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The Phase Relations in the System In_2O_3–TiO_2–MgO at 1100 and 1350°C

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The phase relations in the system In_2O_3–TiO_2–MgO at 1100 and 1350°C are determined by a classical quenching method. In this system, there are four pseudobinary compounds, In_2TiO_5, $MgTi_2O_5$ (pseudobrookite type), $MgTiO_3$ (ilmenite type), and Mg_2TiO_4 (spinel type) at 1100°C. At 1350°C, in addition to these compounds there exist a spinel-type solid solution $Mg_{2-x}In_{2x}Ti_{1-x}O_4$ ($0 \leq x \leq 1$) and a compound $In_6Ti_6MgO_{22}$ with lattice constants $a = 5.9236(7)$ Å, $b = 3.3862(4)$ Å, $c = 6.3609(7)$ Å, $\beta = 108.15(1)°$, and $q = 0.369$, which is isostructural with the monoclinic $In_3Ti_2FeO_{10}$ in the system In_2O_3–TiO_2–MgO. The relation between the lattice constants of the spinel phase and the composition nearly satisfies Vegard's law. $In_6Ti_6MgO_{22}$ extends a solid solution range to $In_{20}Ti_{17}Mg_3O_{67}$ with lattice constants of $a = 5.9230(5)$ Å, $b = 3.3823(3)$ Å, $c = 6.3698(6)$ Å, $\beta = 108.10(5)°$, and $q = 0.360$. The distributions of constituent cations in the solid solutions are discussed in terms of their ionic radius and site preference effect. © 2000 Academic Press

***Key Words*: phase relations; $In_6Ti_6MgO_{22}$; $MgIn_2O_4$; $In_3Ti_2FeO_{10}$; $InFeO_3$; pyrochlore-type.**

INTRODUCTION

In_2O_3 is a useful compound for making transparent and electrically conductive materials at room temperature. The ionic radius of In(III) is located in between those of Lu(III) and Sc(III), which have 6 or above in the coordination number (CN); however, In(III) takes (CN) = 4, 5, 6, or 8 in oxide crystals (1). In a series of investigations for the system In_2O_3–ZnA_2O_4–ZnO at 1350°C (*A*: Fe Ga, or Al), we obtained homologous compounds, $In_2O_3(ZnO)_m$ ($m \geq 3$), $InMO_3(ZnO)_m$ (*M*: Fe or Ga, $m \geq 1$), $(InGaO_3)_2ZnO$, and $InAlO_3(ZnO)_m$ ($m \geq 9$) with $LuFeO_3(ZnO)_m$-type structure, $Fe_2O_3(ZnO)_m$ ($m \geq 8$) with distorted $LuFeO_3(ZnO)_m$-type structure, and $Ga_2O_3(ZnO)_m$ ($m = 7$, 8, 9, and 16) with different types of homologous structures (2–8). Recently, we determined the phase relations in the system In_2O_3–TiO_2–Fe_2O_3 at 1100°C in air and reported a new compound $In_3Ti_2FeO_{10}$, which is polymorphic in the monoclinic and orthorhombic structures (9). The isostructural compounds $In_3Ti_2AO_{10}$, $In_6Ti_6BO_{22}$, and their solid solution $In_{12}Ti_{10}A_2BO_{42}$ were synthesized at elevated temperatures, and the conditions of synthesis and their monoclinic and/or orthorhombic lattice constants were reported (*A*: Al, Cr, Mn, Fe, or Ga; *B*: Mg, Mn, Co, Ni, Cu, or Zn) (10). Their crystal structures (11) are closely related to both the pyrochlore-type and the hexagonal $InFeO_3$ with layered structure (12) in which the In(III) is located in an octahedral site and the Fe(III) is located in a trigonal bipyramidal site. All the X-ray powder diffraction data of these compounds show satellite peaks along the *b* axis in both the monoclinic system and the orthorhombic system. Hereafter we define these compounds as unison-X_1 after (9–10). $R_2Ti_2O_7$ (*R*: Sm–Lu, Y, and Sc) with the cubic pyrochrole-type structure (13, 14) exists; however, no $In_2Ti_2O_7$ was reported (9, 13). In order to determine the thermal stability of the unison-X_1 in which a divalent cation (*B*) exists together with In(III) and Ti(IV), we began by studying the phase relations in the system In_2O_3–TiO_2–*B*O at elevated temperatures. In the present study, we report the phase relations in the system In_2O_3–TiO_2–MgO at 1100°C in which there did not exist ternary compounds, and at 1350°C there existed a solid solution $Mg_{2-x}In_{2x}Ti_{1-x}O_4$ ($0 \leq x \leq 1$) with spinel-type structure between $MgIn_2O_4$ and Mg_2TiO_4 and a compound $In_6Ti_6MgO_{22}$, which is isostructural with the monoclinic $In_3Ti_2FeO_{10}$. It has a solid solution range to $In_{20}Ti_{17}Mg_3O_{67}$.

