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Tl_2MoO_4 at 350 K

K. Friese,[a] G. Madariaga[a] and T. Breczewski[b]

[a]*Departamento de Física de la Materia Condensada, Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain, and* [b]*Departamento Física Aplicada II, Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain. E-mail: wmbfrxxk@lg.ehu.es*

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Abstract

The structure of the title compound, dithallium molybdate, is isotypical with the glaserite structure and Tl_2WO_4. The Mo ion is coordinated tetrahedrally by oxygen, with bond lengths ranging from 1.699 (16) to 1.725 (16) Å, and angles between 107.6 (4) and 111.3 (4)°. The shortest O–O edge length is 2.83 (2) Å. Three independent Tl ions are observed in the structure. The coordination polyhedron around Tl1 can be described as a distorted octahedron, with Tl—O distances of 2.769 (10) Å. Tl2 has a coordination number of 12, with six O atoms at a distance of 2.941 (10) Å and the remaining six at a distance of 3.622 (10) Å. The polyhedron around Tl3 is formed by ten O atoms, with distances ranging between 2.467 (16) and 3.682 (16) Å. The observed bond distances in Tl_2MoO_4 are in good agreement with those in Tl_2WO_4.

Comment

Tl_2MoO_4 was first investigated by Gaultier & Pannetier (1972), who found three phase transitions, presumably all of first order, at temperatures of 776, 673 and 311 K. The lattice parameters given at room temperature are a = 7.919 (5), b = 11.026 (7) and c = 6.179 (5) Å, in space group *Pnam*. Above 323 K, the structure is supposed to be trigonal in space group $P\bar{3}m$, with lattice parameters a = 6.257 (3) and c = 8.085 (4) Å. These authors further reported that the phase transition at 673 K leads to the destruction of the crystals. Later investigations (Sleight *et al.*, 1975) reaffirmed that Tl_2MoO_4 at 298 K is orthorhombic, although the authors reported the non-centrosymmetric space group $Pna2_1$ with similar lattice parameters. They could only observe the phase transitions at 310 and 772 K and did not detect that at 673 K. They also presumed the intermediate phase to have space group $P\bar{3}m$ and proposed the space group $P6_3/mmc$ for the high-temperature phase.

Our investigations corroborate the space group $P\bar{3}m$ for the intermediate phase, which we measured at 350 K. The refinement of the structure shows it to be isostructural with glaserite, $K_3Na(SO_4)_2$ (Okada & Ossaka, 1980), and with Tl_2WO_4 (Okada *et al.*, 1979).

In Tl_2MoO_4 (Fig. 1), the Mo ions are coordinated tetrahedrally by the O atoms, with bond lengths ranging from 1.699 (16) to 1.725 (16) Å, and angles between 107.6 (4) and 111.3 (4)°.

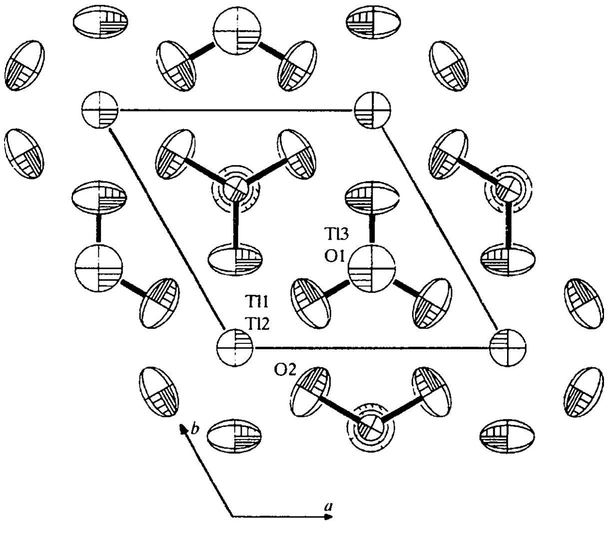

Fig. 1. The *a*,*b* projection of the structure of Tl_2MoO_4. Displacement ellipsoids are drawn at the 50% probability level.

