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Acta Cryst. (1999). C**55**, 1755–1757

Orthorhombic $InFe_{0.33}Ti_{0.67}O_{3.33}$

YUICHI MICHIUE,[a] FRANCISCO BROWN,[b] NOBORU KIMIZUKA,[b] MAMORU WATANABE,[a] MASAHIRO ORITA[c] AND HIROMICHI OHTA[c]

[a]*National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan,* [b]*Centro de Investigaciones en Polimeros y Materiales, Universidad de Sonora, Rosales, Hermesillo, Sonora CP 83000, Mexico, and* [c]*R&D Center, Hoya Corporation, 3-3-1 Musashino, Akishima, Tokyo 196-8510, Japan. E-mail: michiue@nirim.go.jp*

(*Received 6 April 1999; accepted 1 July 1999*)

Abstract

The title compound, indium iron titanium oxide, is closely related to $InFeO_3$, having a hexagonal structure which consists of alternating layers of InO_6 octahedra and FeO_5 trigonal bipyramids. According to substitution of Ti^{4+} for Fe^{3+}, excess O atoms are introduced into the Fe–O trigonal lattice plane of $InFeO_3$. The in-plane arrangement of O atoms can be described as partial occupation on a honeycomb lattice, although large displacement parameters indicate local shifts of O atoms due to repulsive interactions between them.

Comment

Recently, new phases with monoclinic and orthorhombic structures have been found in the system $InFeO_3$–$In_2Ti_2O_7$ (Brown, Flores *et al.*, 1999), and their isostructural compounds were also obtained in various solid-solution systems (Brown, Kimizuka *et al.*, 1999). Structural details of these phases are of interest but complicated due to commensurate or incommensurate satellite reflections (Brown, Flores *et al.*, 1999). This study is the first on the analysis of this family. The average structure of orthorhombic $InFe_{0.33}Ti_{0.67}O_{3.33}$ has been determined using main reflections only, although the crystals showed incommensurate ($q \simeq 0.31a^*$) satellite reflections.

The structure is closely related to that of $InFeO_3$, in which two kinds of coordination polyhedral layers are stacked along the *c* axis; one is an InO_6 octahedral layer and the other is an FeO_5 trigonobipyramidal layer (Giaquinta *et al.*, 1994). The structure of orthorhombic $InFe_{0.33}Ti_{0.67}O_{3.33}$ is given by deformation of the hexagonal $InFeO_3$ structure [a = 3.3270 (2) Å and c = 12.1750 (1) Å]. A considerable amount of Ti^{4+} is substituted for Fe^{3+} in $InFe_{0.33}Ti_{0.67}O_{3.33}$. The charge neutrality is maintained by the introduction of excess O atoms into the Fe–O2 trigonal plane. This phase being clearly distinct from $InFeO_3$, the O3 site, as well as the O2 site, is used to accommodate O atoms. Occupation ratios are greater than 0.5 at both sites and the amount of O atoms in the plane is 1.33 times that of $InFeO_3$. Thus, the arrangement of O atoms in this plane results in a partially occupied honeycomb lattice, as illustrated in Fig. 1(*a*), while $InFeO_3$ gives a fully occupied triangle lattice of O2 sites, as shown in Fig. 1(*b*). An example of prob-

