Lead Trititanate

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Abstract. $PbTi_3O_7$, monoclinic, $P2_1/m$, $a = 10.718$ (5), $b = 3.812$ (1), $c = 6.577$ (7) Å, $\beta = 98.27$ (7)°, $Z = 2$, $D_x = 5.782$ g cm^{-3}. The crystals were prepared by the flux method. The TiO_6 octahedra are connected to each other by corner- and edge-sharing to form a three-dimensional network of the composition Ti_3O_7. The lead atom is surrounded by seven oxygen atoms. The Ti–O distances lie between 1.73 and 2.30 Å, the Pb–O distances between 2.36 and 3.04 Å.

Introduction. The unit-cell dimensions were obtained by the least-squares method based on the 2θ angles measured on a four-circle diffractometer (Rigaku) using monochromated Mo $K\alpha$ radiation ($\lambda = 0.70926$ Å). The intensities were collected by 2θ–ω scanning on the same diffractometer. In the range $\theta \le 60°$, 2528 (2507 unique) reflexions were measured, of which 1616 were 'less-thans'. The systematic absences $0k0$ with $k \ne 2n$ indicated the possible space groups $P2_1/m$ and $P2_1$. The former was assumed because of the distinct concentration of the peaks of the Patterson function $P(u,v,w)$ exclusively in the planes $v = 0$ and $\frac{1}{2}$, and was confirmed by the success of the structure determination. The coordinates of the metal atoms were obtained by the superposition of the Patterson maps. A difference Fourier synthesis revealed the oxygen positions. The structure was refined by the full-matrix least-squares method using the computer program *ORFLS* (Busing, Martin & Levy, 1962). The temperature factor of the lead atom only was assumed to be anisotropic. The conventional R was 0.083 based on the 912 observed structure factors.* The less-thans

* A list of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30399 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atomic coordinates and thermal parameters*

All atoms lie in the special position 2(e) $(x,\frac{1}{4},z)$ of the space group $P2_1/m$. The anisotropic temperature factor was expressed as $\exp{[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hl\beta_{13})]}$.

	x	z	B
Pb	0.15126 (13)	0.00633 (25)	
Ti(1)	0.9001 (5)	0.5538 (9)	0.17 (7)
Ti(2)	0.5640 (5)	0.6955 (9)	0.12 (7)
Ti(3)	0.6571 (5)	0.2559 (9)	0.24 (7)
O(1)	0.0759 (18)	0.4766 (32)	0.13 (27)
O(2)	0.3826 (21)	0.7396 (38)	0.69 (35)
O(3)	0.4803 (23)	0.3535 (40)	1.01 (38)
O(4)	0.9437 (18)	0.8284 (32)	0.11 (27)
O(5)	0.6258 (22)	0.9526 (37)	0.85 (37)
O(6)	0.7116 (19)	0.5602 (34)	0.28 (29)
O(7)	0.8251 (18)	0.2427 (32)	0.16 (28)

	β_{11}	β_{22}	β_{33}	β_{13}
Pb	0.00090 (7)	0.01295 (65)	0.00709 (27)	0.00067 (10)

Table 2. *Interatomic distances* (Å) *calculated by the program ORFFE* (*Busing, Martin & Levy*, 1964)

	Pb		Ti(1)		Ti(2)		Ti(3)
O(4^{iv})	2.36 (2)	O(4)	1.80 (2)	O(5)	1.73 (2)	O(7)	1.82 (2)
O(4^{i})	2.48 (1)	O(1^{i})	1.937 (4)	O(6)	1.92 (2)	O(2^{i})	1.954 (5)
O(4^{v})	2.48 (1)	O(1^{v})	1.937 (4)	O(3^{i})	1.979 (7)	O(2^{v})	1.954 (5)
O(7^{iii})	2.55 (1)	O(1^{vii})	2.02 (2)	O(3^{v})	1.979 (7)	O(5^{ii})	1.97 (3)
O(7^{vi})	2.55 (1)	O(6)	2.03 (2)	O(2)	2.01 (2)	O(6)	2.00 (2)
O(5^{i})	3.04 (2)	O(7)	2.09 (2)	O(3)	2.30 (3)	O(3)	2.09 (2)
O(5^{v})	3.04 (2)						
Average	2.64		1.97		1.99		1.96

O–O	Pb	Ti(1)	Ti(2)	Ti(3)
Minimum	2.65 (3)	2.55 (3)	2.54 (2)	2.54 (2)
Maximum	3.812 (1)	3.01 (2)	2.92 (2)	3.25 (4)
Average	3.30	2.78	2.77	2.78

Pb–Pb: 3.752 (3), 3.812 (1);   Ti–Ti: minimum 3.026 (8)