As pointed out by Moore (1973), in the glaserite structure, and consequently in Tl_2MoO_4, three different monoivalent cations can be observed. These are now discussed.

The coordination around Tl1 can be described as a distorted octahedron, with a Tl—O distance of 2.769 (10) Å. This compares favourably with the distances observed in Tl_2WO_4 [2.70 (7) Å].

Tl2 has a coordination number of 12. Six O atoms are at a distance of 2.941 (10) Å, while the remaining six are at a distance of 3.622 (10) Å. For Tl_2WO_4, the corresponding distances are 2.95 (7) and 3.630 (4) Å. The coordination polyhedron can be described as a 12-coordinate trigonal antiprism, with six additional meridional anions in a hexagonal outline. The ideal point symmetry is $\bar{3}m$.

The polyhedron around Tl3 is formed by ten O atoms. It has ideal point symmetry of $3m$. Again, six of them (O2) form a distorted meridional hexagon, while the three O atoms above share a tetrahedral base with, and the one O atom below forms the apex of, MoO_4 tetrahedra. The Tl3—O1 distance to this apical oxygen is the shortest, at 2.467 (16) Å, followed by the six Tl3—O2 distances of the hexagon [3.178 (16) Å]. The largest distances are formed with the basal O atoms [3.682 (16) Å]. These distances compare well with those observed in Tl_2WO_4: the shortest Tl3—O distance in this compound is 2.46 (6) Å, followed by six distances of 3.18 (6) Å and three more of 3.64 (6) Å.

The shortest O—O distance is found in the Tl3 coordination polyhedron, with a value of 2.78 (2) Å (Tl_2WO_4 2.87 Å), while the shortest O–O edge length in the tetrahedron is 2.83 (2) Å (Tl_2WO_4 2.92 Å).

Bond valence sums, which were calculated according to Brese and O'Keefe (1991), show a too high value for Tl1 in the two compounds (Tl_2MoO_4 1.20; Tl_2WO_4 1.44). For the other two Tl ions, the values are slightly too low in the molybdate (Tl2 0.87; Tl3 0.90) and nearly ideal in the tungstate (Tl2 0.96; Tl3 0.97).

Experimental

Crystals of the title compound were grown from an aqueous solution of Tl_2CO_3 and MoO_3, kept at 313 K for about one month. As the resulting crystals were very thin hexagonal plates, they were placed in a Pt crucible, heated to 923 K and afterwards cooled slowly to 873 K at a rate of 1 K d^{-1}. After rapid cooling to room temperature, the crystals were of a suitable size for single-crystal investigations.

Crystal data

Tl_2MoO_4
$M_r = 568.68$
Trigonal
$P\bar{3}m1$
$a = 6.266\ (1)$ Å
$c = 8.103\ (2)$ Å
$V = 275.52\ (9)$ Å^3
$Z = 2$
$D_x = 6.855$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 2313 reflections
$\theta = 2$–$26°$
$\mu = 60.489$ mm^{-1}
$T = 350\ (1)$ K
Irregular
0.10 × 0.10 × 0.05 mm
Yellow

Data collection

Stoe IPDS diffractometer
Imaging plate scans
Absorption correction:
Gaussian (*X-RED*; Stoe, 1998)
$T_{\rm min} = 0.005$, $T_{\rm max} = 0.041$
2008 measured reflections
237 independent reflections

$R(F^2)_{\rm int} = 0.115$
$\theta_{\rm max} = 26°$
$h = -7 \rightarrow 7$
$k = -7 \rightarrow 7$
$l = -9 \rightarrow 9$
50 standard reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.092$
$S = 1.053$
237 reflections
21 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0468P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 1.31$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.08$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0031 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

