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Crystal Structure of Pseudorhombohedral InFe$_{1-x}$Ti$_x$O$_{3+x/2}$ ($x = 2/3$)

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The structure of pseudorhombohedral-type InFe$_{1-x}$Ti$_x$O$_{3-x/2}$ ($x = 2/3$) was refined by Rietveld profile fitting. The crystal is a commensurate member of a series in a solution range on InFeO$_3$–In$_2$Ti$_2$O$_7$ including incommensurate structures. The structure with the unit cell of $a = 5.9188(1)$, $b = 10.1112(2)$, and $c = 6.3896(1)$ Å, $\beta = 108.018(2)°$, and a space group $P2_1/a$ is the alternate stacking of an edge-shared InO$_6$ octahedral layer and an Fe/Ti–O plane along c*. Metal sites on the Fe/Ti–O plane are surrounded by four oxygen atoms on the Fe/Ti–O plane and two axial ones. Electric conductivities of the order 10^{-4} S/cm were observed for the samples at 1000 K, while the oxide ion transport number is almost zero as no electromotive force was detected by an oxygen concentration cell.

Key Words: **InFe$_{1-x}$Ti$_x$O$_{3+x/2}$; Rietveld analysis; superstructure; composite crystal.**

INTRODUCTION

A large family with two types of layered structures was found in systems In$_2$O$_3$–TiO$_2$–M_2O$_3$ (M = Al, Ga, Cr, Fe) and In$_2$O$_3$–TiO$_2$–M'O (M' = Mg, Mn, Co, Ni, Cu, Zn) (1–4). The phases named Unison-X$_1$ (1) have solution ranges on the pseudobinary line, InMO$_3$–In$_2$Ti$_2$O$_7$. The phase formed in a M-rich region (for example, InMO$_3$/In$_2$Ti$_2$O$_7 > 1$ for M = Fe at 1100°C) has an orthorhombic structure, and the other one in a Ti-rich region (InMO$_3$/In$_2$Ti$_2$O$_7 \leq 1$ for M = Fe at 1100°C) is monoclinic. Both structures give diffraction patterns with a set of strong reflections accompanying weak ones, which are characterized as the superstructure $\mathbf{b} = 3\mathbf{b}_{\text{sub}}$ ($\mathbf{b}_{\text{sub}}$, axis of the sublattice) for InFeO$_3$/In$_2$Ti$_2$O$_7 = 1$. The Positions of weak reflections, however, shift according to the variation of the chemical composition, giving incommensurate spots for samples with the composition deviating from InFeO$_3$/In$_2$Ti$_2$O$_7 = 1$ (1, 2).

Single crystals of the two structure types were grown in the system In$_2$O$_3$–TiO$_2$–Fe$_2$O$_3$ (2, 5), although all crystals obtained so far are incommensurate ones. X-ray diffraction analyses based on only main reflections have clarified that the monoclinic phase has the pseudorhombohedral symmetry (5) and the orthorhombic one has the pseudohexagonal (6). The two structures are closely related to each other, or the stacking variants of each other. The pseudohexagonal type is similar to InFeO$_3$ (7) with a hexagonal cell. The InFeO$_3$ structure is constructed by alternate stacking of two layers along **c***. One is an edge-shared InO$_6$ octahedral sheet, and the other consists of FeO$_5$ trigonal bipyramids. Fe atoms are partially replaced by Ti atoms in the pseudohexagonal Unison-X$_1$. Excess oxygen atoms are introduced into the Fe/Ti–O layer to keep charge neutrality of the whole crystal, which causes an arrangement of oxygen atoms in this layer approximated by the partial occupation at a honeycomb lattice (6). Large thermal parameters U_{11} and U_{22} for oxygen ions on the Fe/Ti–O plane suggested the prominent displacement of the atoms, although observation of satellite reflections implies that such displacements are not random but are to be definitely described by modulation functions. Recently, coordination characters around the Fe/Ti site of the pseudohexagonal Unison-X$_1$ were studied by a super space group approach (8). It was, however, found difficult to apply the same approach to the pseudorhombohedral type because single crystals tried for the analysis were twined.

In the present study, the commensurate structure of the pseudorhombohedral Unison-X$_1$ has been studied by Rietveld profile fitting of powder X-ray diffractions. Electrical properties of the Unison-X$_1$ phases were also investigated.