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EXPERIMENTAL

We used In_2O_3 (99.9%) powders, TiO_2 powders (guaranteed reagent grade), and MgO powders (guaranteed reagent grade) as starting compounds. Prior to mixing the starting compounds, we heated them at 850°C in air for one day. TiO_2 had the rutile-type structure. The experimental facilities, equipment, and methods we employed are described in detail elsewhere (2). About 60 mixtures were made, sealed in Pt tubes, and heated at 1350°C for fixed periods, which was followed by rapid cooling at room temperature in order to establish the phase relations in the present ternary system. At 1100°C, all the starting mixtures were heated in Pt crucibles in air. The specimens obtained were supplied for X-ray powder diffractometry in order to identify the crystal structures and determine the lattice constants. Some specimens were supplied for both electron diffractometry and S.E.M. observation for identification of phase assemblages; the results were consistent with the data obtained by means of powder X-ray diffractometry.

RESULTS AND DISCUSSION

The Phase Relations in the System In_2O_3–TiO_2–MgO at 1100 and 1350°C

The phase relations in the system In_2O_3–TiO_2–MgO at 1100 and at 1350°C are shown in Figs. 1a and 1b. In Table 1(A) and Table 1(B), we list the starting mixtures, heating periods, and phases obtained in the present system.

TABLE 1A
Starting Mixtures, Heating Periods, and Phases Obtained in the System In_2O_3–TiO_2–MgO at 1100°C

In_2O_3 : TiO_2 : MgO = (in a mole ratio)	Heating period (days)	Phases obtained
3:5:1	5 + 7	In_2TiO_5, Mg_2TiO_5
2:7:1	7 + 7	In_2TiO_5, TiO_2, $MgTi_2O_5$
20:50:25	7 + 5	In_2TiO_5, In_2O_3, $MgTiO_3$
35:40:25	5 + 5	In_2O_3, In_2TiO_5, $MgTiO_3$
3:3:4	7 + 9	In_2O_3, $MgTiO_3$, Mg_2TiO_5
2:2:6	13 + 6 + 5	In_2O_3, Mg_2TiO_4, MgO
0:1:2	4 + 4 + 4	Mg_2TiO_4

$MgIn_2O_4$ (spinel-type, $a = 8.864(1)$ Å, *Fd*3*m* (no. 227), JCPDS card no. 40-1402) in the system In_2O_3–MgO (15), Mg_2TiO_4 (spinel-type, $a = 8.4409(3)$ Å, *Fd*3*m* (no. 227), JCPDS card no. 25-1157), $MgTiO_3$ (ilmenite-type, $a = 5.5054$ Å, and $c = 13.898$ Å, $R\bar{3}$ (no. 148), JCPDS card no. 6-0499), $MgTi_2O_5$ (pseudobrookite-type, $a = 9.7501(6)$ Å, $b = 9.9802(6)$ Å, and $c = 3.7483(3)$ Å, *Bbmm* (no. 63), JCPDS card no. 35-792) in the system MgO–TiO_2 (16, 17), and In_2TiO_5 ($a = 7.237$ Å, $b = 3.429$ Å, and $c = 14.86$ Å, *Pnma* (no. 62), JCPDS card no. 30-640) in the system In_2O_3–TiO_2 (18) are already known. At 1100 and 1350°C, there existed Mg_2TiO_4, $MgTiO_3$, and $MgTi_2O_5$ in the system MgO–TiO_2 and In_2TiO_5 in the system In_2O_3–TiO_2. At 1100°C, $MgIn_2O_4$ was not formed from the starting mixture of In_2O_3 and MgO. $MgIn_2O_4$

