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Structure of Indium Iron Oxide

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Abstract

$InFeO_3$ is isostructural with the recently reported $InMnO_3$. The structure of $InFeO_3$ contains layers of In–O octahedra and Fe–O trigonal bipyramids. The trigonal bipyramids have ideal D_{3h} symmetry. This unusual structure is unexpected within the context of known sesquioxide structures.

Comment

Sesquioxides of indium and iron oxides form in both the corundum and C–M_2O_3 structures under the appropriate conditions (Wells, 1984). It is of interest, therefore, to report the structure of $InFeO_3$, which is related to neither the corundum nor the C–M_2O_3 structures. Instead, the structure of $InFeO_3$ resembles most closely the hexagonal rare-earth manganate and rare-earth aluminate structures (Bertaut & Mareschal, 1963; Geller, Jefferies & Curlander, 1975). Although multiphase polycrystalline samples of $InFeO_3$ have been reported in the literature (Nodari, Alebouyeh, Brice, Gerardin & Evrard, 1988; Gerardin, Aqachmar, Alebouyeh & Evrard, 1989) the single-crystal structure has not been determined previously. This unusual layered ABO_3 main group–transition metal oxide is, in fact, isostructural with the recently reported $InMnO_3$ (Giaquinta & zur Loye, 1992).

The structure of $InFeO_3$ is shown in Fig. 1, based on the positional data of Table 1. Bond distances and angles are listed in Table 2. The structure may be described as consisting of alternating layers of octahedra and trigonal bipyramids (Fig. 1). The In atoms are situated within the octahedral interstices of close-packed O(1) layers. All the octahedral interstices are filled. The O(1) layers are separated by Fe—O(2) hexagonal layers of the (6,3) type (Wells, 1977). Fe is coordinated in a trigonal bipyramidal fashion with the apical O atoms coming from the In—O(1) octahedra. The Fe—O(2) layers are staggered such that they repeat with every other layer.

The Fe coordination has ideal D_{3h} symmetry, as found in the isostructural $InMnO_3$ (Giaquinta & zur Loye, 1992). The apical bond in the trigonal bipyramids of $InFeO_3$ is elongated compared to that found in $InMnO_3$; the *c* axis is also significantly longer, although the ionic radii of Mn^{3+} and Fe^{3+} are identical according to Shannon (1976). This elongation of the apical bond, and consequently the *c* axis, is consistent with the presence of an electron in the d_{z^2} orbital for high-spin Fe^{3+} (d^5) *vs* high-spin Mn^{3+} (d^4). Consequently, the difference in *c*-axis lengths between the Mn and Fe compounds can be explained by an elongation and weakening of the axial Fe—O bond which effects a lowering in the energy level of the d_{z^2} orbital. This results in a Fe—O(1) distance that is 0.14 Å longer than the corresponding Mn—O(1) distance, as well as an in-plane trigonal Fe—O(2) distance that is shorter than the apical Fe—O(1) distance in $InFeO_3$, while for $InMnO_3$ the opposite is true.

The difference between both $InMnO_3$ and $InFeO_3$, and the related $YAlO_3$ (Bertaut & Mareschal, 1963; Bertaut *et al.*, 1965) is even more marked. $YAlO_3$ is wider than $InMnO_3$ in the *a* plane (3.678 *vs* 3.398 Å); however, the *c* parameter is dramatically shorter (10.52 *vs* 11.48 Å). The Al—O bond lengths in $YAlO_3$ are surprisingly similar to the Fe—O bond lengths found in $InFeO_3$ even though the *c* axis is almost 2 Å shorter. The in-plane trigonal Al—O distances are 2.12 Å, while the apical Al—O distances are 1.82 Å. The contraction of the *c* axis seems to be related to the coordination requirement of the rare-earth atom. Yttrium wants to increase its coordination from six- to eightfold coordination and the *z*-axis contraction enables the Y atom to bond with two additional next-nearest neighbour O(1) atoms. In the case of In, however, this contraction is neither necessary (In is perfectly content in sixfold coordination) nor possible (the amount of contraction necessary to provide the additional bonding

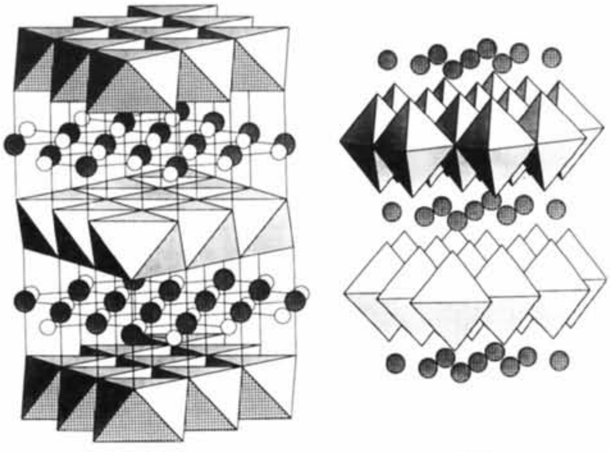
(*a*) (*b*)

