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$Ca_3Mn_2O_7$

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The tricalcium dimanganese heptaoxide ($Ca_3Mn_2O_7$) member of the Ruddlesden–Popper series $Ca_{n+1}Mn_nO_{3n+1}$, *i.e.* with $n = 2$, was previously reported with an *I*-centred tetragonal lattice [a_t = 3.68 and c_t = 19.57 Å] by Fawcett, Sunstrom, Greenblatt, Croft & Ramanujachary [*Chem. Mater.* (1998), **10**, 3643–3651]. It is now found to be orthorhombic, with an *A*-centred lattice [a = 5.2347 (6), b = 5.2421 (2) and c = 19.4177 (19) Å]. The structure has been refined in space group $A2_1am$ using X-ray single-crystal diffraction data and assuming the existence of twin domains related by the $(1\bar{1}0)$ plane. A comparison with the basic perovskite structure $CaMnO_3$ ($n = \infty$) is proposed.

Comment

In order to complete magnetic and electrical measurements on the magnetoresistive manganese oxide perovskite families $Ln_{1-x}Ca_xMnO_3$ (where Ln is a rare earth element), a structural study of these compounds has been developed, including the end compound $CaMnO_3$ ($x = 1$). From the same $CaMnO_3$ preparation, single crystals of a second compound were isolated, exhibiting cell parameters clearly different from those known for $CaMnO_3$ (Poeppelmeier *et al.*, 1982; Taguchi *et al.*, 1989; Aliaga *et al.*, 2001). Scanning electron microscopy measurements, coupled with energy dispersive spectroscopic (EDS) analysis, clearly lead to a Ca_3Mn_2 cationic composition.

The cell parameters of $Ca_3Mn_2O_7$ are consistent with either an orthorhombic or a tetragonal lattice. They depend both on the a_p cubic parameter (a_p = 3.72 Å) of the basic $CaMnO_3$ perovskite cell, with $CaMnO_3$ representing the $n = \infty$ member of the Ruddlesden–Popper series (Ruddlesden & Popper, 1958), and on the face-centred cubic cell of CaO {a_O = 4.8 Å [Tanida & Kitamura, 1981; ref. 41-0421 (ICDD, 1999)]}. The parameters found in the present work differ from those previously published for $Ca_3Mn_2O_7$ ($a_t \simeq a_p$ and $c_t \simeq 4a_p + 2a_O$) $2a_O$) (MacChesney *et al.*, 1967; Tanida & Kitamura, 1981; Fawcett *et al.*, 1998) by the relationships $a \simeq b \simeq a_t 2^{1/2}$ and $c \simeq c_t$.

The symmetry of the present crystal was carefully scrutinized both from Laue diagrams (precession camera) and from the intensity distribution in the X-ray diffraction data. The actual Laue symmetry is *mmm* rather than 4/*mmm*, as shown by the Laue diffraction pattern, and is confirmed from the R_{int} values of 4.49 and 9.73% calculated assuming orthorhombic and tetragonal symmetry, respectively. Moreover, some significant reflections of the type *hkl*, where $h + k = 2n + 1$, were observed and cannot be explained in the tetragonal model.

The present reflection conditions are consistent with the centrosymmetric space group *Amam*, but a satisfactory *R* factor could not be obtained with this symmetry. A new solution was initiated using the direct method calculation program *SIR*97 (Altomare *et al.*, 1999) in the non-centrosymmetric space group $A2_1am$ (No. 36). The standard setting of this group is $Cmc2_1$, but we adopted the non-standard setting in order to keep the pseudo-tetragonal cell along the *c* axis. This space group has already been proposed for the $Ca_3Ti_2O_7$ structure by Elcombe *et al.* (1991) and for $La_{2-2x}Ca_{1+2x}Mn_2O_7$ by Bendersky *et al.* (2001).

The atomic positions were refined to R = 0.023 using the *JANA*2000 structural refinement program (Petříček & Dušek, 2000), with anisotropic displacement parameters for all atoms and assuming the existence of twin domains related by the $(1\bar{1}0)$ plane, due to the similarity of the a and b parameters, with reference to a pseudo-tetragonal cell. The twin ratio was found to be 0.18. This twin model leads to a significant improvement of the *R* factor (0.032 without a twin).

The corresponding structure, with Ca_1 and O_1 atoms in 4*a* crystallographic sites and the other atoms in 8*b* sites, is shown in Fig. 1(*a*). It consists of a stacking of two layers formed by corner-sharing MnO_6 octahedra, separated by a double Ca—O layer. This description is consistent with the usual description of the Ruddlesden–Popper $Ca_{n+1}Mn_nO_{3n+1}$ family, which can also be represented by the formula $CaO[CaMnO_3]_n$, where n is the number of layers of MnO_6 octahedra.

Three types of polyhedra are present in this structure, one per cation, *i.e.* Mn^{4+}, $Ca1^{2+}$ and $Ca2^{2+}$. The Mn^{4+} ions are octahedrally coordinated, and the Mn—O bond distances in the equatorial plane range from 1.856 (5) to 1.899 (5) Å, with apical distances of 1.904 (1) and 1.9193 (4) Å. The corresponding average Mn—O distance is 1.890 (3) Å. Angles within the MnO_6 octahedra range from 88.7 (1) to 92.0 (2)° for O—Mn—O with *cis*-O atoms, and from 177.9 (2) to 178.4 (1)° for O—Mn—O with *trans*-O atoms.

