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Effect of the Chlorine Contents on the Lattice Constants of β-FeOOH

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Synopsis. The lattice constants of β-FeOOH including chlorine and fluorine, were determined by X-ray diffractometry. The chlorine-content dependence of the lattice constants showed that chlorine ions are distributed at random, occupying certain sites of β-FeOOH.

β-FeOOH, also known as akaganeite, is a kind of iron(III) oxide hydroxide. It is formed as a hydrolysis product from iron(III) salt solutions containing Cl^- or F^- ions. It is well known that Cl^- or F^- ions are necessary for the formation of β-FeOOH and that the β-FeOOH thus produced contains Cl or F in the crystal without exception. Recently, Mossbauer spectroscopic studies have indicated that iron atoms exist in two or three different chemical states in the β-FeOOH crystal.[1-4] In a previous paper,[5] we reported on the synthesis of β-FeOOH from various solutions containing different concentrations of Cl^- and F^-, and proposed the possibility that Cl^- and F^- ions are directly bound to Fe^{3+} ions in β-FeOOH.

The present paper reports the variation in the lattice constants of β-FeOOH determined by X-ray diffractometry and its correlation to the difference in Cl and F concentrations in the crystal.

Experimental

Preparation of β-FeOOH. β-FeOOH was prepared by heating Fe(III) solutions containing various concentrations of Cl^- and F^- ions. The details were described previously.[5] The X-ray diffraction patterns and the electron micrographs proved the purity of the β-FeOOH thus synthesized.

Measurement of X-Ray Diffraction Patterns. An X-ray diffractometer was operated with an Fe tube. The powder and the scan speed were 28 kV (6 mA) and 0.25° min^{-1}, respectively.

Analysis of Diffraction Data. The lattice constants were calculated from the 2θ values of the (211) and (400) diffraction lines. The peak positions were determined by drawing the tangent lines on both sides of the diffraction profiles. The diffraction lines of α-Fe_2O_3[6] were used for the correction of the diffraction angle.

Results and Discussion

The structure of β-FeOOH is tetragonal,[7,8] and several observed values of the lattice constants have been reported (*e.g.*, $a=10.48$ Å, and $c=3.023$ Å).

Since Mackay's studies of the crystal,[7] Cl^- and F^- ions have been believed to occupy the hole site in β-FeOOH, but no experimental confirmation has yet been made. We proposed that Cl^- and F^- ions are directly bound to the Fe^{3+} ion in the β-FeOOH crystal.[5] The expansion or the contraction of the lattice in the crystal can be expected without any contradiction if Cl^- and F^- ions are located at certain sites in β-FeOOH.

Table 1. Chlorine and fluorine contents and the observed lattice constants

Sample	Cl/Fe$^{a)}$	F/Fe$^{a)}$	$a^{b)}$/Å	$c^{b)}$/Å
A	0.148	0	10.56	3.035
B	0.143	0	10.54	3.034
C	0.110	0.113	10.51	3.033
D	0.056	0.197	10.48	3.023
E	0.031	0.281	10.46	3.030
F	0.023	0.332	10.46	3.026
G	0.014	0.384	10.46	3.023

a) Cl/Fe and F/Fe are represented as atomic ratios; the error is below 5%. b) The errors are ±0.01 Å and 0.001 Å for *a* and *c*, respectively.

Table 1 shows the Cl and F contents in synthesized β-FeOOH and the observed lattice constants. If β-FeOOH is regarded as non-stoichiometric, the variation in the lattice constants will follow Vegard's law.[9]

$$a = a_0 + px_{Cl} + qx_F, \qquad (1)$$

where x_{Cl}=Cl/Fe, x_F=F/Fe, and p and q are the coefficients concerned with the ion radii and chemical nature of the Cl^- and F^- ions. a_0 is the expected lattice constant of β-FeOOH free from Cl^- or F^-. Practically the estimation of p and q is difficult because of the absence of a compound where the certain sites are completely replaced by Cl^- or F^- ions.

Here, $|p| \gg |q| \approx 0$ can be assumed, since the ionic radius of F^- is almost identical with that of OH^-/O^{2-}. Equation 1 can be reduced as follows:

$$a \fallingdotseq a_0 + px_{Cl}. \qquad (2)$$

The Cl content dependence of the lattice constants is shown in Fig. 1. It is found that the liner relationship is nearly satisfied and that the variation in the lattice constants follows Vegard's law. Namely,

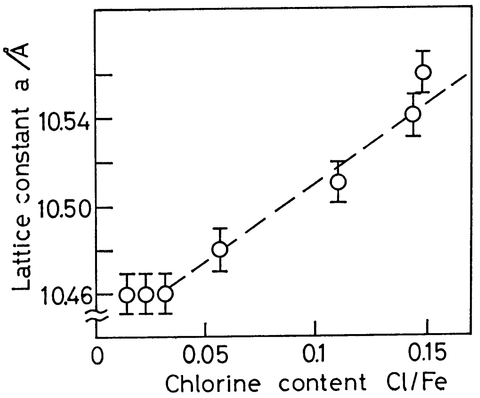

Fig. 1. Chlorine content dependence of the lattice constants *a* of β-FeOOH. *p* in Eq. 2 is estimated to be 0.8 Å.

it is confirmed that, in the β-FeOOH crystal, Cl^- ions are not localized, forming such compound as $FeCl_3$, but the distributed at random, occupying certain sites.

This confirmation is in accordance with the experimental finding that neither the diffraction lines nor the Mössbauer resonant peaks of the Fe(III) compounds were observed other than in the case of β-FeOOH.[10]

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