

Topotactic Oxidation Process from Magnetite to Maghemite Studied by
Rietveld Analysis and ^{119}Sn Mössbauer Spectroscopy

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The topotactic oxidation process from magnetite to maghemite was investigated, using tin substituted magnetite by means of the Rietveld analysis of the powder X-ray diffraction and the ^{119}Sn Mössbauer spectroscopy.

In the study of magnetic substances, hyperfine magnetic field at a diamagnetic probe nucleus provides useful information about chemical bond and magnetic interactions because it is very sensitive to nearest neighbors. Many experimental techniques, such as ^{119}Sn and ^{121}Sb Mössbauer spectroscopy,^{1,2)} ^{111}Cd TDPAC,³⁾ and ^{69}Ga and ^{114}In NMR,⁴⁾ have been developed for these studies. The hyperfine magnetic field at the Sn nucleus ($H(\text{Sn})$), doped in ferrimagnetic spinel, distributes widely from 250 kOe in Ni-ferrite to 45 kOe in Mg-ferrite ($T=85\text{ K}$).¹⁾ Similarly in the topotactic oxidation process from the tin substituted magnetite to maghemite, the $H(\text{Sn})$ changed from 241 kOe to 115 kOe at 4.2 K.⁵⁾ Magnetite (Fe_3O_4) belongs to a typical inverse spinel structure ($\text{Fe}^{3+}[\text{Fe}^{2+}\text{Fe}^{3+}]\text{O}_4$, space group $\text{Fd}\bar{3}\text{m}$, No.227), in which 32(e) positions are occupied by oxide anions, 8(a) positions by Fe^{3+} cations, and 16(d) positions by an equivalent amount of Fe^{3+} and Fe^{2+} cations. Whereas in the maghemite ($\gamma\text{-Fe}_2\text{O}_3$) only B-sites (16(d) position) are different from those of magnetite and may be written as $\text{Fe}^{3+}[\text{Fe}_{5/3}\square_{1/3}]\text{O}_4$, where \square denotes vacancy.

In this study, we will report the topotactic oxidation process from magnetite to maghemite by means of the powder X-ray diffraction and the ^{119}Sn Mössbauer spectroscopy and discuss about the relation between the $H(\text{Sn})$ and the cation distribution during the oxidation process.

Tin substituted magnetite ($\text{Fe}_{3-x}\text{Sn}_x\text{O}_4$, $x<0.20$) was prepared from the alkaline solution containing FeSO_4 and Na_2SnO_3 ,⁶⁾ and was identified to be single phase. The cation distribution in the spinel lattice was determined by the Rietveld method using a Fortran program developed by F. Izumi.⁷⁾

The cubic lattice constants of the $\text{Fe}_{3-x}\text{Sn}_x\text{O}_4$ increased linearly with

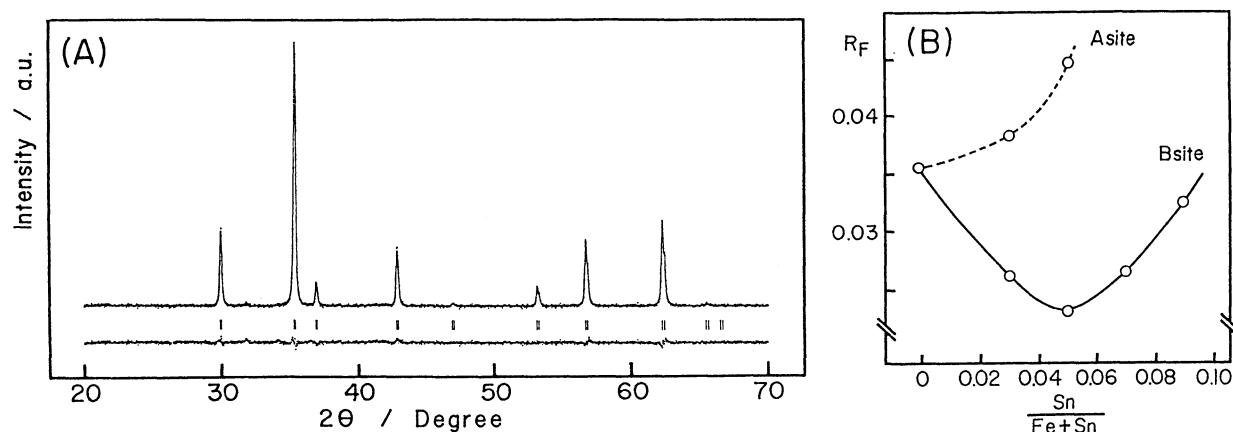


Fig. 1.(A) Rietveld analysis of the tin substituted magnetite ($x=0.10$). The solid line is the best-fit profile and the points are raw data. The difference between them are shown at the bottom. (B) The R_F value is plotted against the mole fraction of the Sn atom on the A or B-site.

