

# Mössbauer study of $\varepsilon$ - $\text{Al}_x\text{Fe}_{2-x}\text{O}_3$ nanomagnets

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**Abstract** A series of  $\text{Al}^{3+}$ -substituted  $\varepsilon$ - $\text{Fe}_2\text{O}_3$  nanomagnets,  $\varepsilon$ - $\text{Al}_x\text{Fe}_{2-x}\text{O}_3$  ( $x = 0, 0.21, 0.40$ ), with large coercive field values was studied by  $^{57}\text{Fe}$  Mössbauer spectroscopy. The hyperfine field and absorption coefficient in the Mössbauer spectra changed with  $x$ . These behaviors can be explained by the selective replacement of  $\text{Fe}^{3+}$  ions with  $\text{Al}^{3+}$  ions. This is the first report on the Mössbauer spectra of metal-substituted  $\varepsilon$ - $\text{Fe}_2\text{O}_3$ .

**Keywords** Mössbauer spectroscopy ·  $\varepsilon$ - $\text{Fe}_2\text{O}_3$  ·  $\varepsilon$ - $\text{Al}_x\text{Fe}_{2-x}\text{O}_3$  · Nanomagnet

## 1 Introduction

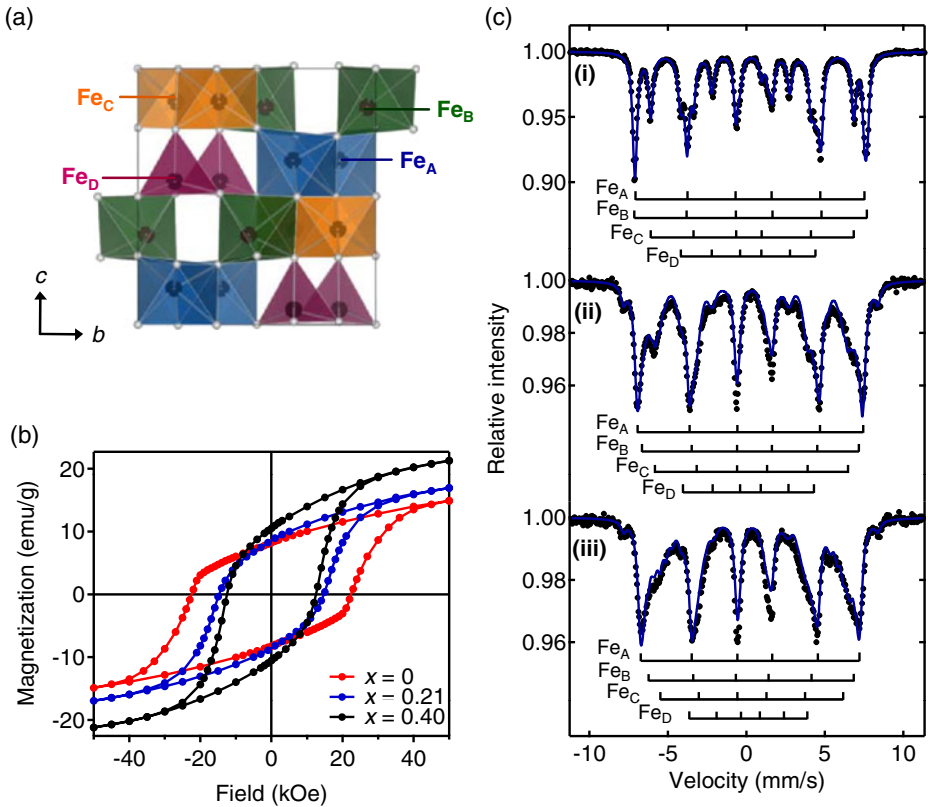
Iron oxide,  $\text{Fe}_2\text{O}_3$ , has four polymorphs at normal pressure and temperature:  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\varepsilon$ -phases [1]. Among these,  $\alpha$ - $\text{Fe}_2\text{O}_3$  with a corundum structure (hematite) and  $\gamma$ - $\text{Fe}_2\text{O}_3$  with a spinel structure (maghemite) exist in nature, and various Mössbauer studies on these phases have been reported [1, 2]. In contrast,  $\varepsilon$ - $\text{Fe}_2\text{O}_3$  is very rare and preparation of a single phase of  $\varepsilon$ - $\text{Fe}_2\text{O}_3$  is difficult. Hence, Mössbauer studies of  $\varepsilon$ - $\text{Fe}_2\text{O}_3$  have been limited to mixed samples containing  $\alpha$ - and  $\gamma$ - $\text{Fe}_2\text{O}_3$  [3]. However, our group successfully synthesized a single phase of  $\varepsilon$ - $\text{Fe}_2\text{O}_3$  in 2004 using a combination of reverse-micelle and sol-gel techniques, and observed an extremely large coercive field value of 20 kOe at room temperature [4–10].

