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Preparation and the Crystal Structure of a New Manganate, $Sr_4Mn_3O_{10}$

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The growth of strontium manganates from melts based on $SrCl_2$–SrF_2 as solvents yielded orthorhombic crystals of composition $Sr_4Mn_{2.964}Pt_{0.036}O_{10}$ (space group *Cmca*, $a = 5.443(2)$, $b = 12.427(4)$, $c = 12.500(4)$ Å, $Z = 4$, $\rho_{cal} = 5.34$ g cm^{-3}). The platinum incorporated in samples originates from the crucible and may be essential for the crystal stabilization. The structure can be derived from a close-packed arrangement of oxygen and strontium atoms, in which some positions are vacant. This results in a more open structure. Manganese and platinum cations occupy all octahedral voids coordinated by the oxygen atoms only. The characteristic feature of the structure is triple groups of face-shared octahedra which are interconnected by common corners into a two-dimensional framework perpendicular to the [010] direction. Stacking in the third dimension is established by Sr–O bonds. © 1988 Academic Press, Inc.

Introduction

Calcium, strontium, and barium manganates exhibit several stoichiometric phases which consist of corner- or face-shared MnO_6 octahedra. The divalent alkali–earth cations are located in larger voids of this framework, coordinated typically by 9 to 12 oxygens. In an ideal case, the manganese cations are tetravalent. Nevertheless, a small amount of Mn^{3+} is generally present due to oxygen deficiency. The phases encountered in the Ca–Mn–O system are all related to the cubic perovskite structure. They are formed of the corner-shared octahedra only. $CaMnO_3$ (*1*) is an orthorhombically distorted perovskite of the $GdFeO_3$ type. Ca_2MnO_3, $Ca_3Mn_2O_7$, and $Ca_4Mn_3O_{10}$ (*2*) are layered (tetragonal) perovskites of the K_2NiF_4, $Sr_3Ti_2O_7$, and $Sr_4Ti_3O_{10}$ type, respectively. Barium manganates on the other hand are hexagonal (or rhombohedral) and display a variety of phases characterized by the number of BaO_3 close-packed layers per hexagonal *c*-parameter. There exist 2-, 4-, 6-, 8-, 9-, 10-, and 15-layer structures of $BaMnO_3$ (*3*).

As to the strontium manganates, two structures have been determined previously—$SrMnO_3$ (*4*) possesses the four-layer structure of the $BaMnO_3$ type and Sr_2MnO_4 (*5*) is of the K_2NiF_4 type. In this paper we describe the preparation and the structure of a new orthorhombic phase of the formula $Sr_4Mn_3O_{10}$.

Preparation

Crystal of strontium manganates were grown by a conventional method from

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melts based on $SrCl_2$–SrF_2(–B_2O_3) as solvent. The growth experiments were performed in a 50-cm^3 platinum crucible with 50 g of the melt, placed in a vertical tube furnace with a crusilite double-spiraled muffle element. The temperature regime was controlled by a PID programmer–controller Eurotherm with an accuracy better than 0.1°C. The cooling speed was 1°C/hr. Compositions of melts and growth ranges of three experiments are summarized in Table I.

The particular compositions of melts were chosen in order to prepare crystals of the layered perovskite Sr_2MnO_3F which is of interest for the ferrodistortive Jahn–Teller ordering of elongated $Mn^{3+}(O,F)_6$ octahedra. Instead of this oxyfluoride, other compounds were obtained. Experimental run 1 yielded tiny black crystals in the form of short hexagonal prisms, which were identified by X-ray powder diffraction as the four-layer hexagonal phase of $SrMnO_3$. Runs 2 and 3 resulted in black crystals in the form of elongated orthorhombic prisms capped by a low pyramid which were later ascribed to the $Sr_4Mn_3O_{10}$ phase. Even though the number of nuclei created during the growth was minimized by spot cooling of the crucible bottom by a platinum rod, the maximum dimension of prepared crystal did not exceed 3 mm. The chemical composition of this new manganite phase was checked by employing an electron microprobe which ruled out any presence of fluorine and showed the Sr/Mn ratio to be slightly greater than 1. In addition, a small amount of platinum was later detected in the crystals.

