Crystal Structure of $InTi_{0.75}Fe_{0.25}O_{3.375}$ and Phase Relations in the Pseudobinary System $InFeO_3$−$In_2Ti_2O_7$ at 1300 °C

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An average structure of incommensurately modulated monoclinic $InTi_{0.75}Fe_{0.25}O_{3.375}$ was determined using single-crystal X-ray diffraction. Unit cell parameters are $a = 5.9207(8)$, $b = 3.4249(5)$, $c = 6.3836(9)$, and $\beta = 107.96(1)$ with $Z = 2$, and the space group is $C2/m$. The structure with pseudorhombohedral symmetry involves two metal positions: M1, practically occupied by In, and M2, by Ti and Fe. Two layers are alternately stacked along the c axis; one is an edge-shared $M1O_6$ octahedral sheet and another consists of bipyramidal coordination at M2 sites. In the bipyramidal layer, a honeycomb lattice 68% occupied by oxygen ions surrounds the M2 site. These oxygen ions are subsequently displaced from their original positions to reduce mutual repulsion. This explains large displacement parameters U_{11} and U_{22} despite the normal U_{33} at the M2 site as well as at the oxygen site. Solid solution for the present phase is limited to $InFeO_3$:$In_2Ti_2O_7$ = 2:3 at 1300 °C according to a phase relations study in the pseudobinary system $InFeO_3$−$In_2Ti_2O_7$. We propose a hypothetical compound with an unusual ABO_3 structure based on a comparison of this compound and related structures.

Introduction

Explorations of new complex metal oxides with simple molar ratios of constituents such as ABO_3, ABO_4, and AB_2O_4 are important. From the viewpoint of structural inorganic chemistry, ABO_3 structures are classified into two groups.[1] The first one contains A and B cations of suitable size for octahedral coordination and tends to adopt sesquioxide structures such as corundom or ilmenite. The second group has A cations comparable in size to oxygen ions and is made up of AO_3 closest-packed layers and linked BO_6 octahedra such as perovskites which represent an important commercial ceramics class. Giaquinta et al.[2] have pointed out that $InMnO_3$ consisting of alternating layers of InO_6 octahedra and MnO_5 trigonal bipyramids is unusual because it belongs to neither of the above structural families. According to their recent review of structural predictions,[3] some other uncommon ABO_3 structures, $PbReO_3$,[4] $KSbO_3$,[5,6] and $LuMnO_3$,[7] have been found so far. Considering the fact that $InMnO_3$ is essentially isostructural to a high-pressure phase $InGaO_3$,[8] all the structure types were originally reported in the 1970s or earlier as well as well-known structures such as perovskite and corundum. Namely, no new ABO_3 structure has been found in the past 20 years.

Our synthetic study of ternary systems, In_2O_3−TiO_2−M_2O_3 (M = Al, Ga, Cr, Fe) and In_2O_3−TiO_2−MO (*M* = Mg, Mn, Co, Ni, Cu, Zn) revealed two groups of orthorhombic (M = Al, Ga, Fe, Cu) and monoclinic (M = Al, Ga, Cr, Fe, Mg, Mn, Co, Ni, Cu, Zn) structures near the composition ratio In:(Ti + M) = 1:1, called Unison-X_1 phases.[9,10] A single-crystal X-ray diffraction study of one of the orthorhombic forms, $InTi_{0.67}Fe_{0.33}O_{3.33}$,[11] showed that the structure has pseudohexagonal symmetry and is understood as a derivative of hexagonal $InFeO_3$[12] isostructural to $InMnO_3$. In this paper we report on monoclinic $InTi_{0.75}Fe_{0.25}O_{3.375}$, which has a new struc-

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ture with pseudorhombohedral symmetry, and is not a distortion of the orthorhombic form. A hypothetical structure with a stoichiometric composition $InFeO_3$, which may belong to unusual ABO_3 structure types, is proposed, extrapolating from this nonstoichiometric phase. Interestingly, the proposed $InFeO_3$ structure is described in the same manner as the hexagonal $InFeO_3$ actually obtained: alternate stacking of two layers of InO_6 octahedra and FeO_5 trigonal bipyramids. Similarities and differences between the structures are discussed in detail. Although the structure should be incommensurately modulated judging from satellite spots, we dealt with the average structure in an analysis by main reflections only. Phase relations in the pseudobinary system $InFeO_3$−$In_2Ti_2O_7$ at 1300 °C were also studied and compared to those at 1100 °C.[9]