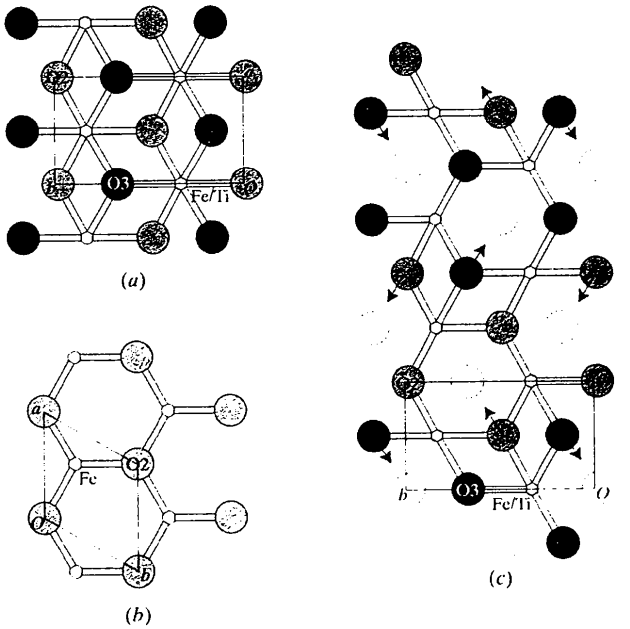

Fig. 1. The atomic arrangement on the plane $z = \frac{1}{4}$ for (*a*) the average structure of $InFe_{0.33}Ti_{0.67}O_{3.33}$ with the O2 and O3 sites partially occupied, (*b*) $InFeO_3$ and (*c*) an example of local structures of $InFe_{0.33}Ti_{0.67}O_{3.33}$. Dotted circles are vacant oxygen sites. Arrows indicate probable displacements of O atoms.

able local structures in the plane of $InFe_{0.33}Ti_{0.67}O_{3.33}$ is shown in Fig. 1(*c*). This explains the fact that the *ab* plane of $InFe_{0.33}Ti_{0.67}O_{3.33}$ was expanded in comparison with $InFeO_3$ in spite of replacement of Fe^{3+} (0.645 Å, in six coordination) by smaller Ti^{4+} (0.605 Å) (Shannon, 1976); the rectangle area defined by *a* and *b* [3.3504 × 5.8341 = 19.5466 Å^2] is about 2% larger than that of $InFeO_3$ converted to an orthohexagonal cell [3.3270 × 3.3270 × $3^{1/2}$ = 19.1719 Å^2].

The In—O1 and apical Fe(Ti)—O1 distances in $InFe_{0.33}Ti_{0.67}O_{3.33}$ are close to those in both $InFeO_3$ [In—O1 2.182 (2) Å and Fe—O1 2.008 (4) Å; Giaquinta *et al.*, 1994] and $InMnO_3$ [In—O1 2.202 (3) Å; Giaquinta & zur Loye, 1992]. In the plane consisting of Fe(Ti), O2 and O3, metal–oxygen distances are widely distributed [Fe(Ti)—O2 1.90 (2)–2.02 (4) Å and Fe(Ti)—O3 1.92 (2)–1.98 (5) Å], while the Fe—O2 distance in $InFeO_3$ is fixed at 1.9208 (1) Å. Significant anisotropy has been observed in the displacement parameters of the O2 and O3 atoms, *i.e.*, the U_{11} [O2 0.094 (9), O3 0.13 (2) Å^2] and U_{22} values [O2 0.064 (10), O3 0.06 (1) Å^2] are unusually large, while the U_{33} values [O2 0.013 (3), O3 0.014 (5) Å^2] are generally normal. Judging from the short O2—O3 distances in Table 2, these large displacement parameters are attributed to the local shifts (shown schematically by arrows in Fig. 1*c*), which probably occur to reduce the repulsion between the O atoms. The coordination character and geometry in this compound should be unambiguously determined by considering positional and/or occupational modulation, the analysis of which, including satellite reflections, is now in progress.

Experimental

A mixture of In_2O_3, TiO_2 and Fe_2O_3 (3:4:1 molar ratio) was heated at 1573 K in air for 1 d to form orthorhombic $InFe_{0.33}Ti_{0.67}O_{3.33}$ in a single phase. The product was reheated at 1943 K for 3 h, cooled to 1773 K at a rate of 1 K min^{-1} and annealed at 1573 K for 2 d.

