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Iron (III) sulfide particles produced by a polyol method

**Ryo Shimizu · Ippei Kubono · Yoshio Kobayashi ·
Yasuhiro Yamada**

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Abstract Iron(III) sulfide Fe_2S_3 particles were produced using a polyol method. Although pyrrhotite $Fe_{1-x}S$ appeared together with Fe_2S_3, the relative yield of Fe_2S_3 changed when the concentration of reagents in the oleylamine changed. Mössbauer spectra of the particles showed superparamagnetic doublets due to Fe_2S_3 at 293 K, along with a hyperfine magnetic splitting of $H = 24.7$ T at 6 K. XRD patterns of the Fe_2S_3 suggested a structure similar to that of greigite Fe_3S_4.

Keywords Iron(III) sulfide · Polyol method · Nanoparticles · X-ray diffraction · Hyperfine magnetic field

1 Introduction

The iron sulfides of pyrite FeS_2, marcasite FeS_2, and pyrrhotite $Fe_{1-x}S$ are commonly available iron(II) compounds. While Fe_3S_4 has been well investigated, iron(III) sulfides are generally unstable under conventional conditions. The possible significance of Fe_2S_3 as a catalyst for coal liquefaction has attracted considerable recent attention [1, 2]. Metastable iron(III) sulfide Fe_2S_3 has been studied for a long time, but its detailed structure and

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R. Shimizu · I. Kubono · Y. Yamada (✉)
Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan
e-mail: yyasu@rs.kagu.tus.ac.jp

Y. Kobayashi
The University of Electro-Communications, 1-5-1 Chofugaoka, Chofu, Tokyo 182-8585, Japan

Y. Kobayashi
RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

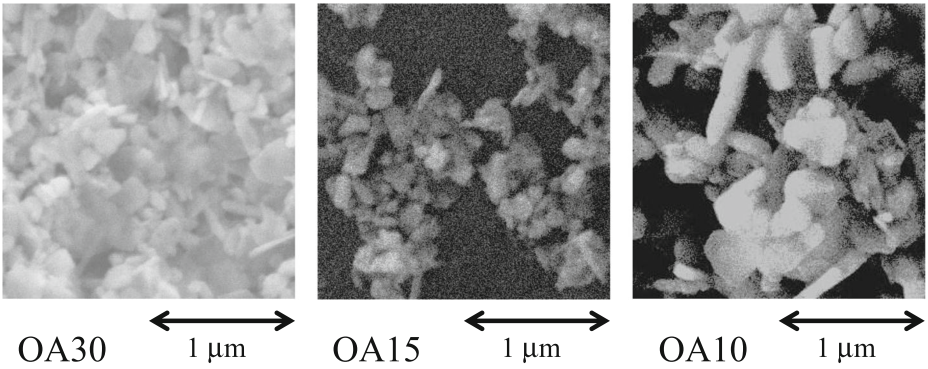

Fig. 1 SEM images of iron sulfide particles

magnetic nature remain unclear. XRD patterns of iron(III) sulfide synthesized in solution have suggested a tetragonal system [3]. Fe_2S_3 formed by mixing ferric chloride and ammonium sulfide was found to have a spinel structure with a lattice size of 9.87 Å [4, 5]. A Mössbauer spectrum of amorphous Fe_2S_3 had hyperfine magnetic splitting of 25.3 (6) T at 4.2 K [6]. EXAFS of Fe_2S_3 has also been measured [7]. The magnetic properties and structures of metastable Fe_2S_3 embedded in pyrrhotite have been discussed [8], and it has been proposed that Fe_2S_3 has a hexagonal structure with ferromagnetic properties. Recently, Lyubutin et al. prepared $Fe_{1-x}S$ nanoparticles by thermal decomposition of a mixture of iron-oleylamine and sulfur oleylamine [9], and Fe_3S_4 nanoparticles were also synthesized by a polyol process [10]. It was further reported that small particles (<9 nm) of γ-Fe_2S_3 have a spinel structure and exhibit paramagnetic properties down to 90 K.