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TABLE 1
Crystallographic Data and Refinement Results for Pseudorhombohedral $InFe_{1-x}Ti_xO_{3+x/2}$ ($x = 2/3$)

Crystal system	Monoclinic
Space group	$P2_1/a$
a (Å)	5.9188(1)
b (Å)	10.1112(2)
c (Å)	6.3896(1)
β (°)	108.018(2)
V (Å^3)	363.64(1)
Z	6
R_{wp} (%)	15.10
R_p	10.96
R_I	4.07
R_F	2.85
S	1.94

TABLE 2
Final Parameters of $InFe_{1-x}Ti_xO_{3+x/2}$ ($x = 2/3$)

Atom	x	y	z	B(Å^2)
In1	0	0	0	1.0(2)
In2	0.022(7)	0.6652(7)	0.0068(9)	0.4(1)
$M1$	0.055(2)	0.844(1)	0.503(2)	0.7(2)
$M2$	0	0.5	0.5	0.1(4)
O1	0.390(9)	0.996(6)	0.135(5)	1.0
O2	0.417(6)	0.671(7)	0.174(5)	1.0
O3	0.359(6)	0.332(7)	0.169(5)	1.0
O4	0.379(5)	0.826(6)	0.505(7)	1.0
O5	0.303(6)	0.538(4)	0.494(8)	1.0

Note. Occupation factors $M1$ and $M2$: Fe, 0.333; Ti, 0.667.

EXPERIMENTAL

In_2O_3, Fe_2O_3, and TiO_2 (99.9% or higher purity) heated at 850°C for 1 day prior to reaction were mixed in a molar ratio of In_2O_3:TiO_2:Fe_2O_3 = 3:4:1 using an agate mortar for about 25 min in ethanol. The mixture was pelletized and heated in a platinum crucible at 1100°C for 9 days, and then cooled to room temperature. After grinding, the sample was pelletized and heated at 1100°C for 7 days. The last process was repeated. Formation of the commensurate phase of the monoclinic (i.e., pseudorhombohedral) Unison-X_1 was confirmed by the X-ray diffraction pattern in which all peaks were indexed by a superlattice with $\mathbf{b} = 3\mathbf{b}_{sub}$.

X-ray diffraction data were collected on a Rigaku Rad 2B diffractometer with graphite-monochromatized Cu$K\alpha$ radiation in a scan range of 20–120° at intervals of 0.02°. The structure was refined by Rietveld profile fitting using the program RIETAN 2000 (9). Initial atomic positions were taken from those of the average structure determined for a single crystal of the incommensurate structure (6). Crystallographic data of pseudorhombohedral $InFe_{1-x}Ti_xO_{3+x/2}$ ($x = 2/3$) and refinement results are given in Table 1. Occupation ratios of Fe and Ti were fixed at $\frac{1}{3}$ and $\frac{2}{3}$ at $M1$ and $M2$ sites because similar scattering abilities of Fe and Ti made it difficult to determine the ratio precisely.

RESULTS AND DISCUSSION

Final structural parameters and the profile fit are given in Table 2 and Fig. 1, respectively. The structure is described by an alternate stacking of two layers along $\mathbf{c}^*$; one is made up of edge-shared InO_6 octahedra and the other consists of bipyramidal coordination around the Fe/Ti site as shown in Fig. 2. Interatomic distances are given in Table 3. Coordination features around the metal sites on the Fe/Ti–O plane are shown in Fig. 3. The $M2$ is surrounded by four oxygen

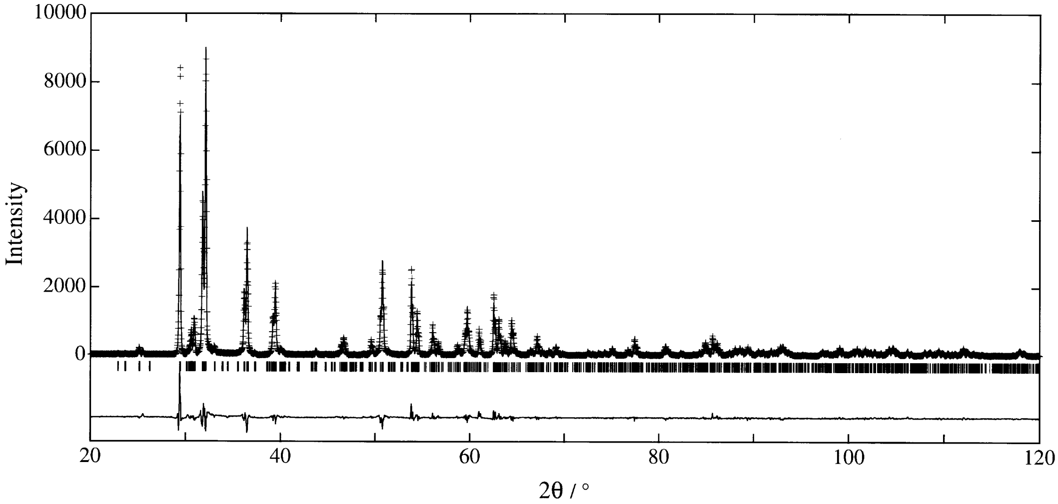

FIG. 1. Final Rietveld fit for pseudorhombohedral-type $InFe_{1-x}Ti_xO_{3+x/2}$ ($x = 2/3$). Observed data are represented by +, and the calculated profile by the solid line. The difference plot is at the bottom.