TABLE I

CRYSTAL GROWTH CONDITIONS

Run no.	SrO (mole%)	$MnO_{1.5}$ (mole%)	SrF_2 (mole%)	$SrCl_2$ (mole%)	B_2O_3 (mole%)	Growth range (°C)
1	40.00	26.67	26.67	—	6.67	1400–1150
2	11.63	7.75	55.04	25.58	—	1250–1000
3	8.33	5.56	58.33	27.78	—	1200–950

Structure Determination

Preliminary lattice constants and the space group *Cmca* were obtained from precession photographs (Mo*Kα*, Zr filtered, $\lambda = 0.71073$ Å). A spherical crystal with $r = 0.33$ mm was used for measurements (Ag*Kα* radiation, Pd filtered, $\lambda = 0.56082$ Å) on a Hilger & Watts four-circle diffractometer controlled by a M 7000 computer. Refined cell parameters were obtained by a least-squares method (*6*) from 25 centered reflections ($5° < \vartheta < 16°$, Ag*Kα*, Pd filtered). The $\omega - 2\vartheta$ scan technique was used to measure all independent reflections with $\sin \vartheta/\lambda \leq 0.6390$ ($h \in (0,6)$, $k \in (0,15)$, $l \in (0,15)$). The learned profile method (*7, 8*) was used for obtaining intensities and their e.s.d.'s. The scan speed varied from 1° to 4° min^{-1} determined from a rapid prescan. The intensities of three standard reflections (4,0,0), (0,8,0), and (0,0,8) measured after every thirty reflections showed no significant variation. Of 511 independent reflections, 71 were classified as unobserved ($I < 1.96\,\sigma(I)$), but these reflections were used in the refinement with $F_{\text{unobs}} = \frac{1}{2} F_{\min}$ and $\sigma(F_{\text{unobs}}) = (1/\sqrt{12})F_{\min}$ ($F_{\min}$ = the minimum observable value of $|F|$). The data were corrected for Lorentz and polarization effects and for absorption ($A^* \in (77.8, 209.7)$, $\mu_{\text{Ag}} \cdot r = 5.52$).

A structure model within the $Sr_4Mn_3O_{10}$ stoichiometry was proposed on the basis of knowledge of the preliminary lattice constants, the space group, and the density of roughly 5 g cm^{-3} by using crystallochemical considerations. This model was used as a starting point in the refinement procedure. The refinement was carried out by a local system of crystallographic programs on a Siemens 7536 computer, minimizing the function $\Sigma_w(|F_o| - |F_c|)^2$ where $1/w = \sigma^2(F_o) + (0.03F_o)^2$.

TABLE II

FRACTIONAL ATOMIC COORDINATES AND TEMPERATURE PARAMETERS [Å^2]

Atom	Site	x	y	z	B_{eq}^{a} or B_{iso}
Sr1	8(f)	0.00000	0.46920(8)	0.14209(8)	0.56(3)
Sr2	8(f)	0.00000	0.26149(8)	0.38923(9)	0.71(3)
Mn,Pt1	4(a)	0.00000	0.00000	0.00000	0.45(6)
Mn2	8(f)	0.00000	0.13129(13)	0.15200(13)	0.38(4)
O1	8(f)	0.00000	0.0370(6)	−0.1466(6)	0.36(12)
O2	8(f)	0.00000	0.2751(7)	0.1492(6)	0.88(14)
O3	16(g)	0.2312(12)	0.1084(4)	0.0367(4)	0.59(8)
O4	8(e)	0.25000	0.1200(6)	0.25000	1.08(13)

[a] $B_{eq} = \frac{4}{3} \Sigma_i \Sigma_j \beta_{ij}\mathbf{a}_i\mathbf{a}_j$ *(10)*.