Fig. 1. Polyhedral representations of (*a*) the octahedral indium coordination (circles represent Fe) and (*b*) the trigonal bipyramidal iron coordination (circles represent In).

contacts would be prohibitively large). This contraction is a function of the rare-earth atom in the *A* site and consequently $InFeO_3$ and $InMnO_3$ are structurally different from $YAlO_3$ and the isostructural $YFeO_3$ (Yamaguchi, Takemura & Yamashita, 1991).

Experimental

Crystal data

$InFeO_3$
$M_r = 218.67$
Hexagonal
$P6_3/mmc$
$a = 3.3270\ (2)$ Å
$c = 12.1750\ (1)$ Å
$V = 116.76\ (2)$ Å^3
$Z = 2$
$D_x = 6.219$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 9\text{-}12°$
$\mu = 15.66$ mm^{-1}
$T = 296$ K
Hexagonal plate
0.08 × 0.08 × 0.02 mm
Brown

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.89$, $T_{\max} = 1.10$
1027 measured reflections
113 independent reflections
85 observed reflections $[I > 3.00\sigma(I)]$

$R_{\text{int}} = 0.028$
$\theta_{\max} = 29.8°$
$h = 0 \rightarrow 4$
$k = -4 \rightarrow 4$
$l = -16 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity variation: no decay

Refinement

Refinement on F
$R = 0.014$
$wR = 0.015$
$S = 1.28$
85 reflections
11 parameters
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.54$ e Å^{-3}
$\Delta\rho_{\min} = -0.74$ e Å^{-3}

Extinction correction: secondary (*TEXSAN*; Swepston, 1985)
Extinction coefficient: $0.2545\ (2) \times 10^{-4}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2A, 2.3.1)

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

$$B_{\text{eq}} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
In	0.0	0.0	0.0	0.48 (2)
Fe	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{4}$	0.32 (3)
O(1)	$\frac{2}{3}$	$\frac{1}{3}$	0.0850 (3)	0.55 (8)
O(2)	0.0	0.0	$\frac{1}{4}$	0.7 (1)

Table 2. *Geometric parameters* (Å, °)

In—In	3.3270 (2)	Fe—O(2) ×3	1.9208 (1)
In—O(1) ×6	2.182 (2)	In—Fe	3.5992 (1)
Fe—O(1) ×2	2.008 (4)	Fe—Fe	3.3270 (2)
O(1)—In—O(1) ×2	99.3 (1)	O(1)—Fe—O(2) ×6	90
O(1)—In—O(1) ×4	80.7 (1)	O(2)—Fe—O(2) ×3	120
O(1)—In—O(1) ×2	180		

Single crystals of $InFeO_3$ were prepared from In_2O_3 (Cerac, 99.99%) and Fe_2O_3 (Cerac, 99.99%) in a Bi_2O_3 (Cerac, 99.9%) flux. Approximately 3 mmol of the binary oxides were ground together under acetone and pelletized. The flux to reactants ratio was 1:1:1. The pellet was heated to 1223 K for 3 d in air on platinum foil and quenched to room temperature. Partial melting occurred during the heating cycle resulting in the formation of dark-brown hexagonal plates of $InFeO_3$ on the surface of the pellets. The flux matrix was weakened with concentrated nitric acid and crystals were separated mechanically. Elemental analysis by energy dispersive spectroscopy (EDS) showed the presence of In and Fe, but no Bi impurities were detected. The metal stoichiometry was confirmed by microprobe to be 1:1.

Careful screening of single crystals by precession methods allowed the selection of single crystals for structure determination. A complete set of precession photos was obtained using a Charles Supper Co. precession camera, with a crystal-to-film distance of 60 mm and a precession angle of 10°, mounted on an Enraf-Nonius 581 Diffractis X-ray generator.

ω scans of several intense reflections, made prior to data collection, had an average width at half height of 0.32° with a take-off angle of 2.8°. Scans of $(0.80 + 0.35\tan\theta)°$ were made at speeds of 0.9-8.0° min^{-1} in ω. The weak reflections $[I < 10\sigma(I)]$ were rescanned a maximum of eight times and the counts accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.8 mm and the crystal-to-detector distance was 173.0 mm. Data were corrected for Lorentz and polarization effects.