Experimental Section

Phase Relations. Samples were prepared by a classical quenching technique. In_2O_3, TiO_2, and Fe_2O_3 (99.9% or higher purity) heated at 850 °C for 1 day prior to reaction were mixed at a molar ratio of In_2O_3:TiO_2:Fe_2O_3 = 1:2x:1−x ($^1/_3 \le x \le {}^6/_7$) using an agate mortar for about 30 min in ethanol. The mixture was pelletized (10 mm in diameter and 1.2 mm thick) and heated in an alumina crucible at 1300 °C for 2 days and then rapidly cooled to room temperature. After grinding, the sample was again pelletized and heated for 3 days. The weight loss of each sample was carefully checked after heating. Identification of the products and confirmation of an equilibrium state were done by powder X-ray diffraction measurements.

Single-Crystal Analysis. A mixture of In_2O_3:TiO_2:Fe_2O_3 = 4:6:1 (in a mole ratio) was heated at 1350 °C for 2 days in air. Single crystals were grown by reheating the product at 1670 °C for 3 h and cooling to 1500 °C at 1 °C/min. Satellite reflections were observed at incommensurate positions analogous to polycrystalline samples prepared by solid-state reactions.[9] Only main reflections were used for the analysis to determine the average structure.

A brown prismatic crystal of 70 × 50 × 150 μm was mounted on a Rigaku AFC7R four-circle diffractometer with a graphite monochromator at 23 °C. Crystallographic data, experimental conditions, and parameters are listed in Table 1. Software package teXsan Version 1.9 (Molecular Structure Corporation, Rigaku Corporation. (1998)) was used for full matrix least-squares refinement based on F^2.

Results

Phase Relations at 1300 °C. In phase relations in the pseudobinary system $InFeO_3$−$In_2Ti_2O_7$ at 1300 °C (Figure 1), Unison-X_1 phases were obtained at $InFeO_3$:$In_2Ti_2O_7$ = 2:3−2:1. Two structure types are known for Unison-X_1, orthorhombic and monoclinic forms.[9] The orthorhombic form has pseudohexagonal structure,[11] which is regarded as a derivative of the hexagonal $InFeO_3$ structure.[12] The monoclinic structure is new, not a monoclinic distortion of the former as discussed in the following section. Hexagonal $InFeO_3$ was unstable at 1300 °C as well as at 1100 °C.[9] This compound was obtained by coprecipitation of $In(OH)_3$ and $Fe(OH)_3$ in a solution followed by heating at 700 °C in air.[14,15] Therefore, three phases, In_2O_3, Fe_2O_3, and orthorhombic Unison-X_1, coexisted in the $InFeO_3$-rich side out of the Unison-X_1 range in Figure 1. No compound with the composition $In_2Ti_2O_7$ was obtained at 1100,[9] 1300, or 1350 °C,[16] even though the ionic radius of In^{3+} in eight coordination (0.923 Å) is located between those of Sc^{3+} (0.87 Å) and Lu^{3+} (0.97 Å),[17] constituents of pyrochlore compounds $Sc_2Ti_2O_7$ and $Lu_2Ti_2O_7$.[16] In_2TiO_5,[18] TiO_2, and monoclinic Unison-X_1 therefore coexisted in the In_2-Ti_2O_7-rich side. Phase relations at 1300 °C (Figure 1) resemble those at 1100 °C. Note, however, that the monoclinic form is limited to $InFeO_3$:$In_2Ti_2O_7$ = 2:3 at 1300 °C, while a wide range of $InFeO_3$:$In_2Ti_2O_7$ = 2:3−