Comparing the MnO_6 octahedra in $Ca_3Mn_2O_7$ with those in $CaMnO_3$ (Poeppelmeier *et al.*, 1982), we note that the Mn—O distances in the equatorial plane of the octahedra are shorter in $Ca_3Mn_2O_7$, while the apical distances are larger, leading to an elongated octahedron in $Ca_3Mn_2O_7$ as opposed to the compressed one in $CaMnO_3$ (1.865 Å for the apical distances, and 1.900 and 1.903 Å for the equatorial ones).

Atoms $Ca1^{2+}$, at $z = 0$ and $z = \frac{1}{2}$, are 12-fold coordinated (usual perovskite coordination), while atoms $Ca2^{2+}$ are ninefold coordinated. Both Ca1 and Ca2 belong to similar CaO layers orthogonal to *c*. The O—O distances in these layers,

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represented by dashed lines in Fig. 1(*b*), clearly show the difference from tetragonal symmetry, due to the MnO_6 octahedral distortion and tilting, which are forbidden in tetragonal symmetry. This projection clearly shows the analogy with the actual *Pnma* symmetry of the $CaMnO_3$ structure.

The average Ca—O distances are 2.646 (4) Å for the Ca1 polyhedra and 2.554 (3) Å for the Ca2 polyhedra, whereas the average Ca—O distance in $CaMnO_3$ is 2.652 Å. Two short Ca2—O distances (<2.3 Å) are observed (Table 1). The average Mn—O and Ca—O distances are in good agreement with those predicted by the ionic radii calculated by Shannon (1976), with $r_{Mn^{4+}} = 0.53$, $r_{Ca1^{2+}} = 1.34$, $r_{Ca2^{2+}} = 1.18$ and $r_{O^{2-}} = 1.35$ Å. Nevertheless, they are shorter than in the $CaMnO_3$ parent phase, but longer than in CaO.

Thus, the present structure can be interpreted as the alternate stacking of reduced $CaMnO_3$-type layers and of expanded CaO-type layers. The principal difference from the structure described by Fawcett *et al.* (1998) results in Mn polyhedra having Mn—O distances differing by ±0.03 Å from those calculated using the Shannon radii, contrasting with an apical Mn—O distance of 2.09 Å with the O atom directed towards the CaO layer. This could be related to the alternate tilt of MnO_6 octahedra, mainly around the *x* and *z* axes (Figs. 1*a* and 1*b*) of 6.8 and 8.3°, respectively, using the formulae of Elcombe *et al.* (1991). These tilt angles, characterized by Mn—O1—Mn 166.5 (1)°, Mn—O2—Mn 158.9 (2)° and Mn—O3—Mn 162.5 (2)°, are quite compatible with the corresponding angles in $CaMnO_3$.

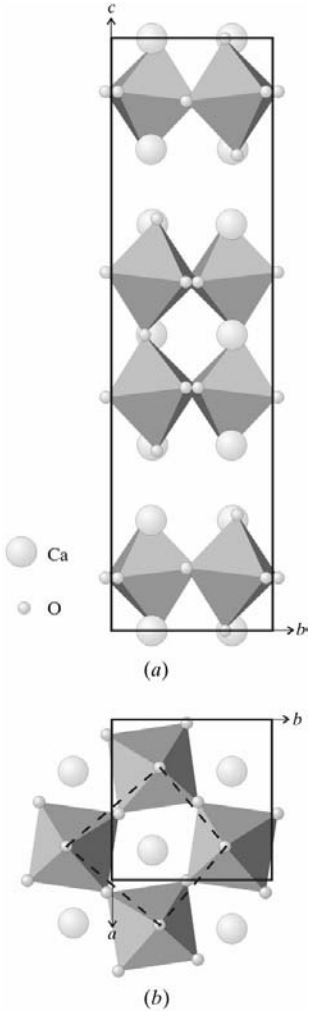

Figure 1
(*a*) The structure of $Ca_3Mn_2O_7$ in the (100) plane. (*b*) The O—O distances viewed along the *c* axis show the difference from tetragonal symmetry.

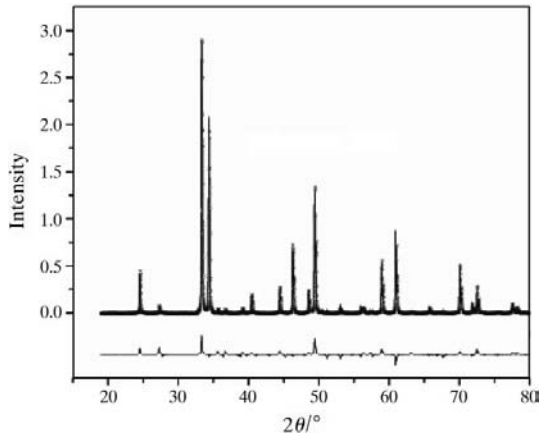

Figure 2
Simulated X-ray diffraction patterns for $Ca_3Mn_2O_7$ in the tetragonal (x) and orthorhombic (—) models. The difference plot is represented at the bottom.