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

	x	y	z	$U_{\rm eq}$
Tl1	0	0	0	0.0444 (5)
Tl2	0	0	1/2	0.0620 (6)
Tl3	2/3	1/3	0.17374 (10)	0.0568 (5)
Mo	2/3	1/3	0.6878 (2)	0.0346 (6)
O1	2/3	1/3	0.478 (2)	0.094 (7)
O2	0.1852 (9)	−0.1852 (9)	0.2350 (15)	0.100 (4)

Table 2. *Selected geometric parameters (Å, °)*

Tl1—O2 (× 6)	2.769 (10)	Tl3—O2^{i} (× 3)	3.682 (16)
Tl2—O2 (× 6)	2.941 (10)	Mo—O1	1.699 (16)
Tl2—O1 (× 6)	3.622 (10)	Mo—O2^{ii} (× 3)	1.725 (16)
Tl3—O1	2.467 (16)	O1—O2^{ii}	2.83 (2)
Tl3—O2 (× 6)	3.178 (16)	O2—O2^{iii}	2.78 (2)
O2—Tl1—O2^{iv}	180.0 (4)	O2—Tl2—O1^{viii}	130.3 (4)
O2—Tl1—O2^{v}	77.9 (4)	O2—Tl2—O1^{ix}	112.1 (4)
O2—Tl1—O2^{vi}	102.1 (4)	O2—Tl2—O1^{ii}	49.7 (4)
O2—Tl2—O2^{v}	72.6 (4)	O1—Mo—O2^{ii}	111.3 (4)
O2—Tl2—O2^{vii}	107.4 (4)	O2^{ii}—Mo—O2^{x}	107.6 (4)
O2—Tl2—O1	67.9 (4)		

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

The computations were carried out with the coordinates of Tl_2WO_4 (Okada *et al.*, 1979) as the starting model. Due to the high anisotropic displacement parameters of the O atoms, a refinement with split positions for these atoms was attempted. However, this did not lead to a significantly better model and so this refinement was discarded.

Data collection: *EXPOSE* (Stoe, 1997). Cell refinement: *EXPOSE*. Data reduction: *X-RED* (Stoe & Cie, 1998). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1242). Services for accessing these data are described at the back of the journal.

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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*

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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-

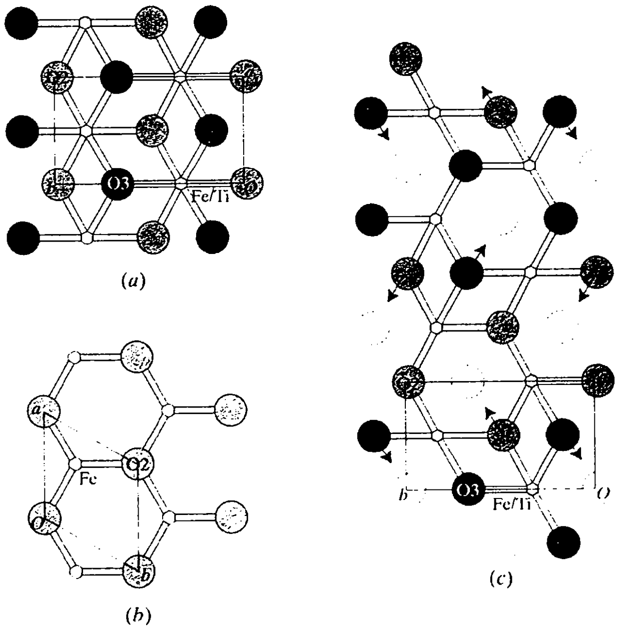

Fig. 1. The atomic arrangement on the plane $z = \frac{1}{4}$ for (*a*) the average structure of $InFe_{0.33}Ti_{0.67}O_{3.33}$ with the O2 and O3 sites partially occupied, (*b*) $InFeO_3$ and (*c*) an example of local structures of $InFe_{0.33}Ti_{0.67}O_{3.33}$. Dotted circles are vacant oxygen sites.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