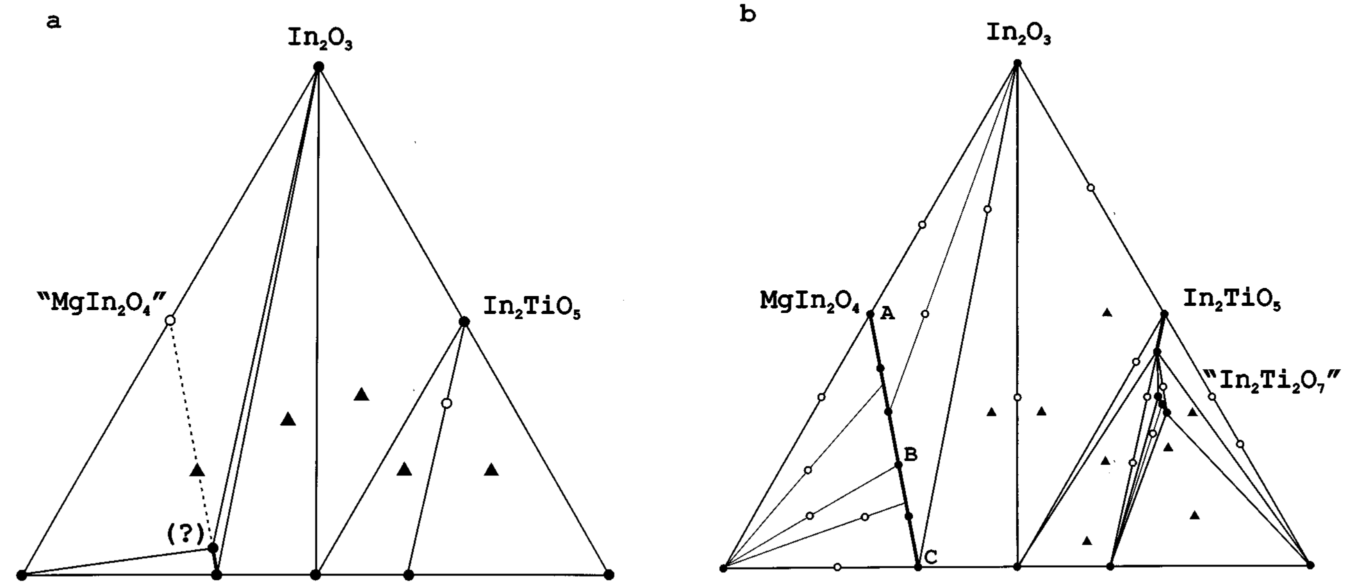

FIG. 1. (a) The phase relations in the system In_2O_3–TiO_2–MgO at 1100°C. (b) The phase relations in the system In_2O_3–TiO_2–MgO at 1350°C (symbols ● denotes that a single phase exists, ○ denotes that two phases coexist, and ▲ denotes that three phases coexist. (A) The phase on the A ($MgIn_2O_4$)–B ($Mg_{1.5}InTi_{0.5}O_4$)–C (Mg_2TiO_4) has the spinel structure. (B) In_2TiO_5 has a solid solution range to the direction to $MgTi_2O_5$. The solid solution range is $x = 0$–0.105 in $Mg_xIn_{2-2x}Ti_{1+x}O_5$. (C) A solid solution range of $In_6Ti_6MgO_{22}$ is to $In_{20}Ti_{17}Mg_3O_{67}$, (In_2O_3 : TiO_2 : MgO = 3:6:1 to 10:17:3 mole ratio).

