

Structure of Calcium Manganese Oxide $\text{Ca}_2\text{Mn}_3\text{O}_8$

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Abstract. $\text{Ca}_2\text{Mn}_3\text{O}_8$, monoclinic, $C2/m$, $a = 11.014$ (4), $b = 5.851$ (3), $c = 4.942$ (2) Å, $\beta = 109.73$ (5)°, $Z = 2$, $d_{\text{calc}} = 4.13$ g cm⁻³. The structure was solved using powder diffraction data. Later, when single crystals became available, 1628 independent F values were refined to $R = 0.024$. This is the first reported example of a compound possessing prismatically coordinated Ca^{2+} ions. They separate $\text{Mn}_3\text{O}_8^{4-}$ sheets formed by edge-sharing of distorted MnO_6 octahedra.

Introduction. The low-temperature synthesis of $\text{Ca}_2\text{Mn}_3\text{O}_8$ from a carbonate precursor has been discussed by Horowitz & Longo (1978) and Clavenna, Longo & Horowitz (1977). A preliminary structure for the material was reported by Ansell, Longo & Horowitz (1978).

Single crystals used in the more recent experiments were prepared in a CaCl_2 flux during attempts to grow crystals of the Mn-rich compositions CaMn_3O_6 or CaMn_4O_8 . When these mixtures were heated in a Pt crucible at 1123 K in air for 3 d, cooled, and washed with water, only crystals of $\text{Ca}_2\text{Mn}_3\text{O}_8$ remained. 3328 intensity data with $0^\circ < 2\theta < 50^\circ$ (Mo $K\alpha$ radiation) (including systematic absences) were collected with a small irregular crystal of approximate dimensions $0.29 \times 0.22 \times 0.19$ mm on an Enraf–Nonius CAD-4 diffractometer. A variable scan rate ($4\text{--}20^\circ \text{ min}^{-1}$) was used for data collection, with fast scans for intense reflections and slower ones for weaker reflections. Using the parameters from the powder determination, 1628 reflections having $F_o > 3\sigma(I)$ were refined, using least-squares procedures, to an R value of 0.024 ($wR = 0.030$).^{*} During the final cycles of refinement, all atoms were assigned anisotropic thermal parameters. Ca and

Mn were corrected for anomalous dispersion (f' being 0.203 and 0.295, and f'' being 0.306 and 0.729 for Ca and Mn respectively). Unit weights were applied to F values. An extinction correction of the form $|F_c|(I + gI_c)^{-1}$ (Stout & Jensen, 1968) was applied to F_o where the parameter g was refined in the least squares and converged to a value of 0.28569×10^{-4} . $N(z)$ and Hamilton (1965) significance terms showed conclusively that the space group was $C2/m$ and not Cm or $C2$. Final atomic and thermal parameters are listed in Table 1 and bond lengths are shown in Fig. 1. Fig. 2 gives a stereoscopic view illustrating the layered nature of the structure and the packing of the polyhedra depicted in Fig. 1. All calculations were performed with a PDP-11/60 computer (Enraf–Nonius, 1979).

Discussion. The powder and single-crystal refinements give essentially the same results; with the positional parameters from the single-crystal determination being within four standard deviations of those calculated from the Simplex powder refinement. The interatomic distances and angles that are reported and discussed are those calculated from the single-crystal refinement.

The overall structure of $\text{Ca}_2\text{Mn}_3\text{O}_8$ can be simply described as infinite sheets of $\text{Mn}_3\text{O}_8^{4-}$ held together by Ca^{2+} ions (Fig. 2). The sheets are formed by a pair of close-packed O layers with three-quarters of the available octahedral sites filled with Mn^{4+} in an ordered

Table 1. Fractional atomic coordinates ($\times 10^5$) and equivalent isotropic thermal parameters

	x	y	z	B_{eq} (Å ² × 10 ²)
Ca	72442 (3)	0	66593 (7)	40
Mn(1)	0	0	50000	22
Mn(2)	0	25914 (4)	0	24
O(1)	10059 (7)	22158 (15)	39171 (17)	41
O(2)	59726 (11)	50000	90202 (25)	40
O(3)	60385 (11)	0	96258 (26)	44

* Lists of structure factors, anisotropic thermal parameters and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36667 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