Table 1. Crystallographic Data and Conditions for Data Collection and Refinement for $InTi_{0.75}Fe_{0.25}O_{3.375}$

formula weight	218.70
crystal system	monoclinic
space group	$C2/m$
a (Å)	5.9207(8)
b	3.4249(5)
c	6.3836(9)
β (°)	107.96(1)
V (Å^3)	123.14(3)
Z	2
Dx (g/cm^3)	5.90
μ (Mo Kα) (mm^{-1})	13.00
radiation	Mo Kα (0.71069 Å)
refinement of cell parameters	25 reflections (40.6° ≤ θ ≤ 42.3°)
scan mode	$\omega - 2\theta$
2θ max.	100° (0≤ h≤ 12, 0 ≤ k ≤ 7, −13 ≤ l ≤ 13)
standard reflections	3 every 200 (variation within 2.5%)
reflections measured	1380
reflections used for calculation	722
absorption correction	experimental (ψ-scan)
transmission factor	0.996−0.575
extinction coefficient[a]	6.5(3) × 10^{-6}
final R_1, wR_2[b]	0.0288, 0.0538 (weight factor: $w = 1/\sigma(F_o)^2$)
$\Delta\rho_{min}$, $\Delta\rho_{max}$	−1.58, 1.47 (e/Å^3)

[a] Type 2 Gaussian isotropic (ref 13). [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $I > 2\sigma(I)$ and w$R_2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4)^{1/2}$.

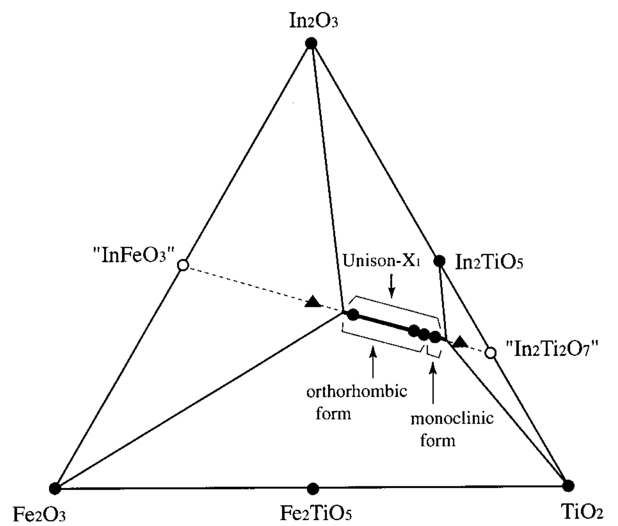

Figure 1. Phase relations at 1300 °C. Filled circles, one phase exists; open circles, two phases coexist; triangles, three phases coexist. Unison-X_1 phases are on the thick line in the pseudobinary system $InFeO_3$−$In_2Ti_2O_7$. The structure of the monoclinic Unison-X_1 is new, not a distortion of the orthorhombic form.

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Table 2. Fractional Coordinates, Occupation Ratios, and Displacement Parameters (Å^2) for $InTi_{0.75}Fe_{0.25}O_{3.375}$[a]

position	occupancy	x	y	z	B_{eq}
M1 (In/Ti)	0.93(2)/0.07	0	0	0	0.623(5)
M2 (Ti/Fe/In)	0.690(8)/0.25/0.060	0.5	0	0.5	2.46(2)
O1	1	0.6103(4)	0	0.8332(4)	1.07(4)
O2	0.68(1)	0.663(1)	0.5	0.493(1)	5.9(2)

position	U_{11}	U_{22}	U_{33}	U_{13}
M1	0.0066(1)	0.0070(1)	0.0103(1)	0.00294(9)
M2	0.0325(6)	0.0512(8)	0.0057(4)	−0.0002(3)
O1	0.014(1)	0.017(1)	0.009(1)	0.0025(8)
O2	0.106(7)	0.092(7)	0.020(4)	0.010(4)

[a] Temperature factors take the form $\exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$. $B_{eq} = (^4/_3)\Sigma_i\Sigma_j\, \beta_{ij}a_ia_j$. $U_{ij} = \beta_{ij}/2\pi^2 a_i^* a_j^*$. U_{12} and U_{23} are 0 for all atoms.