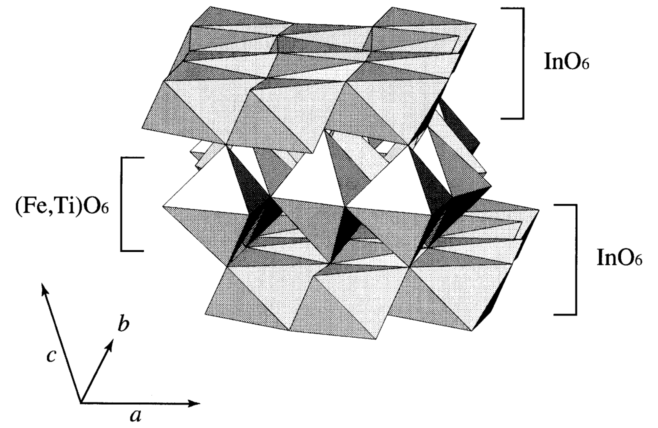

FIG. 2. Structure of pseudorhombohedral-type $InFe_{1-x}Ti_xO_{3+x/2}$ ($x = 2/3$) represented by coordination polyhedra.

atoms on the Fe/Ti–O plane with distances between 1.84(4) and 1.90(6) Å. This metal site is a 6-coordination site including two axial *M*2–O1 bonds. The *M*1 site is also a 6-coordination site, although one of the O5 atoms is rather distant from the *M*1 site (2.13(4) Å) compared with the other three O atoms on the Fe/Ti–O plane.

X-ray and electron diffractions for samples of a composition ratio that deviated from Fe/Ti $= \frac{1}{2}$ showed some reflections displaced along **b***, which makes it impossible to index the reflections by a set of three vectors. The incommensurate character is seen in both the pseudorhombohedral and pseudohexagonal phases. The four-dimensional super space group approach for the pseudohexagonal type has led to the conclusion that the structure is properly described as a composite crystal (8); that is, the structure consists of two subsystems with different periods. It seems that the same interpretation is applicable to the structure of pseudorhombohedral type. The whole structure is taken as a combination of two subsystems. The first subsystem contains the InO_6 octahedral sheet (In1, In2, O1, O2, and O3) and the metal atoms on the Fe/Ti–O plane (*M*1, *M*2), while the second one consists of oxygen atoms on the Fe/Ti–O plane (O4, O5). Two subsystems have the same period in **a** and **c** axes, but a different one in **b**. The structure on the Fe/Ti–O plane is based on the fundamental structure given in Fig. 4, where metal atoms are arranged on a *C*-centered lattice with period *a* and b_1 and oxygen atoms are on another *C*-centered lattice with *a* and b_2. In this basic structure, O–O distances are sufficient for the distance between oxygen atoms, but the metal–oxygen distance is too short in parts. The oxygen and metal atoms shift so as to reduce repulsive interactions between them while keeping long enough O–O distances. It is reasonable for an oxygen atom to shift toward the center of a triangle consisting of three metal atoms to keep enough distance between all metal atoms

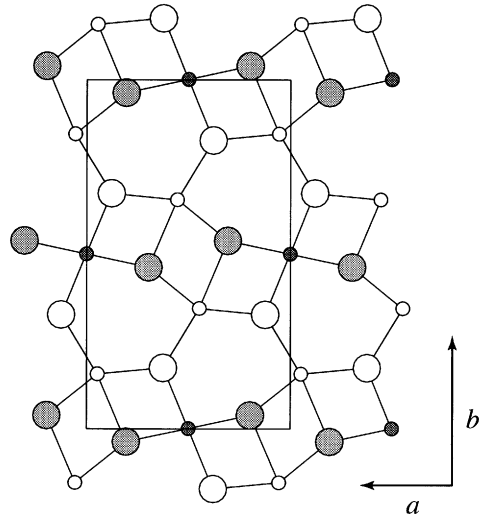

FIG. 3. Atomic arrangement in the slab at $z \approx 0.5$. Small open circles are *M*1, small filled circles *M*2, large open circles O4, and large filled circles O5.