Symmetry code

i	$1-x$,	$\frac{3}{4}$,	$1-z$
ii	x,	$\frac{1}{4}$,	$-1+z$
iii	$1-x$,	$\frac{3}{4}$,	$-z$
iv	$-1+x$,	$\frac{1}{4}$,	$-1+z$
v	$1-x$,	$-\frac{1}{4}$,	$1-z$
vi	$1-x$,	$-\frac{1}{4}$,	$-z$
vii	$1+x$,	$\frac{1}{4}$,	z

were not used for the structure refinement. The atomic scattering factors were taken from Hanson, Herman, Lea & Skillman (1964). The absorption correction was not applied ($\mu R = 0.43$).
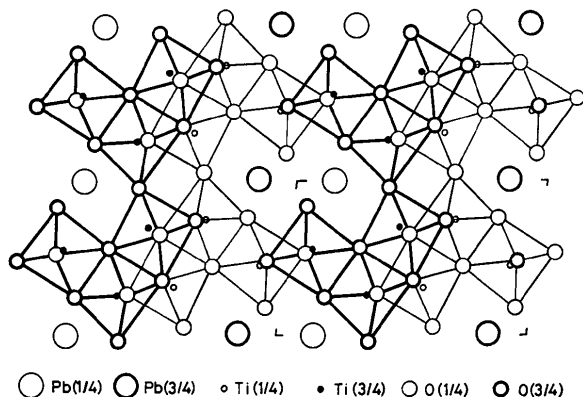

○ Pb(1/4) ◯ Pb(3/4) ○ Ti(1/4) • Ti(3/4) ○ O(1/4) ◯ O(3/4)

Fig. 1. The structure of $PbTi_3O_7$ projected on to (010). The fractional y coordinates of the atoms are given in parentheses after the chemical symbols.

Discussion. Table 1 lists the atomic coordinates and thermal parameters, Table 2 the interatomic distances. Fig. 1 depicts the way in which the TiO_6 octahedra are connected. The lead atom is surrounded by seven oxygen atoms, whereas the same atom in $PbTiO_3$ has eight oxygen nearest neighbours. The Ti_3O_7 group forms a three-dimensional network instead of a sheet as in $Na_2Ti_3O_7$ (Andersson & Wadsley, 1961).

The calculations were carried out on the FACOM 270-20 of this Institute.

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Tricarbonyl-1-*syn*-(1',2'-dihydro-2'-oxo-1'-oxa-azulen-3'-yl)-*h*⁵-pentadienylmanganese

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Abstract. Monoclinic, $P2_1/c$, $a = 13.249(5)$, $b = 7.178(4)$, $c = 15.662(6)$ Å, $\beta = 96.66(3)°$. $C_{17}H_{11}O_5Mn$, $M = 350.2$, $Z = 4$, $D_c = 1.57$ g cm^{-3}. Tropone reacts with decacarbonyldimanganese to yield a tricarbonylmanganese complex. The molecules contain an approximately planar oxa-azulenone system with an open π-pentadienyl side chain to which is bonded a tricarbonylmanganese group. Formation of the ligand has involved a hydrogen-elimination reaction between two tropone molecules.

Introduction. The preparation of the title compound has been reported earlier (Barrow, Mills, Haque & Pauson, 1971). The crystals, red monoclinic needles, were air-stable and unaffected by X-rays. Approximate cell dimensions were obtained from precession and Weissenberg photographs. The reciprocal lattice symmetry and systematic absences uniquely specified space group $P2_1/c$ (C^5_{2h}, No. 14). A crystal with dimensions $0.39 \times 0.13 \times 0.15$ mm, μ(Mo $K\alpha$) = 9.46 cm^{-1}, was selected for intensity measurements.

The intensities (for $\theta < 25°$) were collected on a Hilger and Watts computer-controlled single-crystal four-circle X-ray diffractometer (Edwards, Bowden, Standeven & Mills, 1966) with Zr-filtered Mo $K\alpha$ radiation and an $\omega/2\theta$ step-scanning mode. Orientation matrices were calculated by a least-squares method which utilized reflexion positions determined by a peak-finder program. Cell parameters were calculated, by the least-squares method, from the θ values of reflexions measured at both positive and negative $\omega/2\theta$ offsets. The intensities were corrected for Lorentz and polarization effects but not for absorption. 2592 independent reflexions were obtained; this analysis is based on the 1009 reflexions with $F > 6\sigma(F)$, where $\sigma(F)$ was derived from counting statistics. The large proportion of statistically non-significant reflexions was a consequence of an unusually large mosaic spread which gave rise to ill-defined diffracted beams of low peak height. Structure solution was by Fourier methods and refinement by least-squares methods to minimize $\sum w(F_o - k|F_c|)^2$. All hydrogen atoms were located from difference syntheses. The positional coordinates of hydrogens H(4) and Hx(4) were refined whilst the other hydrogen atoms were placed at calculated locations, [r(C–H) = 1.09 Å]. The temperature factors for the