta = 0.88$ mm/s, $2\varepsilon = -0.25$ mm/s, $H = 314$ kOe) and one of the doublets of Fe_2S_3 (B; $\delta = 0.53$ mm/s, $\Delta E_q = 0.72$ mm/s) had similar Mössbauer parameters as those observed at room temperature (Fig. 2), except for the effects of a secondary Doppler shift. However, the other doublet of Fe_2S_3 (A) showed superparamagnetic relaxation at 6 K ($\delta = 0.49$ mm/s,

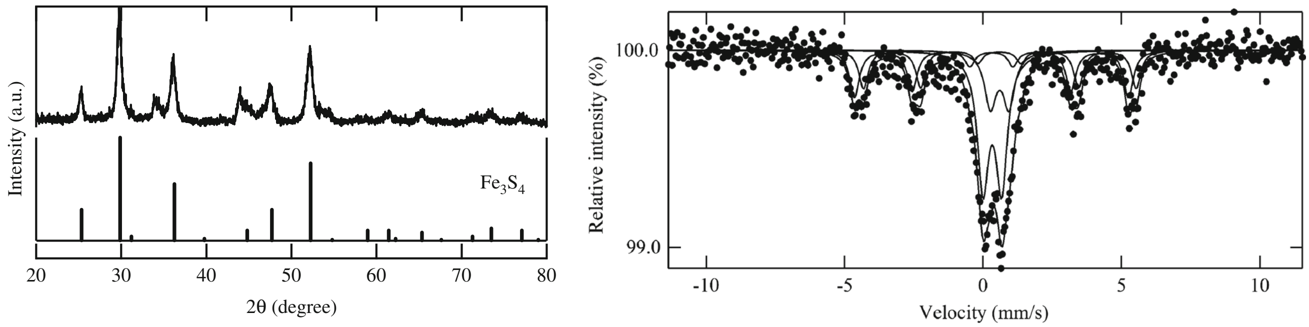

Fig. 4 XRD pattern (left) and room-temperature Mössbauer spectrum (right) of iron sulfide particles heated at 100 °C for 48 h. The XRD pattern for Fe_3S_4 (JCPDS Card No. 16-0713) is shown for comparison

$H = 188$ kOe, relaxation time $\tau = 4.01 \times 10^{-8}$ s). Fe_2S_3 has been reported to have a sextet with 253 kOe at 4 K [3]; however, the particle size was too small for the sextet absorption to be observed in the present experiment. The results were similar to those previously reported [3], which indicates an antiferromagnetic character at low temperatures with two distinct iron sites. However, one site showed no magnetic splitting, even at low temperatures, which may be due to the small particle size.

Figure 3 shows XRD patterns for the samples. Assignments of $Fe_{1-x}S$, α-Fe, and Fe_3O_4 were made based on the ICDD-PDF database ($Fe_{1-x}S$: PDF #29-0724, α-Fe: PDF #87-0721, Fe_3O_4: PDF #19-0629). The relative yields of $Fe_{1-x}S$, α-Fe, and Fe_3O_4 were in good agreement with the Mössbauer spectra. Besides these well assigned XRD peaks, unassigned XRD peaks were observed for the S2–S6 particles. The peaks marked 'X' in Fig. 3 may correspond to Fe_2S_3 with a long-range periodic structure. The XRD patterns obtained here are different from those patterns of heavily contaminated samples reported in the literature [2].

The Fe_2S_3 obtained in this work showed two sets of doublets in the room-temperature Mössbauer spectra, and one of the doublets showed broad absorption caused by relaxation at low-temperature. This may be due to the small crystallite size of Fe_2S_3 in the S3 particles. If the crystallite size is sufficiently large, then the absorption should be a sextet because of the long relaxation time. The S3 particles were annealed for 48 h at 100 °C to enlarge the crystallite size. The annealed particles were then measured using XRD and Mössbauer spectroscopy at room temperature (Fig. 4). The XRD pattern indicated Fe_3S_4 (greigite); therefore, the S3 particles consisted of $Fe_{1-x}S$ and Fe_2S_3 that were changed to Fe_3S_4 by annealing. The Mössbauer spectrum had two sets of doublets ($\delta = 0.60$ mm/s, $2\varepsilon = 0.67$ mm/s and $\delta = 0.34$ mm/s, $\Delta E_q = 0.67$ mm/s) and sextets ($\delta = 0.60$ mm/s, $2\varepsilon = 0.01$ mm/s, $H = 306$ kOe and $\delta = 0.30$ mm/s, $2\varepsilon = 0.00$ mm/s, $H = 307$ kOe). The sextets were assigned to Fe_3S_4 and the doublets were interpreted as superparamagnetism of small Fe_3S_4 particles. The two sets of doublets may due to the spinel structure of Fe_3S_4. Similar results have been reported, where Fe_2S_3 changed to Fe_3S_4 when heated in a vacuum at 150 °C [2], which is consistent with the present results. Thus, the newly found Fe_2S_3 is stable only when the crystallite size is small.

Conclusion

Iron sulfide particles were prepared by the polyol method. Hexagonal plate-like $Fe_{1-x}S$ particles of 2–3 µm in size were obtained without HD. In contrast, 100–200 nm sized Fe_2S_3 particles were produced in the presence of HD. Although the newly found Fe_2S_3 particles had long-range periodic structure, as indicated by sharp XRD peaks, the Mössbauer spectra of Fe_2S_3 showed superparamagnetic nature due to its small crystallite size. The Fe_2S_3 particles were changed to Fe_3S_4 (greigite) by heating at 100 °C. The polyol method with ferrocene and HD was demonstrated as a practical method for the production of iron sulfide particles, where the Fe_2S_3 phase is stabilized only in nanoparticles.

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