TABLE 1B
Starting Mixtures, Heating Periods, and Phases Obtained in the System In_2O_3–TiO_2–MgO at 1350°C

In_2O_3 : TiO_2 :MgO = (in a mole ratio)	Heating period (days)	Phases obtained
1 : 1 : 3	6 + 6	spinel
1 : 1 : 1	6 + 6	In_2O_3,$MgTiO_3$
1 : 3 : 1	6 + 6	In_2TiO_5,$MgTi_2O_5$
0 : 1 : 2	5 + 5	spinel
0 : 1 : 1	5 + 5	$MgTiO_3$
2 : 0 : 1	5	In_2O_3, $MgIn_2O_4$
1 : 0 : 2	5	$MgIn_2O_4$, MgO
0 : 1 : 4	4 + 6	MgO, Mg_2TiO_4
7 : 1 : 2	4 + 6	In_2O_3, spinel
1 : 1 : 8	4 + 6	MgO, spinel
1 : 3 : 0	6 + 6 + 6	In_2TiO_5, TiO_2
3 : 1 : 0	6 + 6	In_2O_3, In_2TiO_5
1 : 1 : 0	5 + 5	In_2TiO_5
0 : 2 : 1	6 + 4	$MgTi_2O_5$
30 : 80 : 19	6 + 4	$MgTi_2O_5$, X_1, TiO_2
3 : 8 : 19	6 + 5	spinel
4 : 4 : 17	6 + 6	spinel
3 : 3 : 4	5 + 5	In_2O_3, spinel, $MgTiO_3$
6 : 1 : 8	6 + 6	spinel
3 : 4 : 3	4 + 5	In_2O_3, $MgTiO_3$, In_2TiO_5
4 : 5 : 1	5 + 5	In_2TiO_5, $MgTiO_3$
5 : 1 : 4	6 + 6	In_2O_3, spinel
4 : 1 : 12	6 + 5	spinel, MgO
1 : 2 : 7	4 + 5	spinel, MgO
6 : 13 : 1	5 + 5	X_1, In_2TiO_5, TiO_2
5 : 12 : 3	5 + 4	X_1, $MgTi_2O_5$
2 : 15 : 3	4 + 5	X_1, $MgTi_2O_5$, TiO_2
14 : 23 : 3	4 + 4	X_1, In_2TiO_5
26 : 47 : 7	5	X_1, In_2TiO_5
13 : 23 : 4	5	X_1
1 : 12 : 7	5	$MgTiO_3$, $MgTi_2O_5$, In_2TiO_5
4 : 7 : 1	5 + 5	X_1, In_2TiO_5
10 : 17 : 3	5 + 5	X_1
3 : 6 : 1	5 + 5	X_1
3 : 5 : 1	5 + 5	In_2TiO_5, $MgTi_2O_5$
6 : 11 : 2	5 + 5	X_1, $MgTi_2O_5$

TABLE 2
Lattice Constants of the Pseudobinary Compounds in the System In_2O_3–TiO_2–MgO at 1100°C

Compounds		Lattice constants (Å)
$MgIn_2O_4$	cubic	$a = 8.864(1)$
Mg_2TiO_4	cubic	$a = 8.441(1)$
$MgTiO_3$	hexagonal	$a = 5.054(1)$ $c = 13.893(1)$
$MgTi_2O_5$	orthorhombic	$a = 9.741(1)$ $b = 9.991(1)$ $c = 3.7442(5)$
In_2TiO_5	orthorhombic	$a = 7.233(1)$ $b = 3.489(2)$ $c = 14.856(6)$