$\varepsilon$ - $\text{Fe}_2\text{O}_3$  has an orthorhombic crystal structure in the  $Pna2_1$  space group ( $a = 5.102 \text{ \AA}$ ,  $b = 8.781 \text{ \AA}$ ,  $c = 9.466 \text{ \AA}$ ) with four nonequivalent  $\text{Fe}^{3+}$  sites, i.e., distorted

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**Fig. 1** **a** Crystal structure of  $\epsilon$ - $\text{Fe}_2\text{O}_3$ , **b** magnetization versus external magnetic field plots for  $\epsilon$ - $\text{Al}_x\text{Fe}_{2-x}\text{O}_3$  ( $x = 0, 0.21, 0.40$ ) at room temperature, and **c** Mössbauer spectra of  $\epsilon$ - $\text{Al}_x\text{Fe}_{2-x}\text{O}_3$  at room temperature for  $x =$  (i) 0, (ii) 0.21, and (iii) 0.40. Black dots and blue lines represent the observed and fitted spectra, respectively

octahedral  $\text{Fe}_A$  and  $\text{Fe}_B$  sites, regular octahedral  $\text{Fe}_C$  site, and tetrahedral  $\text{Fe}_D$  site (Fig. 1a) [10]. In addition, we have synthesized metal-substituted  $\epsilon$ -iron oxide ( $\epsilon$ - $\text{M}_x\text{Fe}_{2-x}\text{O}_3$ ,  $\text{M} = \text{Al}, \text{Ga}, \text{In}$ ) [11–14]. Figure 1b shows the magnetic hysteresis loops of  $\epsilon$ - $\text{Al}_x\text{Fe}_{2-x}\text{O}_3$  [13].  $\epsilon$ - $\text{Ga}_x\text{Fe}_{2-x}\text{O}_3$  and  $\epsilon$ - $\text{Al}_x\text{Fe}_{2-x}\text{O}_3$  show high-frequency millimeter wave absorption, while  $\epsilon$ - $\text{In}_x\text{Fe}_{2-x}\text{O}_3$  exhibits a phase transition between ferrimagnetism and antiferromagnetism [11–13, 15]. In this paper, we report  $^{57}\text{Fe}$  Mössbauer spectra of  $\text{Al}^{3+}$ -substituted  $\epsilon$ - $\text{Fe}_2\text{O}_3$ .

## 2 Experimental section

A series of  $\epsilon$ - $\text{Al}_x\text{Fe}_{2-x}\text{O}_3$  ( $x = 0, 0.21, 0.40$ ) spherical nanoparticles with average sizes of 24–54 nm were synthesized using the methods reported in our previous paper [13]. The  $^{57}\text{Fe}$  Mössbauer spectra of  $\epsilon$ - $\text{Al}_x\text{Fe}_{2-x}\text{O}_3$  were measured at room temperature in a transmission geometry using a  $^{57}\text{Co}/\text{Rh}$  source. The obtained spectra were analyzed with WinNormos software using the least squares method.