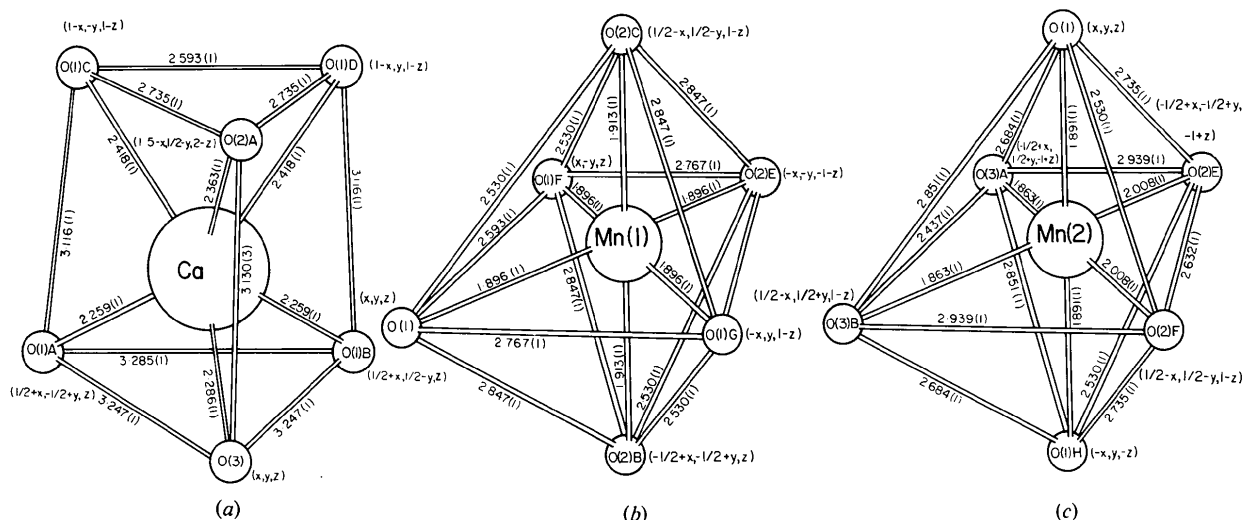


Fig. 1. The coordinates of O atoms around metal atoms. (a) CaO_6 polyhedra, and octahedral coordinations about (b) Mn(1) and (c) Mn(2). Distances in Å.

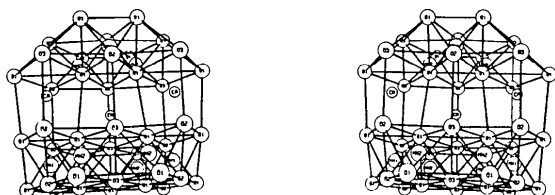


Fig. 2. A stereoscopic illustration showing the layered nature of $\text{Ca}_2\text{Mn}_3\text{O}_8$ when the polyhedra in Fig. 1 are packed.

way. The sheets are stacked perpendicular to the a axis and have alternate O octahedra in alternate rows left vacant. All octahedra share only edges with each other. One-third of the manganese, Mn(1), are in the d ($2/m$) position which provides a fairly symmetrical octahedral coordination of four O atoms at 1.896 (1) Å and two more at 1.913 (1) Å for an average Mn—O distance of 1.902 (1) Å. Angles within the Mn(1) O_6 octahedra range from 83.3 (1) to 96.8 (1)° for O—Mn—O with adjacent O atoms and are 180° for O—Mn—O with non-adjacent O atoms. The other two-thirds of the Mn^{4+} ions, Mn(2), are in a less-symmetrical environment, b (2), and have two O atoms at 1.863 (1) Å, two at 1.891 (1) Å, and two at 2.008 (1) Å for an average Mn—O distance of 1.917 (1) Å. Angles within the Mn(2) octahedra range from 81.7 (1) to 98.7 (1)° for O—Mn—O with adjacent O and are from 166.7 (1) to 172.1 (1)° for O—Mn—O.

The nearly close-packed O layers of the structure stack with the cations in an $A \cdot \text{Mn} \cdot B \cdot \text{Ca} \cdot B \cdot \text{Mn} \cdot C \cdot \text{Ca} \cdot C \cdot \text{Mn} \cdot A \cdot \text{Ca}$ sequence, which provides octahedra for the Mn^{4+} and trigonal prisms for the Ca^{2+} . One-quarter of the possible trigonal prisms are filled in such a way as to give isolated chains of edge-shared prisms. This arrangement puts an empty

octahedron and an empty tetrahedron on opposite sides of every trigonal prism. As might be expected, the Ca^{2+} moves toward the O of the empty octahedron [$\text{Ca—O} = 2.259$ (1) Å] and away from the empty tetrahedron [$\text{Ca—O} = 2.418$ (1) Å].

There are three different types of O atom in $\text{Ca}_2\text{Mn}_3\text{O}_8$. O(1) is coordinated by two Mn^{4+} and two Ca^{2+} ions, O(2) is coordinated by three Mn^{4+} ions and one Ca^{2+} ion, and O(3) has only two Mn^{4+} ions and one Ca^{2+} ion coordinated to it.