synthesized at 1350°C was decomposed to In_2O_3 and MgO at 1100°C. $In_6Ti_6MgO_{22}$, which was synthesized at 1350°C was decomposed to In_2TiO_5, $MgTi_2O_5$, and TiO_2 at 1100°C. We concluded that there exists no ternary compounds in the present ternary system at 1100°C. The lattice constants for each compound in a single-phase state which we obtained in the pseudo-binary systems were identical within experimental errors to those in the above JCPDS cards. (See Table 2). At 1350°C, there are a spinel phase with a solid solution range $Mg_{2-x}Ti_{1-x}In_{2x}O_4$ ($0 \leq x \leq 1$) between $MgIn_2O_4$ and Mg_2TiO_4, a solid solution of In_2TiO_5 to the direction of the $MgTi_2O_5$ phase, $In_{2-2x}Mg_xTi_{1+x}O_5$ ($x = 0$–0.105), and an $In_6Ti_6MgO_{22}$ phase with a solid solution range to $In_{20}Ti_{17}Mg_3O_{67}$, which is isostructural with the monoclinic $In_3Ti_2FeO_{10}$ (9–11, 19). The relation between the lattice constant of the spinel phase and x in $Mg_{2-x}Ti_{1-x}In_{2x}O_4$ is shown in Fig. 2. We concluded that the relation nearly satisfies Vegard's law. Since both $MgIn_2O_4$ and Mg_2TiO_4 have inversed spinel-type structure (20), we can reasonably postulate the following cationic distribution in a whole range of the solid solution: $(In)\{MgIn\}O_4$–$(In_{1-y}Mg_y)\{MgIn_{1-y}Ti_y\}O_4$–$(Mg)\{MgTi\}O_4$. Parentheses signifies the tetrahedral site and brackets denote the octahedral one in the spinel structure ($0 \leq y \leq 1$). Shannon (1) estimated the ionic radii for In(III), Mg(II), and Ti(IV) as (In(III)): 0.62 Å, (Mg(II)): 0.57 Å, {In(III)}: 0.800 Å, {Mg(II)}: 0.72 Å, {Ti(IV)}: 0.605 Å. If we take the above ionic sizes for each ion and the following relations for the lattice constant for the spinel, $a = \{(8/3 \times 3^{1/2})\} \times (\text{tet.bond})\} + (8/3) \times (\text{oct.bond})\}$, assuming $u = 0.25$ (18), we can reasonably explain the inclination

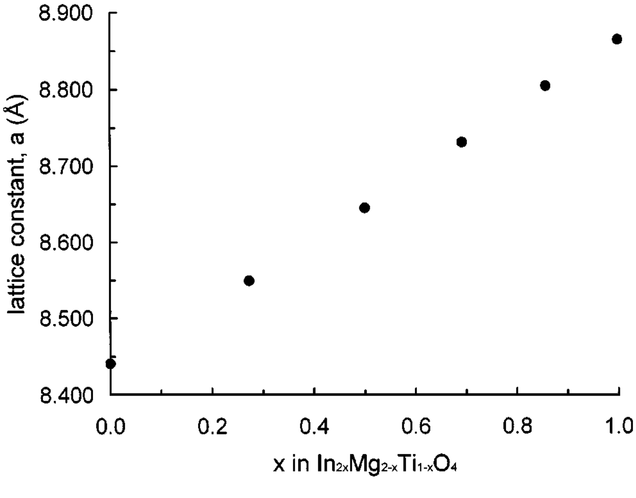

FIG. 2. The relation between the lattice constants of the spinel phase and the chemical composition x in $Mg_{2-x}In_{2x}Ti_{4-x}O_4$ synthesized at 1350°C.

in Fig. 2. Here, we can estimate (tet.bond) and (oct.bond) as

$$(\text{tet.bond}) = 0.62 + 1.40 = 2.02\,\text{Å},$$

$$(\text{oct.bond}) = (1/2)\times(0.8 + 0.72) + 1.40 = 2.16\,\text{Å},$$

for (In){MgIn}O_4,

$$(\text{tet.bond}) = 0.57 + 1.40 = 1.97\,\text{Å},$$

$$(\text{oct.bond}) = (1/2)(0.72 + 0.605) + 1.40 = 2.06\,\text{Å}$$

for (Mg){MgTi}O_4.