Crystal data

$InFe_{0.33}Ti_{0.67}O_{3.33}$
M_r = 218.62
Orthorhombic
Cmcm
a = 3.3504 (3) Å
b = 5.8341 (7) Å
c = 12.070 (5) Å
V = 235.92 (7) Å^3
Z = 4
D_x = 6.155 Mg m^{-3}
D_m not measured

Mo *K*α radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 26.0–27.1°
μ = 13.795 mm^{-1}
T = 296.2 K
Plate
0.26 × 0.13 × 0.04 mm
Brown

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
T_{min} = 0.183, T_{max} = 0.567
1416 measured reflections
708 independent reflections

492 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
θ_{max} = 50.07°
$h = 0 \rightarrow 7$
$k = -12 \rightarrow 12$
$l = 0 \rightarrow 26$
3 standard reflections every 200 reflections intensity decay: 0.08%

Refinement

Refinement on F^2
$R(F)$ = 0.032
$wR(F^2)$ = 0.057
S = 3.957
708 reflections
25 parameters
Weighting scheme based on measured s.u.'s
$(\Delta/\sigma)_{max}$ = 0.043

$\Delta\rho_{max}$ = 1.17 e Å^{-3}
$\Delta\rho_{min}$ = −1.15 e Å^{-3}
Extinction correction: Zachariasen (1967) type 2, Gaussian isotropic
Extinction coefficient: 4.3 (2) × 10^{-6}
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	Occupancy	x	y	z	U_{eq}
In	1.00	0	0	0	0.00923 (7)
Fe	0.33	0	1/3	1/4	0.0371
Ti	0.67	0	0.333 (1)	1/4	0.0371 (5)
O1	1.00	0	0.3301 (6)	0.0846 (2)	0.0114 (6)
O2	0.74	0	0.988 (6)	1/4	0.057 (4)
O3	0.59	0	0.673 (8)	1/4	0.068 (6)

Table 2. *Selected bond lengths (Å)*

In—O1	2.180 (4)	Fe/Ti—O2^{vii}	2.02 (4)
In—O1^{i}	2.180 (4)	Fe/Ti—O2^{v}	1.90 (2)
In—O1^{ii}	2.198 (2)	Fe/Ti—O3	1.98 (5)
In—O1^{iii}	2.198 (2)	Fe/Ti—O3^{iii}	1.92 (2)
In—O1^{iv}	2.198 (2)	Fe/Ti—O3^{v}	1.92 (2)
In—O1^{v}	2.198 (2)	O2—O3	1.83 (2)
Fe/Ti—O1	1.996 (3)	O2—O3^{viii}	1.99 (1)
Fe/Ti—O1^{vi}	1.996 (3)	O2—O3^{ix}	1.99 (1)
Fe/Ti—O2^{iii}	1.90 (2)		

Symmetry codes: (i) $x, -y, -z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, -z$; (iii) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (iv) $x-\frac{1}{2}, \frac{1}{2}-y, -z$; (v) $\frac{1}{2}+x, y-\frac{1}{2}, z$; (vi) $x, y, \frac{1}{2}-z$; (vii) $x, y-1, z$; (viii) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (ix) $x-\frac{1}{2}, \frac{1}{2}+y, z$.

Although the structure (Laue class *mmm*) has a pseudo-hexagonal symmetry, Laue class 6/*mmm* was ruled out by an intensity check of equivalent reflections using *Rigaku/AFC Diffractometer Control Software* (Rigaku, 1998). Reflection conditions are *h* + *k* = 2*n* for *hkl* and *l* = 2*n* for *h*0*l*, which gives possible space groups *C*2*cm* and *Cmcm*. Positional parameters of $InFeO_3$ (Giaquinta *et al.*, 1994) were used as initial values of refinement. Ti atoms were substituted for two thirds of Fe atoms according to the chemical composition of a starting mixture in the crystal-growth process. The additional oxygen site, O3, was found by difference Fourier syntheses. Occupational parameters at the O2 and O3 sites were refined under the condition that a sum of these oxygen contents is fixed to 5.33 per unit cell so as to keep charge neutrality in the unit cell.

