Mn-Substitution Effects on the Magnetic and Zero-Field Ferromagnetic Resonance Properties of ε-Fe_2O_3 Nanoparticles

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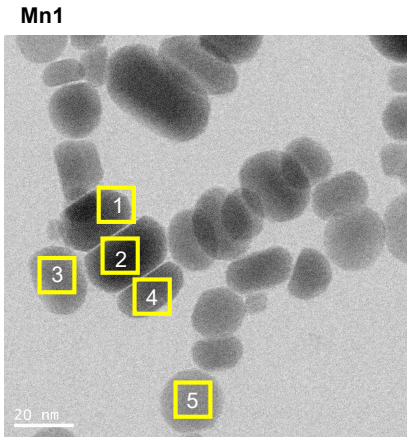
§ 1. STEM quantitative analysis



Sample	[Mn]/[Mn+Fe]
1	0.05
2	0.05
3	0.05
4	0.05
5	0.04

Figure S1. STEM images of **Mn1** with quantitative analysis.

§ 2. Phase diagram

Additional samples were prepared with a targeted feed ratio of [Mn]/[Mn + Fe] as 0.15 (**Mn3**), 0.2 (**Mn4**), 0.25 (**Mn5**), and 0.3 (**Mn6**). Iron oxy-hydroxide (β-FeO(OH)) sol and $Mn(NO_3)_2$ were added to 420 mL water with the following amounts of Fe (n_{Fe}) in β-FeO(OH) and Mn (n_{Mn}): (n_{Fe}, n_{Mn}) = (8.52, 1.50 mmol) for **Mn3**, (8.02, 2.00 mmol) for **Mn4**, (7.51, 2.51 mmol) for **Mn5**, and (7.01, 3.01 mmol) for **Mn6**. The observed x values are almost the same as the target values (i.e., 0.15 for **Mn3**, 0.20 for **Mn4**, 0.25 for **Mn5**, and 0.29 for **Mn6**).

The PXRD patterns of samples **Mn3**–**Mn6** were measured and analyzed (Fig. S2a). The ε-phase, β-phase, and spinel-phase for **Mn3** are 49.3%, 5.8%, and 44.9%, while those for **Mn4** are 15.4%, 0.2%, and 84.4%, respectively. At higher Mn ratios, the ε-phase is not formed. **Mn5** contains 7% of the β-phase and 93% of the spinel-phase, whereas **Mn6** contains 1.8% of the β-phase and 98.2% of the spinel-phase. Figure S2b shows the phase diagram.