### 3 Results and discussion

Figure 1c(i) shows the Mössbauer spectrum of the sample for  $x = 0$ , which consists of four sextets with line area ratios of 3:2:1:1:2:3. These four sextets belong to the four Fe<sup>3+</sup> (Fe<sub>A</sub>, Fe<sub>B</sub>, Fe<sub>C</sub>, and Fe<sub>D</sub>) sites in  $\varepsilon$ -Fe<sub>2</sub>O<sub>3</sub>. Least squares analysis indicates that the hyperfine field (HF) values of Fe<sub>A</sub>, Fe<sub>B</sub>, Fe<sub>C</sub>, and Fe<sub>D</sub> sites are 45.3, 46.0, 40.1, and 26.6 T, respectively. The isomer shift (IS) values of the Fe<sub>A</sub>–Fe<sub>D</sub> sites are 0.35, 0.39, 0.37, and 0.19 mm/s, respectively, while the quadrupole shift (QS) values are  $-0.23$ ,  $-0.22$ ,  $0.00$ , and  $-0.17$  mm/s, respectively. These observed Mössbauer parameters correspond to the previously reported values [1, 3, 6, 7, 15].

Figure 1c(ii) and (iii) show the Mössbauer spectra of the samples  $x = 0.21$  and  $0.40$ , respectively. In the case of magnetic materials, the HF value of an Fe<sup>3+</sup> ion depends on the product of the number of nearest neighboring Fe<sup>3+</sup> ions ( $Z$ ) and the superexchange interaction between the center Fe<sup>3+</sup> ion and the neighboring Fe<sup>3+</sup> ions through O<sup>2-</sup> ions ( $J_{ex}$ ). Hence, when a magnetic Fe<sup>3+</sup> ( $S = 5/2$ ) is substituted by a diamagnetic Al<sup>3+</sup> ( $S = 0$ ), one sextet for each Fe<sup>3+</sup> site is split into several sextets due to the appearance of reduced  $Z$  integers ( $Z - 1$ ,  $Z - 2$ , ...). Thus, we analyzed the Mössbauer spectra for  $x = 0.21$  and  $0.40$  using more than one sextet assuming that only Fe<sub>D</sub> site is replaced by Al<sup>3+</sup> ion, since Fe<sub>D</sub> site is expected to be replaced by Al<sup>3+</sup> ion on the basis of our previous knowledge. Consequently, the average HF values of the Fe<sub>A</sub>, Fe<sub>B</sub>, Fe<sub>C</sub>, and Fe<sub>D</sub> sites for the sample  $x = 0.21$  are 44.6, 42.7, 37.5, and 26.0 T, the IS values are 0.38, 0.38, 0.34, and 0.19 mm/s, the QS values are  $-0.29$ ,  $-0.25$ ,  $-0.02$ , and  $-0.13$  mm/s, and the relative absorption intensities are 1, 1, 1, and 0.4, respectively. For the sample  $x = 0.40$ , the HF values of Fe<sub>A</sub>–Fe<sub>D</sub> sites are 42.9, 39.4, 35.2, and 24.4 T, the IS values are 0.38, 0.33, 0.34, and 0.19 mm/s, the QS values are  $-0.30$ ,  $-0.28$ ,  $-0.02$ , and  $-0.13$  mm/s, and the relative absorption intensities are 1, 1, 1, and 0.2, respectively. In these samples,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is contained as an impurity.

As the degree of Al<sup>3+</sup> substitution increased, the HF values of the Fe<sub>A</sub>–Fe<sub>D</sub> sites gradually decreased, and the absorption intensity of the Fe<sub>D</sub> site significantly decreased. These behaviors can be understood by considering that the Al<sup>3+</sup> ion selectively replaces the Fe<sub>D</sub> site. This interpretation corresponds to the results of the XRD patterns in our previous paper [13]. Al<sup>3+</sup> ions predominantly substitute for the tetrahedral Fe<sub>D</sub> site because Al<sup>3+</sup> ions have difficulty replacing the octahedral Fe<sup>3+</sup> sites due to the smaller ionic radius of octahedral Al<sup>3+</sup> (0.535 Å) compared to that of Fe<sup>3+</sup> (0.645 Å) [16]. Hence, Al<sup>3+</sup> ions prefer to substitute for the smaller tetrahedral Fe<sup>3+</sup> site.

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