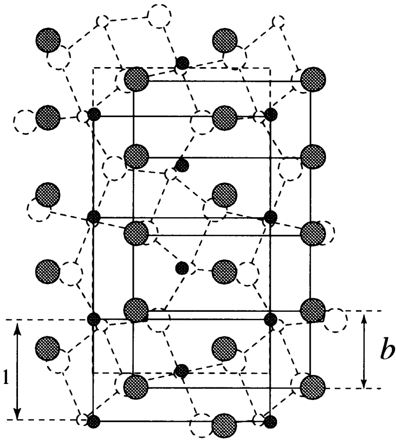

FIG. 4. Hypothetical arrangement of atoms in the slab at $z \approx 0.5$ based on a composite crystal model. Small circles are metal atoms and large circles are oxygen atoms of the basic structure. The real structure is drawn by dotted circles and lines.

TABLE 3
Selected Interatomic Distances (Å) in $InFe_{1-x}Ti_xO_{3+x/2}$ ($x = 2/3$)

In1–O1 × 2	2.20(5)	*M*1–O2	2.02(3)
–O2 × 2	2.19(6)	–O3	2.00(4)
–O3 × 2	2.31(6)	–O4	1.92(3)
		–O4	2.01(6)
In2–O1	2.08(6)	–O5	1.90(4)
–O1	2.09(6)	–O5	2.13(4)
–O2	2.17(6)		
–O2	2.25(3)	*M*2–O1 × 2	2.22(3)
–O3	2.19(3)	–O4 × 2	1.90(6)
–O3	2.26(6)	–O5 × 2	1.84(4)

surrounding the oxygen atom. Thus, the second model also gives the real structure drawn by dotted circles in the figure.

The interpretation of the structure based on the composite crystal model in Fig. 4, which may seem rather unnatural, is useful for understanding the structural variation including the incommensurate structure. Namely, it should be supposed that the ratio b_1/b_2 becomes irrational. In this case four vectors are necessary to define the positions of all reflections: **a** and **c** commonly in the two subsystems, and $\mathbf{b}_1$, $\mathbf{b}_2$. In the commensurate structure with $b_1{:}b_2 = 4{:}3$, an extended vector $\mathbf{b} = 3\mathbf{b}_1 = 4\mathbf{b}_2$ was used instead of $\mathbf{b}_1$ and $\mathbf{b}_2$, which makes it possible to index all reflections by a set of three vectors. Complete description of the incommensurate structure requires the determination of the Fourier coefficients of modulation functions as done for the pseudohexagonal type. It is probable that modulation functions of the pseudorhombohedral structure are similar to those of the pseudohexagonal, because the two structures have similar basic structures on the Fe/Ti–O plane. It should be commonly observed that oxygen and metal atoms in two subsystems are displaced so as to reduce repulsive interactions between them.

The composite crystal model gives the relation between the chemical composition and the b_1/b_2 ratio. The first subsystem contains $2(\mathrm{InFe}_{1-x}\mathrm{Ti}_x\mathrm{O}_2)$ atoms in the unit cell based on $\{\mathbf{a}, \mathbf{b}_1, \mathbf{c}\}$. Two oxygen atoms of the second subsystem are included in the unit cell based on $\{\mathbf{a}, \mathbf{b}_2, \mathbf{c}\}$, that is $2(b_1/b_2)\mathrm{O}$ atoms in the unit cell based on $\{\mathbf{a}, \mathbf{b}_1, \mathbf{c}\}$. As a whole structure, $2(\mathrm{InFe}_{1-x}\mathrm{Ti}_x\mathrm{O}_2) + 2(b_1/b_2)\mathrm{O} = 2(\mathrm{InFe}_{1-x}\mathrm{Ti}_x\mathrm{O}_{2+b1/b2})$ atoms are included in the unit cell based on $\{\mathbf{a}, \mathbf{b}_1, \mathbf{c}\}$. As the chemical formula is given by $\mathrm{InFe}_{1-x}\mathrm{Ti}_x\mathrm{O}_{3+x/2}$, the ratio of cell dimensions of the two subsystem is given using the x parameter, $b_1/b_2 = 1 + x/2$. Thus, the ratio b_1/b_2 is varied according to the variation of the Fe/Ti ratio, although this relationship is valid under the condition of no defects.

Oxygen ion conduction was expected for Unison-X_1 phases, because the arrangement of oxygen ions on the Fe/Ti–O plane is rather irregular compared with that on the Fe–O plane in hexagonal InFeO_3, the full occupation at the triangle lattice sites. Electric conductivity was measured between room temperature and 1073 K for pseudohexagonal and pseudorhombohedral Unison-X_1 phases. The observed conductivities were thermally activated and of the order of 10^{-4} S/cm at 1000 K. No electromotive force was, however, detected by an oxygen concentration cell. It was concluded that the oxide ion transport number is almost zero and the observed conductivity is not ionic but electronic.

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