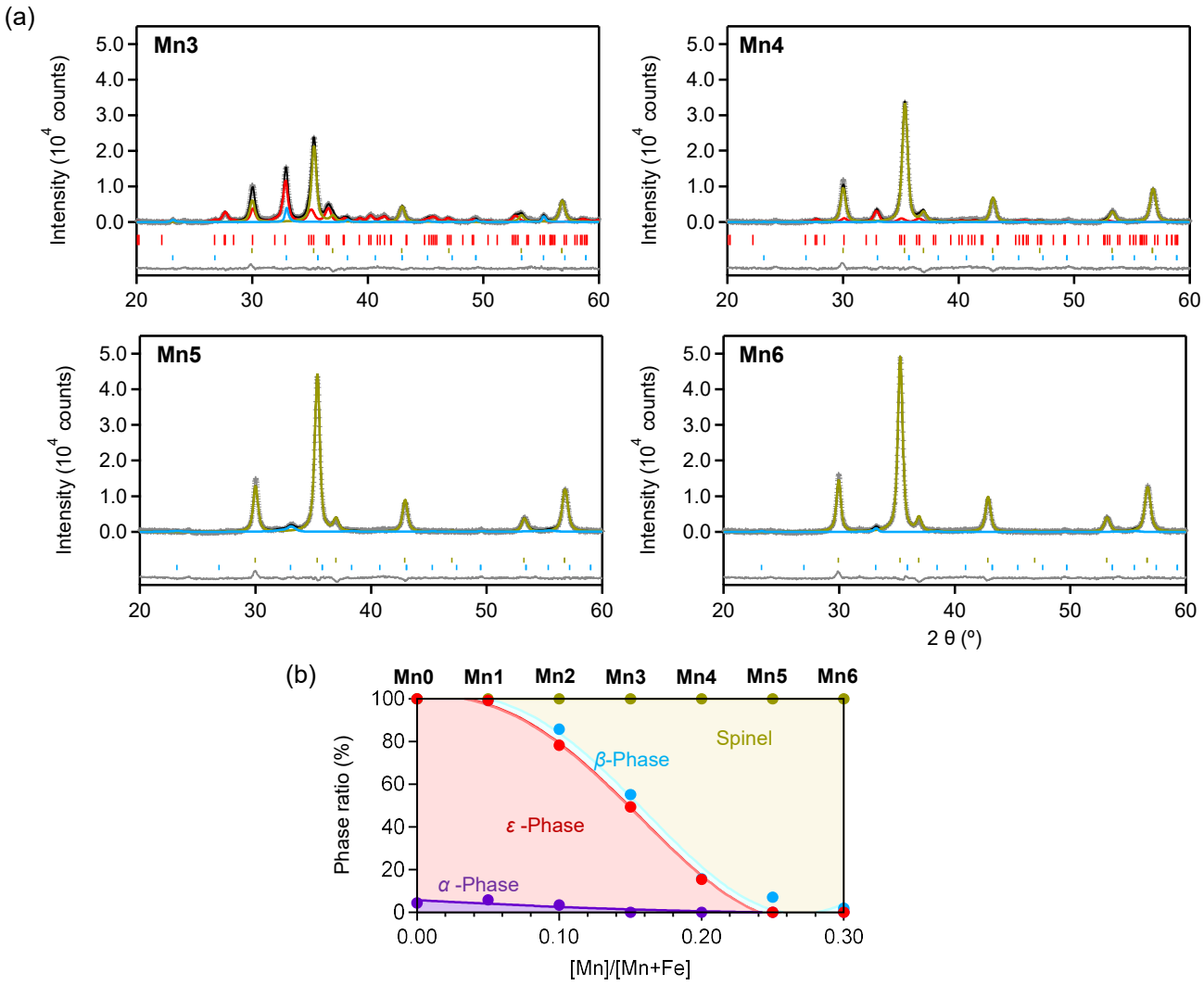


Figure S2. (a) PXRD patterns with Rietveld analyses. Grey dots, black lines, and grey lines indicate the observed pattern, the calculated pattern, and their difference, respectively. Red, blue, and gold lines denote the calculated patterns for the ε-phase, β-phase, and spinel-phase, respectively. Red, blue, and gold bars indicate the calculated Bragg positions for the ε-phase, β-phase, and spinel-phase, respectively. (b) Phase composition of oxides with respect to the [Mn]/[Mn+Fe] ratio measured by XRF.

§ 3. Crystal structure parameters

Table S1. Structural parameters of the ε-phase obtained from Rietveld analysis of the PXRD patterns. CCDC-2380301, CCDC-2380300 and CCDC-2380302 contain structural information of the ε-Fe_2O_3 phase for **Mn0**, **Mn1**, and **Mn2**, respectively, in a crystallographic information file format. These files are available from the Cambridge Crystallographic Data Centre at https://www.ccdc.cam.ac.uk/structures/.