Our results on $\text{Ca}_2\text{Mn}_3\text{O}_8$ represent the first complete single-crystal determination for this structure type and support the earlier results of Oswald & Wampetich (1967) on $\text{Cd}_2\text{Mn}_3\text{O}_8$ and $\text{Mn}_2\text{Mn}_3\text{O}_8$. In $\text{Ca}_2\text{Mn}_3\text{O}_8$, the average Mn—O distances for the two different Mn^{4+} [1.902 (1) and 1.917 (1) Å] are similar but definitely longer than those reported for $\text{Cd}_2\text{Mn}_3\text{O}_8$ (1.86, 1.87 Å). They are closer to those reported by Riou & Lecerf (1975) for $\text{Co}_2\text{Mn}_3\text{O}_8$ (1.89 and 1.91 Å) which has similar $\text{Mn}_3\text{O}_8^{4-}$ layers. There is excellent agreement between our distances and those predicted from the ionic radii of Shannon (1976) for octahedral Mn^{4+} (0.53 Å) and O^{2-} in fourfold coordination (1.38 Å). Our average Ca—O distance (2.34 Å) is also in good agreement with that predicted (2.35 Å) from the ionic radii of Shannon (1976).

The most striking feature of this structure is the trigonal-prismatic coordination found for the Ca^{2+} . We know of no other compound in which the Ca^{2+} ion has this coordination. In fact, trigonal-prismatic coordination of cations in oxides is very unusual. It can, where found, be correlated (Delmas, Fouassier & Hagenmuller, 1976) with compounds in which the O is involved in covalent interactions with cations, as is the case in the $\text{Mn}_3\text{O}_8^{4-}$ layers of this structure. A similar situation is found for a whole series of compounds

described by the general formula $A_x\text{MO}_2$ (Fouassier, Delmas & Hagenmuller, 1975) where $A = \text{Na}, \text{K}$ and $M = \text{Cr}, \text{Mn}, \text{Co}$. These materials can be described as covalent MO_2^{n-} layers stacked to give trigonal-prismatic coordination for the A cation which holds the anion sheets together.

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$\text{Sr}_9\text{Mg}_{38}$: Structural Redetermination of ‘ SrMg_4 ’

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Abstract. $\text{Sr}_9\text{Mg}_{38}$, hexagonal, $P6_3/mmc$, $a = 10.500$ (2), $c = 28.251$ (3) Å, $Z = 2$, $D_c = 2.11 \text{ Mg m}^{-3}$, $\mu(\text{Mo } K\alpha) = 9.7 \text{ mm}^{-1}$. The final R value is 0.061 for 446 independent reflexions. This study is a structural redetermination of the phase SrMg_4 , $Z = 18$, already known in the literature. The presence of four further Mg atoms is detected, changing the stoichiometry to $\text{Sr}_9\text{Mg}_{38}$. The atomic coordination of several atoms is increased, and their coordination polyhedra become more regular.

Introduction. During a crystal-chemical analysis of the binary phases formed by the alkaline-earth elements, some anomalous features were observed in the structure of the compound SrMg_4 , determined by Wang, Kanda, Miskell & King (1965): (a) The measured density, 2.11 Mg m^{-3} , appears greater than the calculated one, 2.03 Mg m^{-3} . (b) The volume contraction, calculated on the basis of the elemental volumes, is negative ($\Delta V = -1.1\%$); in other words, an expansion is observed in the compound as regards the elements. This behaviour, which is very unusual for an intermetallic phase, is opposite to that of the other Sr–Mg phases, which show normally positive values of $\Delta V\%$ (8.3 for SrMg_2 , 4.8 for $\text{Sr}_6\text{Mg}_{23}$ and 1.8 for $\text{Sr}_2\text{Mg}_{17}$). (c) In the unit cell, holes are recognizable corresponding to the 4(f) equipoint of the

space group $P6_3/mmc$ ($\frac{1}{3}, \frac{2}{3}, z$ with $z \simeq 0.65$) which are large enough to be filled by Mg atoms. The occurrence of these voids, which are infrequent in intermetallic compounds, causes some coordination polyhedra to be incomplete (e.g. icosahedra with a missing vertex).

All these circumstances suggested the opportunity of a redetermination of the structure.

A prismatic single crystal of mean dimensions $0.19 \times 0.15 \times 0.07 \text{ mm}$ was isolated from a sample of composition SrMg_5 , melted in a sealed iron crucible and slowly cooled. Symmetry and extinctions were consistent with the space group $P6_3/mmc$ already found by Wang *et al.* (1965). Data collection was carried out on an Enraf–Nonius CAD-4 four-circle automatic diffractometer in the ω -scan mode using graphite-monochromated Mo $K\alpha$ radiation. 1807 reflexions were measured in the θ range $3\text{--}25^\circ$ and corrected for Lorentz, polarization and absorption effects, applying the semi-empirical correction of North, Phillips & Mathews (1968), by use of ψ -scan data of four top reflexions. Averaging gave 949 independent reflexions. Lattice constants were determined by least-squares refinement of the angular values of 25 reflexions centered on the diffractometer. The positional parameters reported by Wang *et al.* (1965) were assumed as starting values for a full-matrix least-squares refinement in $P6_3/mmc$ with *SHELX 76*