Calculations were performed on a MicroVAX 3500 with the use of *TEXSAN* crystallographic software (Sweptson, 1985). The In and transition-metal positions were determined by direct methods (Sheldrick, 1985). O-atom positions were determined by the examination of difference electron density maps.

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Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71436 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1059]

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Structure of $SrMo_5O_8$ Containing Chains of Bioctahedral Mo_{10} Clusters

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Abstract

The title compound, strontium pentamolybdate, is isostructural with $LaMo_5O_8$ and therefore contains bioctahedral $Mo_{10}O_{18}$ cluster units strongly linked by Mo(1)—Mo(1) intercluster bonds of 2.7651 (9) Å to form infinite molybdenum oxide chains. These are interconnected through Mo—O—Mo bonds to create four-sided channels, in which the Sr^{2+} cations are located. The Mo—Mo distances within the Mo_{10} cluster lie between 2.6034 (6) and 2.8324 (9) Å (average 2.740 Å). The Mo—O distances range between 1.902 (4) and 2.148 (4) Å (average 2.062 Å). The Sr^{2+} cation is surrounded by ten O atoms at distances ranging from 2.529 (4) to 2.935 (4) Å, with an eleventh O atom at 3.219 (4) Å.

Comment

The present work constitutes part of our program on the study of the structural and physical properties of the compounds MMo_5O_8 (M = Ca, Sr, Ba, Sn, Pb, La, Ce, Pr, Nd, Sm, Eu and Gd), containing chains of bioctahedral Mo_{10} clusters. The prototype compound $LaMo_5O_8$ was synthesized by Hibble, Cheetham, Bogle, Wakerley & Cox (1988). Later isostructural compounds were obtained with other light rare earths (RE) such as Ce, Pr, Nd, Sm, Eu and Gd (Gougeon, Gall & Sergent, 1991; Gall, 1990, 1993), as well as with elements of Group IVB (Sn: Gougeon, Potel & Sergent, 1990; and Pb: Dronskowski & Simon, 1989; Dronskowski, Simon & Mertin, 1991) and alkaline-earth metals (Ca: Torardi & McCarley, 1981; Sr: Gougeon, Gall & Sergent, 1991; and Ba: McCarley, Schimek, Chen & Nagaki, 1992). We present here the crystal structure of $SrMo_5O_8$.

The structure type MMo_5O_8 has been described previously in detail by many authors (Hibble, Cheetham, Bogle, Wakerley & Cox, 1988; Dronskowski & Simon, 1989; Gougeon, Potel & Sergent, 1990). Its basic structural building block is the bioctahedral cluster unit $Mo_{10}O_{18}$, which results from the metal-edge condensation of two Mo_6O_{12}-type cluster units (Fig. 1). The $Mo_{10}O_{18}$ cluster units are linked on opposite edges *via* common O atoms to form infinite chains in which the Mo_{10} clusters are strongly linked through intercluster Mo—Mo bonds (Fig. 2*a*). These chains, which run parallel to the *a* axis, then interlink through O atoms to create one-dimensional four-sided channels where the cations reside (Fig. 2*b*).

The Mo—Mo distances within the double-octahedron range between 2.6034 (6) and 2.8324 (9) Å, with the shortest of these occurring between the apical atoms Mo(3) and Mo(4) and the largest between the Mo(5) atoms of the shared edge. The average value is 2.740 Å and does not change significantly from those observed in the other compounds with divalent ($SnMo_5O_8$ 2.746 Å and $PbMo_5O_8$ 2.745 Å) or trivalent cations ($RE^{3+}Mo_5O_8$ 2.746–2.750 Å). The intercluster distances are 2.7651 (9), 3.0380 (6) (× 2) and 3.0869 (6) Å (× 2) and are close to the corresponding distances in $SnMo_5O_8$ [2.796 (1), 3.037 (1) (× 2) and 3.089 (1) Å (× 2)] and $PbMo_5O_8$ [2.784 (5), 3.034 (4) (× 2) and 3.083 (3) Å (× 2)]. On the other hand, the two short-

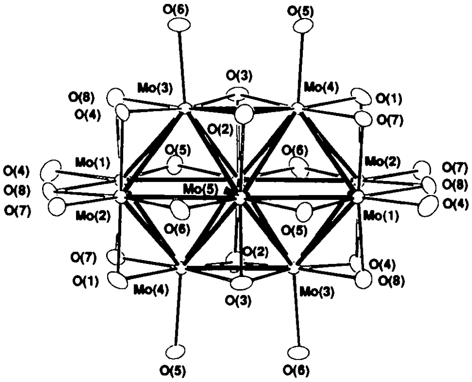

Fig. 1. The $Mo_{10}O_{18}$ cluster unit and its eight additional corner-linked O atoms. The inversion centre occurs at the middle of the Mo(5)—Mo(5) bond.

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