Table 3. Selected Data and Parameters Based on Structure Models

model	1	2	3	4	5
M1 site:					
In	1	1	0.903(4)	0.91(2)	0.93(2)
Ti					0.07
Fe				0.09	
B_{eq} (Å^2)	0.595(6)	0.620(5)	0.625(5)	0.615(4)	0.623(5)
M2 site:					
In				0.065	0.060
Ti	0.75	0.27(2)	0.75	0.75	0.690(8)
Fe	0.25	0.73	0.25	0.185(9)	0.25
B_{eq} (Å^2)	2.00(3)	2.38(2)	2.37(2)	2.45(2)	2.46(2)
O2 site:					
O	0.6875	0.70(1)	0.67(1)	0.68(1)	0.68(1)
B_{eq} (Å^2)	6.2(3)	5.9(2)	6.1(2)	5.8(2)	5.9(2)
$R1$ (%)	3.81	2.88	3.05	2.95	2.88
wR (%)	7.33	5.43	5.44	5.28	5.38
chemical formula	$InTi_{0.75}Fe_{0.25}O_{3.375}$	$InTi_{0.27}Fe_{0.73}O_{3.40}$	$In_{0.903}Ti_{0.75}Fe_{0.25}O_{3.34}$	$In_{0.975}Ti_{0.75}Fe_{0.275}O_{3.36}$	$In_{0.99}Ti_{0.76}Fe_{0.25}O_{3.36}$
total charge	0	−0.53	−0.22	+0.03	+0.04

1:1 was seen for the monoclinic form at 1100 °C.[9] In other words, the orthorhombic form expanded and the monoclinic form contracted at 1300 °C compared to 1100 °C, implying that the orthorhombic/monoclinic boundary shifts toward $In_2Ti_2O_7$ with increasing temperature.

Structure Determination of $InTi_{0.75}Fe_{0.25}O_{3.375}$. Fractional coordinates, occupancies, and displacement parameters of $InTi_{0.75}Fe_{0.25}O_{3.375}$ (monoclinic Unison-X_1) are listed in Table 2. Great care was paid in determining occupation ratios at the metal (M1 and M2) and O2 sites in this nonstoichiometric compound. At initial stages of the refinement, the M1 site was allotted for In and the M2 site was for Ti and Fe, analogous to $InTi_{0.67}Fe_{0.33}O_{3.33}$ (orthorhombic Unison-X_1).[11] An occupation factor at the O2 site was fixed to keep charge neutrality of the whole crystal. The results are shown as model 1 in Table 3, which was taken as a basic model and modified as follows. Refinement of the Ti/Fe ratio at the M2 site and the occupation factor at the O2 site resulted in considerable improvement of reliability factors (model 2). The obtained Ti/Fe ratio appears, however, unreasonable for the monoclinic phase, judging from phase relation studies. The charge discrepancy between cations (metal ions) and anions (oxygen ions) was significant because the occupation factor at the O2 increased little despite the considerable decrease in positive charges due to the decrease in the Ti^{4+}/Fe^{3+} ratio at the M2 site. We tried another model (model 3) by introducing vacancies at the M1 site which gave similar R values to those in model 2. Charge neutrality was poor, however, because the decrease in the occupation factor at the O2 site was too small to compensate for the decrease in positive charge due to the introduction of In vacancies. These results imply, first, electrons in model 1 should decrease at the M1 site and/or increase at the M2 site, and second, total cation charge (i.e., metal ions) should not differ greatly from those in model 1 because anions (i.e., oxygen ions) seem rather independent of occupation ratios at metal sites, as is shown by models 2 and 3, giving roughly similar occupation ratios at the O2 site. These requirements are satisfied by (i) combining Fe substitution for part of In at the M1 site and In substitution for part of Fe at the M2 site (model 4), or (ii) combining Ti substitution for part of In at the M1 site and In substitution for part of Ti at the M2 site (model 5). Fitting was equally good for both models (Table 3). Charge neutrality was also fairly good. Although the two models are equally acceptable at this stage, model 5 was taken as the final model (Table 2) because Ti substitution is commonly applicable to other isostructural compounds, $InTi_xM_{1-x}O_{3+x/2}$ (M = Al, Ga, Cr, etc.) actually synthesized.[10] The chemical composition of the crystal, which may deviate from that of the starting mixture due to the evaporation of certain species in crystal growth, could not be determined precisely because of the inhomogeneity of the crystal growth product and too much fluctuation in electron probe microanalysis. We used the chemical composition of the starting mixture, $InTi_{0.75}Fe_{0.25}O_{3.375}$, as a nominal composition because few deviations from this were seen in models 4 and 5. Note that occupation factors at the M2 and O2 sites may have been overestimated, leading to large displacement parameters at both sites, but this was ruled out because in model 2 the Ti/Fe ratio refinement at the M2 site increased electrons at this site (i.e., decreased the Ti/Fe ratio) with little change