Data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku, 1998). Cell refinement: *Rigaku/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1998). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

YM is grateful to Dr Mitsuko Onoda in NIRIM for helpful discussion.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OH1115). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1757–1759

Refinement of $CaBa_2(HPO_4)_2(H_2PO_4)_2$

LOTFI BEN TAHAR,[a] LEILA SMIRI[a] AND AHMED DRISS[b]

[a]*Département de Chimie, Faculté des Sciences de Bizerte, 7021 Zarzouna, Bizerte, Tunisia, and* [b]*Département de Chimie, Faculté des Sciences, 1060 Campus Universitaire, Tunis, Tunisia. E-mail: leila.smiri@fsb.rnu.tn*

(Received 11 January 1999; accepted 29 June 1999)

Abstract

The structural model proposed previously for calcium dibarium bis(hydrogenphosphate) bis(dihydrogenphosphate) from X-ray powder data is confirmed by the present single-crystal study. The structure consists of infinite $[Ca(HPO_4)_2(H_2PO_4)_2]$ anionic chains built up from CaO_6, HPO_4 and H_2PO_4 polyhedra linked *via* Ca—O—P bonds. These chains are held together by nine-coordinate Ba^{2+} cations. A two-dimensional network of hydrogen bonds contributes to the linkage of these chains.

Comment

The alkaline earth phosphates $M_3(PO_4)_2$, MHPO$_4$ and $M(H_2PO_4)_2$ (M = Mg, Ca, Sr or Ba) have been studied extensively for their applications in different areas. Mixed alkaline earth phosphates, $M_2M'(PO_4)_2$, have also been studied. However, to our knowledge, there is very scant information on mixed alkaline earth hydrogenphosphates.

Our research efforts have focused on synthesizing new compounds of mixed alkaline earth phosphates. The title compound has recently been prepared and its structure based on X-ray powder diffraction data has been reported (Toumi *et al.*, 1997), but no attempt was made to locate the H atoms. Nevertheless, some hydrogen bonds were suggested on the basis of O···O contacts. Using hydrothermal synthesis, we have successfully obtained single crystals of this compound in order to refine the structure, including the hydrogen-bond system.

The structure of $CaBa_2(HPO_4)_2(H_2PO_4)_2$ is shown in Fig. 1. It consists of infinite chains of corner-sharing CaO_6 octahedra and H_2P1O_4 and $HP2O_4$ tetrahedra running along the *a* axis. Each CaO_6 centre is bridged to its neighbours by two pairs of P2 groups; thus, the Ca–Ca linkage is *via* Ca—O—P—O—Ca bonds. The two remaining *trans* corners of the octahedron, O4, are shared with two P1 groups. The polyhedral connectivity leads to infinite $[Ca(HPO_4)_2(H_2PO_4)_2]$ anionic chains. These chains are crosslinked by the Ba^{2+} cations. Further linkages are provided by hydrogen bonds.

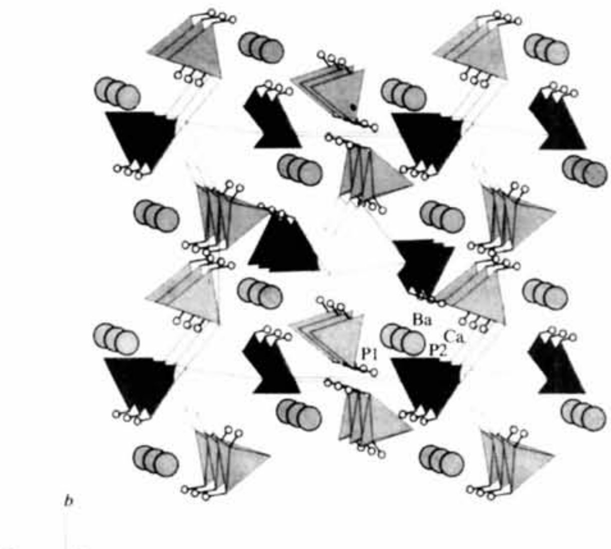

Fig. 1. Polyhedral view of the structure of $CaBa_2(HPO_4)_2(H_2PO_4)_2$. Ba^{2+} ions and H atoms are represented by spheres of arbitrary radii.

The Ba^{2+} ion is coordinated to nine O atoms located within 3.1 Å. These BaO_9 polyhedra are connected *via* atoms O7 to form infinite strings running along the *a*