We have produced various iron sulfide particles using a polyol method, and obtained a mixture of FeS, Fe_3S_4, and Fe_2S_3 by varying the ratios of starting materials [11]: a mixture of ferrocene, 1,2-hexadecanediol (HD), and 1-octadecanethiol (OT) in oleylamine (OA). The composition of the iron sulfide particles varied according to the ratio of HD to OT. When the concentration of HD was low, $Fe_{1-x}S$ plate-like particles 1-3 μm in size were produced, whereas 100-200 nm Fe_2S_3 particles were obtained at higher HD concentrations. In the present study, we found that the concentration of the reagents (with a fixed mixture ratio of ferrocene/HD/OT) in OA influenced the yield of Fe_2S_3, and we identified optimal conditions for the production of Fe_2S_3.

2 Experimental

The procedure used to produce the iron sulfide particles employed in this study was almost the same as that described in our previous paper [11]. A mixture of ferrocene (2 mmol), HD (8 mmol), OT (8 mmol), and OA (10-30 mL) was stirred for 1 h at room temperature, and then refluxed for 2 h at 320 °C under Ar flow. Here, we present data from three samples: OA30, OA15, and OA10, which were produced in 30, 15, and 10 mL of OA, respectively, while the same amounts of the other reagents (ferrocene/HD/OT) were added to different amounts of OA. The resultant particles were investigated by Mössbauer spectroscopy, X-ray diffraction (XRD; Rigaku, RINT2500, Cu-Kα), and scanning electron microscopy (SEM; Jeol, JSM7001F).

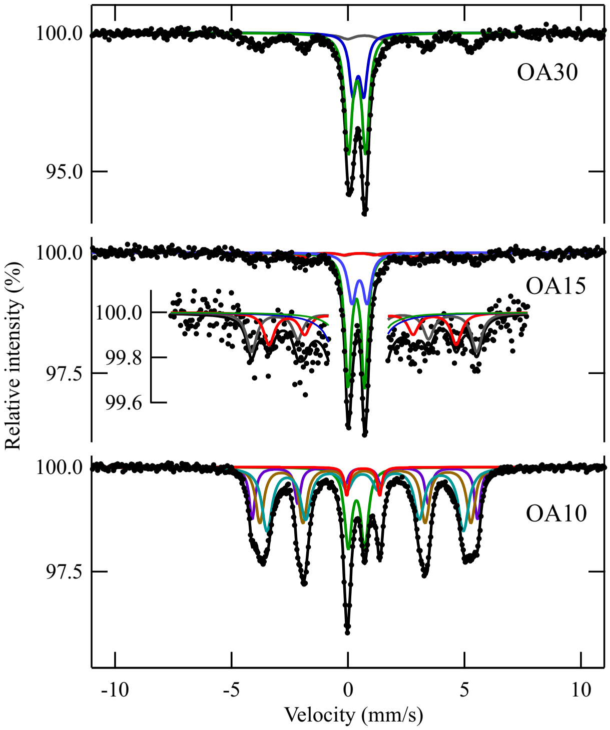

Fig. 2 Mössbauer spectra of iron sulfide particles measured at 293 K

3 Results and discussion

In order to determine the effect of changes in the amount of solvent OA on the size of the resulting particles, SEM images of the particles were obtained (Fig. 1). The particles produced at the lower concentrations of reagents (in larger amounts of solvent OA), OA30 and OA15, had a rough surfaces and were 100-200 nm in size, and no significant differences between them were observed. The particles produced in OA10, at the highest concentration of the reagents, were larger (300-700 nm) and crystalline. The particle size and shape changed dramatically after changing the amount of solvent OA from 15 mL to 10 mL while adding the same amounts of ferrocene, HD, and OT reactants. The solvent OA prevented the aggregation of precipitates produced in the solution, and larger particles were obtained from the more concentrated solution.