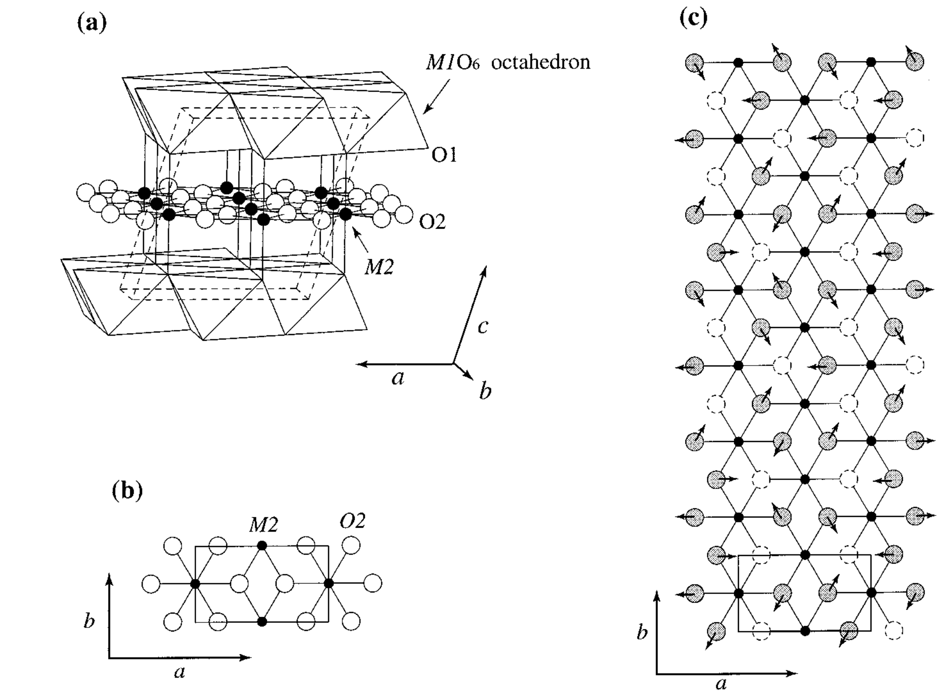

Figure 2. (a) Structure of $InTi_{0.75}Fe_{0.25}O_{3.375}$ projected along a direction slightly tilted from the *b* axis. The M1 site is at about the center of the $M1O_6$ octahedron. (b) Atomic arrangement in the slab at $z \approx {}^1/_2$. The occupation ratio at the O2 site is 0.68. (c) Example of probable local arrangements in the slab at $z \approx {}^1/_2$. Small filled circles are metal ions, large shaded circles oxygen ions, and dotted circles vacancies. Arrows indicate probable positional displacement of oxygen ions from their original positions.