the tin concentration in the range $x < 0.20$, suggesting a homogeneous incorporation of the tin into the spinel lattice. The Sn^{4+} ions are believed to occupy only the B-sites (16(d) position) in the spinels from many experimental evidences. However, it is worthwhile to determine the Sn site for the sample prepared by a wet method. Furthermore, the determination of the Sn site is important for the discussion about the $H(\text{Sn})$. Figure 1(A) shows the final result of the Rietveld analysis for $\text{Fe}_{3-x}\text{Sn}_x\text{O}_4$ ($x=0.10$) and Fig. 1(B) plots the R_F value against the mole fraction of Sn on the A or B-site. The final structural parameters for $x=0.10$ are summarized in Table 1. Figure 1(B) shows clearly that the Sn atoms occupy B-sites with the mole fraction of 0.05, i.e. the cation distribution could be described as $(\text{Fe}^{3+})[\text{Fe}_{0.8}^{3+}\text{Fe}_{1.1}^{2+}\text{Sn}_{0.1}^{4+}]\text{O}_4$ assuming an electrical neutrality condition, $2\text{Fe}^{3+} = \text{Sn}^{4+} + \text{Fe}^{2+}$. Furthermore, the incorporated mole fraction of the Sn in the B-site agrees very well with that expected from the stoichiometry in the preparation. Figure 2 plots the lattice constants ($T=293\text{ K}$) against the heating time at $100\text{ }^\circ\text{C}$ for the $x=0$ and 0.05 samples. These samples remained single-phase spinels during the oxidation process and the lattice constants continuously decreased with increasing the heating time. This fact suggests that continuous solid solutions are formed between magnetite and maghemite containing the Sn atom in the B-site. Table 1 shows structural parameters for the tin substituted maghemite, which was obtained after 100 hours heating of $\text{Fe}_{3-x}\text{Sn}_x\text{O}_4$ ($x=0.05$) at $100\text{ }^\circ\text{C}$. The mole fraction of Sn in the B-site and the occupation factor at this site could not be determined independently from the Rietveld analysis. Therefore, the mole fraction of Sn in the B-site was assumed to be $8x/15$ on the basis of the oxidation equation ($4\text{Fe}_{3-x}\text{Sn}_x\text{O}_4 + \text{O}_2 \rightarrow 6\text{Fe}_{2-2x/3}\text{Sn}_{2x/3}\text{O}_3$) and the expected cation distribution in the spinel

Table 1. Structural parameters refined by the Rietveld analysis. (A) $\text{Fe}_{3-x}\text{Sn}_x\text{O}_4$ ($x=0.1$), (B) Oxidation product of the $x=0.05$ sample at 100°C

Atom	Position	Occupation	$x=y=z$	$B/\text{\AA}^2$	$a/\text{\AA}$	R_F
Fe	8(a)	1	0			
(A) Fe(95%)+Sn(5%)	16(d)	1	5/8	0.50(5) ^{b)}	8.428(1)	0.023
O	32(e)	1	0.379(1)			
Fe	8(a)	1	0			
(B) Fe(97.3%)+Sn(2.7%)	16(d)	0.84(1)	5/8	0.60(6) ^{b)}	8.350(1)	0.030
O	32(e)	1	0.377(1)			

a) $R_F = \sum |\sqrt{I_{\text{obs}}} - \sqrt{I_{\text{cal}}}| / \sum \sqrt{I_{\text{obs}}}$. b) Overall isotropic thermal parameter.

lattice $((\text{Fe}^{3+})[\text{Fe}_{5/3-16x/9}^{3+}\text{Sn}_{1/3-8x/9}^{4+}\text{O}_4])$. The occupation factor at the B-site thus obtained was 0.84 and this value is almost consistent with that expected for the tin substituted maghemite ($5/6=0.833$).

^{119}Sn Mössbauer spectra and the distributions of the $H(\text{Sn})$ as a function of the heating time are shown in Fig. 3 for the $x=0.05$ sample. With increasing the heating time in air at 100°C , the absorption became broad due to the superposition of several components having different hyperfine fields. However, as is apparent from Fig. 3(B), the distribution of the $H(\text{Sn})$ does not change continuously but the $H(\text{Sn})$ peak corresponding to Fe_3O_4 becomes weaker and a new peak corresponding to $\gamma\text{-Fe}_2\text{O}_3$ appears. The hyperfine field at 293 K corresponding to magnetite and maghemite were determined to be 208 and 131 kOe, respectively, and consistent with previous values.⁵⁾ The conflicting results from the X-ray and the Mössbauer techniques may arise from the fact that the former reflects the averaged bulk structure whereas the latter reflects only the nearest neighbors at

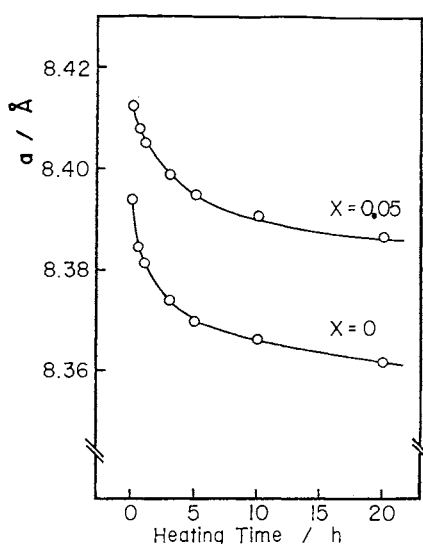


Fig. 2. Cubic lattice constant (293 K) against the heating time for tin substituted magnetite.