During the refinement, it was found that the temperature tensor of the atom Mn1 in site 4(a) was not positive definite as if this position is partly occupied by some heavier atom. This suspicion was confirmed by an analysis on the electron microprobe (JEOL JXA 733) which showed that the samples contained about 1% platinum. This fact was in good agreement with results of the subsequent structural refinement where the 4(a) site was allowed to be occupied by manganese and platinum atoms. The platinum occupancy was refined to 0.036(6) and this gives the final formula of $Sr_4Mn_{2.964}Pt_{0.036}O_{10}$, which means that the content of platinum is approximately 1.03%. The common temperature tensor for the 4(a) site became positive definite and reasonable.

TABLE III

ANISOTROPIC TEMPERATURE PARAMETERS ($\times 10^5$) OF NONOXYGEN ATOMS IN THE FORM $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hk - 2\beta_{23}kl)$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sr1	368(38)	78(7)	120(7)	0	0	4(4)
Sr2	403(39)	69(7)	198(7)	0	0	−1(4)
Mn,Pt1	329(87)	78(15)	77(16)	0	0	4(9)
Mn2	269(58)	59(10)	73(10)	0	0	15(7)

TABLE IV

INTERATOMIC DISTANCES (Å) AND SELECTED BOND ANGLES (°)

(a) Distances and angles in octahedrons^a

Mn1–O1	1.889(7)	Mn2–O1^{i}	2.093(8)
–O1^{i}	1.889(7)	–O2	1.787(9)
–O3	1.900(6)	–O3	1.935(6)
–O3^{i}	1.900(6)	–O3^{iii}	1.935(6)
–O3^{ii}	1.900(6)	–O4	1.836(1)
–O3^{iii}	1.900(6)	–O4^{iii}	1.836(1)
O1 –Mn1–O1^{i}	180.0	O1^{i} –Mn2–O2	177.0(3)
O1 –Mn1–O3	93.5(2)	O1^{i} –Mn2–O3	80.2(2)
O1 –Mn1–O3^{i}	86.5(2)	O1^{i} –Mn2–O3^{iii}	80.2(2)
O1 –Mn1–O3^{ii}	86.5(2)	O1^{i} –Mn2–O4	86.9(3)
O1 –Mn1–O3^{iii}	93.5(2)	O1^{i} –Mn2–O4^{iii}	86.9(3)
O1^{i} –Mn1–O3	86.5(2)	O2 –Mn2–O3	97.6(3)
O1^{i} –Mn1–O3^{i}	93.5(2)	O2 –Mn2–O3^{iii}	97.6(3)
O1^{i} –Mn1–O3^{ii}	93.5(2)	O2 –Mn2–O4	95.1(3)
O1^{i} –Mn1–O3^{iii}	86.5(2)	O2 –Mn2–O4^{iii}	95.1(3)
O3 –Mn1–O3^{i}	180.0	O3 –Mn2–O3^{iii}	81.2(3)
O3 –Mn1–O3^{ii}	97.0(3)	O3 –Mn2–O4	90.2(2)
O3 –Mn1–O3^{iii}	83.0(3)	O3 –Mn2–O4^{iii}	165.5(3)
O3^{i} –Mn1–O3^{ii}	83.0(3)	O3^{iii} –Mn2–O4	165.5(3)
O3^{i} –Mn1–O3^{iii}	97.0(3)	O3^{iii} –Mn2–O4^{iii}	90.2(2)
O3^{ii} –Mn1–O3^{iii}	180.0	O4 –Mn2–O4^{iii}	95.6(1)