Simulations of X-ray diffraction powder patterns with *JANA*2000 (Fig. 2) in both models show very small differences. This outlines, in the present case, the difficulty of refining the structure with standard X-ray powder diffraction patterns.

Experimental

The initial sample preparation consisted of a mixture of CaO, prepared by decarbonation of $CaCO_3$ at 1273 K, and MnO_2 (Aldrich) in stoichiometric proportions, to produce $CaMnO_3$. The mixture was heated to 1273 K and crushed, three times in succession, so as to obtain a good sample homogeneity, and was then compressed in an isostatic press at 3×10^7 Pa in the form of a rod (5 × 50 mm) before sintering at 1673 K for 12 h in air. Crystal growth was carried out in a four-mirror optical floating-zone furnace (Crystal Systems Inc. FZT 10000 H III P). The samples were set to rotate in opposite directions at 20 revolutions per minute and were grown in an oxygen flow at atmospheric pressure, at a feeding speed of 10 mm h^{-1}. It is important to state that the previous ceramic synthesis of $Ca_3Mn_2O_7$ could only be performed under a high pressure of oxygen (3200 psi; 1 psi ≃ 6.895×10^3 Pa) (MacChesney *et al.*, 1967).

Crystal data

$Ca_3Mn_2O_7$
$M_r = 342.1$
Orthorhombic, $A2_1am$
$a = 5.2347$ (6) Å
$b = 5.2421$ (2) Å
$c = 19.4177$ (19) Å
$V = 532.83$ (8) Å^3
$Z = 4$
$D_x = 4.266$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 11$–24°
$\mu = 7.61$ mm^{-1}
$T = 298$ K
Prism, black
0.12 × 0.07 × 0.02 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: Gaussian (*JANA*2000; Petříček & Dušek, 2000)
T_{min} = 0.619, T_{max} = 0.865
10 766 measured reflections
1516 independent reflections (plus 1318 Friedel-related reflections)
745 reflections with $I > 3\sigma(I)$
R_{int} = 0.045
θ_{max} = 50°
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -41 \rightarrow 41$
3 standard reflections
frequency: 60 min
intensity decay: 0.2%

Refinement

Refinement on F
R = 0.023
wR = 0.015
S = 1.45
1516 reflections
59 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.39 e Å^{-3}
$\Delta\rho_{min}$ = −1.13 e Å^{-3}
Extinction correction: B-C type 1, Gaussian isotropic (Becker & Coppens, 1974)
Extinction coefficient: 0.008 (2)
Absolute structure: (Flack, 1983)
Flack parameter = 0.45 (6)

Table 1
Selected interatomic distances (Å).

Mn—O1	1.9193 (4)	Ca1—O3^{iii}	2.548 (3)
Mn—O2^{i}	1.873 (4)	Ca1—O3^{v}	2.996 (4)
Mn—O2^{ii}	1.900 (5)	Ca1—O3^{viii}	2.548 (3)
Mn—O3	1.857 (5)	Ca1—O3^{ii}	2.996 (4)
Mn—O3^{ii}	1.885 (4)	Ca2—O2^{vi}	2.884 (4)
Mn—O4	1.9048 (10)	Ca2—O2^{ii}	2.406 (3)
Ca1—O1	2.755 (5)	Ca2—O3^{iii}	2.293 (4)
Ca1—O1^{iii}	2.499 (5)	Ca2—O3^{ii}	2.598 (4)
Ca1—O1^{iv}	2.856 (3)	Ca2—O4	2.526 (4)
Ca1—O1^{v}	2.393 (3)	Ca2—O4^{iii}	2.730 (4)
Ca1—O2^{vi}	2.694 (4)	Ca2—O4^{ix}	2.2968 (11)
Ca1—O2^{v}	2.391 (3)	Ca2—O4^{x}	2.438 (2)
Ca1—O2^{vii}	2.694 (4)	Ca2—O4^{ii}	2.821 (2)
Ca1—O2^{ii}	2.391 (3)		

Symmetry codes: (i) $x, y-1, z$; (ii) $\frac{1}{2}+x, 1-y, z$; (iii) $1+x, y, z$; (iv) $\frac{1}{2}+x, -y, -z$; (v) $\frac{1}{2}+x, 1-y, -z$; (vi) $1+x, y-1, z$; (vii) $1+x, y-1, -z$; (viii) $1+x, y, -z$; (ix) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$; (x) $\frac{1}{2}+x, -y, z$.

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1994); cell refinement: *CAD*-4-*PC Software*; data reduction: *JANA*2000 (Petříček & Dušek, 2000); program(s) used to solve structure: *JANA*2000 and *SIR*97 (Altomare *et al.*, 1999) program(s) used to refine structure: *JANA*2000; molecular graphics: *ATOMS* (Dowty, 1997); software used to prepare material for publication: *JANA*2000.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1169). Services for accessing these data are described at the back of the journal.

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