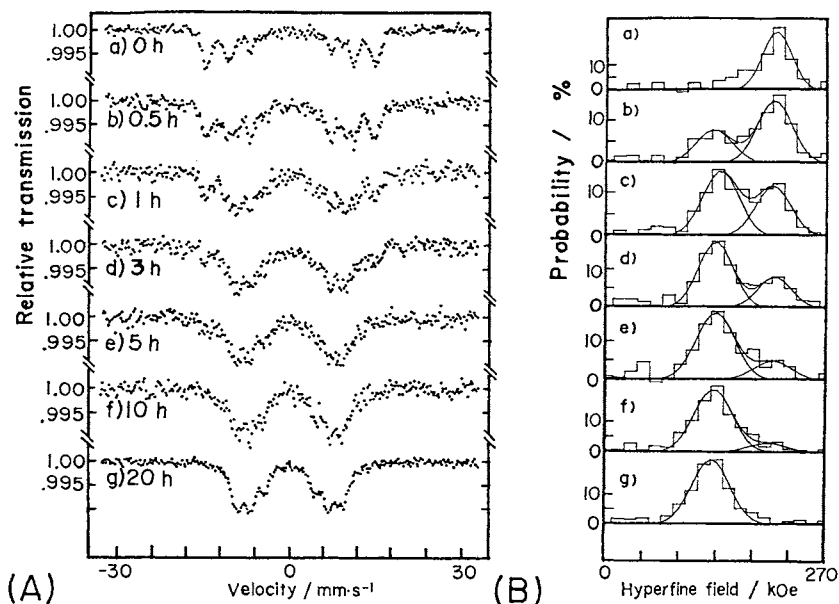


Fig. 3. (A) A series of ^{119}Sn Mössbauer spectra (293 K) as a function of the heating time at 100°C and (B) the distribution of the $H(\text{Sn})$.

A and B-sites. According to Lyubutin et al., the $H(\text{Sn})$ is very sensitive to the nearest neighbors and is semiempirically expressed as,⁸⁾

$$H(\text{Sn}) = m H(\text{A}) + n H(\text{B}),$$

where $H(\text{A})$ is a supertransferred field from the A-site through A-O-B bond, $H(\text{B})$ is a direct transferred field from the B-site, and m and n are the numbers of the magnetic nearest neighbors at the A

and B-site, respectively. In the case of magnetite, there are six Fe^{3+} at the A-site and three Fe^{3+} and three Fe^{2+} at the B-site as the nearest neighbors, respectively. Whereas in maghemite, only B-site is different from magnetite and occupied by five Fe^{3+} and one vacancy. Using these relations and observed $H(\text{Sn})$ values, $H(\text{A})$ and $H(\text{B})$ from Fe^{3+} and Fe^{2+} were estimated by Shigematsu et al.⁵⁾ These nearest neighbors are schematically shown in Fig. 4, where one Fe^{3+} in the B-site is replaced by a Fe^{2+} because of the local charge neutrality. In the oxidation process from Fe_3O_4 to $\gamma\text{-Fe}_2\text{O}_3$, there are two steps, (1) diffusion of 1/6 of the iron atom from the B-site to the surface, (2) oxidation of the Fe^{2+} to Fe^{3+} at the B-site. Then, one of the possible explanation for the step-wise change of $H(\text{Sn})$ in Fig. 3(B) may be due to the difference between rate constants of these two steps. If step (2) is much faster than that of step (1), the nearest neighbors seen by ^{119}Sn Mössbauer spectroscopy is restricted to two models shown in Fig. 4. This is quite reasonable because the local charge neutrality condition is always satisfied because of the electron hopping between B-sites.

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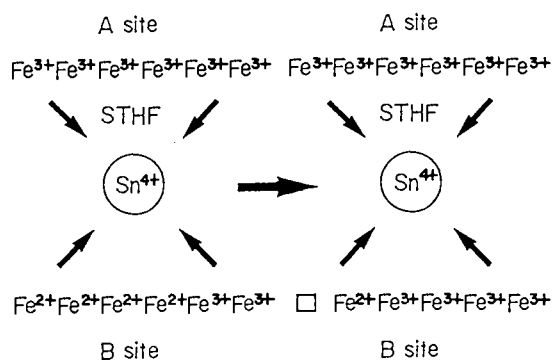


Fig. 4. Tin nearest neighbors in magnetite and maghemite.