(b) Coordination of strontium atoms and cation–cation distances

Atoms	Multiplicity	Distance
Sr1–O1	2	2.723(2)
–O1	1	2.642(7)
–O2	1	2.414(9)
–O3	2	2.621(6)
–O3	2	2.840(6)
–O4	2	2.680(5)
Sr2–O1	1	2.544(8)
–O2	2	2.769(2)
–O2	1	3.005(8)
–O2	1	3.281(8)
–O3	2	2.572(6)
–O3	2	2.756(5)
–O4	2	2.824(5)
Mn1–Mn2	2	2.504(16)
Mn1–Sr1	4	3.272(5)
–Sr2	2	3.271(10)
Mn2–Sr1	1	3.268(19)
–Sr1	2	3.388(11)
–Sr2	2	3.208(10)
–Sr2	1	3.378(20)

[a] Symmetry code: (i) $-x, -y, -z$; (ii) $x, -y, -z$; (iii) $-x, y, z$.

The full-matrix least-squares refinement (max. $\Delta/\delta < 0.01$) converged to $S = 1.25$, $R_w = 0.056$, and $R = 0.048$. For the observed reflections, $R_w = 0.051$ and $R = 0.040$. The secondary extinction correction was made (Becker and Coppens (*9*), type II) and the mean particle size was refined to $5.5(5) \times 10^{-5}$ cm. The maximum residual electron density determined from final difference Fourier maps was 0.24 e/Å^3. The final atomic parameters are summarized in Tables II and III. The interesting bond distances and angles are given in Table IV.

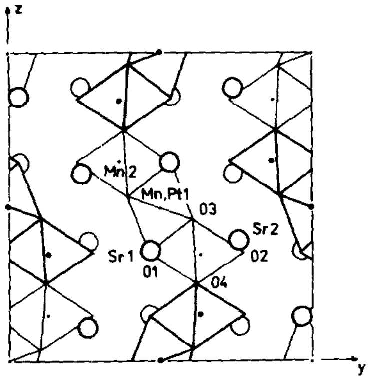

FIG. 1. The structure of $Sr_4Mn_{2.964}Pt_{0.036}O_{10}$. ($MnO_6$ octahedra and Sr cations marked by the full lines are located at the $x = 0.5$ level; the others are at $x = 0$.)

Discussion

The building elements of the $Sr_4Mn_{2.964}Pt_{0.036}O_{10}$ structure are triple groups of face-shared $(Mn,Pt)O_6$ octahedra (see Fig. 1). The platinum cations are located only in central octahedra. The triple groups are linked up by corners of terminal octahedra into a two-dimensional framework perpendicular to the [010] direction. Separate sheets of interconnected octahedra are bonded by strontium cations in two nonequivalent sites. One strontium site is linked to 10 oxygen ions at the distance 2.41–2.84 Å, the second site to 9 oxygens at the bonding distance 2.54–2.82 Å, and two others at 3.01 and 3.28 Å.

Isomorphous structures have been reported previously for $Ba_4(Ti,Pt)_2PtO_{10}$ (*11*) and $Cs_4Ni_3F_{10}$ (*12*). As pointed out in Ref. 11, the structure can be derived from a hexagonal stacking of eight close-packed (011) planes of oxygen and strontium atoms in which some positions are vacant. The composition of these planes is $Sr_2O_5\square$. In the vicinity of vacancies, the atomic arrangement is distorted. The vacancies are ordered along the [100] direction and form "channels" between the sheets of interconnected $(Mn,Pt)P_6$ octahedra. The walls of these channels are built of strontium and oxygen atoms arranged as in the NaCl structure.

It is probable that the platinum incorporated in our compound played an essential role in the formation of the $Sr_4Mn_3O_{10}$ phase. This can be concluded from the failure of our attempts to prepare uncontaminated $Sr_4Mn_3O_{10}$ from carbonates by the solid-state reactions. We note that similar behavior is reported for barium titanates where the synthesis of hexagonal perovskite phase does require the presence of platinum or some other transition metals (*11*). Their *d*-electrons are assumed to enable the direct cation–cation bonding in face-shared octahedra which may stabilize the hexagonal or hexagonal-related structures.

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