		Mn0	**Mn1**	**Mn2**
Phase ratio (wt.%)		95.7(3)	93.9(3)	74.9(4)
a (Å)		5.0907(4)	5.0978(4)	5.1031(4)
b (Å)		8.7922(8)	8.7823(7)	8.7759(8)
c (Å)		9.4764(5)	9.4694(5)	9.4661(7)
V (Å^3)		424.15(6)	423.95(5)	423.93(6)
R_{wp} (%)		0.43	0.46	0.42
S		0.537	0.085	0.092
Mn	A	0	0.0(6)	0.0(6)
Occupancy (%)	B	0	0.2(2)	0.4(3)
	C	0	0.0(4)	0.0(4)
	D	0	0	0
A	*x*/*a*	0.314(4)	0.312(4)	0.315(3)
	y/*b*	0.345(2)	0.348(2)	0.345(2)
	z/*c*	0.155(9)	0.153(7)	0.154(6)
B	*x*/*a*	0.321(2)	0.323(2)	0.324(2)
	y/*b*	0.030(1)	0.028(1)	0.027(1)
	z/*c*	0.363(9)	0.361(7)	0.359(6)
C	*x*/*a*	0.311(2)	0.310(1)	0.317(1)
	y/*b*	0.658(1)	0.659(1)	0.656(1)
	z/*c*	0.374(8)	0.375(7)	0.375(6)
D	*x*/*a*	0.195(3)	0.191(3)	0.195(2)
	y/*b*	0.850(2)	0.850(2)	0.853(1)
	z/*c*	0.077(9)	0.076(7)	0.073(6)
O1	*x*/*a*	0	0	0
	y/*b*	0	0	0
	z/*c*	0	0	0
O2	*x*/*a*	0.012(6)	0.023(6)	0.012(6)
	y/*b*	0.325(3)	0.319(2)	0.324(3)
	z/*c*	0.015(1)	0.013(9)	0.003(8)
O3	*x*/*a*	0.034(7)	0.028(6)	0.040(6)
	y/*b*	0.652(5)	0.651(4)	0.649(4)
	z/*c*	0.013(1)	0.015(9)	0.014(8)
O4	*x*/*a*	0.156(10)	0.156(8)	0.159(8)
	y/*b*	0.503(4)	0.509(3)	0.508(4)
	z/*c*	0.252(9)	0.246(7)	0.253(6)
O5	*x*/*a*	0.157(8)	0.168(9)	0.166(9)
	y/*b*	0.833(4)	0.832(4)	0.833(4)
	z/*c*	0.264(9)	0.265(7)	0.265(7)
O6	*x*/*a*	0.172(8)	0.172(7)	0.172(8)
	y/*b*	0.159(6)	0.156(5)	0.160(5)
	z/*c*	0.234(9)	0.235(7)	0.234(6)

§ 4. Magnetic properties of Mn6

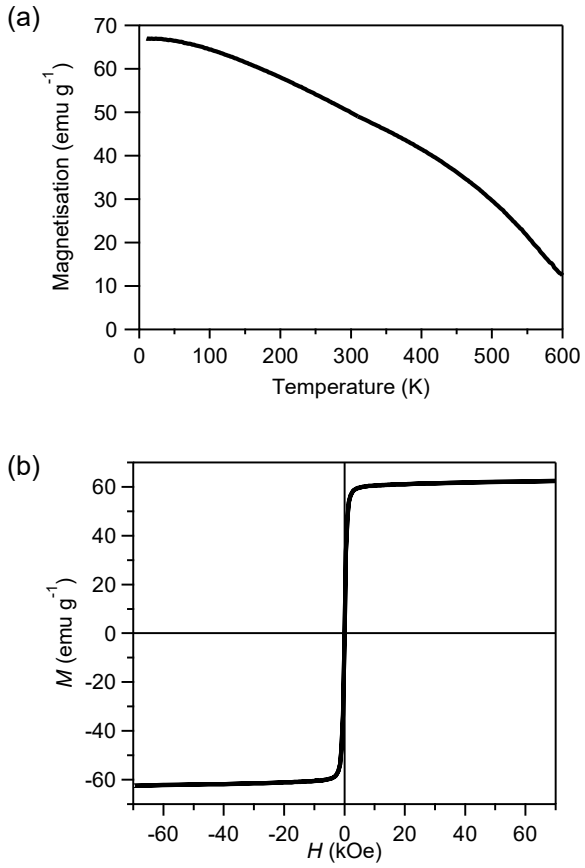


Figure S3. Magnetic properties of **Mn6**. (a) FCM curves in an external field of 1 kOe. (b) Magnetisation versus external magnetic field curve at 300 K.