Then the difference between the lattice constants is [the lattice constant of (In){MgIn}O_4]-[the lattice constant of (Mg){MgTi}O_4] = 0.34 Å. (See the experimental value 0.4 Å in Fig. 2.) Here we adopted 1.40 Å for the ionic radius of oxygen ion (1). We think that the present experimental value and the estimated value from the spherical model are rather consistent with each other. Although there exists $R_2Ti_2O_7$ (R: Sm–Lu, Y, and Sc) with cubic pyrochlore-type structure in the system R_2O_3–TiO_2 at elevated temperatures, as we mentioned above, no $In_2Ti_2O_7$ with pyrochlore-type structure has been reported (9, 13, 14). As shown in Fig. 1, there does not exist $In_2Ti_2O_7$ at 1100 and 1350°C in the present work; however, there is $In_6Ti_6MgO_{22}$, which is isostructural with the monoclinic $In_6Ti_6ZnO_{22}$, (19). As we showed in (9), the crystal structure of monoclinic $In_3Ti_2FeO_{10}$ has a close relation to that of the pyrochlore-type structure, which was clarified by both powder X-ray diffractometry and electron diffractometry. Between their lattice constants, there are the following approximate relations: $\mathbf{a}_m = (-1/4)\mathbf{a}_p + (-1/2)\mathbf{b}_p + (-1/4)\mathbf{c}_p$, $\mathbf{b}_m = (-1/4)\mathbf{a}_p + (0)\mathbf{b}_p + (1/4)\mathbf{c}_p$, $\mathbf{c}_m = (1/4)\mathbf{a}_p + (-1/2)\mathbf{b}_p + (1/4)\mathbf{c}_p$, and $\beta(°) = 109.47$, where $\mathbf{a}_m$, $\mathbf{b}_m$, $\mathbf{c}_m$, and β are the unit cell vectors of the $In_3Ti_2FeO_{10}$, and $\mathbf{a}_p$, $\mathbf{b}_p$, and $\mathbf{c}_p$ are those of the cubic pyrochlore with $a_p = b_p = c_p$. The lattice constants of $In_6Ti_6MgO_{22}$ and $In_{20}Ti_{17}Mg_3O_{67}$ are listed in Table 3. The single-crystal structure analyses for the orthorhombic $In(Ti_{0.67}Fe_{0.33})O_{3.33}$ (11), the monoclinic $In(Ti_{0.75}Fe_{0.25})O_{3.38}$ (19), and the monoclinic $(In_{0.92}Ti_{0.08})(Ti_{0.85}Zn_{0.15})O_{3.38}$ (19) were recently carried out using single-crystal diffractometry, and it was clarified that their crystal structures are closely related to that of the hexagonal $InFeO_3$ with layered structure consisting of alternating layers of InO_6 octahedra and FeO_5 trigonal bipyramids (12). Since all the compounds $In_6Ti_6BO_{22}$ (B: Mg, Mn, Co, Ni, Cu, or Zn), which we made from a mixture of $In_2O_3 : TiO_2 : BO = 3 : 6 : 1$ (in a mole ratio), were identified to be isostructural with each other by means of powder X-ray diffractometry (10), we conclude that {0.92In(III) and 0.08 Ti(IV)} take the site I and {0.85Ti(IV) and 0.15B(II)} take the site II in both $In_6Ti_6ZnO_{22}$ and $In_6Ti_6MgO_{22}$. Therefore, Ti(IV) in $In_6Ti_6MgO_{22}$ takes both crystallographic sites as in $In_6Ti_6ZnO_{22}$. Comparing the relative intensities of powder X-ray diffraction peaks of the monoclinic $In_{20}(Ti_{17}Mg_3)O_{67}$ with those of the monoclinic $In(Ti_{0.75}Fe_{0.25})O_{3.38}$, we conclude that {Ti(IV) and Mg(II)} take the same crystallographic site as {Ti(IV) and Fe(III)} in $In(Ti_{0.75}Fe_{0.25})O_{3.38}$. In Table 4, we summarize the distributions of all the cations in the unison-X_1 compounds. The In(III) in unison-X_1 in the systems In_2O_3–TiO_2–Fe_2O_3, In_2O_3–TiO_2–ZnO, and In_2O_3–TiO_2–MgO take site I, both the Mg and the Zn take site II, and the Ti(IV) takes site II; however, a part of Ti(IV) takes site I in the system In_2O_3–TiO_2–BO (B: Mg or Zn) also. As we mentioned above, both Mg(II) and In(III) take both the tetrahedral site and the octahedral site in the spinel solid solutions. We conclude that both In(III) and Mg(II) take from 4 to 6, Ti(IV) takes 5 to 6 in the coordination number in the system In_2O_3–TiO_2–MgO at 1350°C in air. Considering each ionic size and electronic structure of all the cations and the CN of site I and site II, we think that the data in Table 4 are quite reasonable. The crystal structural relations between the pyrochlore, the hexgonal $InFeO_3$, and the unison-X_1 will be clarified soon (21).