Mössbauer spectra of the particles were measured at 293 K (Fig. 2), and the Mössbauer parameters are summarized in Table 1. The OA30 spectrum was fitted to a combination of two sets of doublets and a sextet; the doublets were assigned to Fe_2S_3 and the sextet was assigned to $Fe_{1-x}S$ according to the analysis performed in our previous study [11]. Although $Fe_{1-x}S$ should consist of several sets of sextets because of the different Fe sites in the lattice [12], it was fitted to a single sextet because the absorptions were too weak to distinguish the individual sextets. The OA15 sample had a Mössbauer spectrum very similar to that of OA30, whereas the peak shapes of the hyperfine magnetic component were different. The hyperfine magnetic component of OA15 was fitted into two sets of sextets, which were assigned to $Fe_{1-x}S$ and Fe_2S_3 from their Mössbauer parameters. The yield of $Fe_{1-x}S$ was

Table 1 Mössbauer parameters of the iron sulfide particles

Sample	Temperature	Component	δ mm/s	ΔE_Q mm/s	H T	Γ mm/s	Area int.
OA30	293 K	$Fe_{1-x}S$	0.71(4)	0.04(3)	28.3(1)	0.74(4)	28 %
		Fe_2S_3 (A)	0.38(1)	0.73(2)		0.37(1)	49 %
		Fe_2S_3 (B)	0.44(2)	0.47(4)		0.36(3)	23 %
OA30	6 K	$Fe_{1-x}S$	0.88(1)	-0.24(2)	31.2(1)	0.71(3)	39 %
		Fe_2S_3 (A)	0.52(1)	0.67(1)		0.90(3)	41 %
		Fe_2S_3 (B)(DHMF)	0.53(3)	0.01(5)	16.0*		20 %
OA15	293 K	$Fe_{1-x}S$	0.67(3)	0.04(5)	29.9(2)	0.53(9)	11 %
		Fe_2S_3 (A)	0.35(1)	0.71(1)		0.33(2)	54 %
		Fe_2S_3 (B)	0.49(3)	0.65(2)		0.42(3)	26 %
		Fe_2S_3 (HMF)	0.54(3)	0.16(6)	24.8(2)	0.54(11)	9 %
OA15	6 K	$Fe_{1-x}S$	0.87(2)	-0.14(4)	31.5(1)	0.59(6)	11 %
		Fe_2S_3 (A)	0.49(1)	0.82(1)		0.75(3)	32 %
		Fe_2S_3 (B)(DHMF)	0.49(3)	0.12(5)	16.2*		20 %
		Fe_2S_3 (HMF)	0.58(2)	-0.10(4)	24.7(1)	1.03(5)	38 %
OA10	293 K	$Fe_{1-x}S$ (A)	0.71(1)	0.06(1)	28.1(1)	0.43(5)	29 %
		$Fe_{1-x}S$ (B)	0.67(1)	0.12(1)	26.2(1)	0.52(2)	36 %
		$Fe_{1-x}S$ (C)	0.67(1)	0.08(1)	30.1(1)	0.31(2)	17 %
		$Fe_{1-x}S$ (D)	0.65(1)	1.41(2)		0.23(2)	3 %
		Fe_2S_3 (A)	0.35(1)	0.71(1)		0.37(1)	15 %

*Hyperfine magnetic field at the mode of the distribution

larger in OA30 than in OA15, showing a tendency that the yield of $Fe_{1-x}S$ increases in lower concentration of the reagent in OA. Particles were also produced in further lower concentration adding 60 mL of OA, and the yield of $Fe_{1-x}S$ increased to 46 %. Therefore, it was expected that yield of $Fe_{1-x}S$ decreases (and the yield of Fe_2S_3 increases) at higher concentration, but the Mössbauer spectrum of OA10 was significantly different from those of OA30 and OA15. The relative yield of $Fe_{1-x}S$ increased, and the $Fe_{1-x}S$ spectrum was fitted into three sets of sextets and a doublet, clearly showing the different Fe sites in the $Fe_{1-x}S$ lattice. It was found that OA15 was the optimal concentration for production of Fe_2S_3.