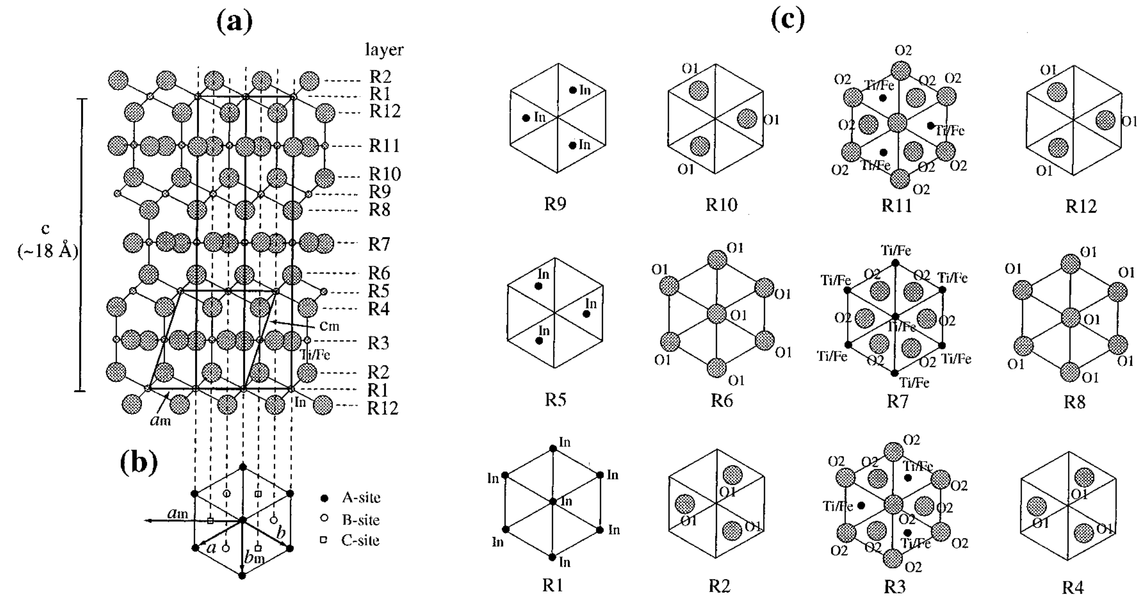

Figure 3. Idealized rhombohedral structure of $InTi_{0.75}Fe_{0.25}O_{3.375}$ (monoclinic Unison-X_1). (a) Projection along [1 1 0] (in hexagonal axes). a_m and c_m are axes of the monoclinic cell. (b) Closest packing sites, A, B, and C, projected along [0 0 1]. a_m and b_m are axes of the monoclinic cell. (c) 12 layers projected along [0 0 1]. The occupation ratio is 0.68 at the O2 site.

in the equivalent displacement parameter B_{eq}. Occupation factors and displacement parameters at the O2 site were roughly similar among the five models. Explanations for unusually large displacement parameters at these sites will be given in the following paragraph.

The structure with pseudorhombohedral symmetry is formed by alternate stacking of two layers: one is made up of edge-shared $M1O_6$ octahedra and another consists of bipyramidal coordination around the M2 site (Figure 2a). The octahedral layer is common, while some peculiarity is seen in the bipyramidal, which contains axial M2−O1 bonds and in-plane M2−O2 bonds. The O2 site in the slab at $z \approx {}^1/_2$ forms a honeycomb lattice surrounding the M2 (Figure 2b). The occupation ratio at the O2 site is 0.68, meaning that 4.1 (=0.68 × 6) positions among 6 around one metal ion are actually occupied on the average by oxygen ions. Primary images of local structures and coordination features in this slab are given from present data, although a complete structure analysis including satellite reflections is necessary for accurate discussion. In an example of probable local arrangements in the slab (Figure 2c), 44 of 64 sites were occupied by oxygen atoms and the rest vacant. Oxygen ions may subsequently be displaced

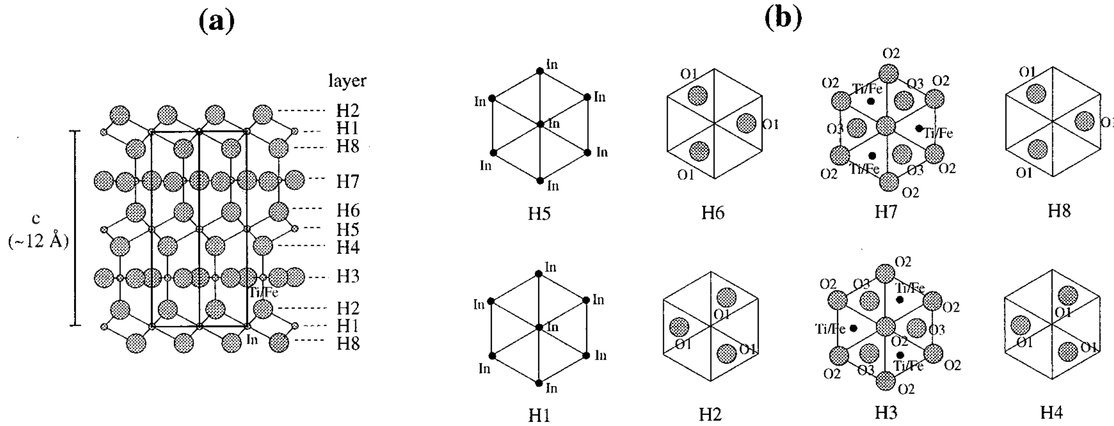

Figure 4. (a) Idealized hexagonal structure of $InTi_{0.67}Fe_{0.33}O_{3.33}$ (orthorhombic Unison-X_1) projected along [1 1 0]. (b) 8 layers projected along [0 0 1]. The occupation ratio is 0.74 at the O2 site and 0.59 at the O3.

