

Redetermination of CaMn_2O_4

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The title compound, calcium dimanganese tetraoxide, CaMn_2O_4 , was synthesized hydrothermally and is made up of edge-sharing Mn^{3+} distorted octahedral layers and eight-coordinate Ca^{2+} centered polyhedral layers.

Comment

The use of alkali metal hydroxides as a mineralizer for hydrothermal production of single metal oxide crystals has been known for some time (Kolb *et al.*, 1973; Demianets, 1978). We became interested in using hydrothermal techniques to synthesize novel transition metal borates, and found that these anions can act as co-mineralizers to give large single crystals of several significant metal oxides, including the title compound.

CaMn_2O_4 is one of the most dense forms of the AB_2O_4 structure type (Fei *et al.*, 1999). As the original structure solution of CaMn_2O_4 was performed using a multiple film technique (Couffon *et al.*, 1964), we felt that a modern structure solution was needed. The unit-cell parameters of the original determination [$a = 9.71$ (2), $b = 10.03$ (2), $c = 3.162$ (5) Å, $V = 307$ Å³] are comparable to ours, but are of much lower precision.

The structure of CaMn_2O_4 is made up of edge-sharing MnO_6 octahedral dimers with eight-coordinate calcium-centered polyhedra (Fig. 1). The edge-sharing Mn_2O_{10} dioctahedra also vertex share to other Mn_2O_{10} dioctahedra via elongated Mn—O bonds. The elongated Mn—O bonds are due to the Jahn–Teller distortions expected for high-spin d^4 systems. The connectivity gives rise to a layered herring-bone structure, similar to that seen in a number of oxide materials (Reid, 1967; Reid *et al.*, 1967, 1968). The structure of the title compound is related to that of CaFe_2O_4 (Decker & Kasper, 1957) which crystallizes in space group $Pnam$ and has cell constants $a = 9.23$, $b = 10.705$ and $c = 3.024$ Å. Both compounds are made up of herring-bone layers of linked M_2O_{10} dimers, but the connectivity of the dioctahedra are in different orientations (Fig. 2). In both structures, these layers are held together by interactions to the calcium ions between them.

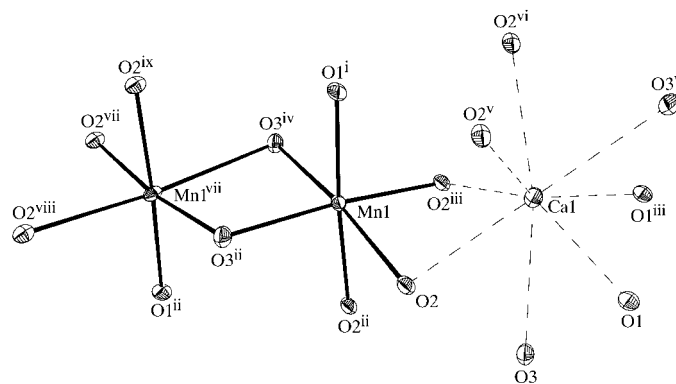


Figure 1

The connectivity of CaMn_2O_4 showing 70% probability displacement ellipsoids. [Symmetry codes (i)–(iv) as in Table 1; (v) $x, y, \frac{3}{2} - z$; (vi) $x - 1, y, \frac{3}{2} - z$; (vii) $x - 1, \frac{1}{2} - y, 1 - z$; (viii) $x, \frac{1}{2} - y, 1 - z$; (ix) $1 - x, y - \frac{1}{2}, z$.]

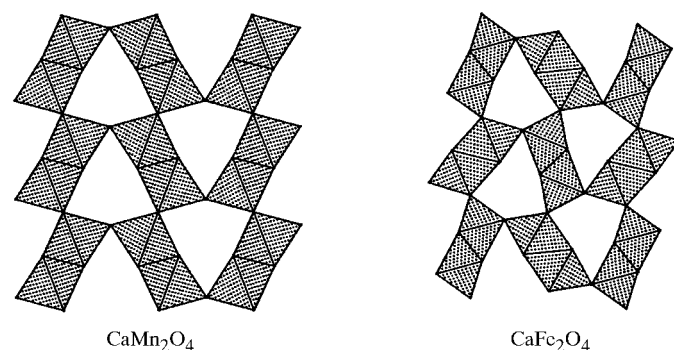


Figure 2

Comparison of the herring-bone structures of CaMn_2O_4 and CaFe_2O_4 .

There is one unique manganese metal site, which is on a general position. The average equatorial Mn—O bond is 1.92 (3) Å, and the elongated axial bonds are 2.3661 (11) and 2.4637 (12) Å (see Table 1 for selected bond lengths and angles). These distances are comparable to those reported by Couffon *et al.* (1964), *i.e.* between 1.90 and 1.97 Å for the four equatorial bonds, and 2.39 and 2.46 Å for the two axial bonds. The unique Ca atom sits on a crystallographic mirror ($x, y, \frac{3}{4}$). The average Ca—O bond length is 2.4 (1) Å. Of the three unique O atoms, O1 and O3 sit on special positions, a mirror ($x, y, \frac{3}{4}$) and a twofold rotation axis ($x, \frac{3}{4}, \frac{1}{2}$), respectively, and O2 resides on a general position.