TABLE 3
Lattice Constants of the Monoclinic unison-X_1

Compound	a (Å)	b (Å)	c (Å)	β (°)	q^a	V (Å^3)
$In_6Ti_6MgO_{22}$	5.9236(7)	3.3862(4)	6.3609(6)	108.15(1)	0.369	121.2
$In_{20}Ti_{17}Mg_3O_{67}$	5.9230(5)	3.3823(3)	6.3698(6)	108.10(5)	0.360	121.3

[a] For a definition of q, see the Refs. (9, 10).

TABLE 4
Distribution of the Cations in the unison-X_1

Compound	Site (I)	Site (II)	(In){Ti_xFe_{1-x}}$O_{3+x/2}$
o-$In_3Ti_2FeO_{10}$ (11)	In(III)	2/3Ti(IV) + 1/3Fe(III)	(In){$Ti_{0.67}Fe_{0.33}$}$O_{3.333}$
m-$In_8Ti_6Fe_2O_{27}$ (19)	In(III)	3/4Ti(IV) + 1/4Fe(III)	(In){$Ti_{0.75}Fe_{0.25}$})$O_{3.375}$
m-$In_{20}Ti_{17}Mg_3O_{67}$	In(III)	0.85Ti(IV) + 0.15Mg(II)	(In){$Ti_{0.85}Mg_{0.15}$})$O_{3.350}$
r-$In_6Ti_6ZnO_{22}$ (19)[a] site(I): 0.92In(III) + 0.08Ti(IV) site(II): 0.85Ti(IV) + 0.15Zn(II) $(In(III)_{0.92}Ti(IV)_{0.08})$\{$Ti(IV)_{0.85}Zn_{0.15}$\}$O_{3.375}$			
m-$In_6Ti_6MgO_{22}$ site(I): 0.92In(III) + 0.08Ti(IV) site(II): 0.85Ti(IV) + 0.15Mg(II) $(In(III)_{0.92}Ti(IV)_{0.08})$\{$Ti(IV)_{0.85}Mg_{0.15}$\}$O_{3.375}$			

Note. o signifies orthorhombic, m signifies monoclinic, and r signifies rhombohedral.

[a] The crystal structure of m-$In_6Ti_6MgO_{22}$ is slightly distorted from that of r-$In_6Ti_6ZnO_{22}$. The cation site(I) is located in the layer of the oxygen-octahedra. The cation site(II) is located in the layer of the trigonal cation sublattice points along with the oxygen on the honeycomb anion sublattice. The oxygen CN of the site(II) is between 5 and 6.

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