Table 4. Interatomic Distances for $InTi_{0.75}Fe_{0.25}O_{3.375}$

atom	atom	multiplicity	distance (Å)
M1	O1	×4	2.218(2)
	O1	×2	2.223(2)
average			2.220
M2	O1	×2	2.023(3)
	O2	×4	1.974(4)
	O2	×2	1.980(8)
average			1.988

from their original positions to reduce mutual repulsion (arrows, Figure 2c). This explains large displacement parameters U_{11} and U_{22} despite normal U_{33} at the M2 site as well as at the O2 site (Table 2), similar to metal (Ti/Fe) and oxygen ions in orthorhombic Unison-X_1, $InTi_{0.67}Fe_{0.33}O_{3.33}$.[11] Selected interatomic distances are listed in Table 4. In-plane M2−O2 bonds are longer than those of related structures, $InTi_{0.67}Fe_{0.33}O_{3.33}$ (1.94 Å average[11]) and $InFeO_3$ (1.9208(1) Å).[12] This is concerned with the expansion of the rectangle defined by unit cell dimensions, $a \times b$: 20.278 Å^2 for $InTi_{0.75}Fe_{0.25}O_{3.375}$, 19.547 Å^2 for $InTi_{0.67}Fe_{0.33}O_{3.33}$, and 19.172 Å^2 for $InFeO_3$ (in the orthohexagonal cell). The variation in *ab* area coincides with the fact that oxygen ions on the M2−O2 plane are most condensed in $InTi_{0.75}Fe_{0.25}O_{3.375}$ and the least in $InFeO_3$. The more oxygen ions in the M2−O2 plane, the larger the *ab* area for reducing electrostatic repulsion between oxygen ions, elongating in-plane M2−O2 distances.

Discussion

The structure of $InTi_{0.75}Fe_{0.25}O_{3.375}$ (monoclinic Unison-X_1) is closely related to that of $InTi_{0.67}Fe_{0.33}O_{3.33}$ (orthorhombic Unison-X_1) because the orthorhombic form is also constructed by alternate stacking of InO_6 octahedral and (Ti/Fe)$O_{5+\alpha}$ bipyramidal layers.[11] The two structures differ essentially in filling by metal and oxygen ions compared to Figures 3 and 4, where structural distortion is ignored and ideal symmetry is used for simplicity: a rhombohedral lattice for the monoclinic and a hexagonal lattice for the orthorhombic. Minor components at metal sites, Ti at the M1 site and In at the M2 site, are ignored in Figure 3. All metal and oxygen ions are positioned at the three sites, A, B, and C, defined by closest packing (Figure 3b). The rhombohedral form consists of 12 layers, R1, R2, ..., R12,

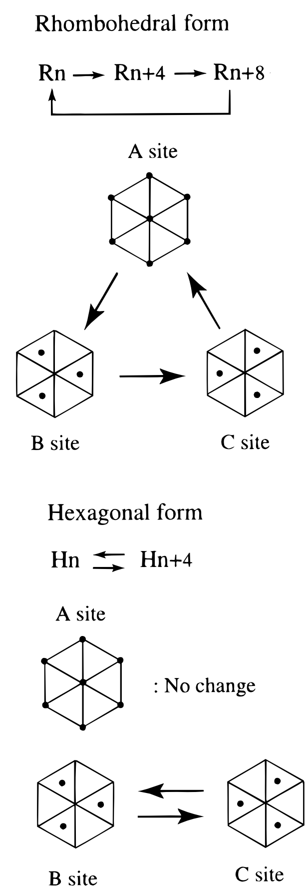

Figure 5. Relationships between layers forming structures.

stacked along the *c* axis (in a hexagonal setting, Figure 3c), while the hexagonal form consists of 8 layers, H1, H2, ..., H8 (Figure 4b). The first four layers R1−R4 in the rhombohedral form are identical to those in the hexagonal, H1−H4 (Figure 4b), except that occupation ratios at oxygen sites differ slightly between R3 and H3. Other layers are made from these four layers by simple rules differing between the two structures (Figure 5). In rhombohedral stacking, ions at A sites in the *n*th layer go to B sites in the (4+*n*)th layer, and those at B sites go to C sites in the latter, while those at C sites in the former go to A sites in the latter. Indium ions occupy A sites in layer R1, B sites in R5, and C sites in R9. Indium positions are described by a repetition of |ABC|ABC|... along the *c* axis. Oxygen ions at C sites in layer R2 occupy A sites in R6 and then B sites in R10. Ti and Fe ions are at C sites in layer R3, A sites in R7, and B sites in R11. The unit of repetition for Ti and Fe is |CAB|. Another rule is applied for the hexagonal form. Ions at A sites in the *n*th layer remain at A sites in the $(4+n)$th layer, but those at B sites in the former go to C sites in the latter, and those at C sites in the former go to B sites in the latter. Indium ions on layers H1 and H5 are always at A sites. Oxygen ions at C sites in layer H2 occupy B sites in H6. Ti and Fe ions are at C sites on layer H3 and B sites on H7, but never occupy A sites. Metal positions (i.e., In, Ti, and Fe) are described by a repetition of |ACBACB |ACBACB|... along the *c* axis in rhombohedral stacking, while |ACAB|ACAB|... in the hexagonal. This difference leads to rather different diffraction patterns for powder samples of the two phases. At first sight, diffraction patterns of monoclinic Unison-X_1 resemble those of fluorite-related structures such as pyrochlore because the fluorite structure has basically the same packing mode of metal ions to that of the rhombohedral form (Figure 3).