A face-indexing analytical absorption correction was applied based on a data crystal bound by faces of the forms {100}, {010}, {001} and {011}, with face-to-center distances of 0.408, 0.192, 0.168 and 0.210 mm, respectively.

Experimental

Black hexagonal rods of the title compound were synthesized hydrothermally in silver tubes. The reaction mixture was composed of a 1:1:1:19.5 ratio of B_2O_3 (15 mg, 0.215 mmol), Mn_2O_3 (34 mg, 0.215 mmol), $\text{Ca}(\text{OH})_2$ (16 mg, 0.215 mmol), and 10.5 M NaOH (0.4 ml, 4.20 mmol), all of analytical grade from Aldrich. The reactants were loaded into a silver tube, which was welded shut and then placed in an autoclave. Sufficient water was added to the autoclave to

produce a counter-pressure of 230 MPa at 873 K. The reaction was held at 873 K for 3 d. The yield was 98% based on Mn. Boron oxide was found not to be needed to obtain the product, but its inclusion in the reaction improves crystal growth in terms of both size and quality.

Crystal data

CaMn ₂ O ₄	Mo K α radiation
$M_r = 213.96$	Cell parameters from 41 reflections
Orthorhombic, <i>Pbcm</i>	$\theta = 7.53\text{--}17.48^\circ$
$a = 3.1546(6) \text{ \AA}$	$\mu = 9.787 \text{ mm}^{-1}$
$b = 9.988(2) \text{ \AA}$	$T = 293(2) \text{ K}$
$c = 9.6769(19) \text{ \AA}$	Hexagonal rod, black
$V = 304.90(10) \text{ \AA}^3$	$0.816 \times 0.384 \times 0.336 \text{ mm}$
$Z = 4$	
$D_x = 4.661 \text{ Mg m}^{-3}$	

Data collection

Siemens R3m/V diffractometer	$\theta_{\text{max}} = 35.07^\circ$
$\omega/2\text{-}\theta$ scans	$h = -5 \rightarrow 5$
Absorption correction: analytical	$k = -16 \rightarrow 16$
$T_{\text{min}} = 0.175$, $T_{\text{max}} = 0.256$	$l = -15 \rightarrow 15$
5238 measured reflections	3 standard reflections
706 independent reflections	every 97 reflections
701 reflections with $I > 2\sigma(I)$	intensity decay: 6.2%
$R_{\text{int}} = 0.043$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.011$
$R(F) = 0.022$	$\Delta\rho_{\text{max}} = 0.56 \text{ e \AA}^{-3}$
$wR(F^2) = 0.052$	$\Delta\rho_{\text{min}} = -1.41 \text{ e \AA}^{-3}$
$S = 1.332$	Extinction correction: <i>SHELXTL-Plus</i> (Sheldrick, 1998)
706 reflections	Extinction coefficient: 0.161 (11)
42 parameters	
$w = 1/[\sigma^2(F_o^2) + (0.0218P)^2 + 0.3104P]$	

The minimum electron-density peak is located 0.67 \AA from the Mn1 atom.

Data collection: *P3 Software* (Siemens, 1989); cell refinement: *P3 Software*; data reduction: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to solve structure: *SHELXTL-Plus*; program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

Table 1

Selected geometric parameters (\AA , $^\circ$).

Mn1—O1 ⁱ	1.8978 (7)	Ca1—O1	2.2819 (15)
Mn1—O2 ⁱⁱ	1.9053 (10)	Ca1—O1 ⁱⁱⁱ	2.3169 (15)
Mn1—O2 ⁱⁱⁱ	1.9236 (10)	Ca1—O2	2.3825 (10)
Mn1—O3 ⁱⁱ	1.9612 (10)	Ca1—O2 ⁱⁱⁱ	2.4573 (11)
Mn1—O2	2.3661 (11)	Ca1—O3	2.6372 (5)
Mn1—O3 ^{iv}	2.4637 (12)		
O1 ⁱ —Mn1—O2 ⁱⁱ	175.61 (5)	O2 ⁱⁱⁱ —Mn1—O2	94.11 (4)
O1 ⁱ —Mn1—O2 ⁱⁱⁱ	94.28 (5)	O3 ⁱⁱ —Mn1—O2	88.37 (4)
O2 ⁱⁱ —Mn1—O2 ⁱⁱⁱ	81.61 (5)	O1 ⁱ —Mn1—O3 ^{iv}	91.11 (4)
O1 ⁱ —Mn1—O3 ⁱⁱ	93.47 (4)	O2 ⁱⁱ —Mn1—O3 ^{iv}	90.17 (3)
O2 ⁱⁱ —Mn1—O3 ⁱⁱ	90.73 (3)	O2 ⁱⁱⁱ —Mn1—O3 ^{iv}	86.44 (4)
O2 ⁱⁱⁱ —Mn1—O3 ⁱⁱ	171.62 (4)	O3 ⁱⁱ —Mn1—O3 ^{iv}	90.21 (2)
O1 ⁱ —Mn1—O2	95.19 (5)	O2—Mn1—O3 ^{iv}	173.61 (3)
O2 ⁱⁱ —Mn1—O2	83.62 (4)		

Symmetry codes: (i) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$; (ii) $1-x, 1-y, 1-z$; (iii) $x-1, y, z$; (iv) $-x, 1-y, 1-z$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1001). Services for accessing these data are described at the back of the journal.

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