The doublet observed at 293 K can be assigned to small Fe_2S_3 particles. As bulk Fe_2S_3 should be ferromagnetic, the doublet could result from the superparamagnetic behavior of small particles. Ferromagnetic Fe_2S_3 was observed at 293 K in OA15, but the relative intensity in the spectrum was very small. To clarify the effect of this superparamagnetism, the same samples were measured at 6 K (Fig. 3). The Mössbauer spectrum of OA30 at 6 K (Fig. 3a) showed the $Fe_{1-x}S$ sextet ($H = 31.2$ T) clearly. The area intensity of the $Fe_{1-x}S$ sextet was higher at 6 K than at 293 K, and the small portion of the doublet was due to the superparamagnetism of Fe_2S_3. Besides the $Fe_{1-x}S$ sextet and the Fe_2S_3 doublet, a broad

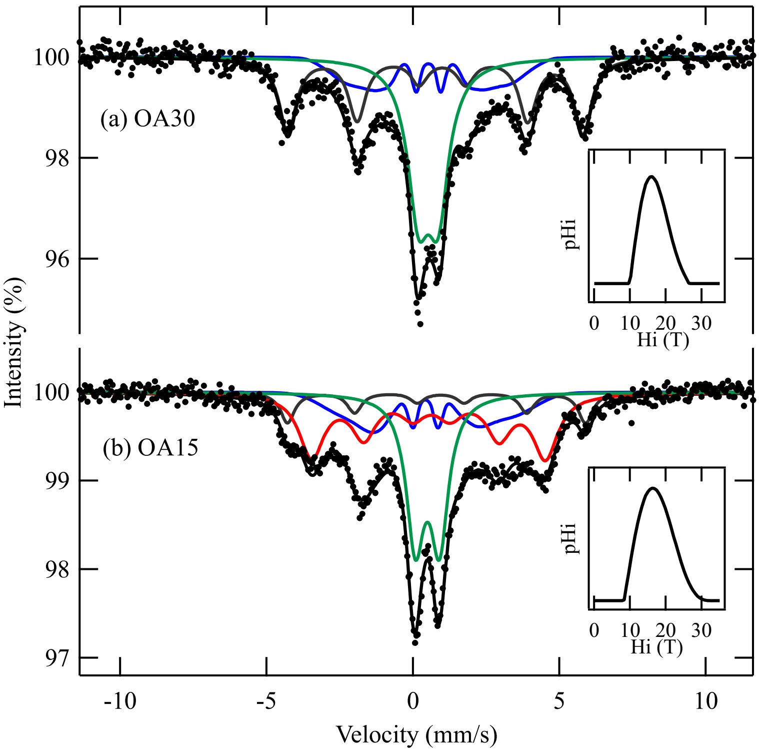

Fig. 3 Mössbauer spectra of iron sulfide particles measured at 6 K

absorption due to the distributed hyperfine magnetic field H was observed. The distribution of H had a maximum at 16.0 T, as shown in the Fig. 3a. A Mössbauer spectrum of OA15 measured at 6 K is shown in Fig. 3b. The intensity of the sextet ($H = 24.7$ T) increased, which was assigned to Fe_2S_3. This H value was in good agreement with the value reported in the literature [6]. Broad absorptions of a distributed hyperfine magnetic field H (maximum at 16.2 T) were also observed in the spectrum, and these were due to either the small crystal size or defects in the Fe_2S_3. The same doublet was also observed at 6 K, and its isomer shift was in the region of Fe(III) species. Although the OA30 and OA15 spectra measured at 293 K were almost identical, Fe_2S_3 with $H = 24.7$ T was observed only in OA15. This indicates that larger Fe_2S_3 crystals were present in the OA15.

XRD patterns of the iron sulfide particles are shown in Fig. 4. The OA30 and OA15 samples had similar XRD patterns, which were a combination of Fe_2S_3 [11] and Fe_7S_8 [13], whereas the OA10 sample had an Fe_7S_8 pattern without Fe_2S_3. The XRD patterns were in good agreement with the assignments made on the basis of the Mössbauer spectra. As XRD is only sensitive to long-range periodic structure, it cannot detect amorphous Fe_2S_3. Fe_7S_8 is one of the various types of pyrrhotite $Fe_{1-x}S$, and was reported to have vacancy ordering in the FeS lattice [13]. The Fe_2S_3 XRD pattern observed in this experiment did not correspond to that reported previously in the literature [3, 4]. As Fe_2S_3 appeared along with pyrrhotite in our experiment, Fe_2S_3 was considered to have a structure similar to that of pyrrhotite. The S atoms occupy a face-centered-cubic (fcc) lattice, and Fe atoms occupy only Oh position in pyrrhotite FeS, whereas Fe atoms occupy both Oh and Td positions