As pointed out elsewhere,[11] orthorhombic Unison-X_1 can be regarded as a nonstoichiometric form of hexagonal $InFeO_3$. This stoichiometric structure is isostructural to $InMnO_3$[2] and consists of two layers of InO_6 octahedra and FeO_5 trigonal bipyramids. Layers H3 and H7 in the nonstoichiometric form (Figure 4b) are replaced by layers H3′ and H7′ (Figure 6a) in the stoichiometric form. Fe^{3+} ions are substituted for all Ti^{4+} ions in the nonstoichiometric form to give a stoichiometric compound. Excess oxygen ions were removed from H3′ and H7′ layers to keep the charge neutrality in the whole crystal. The same modification applied to monoclinic Unison-X_1 gives a hypothetical compound with stoichiometric composition $InFeO_3$ (rhombohedral $InFeO_3$); layers R3, R7, and R11 in Figure 3c are replaced by layers R3′, R7′, and R11′ in Figure 6b. All Ti^{4+} ions in the nonstoichiometric form are replaced by Fe^{3+} ions, removing additive oxygen ions. Thus, two layers of InO_6 octahedra and FeO_5 trigonal bipyramids are seen and oxygen ions in Fe−O2 planes form a triangle lattice in rhombohedral $InFeO_3$. The stoichiometric structures, hexagonal and rhombohedral $InFeO_3$, belong to unusual ABO_3 types from the viewpoint of structural inorganic chemistry. $InMnO_3$[2] and $InGaO_3$ (under high pressure[8]) isostructural to hexagonal $InFeO_3$ and similar structures ($YAlO_3$[19] and $RMnO_3$, R═Lu, Yb, Er, etc.[20,21]) were synthesized, but not rhombohedral $InFeO_3$ or isostructural compounds, so far. This suggests that the rhombohedral structure is more unstable than the hexagonal form and additive oxygen ions may have to be introduced into Fe−O2 planes to stabilize the rhombohedral structure. Attempts to synthesize rhombohedral $InFeO_3$, a new ABO_3 structure, are worth trying because all ABO_3 structure types were originally reported in the 1970s or earlier.

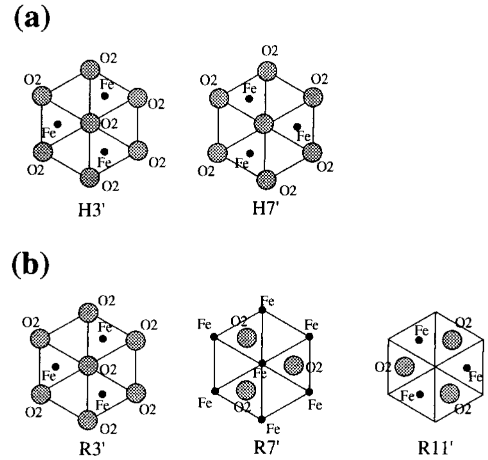

Figure 6. (a) Layers in the hexagonal $InFeO_3$ structure. H3′ and H7′ are substituted for H3 and H7 in Figure 5. (b) Layers in the hypothetical $InFeO_3$ structure with rhombohedral symmetry. R3′, R7′, and R11′ are substituted for R3, R7, and R11 in Figure 4.

Supporting Information Available: Bond angles and tables of observed and calculated structure factors for monoclinic $InTi_{0.75}Fe_{0.25}O_{3.375}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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