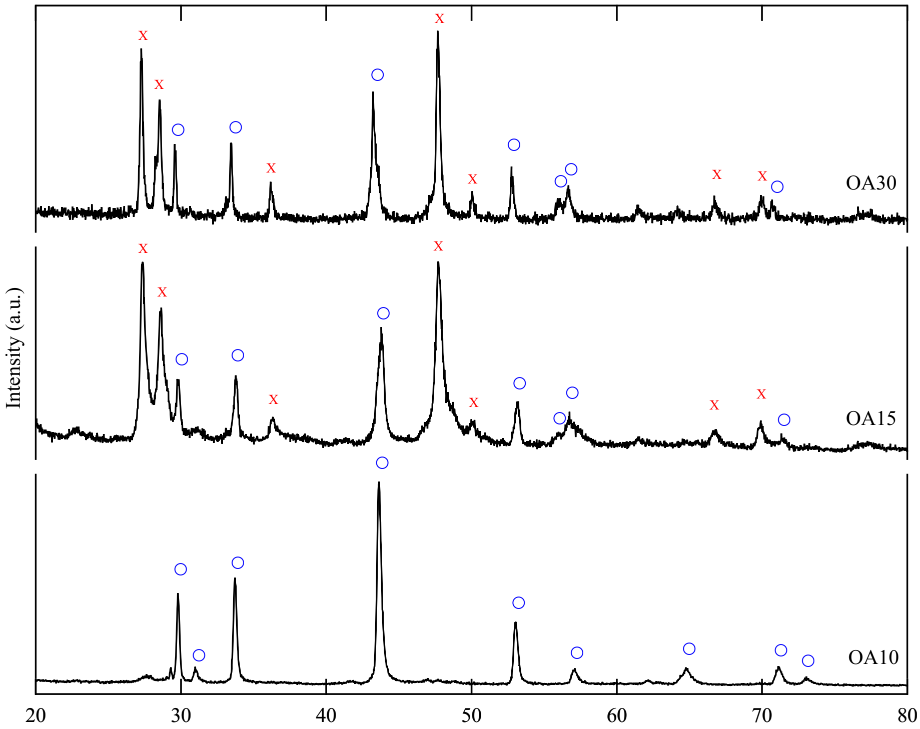

Fig. 4 XRD patterns of iron sulfide particles. Fe_2S_3 (x) and Fe_7S_8 (o) were observed simultaneously

in Fe_3S_4. It has been proposed that Fe_2S_3 has a spinel structure analogous to maghemite γ-Fe_2O_3 [10]. In this case, cation vacancies occur in the Oh position of the greigite Fe_3S_4.

We performed calculations to estimate the structure of Fe_2S_3. When we assumed that Fe_2S_3 has a structure analogous to maghemite γ-Fe_2O_3, the estimated XRD pattern did not coincide with the observed pattern. When we tentatively assumed that the Fe_2S_3 lattice had 33.3 % vacancies in the Td-position Fe of the spinel greigite Fe_3S_4 and that the lattice constant was enlarged to $a = 1.08$ nm, the XRD pattern calculated using the RIETAN program [14] coincided fairly well with the observed pattern in the region of $2\theta < 30°$. DFT calculation of the structure was performed using WIEN2k [15], and the Fe atoms in the Oh and Td positions were estimated to have hyperfine magnetic fields of $H = 22$ and 24 T, respectively. This calculation was also in agreement with our experimental results. As the Fe_2S_3 particles obtained in this study were contaminated by amorphous Fe_2S_3 and $Fe_{1-x}S$, synthesis of pure Fe_2S_3 is required to confirm the exact lattice structure.

4 Conclusion

Metastable Fe_2S_3 particles were successfully produced by a polyol method. Optimal conditions for the production of particles containing crystalline Fe_2S_3 were determined, although the resulting particles still contained amorphous Fe_2S_3 and $Fe_{1-x}S$. The XRD pattern of the Fe_2S_3 lattice was observed, and the Mössbauer spectrum of the Fe_2S_3 lattice showed a hyperfine magnetic field $H = 24.7$ T at 6 K. The results suggest that the Fe_2S_3 lattice had a spinel greigite Fe_3S_4 structure with Fe vacancies in the Td position.

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