A Single Crystal Study of Eight-Layer Barium Manganese Oxide, BaMnO$_3$

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A single crystal study of hydrothermally prepared eight-layer BaMnO$_3$ has been carried out which confirms the (Zhdanov notation) 121121 layer stacking scheme for the BaO$_3$ layers. The MnO$_6$ octahedra share faces in strings of four, and these strings are connected to each other by corner sharing. The compound has an hexagonal unit cell of dimensions $a = 5.667 \pm 0.003$ and $c = 18.738 \pm 0.009$ Å, probable space group $P6_3/mmc$, $Z = 8$. Its structure has been determined from 352 independent reflections, of which 242 were considered observed, collected manually by a counter technique and refined to a conventional R value of 0.079.

Introduction

A discussion of structure relations in mixed metal oxides which could be described in terms of close packed layers of composition AO$_3$ has been given by Katz and Ward (*1*). For the system BaMnO$_{3-x}$, Negas and Roth (*2*) have carried out an extensive investigation in which the relationships among the 2-, 4-, 6-, 8-, 10-, and 15-layer modifications were studied and rationalized. In addition to these modifications, a nine-layer (9L) phase has also been reported (*3, 4*).

Single crystals of the eight-layer modification were grown by Negas and Roth (*2*) in sealed platinum tubes at temperatures between 1250°C and 1350°C. Crystals for the current study were prepared hydrothermally. Preliminary powder work suggested that the sample consisted mainly of the 9L phase. However, the crystals selected for study had hexagonal *c* axes of about 18.8 Å, which corresponds to an 8L structure. We decided to take the opportunity to carry out the first single crystal study of an 8L ABO$_3$ structure.

The hydrothermal reaction between Ba(OH)$_2$ · 8H$_2$O and MnO$_2$ was carried out in a collapsible gold ampoule at 700°C and 3000 atm for about 8 hr. The black product contained a microcrystalline powder and a few hexagonal plates. The powder pattern obtained from a sample of this product showed only the 9L phase, but the crystals used in this study were found to have the 8L structure. Mixed polytypes were also observed (*3*) in the SrMnO$_3$ system in which crystals of the 2L phase were found in the predominantly 4L product.

The 8L phase prepared in this reaction is believed to be very nearly stoichiometric due to the oxidizing nature of the hydrothermal experiment. The nonstoichiometric 8L phase prepared by Negas and Roth (*2*) in high-temperature solid state preparations could be converted to a stoichiometric composition by thermal treatment in an oxidizing atmosphere.

Experimental Methods

The crystal chosen was a black hexagonal plate approximately 0.08 mm in diameter and 0.04 mm thick. Precession photographs indicated the probable space group to be one of $P\bar{6}2c$, $P6_3mc$, or $P6_3/mmc$. The hexagonal unit cell parameters of $a = 5.67$ and $c = 18.77$ Å were close to those reported (*2*). However, a least squares refinement using the setting angles of 12 well centered reflections measured in a Picker automated diffractometer using graphite monochromatized Mo radiation gave $a = 5.667 \pm 0.003$ and $c = 18.738 \pm 0.009$ Å. A full rotation photograph around c confirmed the axial length. Taking $Z = 8$, the X-ray density has the reasonable value

TABLE I

ATOMIC PARAMETERS FOR $Ba_8Mn_8O_{24}$[a] SPACE GROUP $P6_3/mmc$ (No. 194)

Atom	Position	x	y	z	U_{12}[b]	U_{33}[b]
Ba(1)	2a	0	0	0	11 (8)	132 (22)
Ba(2)	2b	0	0	1/4	19 (9)	202 (26)
Ba(3)	4f	1/3	2/3	0.1285 (2)	16 (4)	109 (14)
Mn(1)	4f	1/3	2/3	0.5517 (4)	19 (10)	74 (33)
Mn(2)	4f	1/3	2/3	0.6857 (4)	29 (11)	35 (27)

					U	
O(1)	6g	1/2	0	0	74 (65)	
O(2)	6h	0.5202 (53)	0.0404	1/4	214 (91)	
O(3)	12k	0.8126 (22)	0.6252	0.1197 (10)	19 (37)	

[a] Thermal parameters have been multiplied by 10^4.

[b] $U_{11} = U_{22} = 2U_{12}$ and $U_{13} = U_{23} = 0$.

of 6.12 g/cc. However, no density measurement or chemical analysis was carried out on the mixture of phases from which the crystals were obtained.

Data were collected manually on a General Electric XRD-5 diffractometer with a single crystal orienter. A total of 1191 reflections were measured, using Zr-filtered Mo radiation, pulse height discrimination, and a scintillation counter. The θ–2θ scan technique was used at 2° 2θ/min for 80 sec. Background was counted for 20 sec at each end of the 2.67° scan range.

After averaging symmetry related reflections

there were 352 independent reflections of which 242 were greater than 5 counts above background (approximately 2σ for the background) and were considered observed. An absorption correction was attempted, but since it resulted in no improvement in the final agreement, it was not used.

Structure Refinement

A statistical analysis of the reflection intensities indicated that the structure was centrosymmetric; therefore the probable space group is

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

[Table of observed and calculated structure factors — dense numerical data columns omitted]

[a] The columns are l, $10|F_o|$, $10F_c$.

* Unobserved reflections.

$P6_3/mmc$. Two eight-layer stacking sequences are possible in this space group. In the Zhdanov notation these are 44, which corresponds to 75% cubic layers (adjacent layers different) and 25% hexagonal layers (adjacent layers alike), and 121121, which corresponds to 75% hexagonal layers and 25% cubic layers. Negas and Roth (2) established from powder data that the second arrangement was correct, and this was confirmed in our study.

Omitting the 110 and 220 reflections, which were obviously affected by extinction, an isotropic least squares refinement with unit weights resulted in a conventional R of 9.9%. Refinement was continued with metal atoms anisotropic. By applying the real and imaginary anomalous dispersion corrections (5), an initial difficulty with nonpositive-definite temperature factors was overcome, and convergence was obtained (maximum shift/error of 0.003) with a conventional R of 7.9%. The corresponding parameters are listed in Table I.

The calculated and observed structure factors, listed in Table II, were examined for discrepancies. Since the weaker reflections showed the poorest agreement, a Hughes type weighting scheme (6) was applied to reflections for which $F_{obs} < 35.0$. The scheme was: $w = 1/\sigma^2$ with $\sigma = 35.0/F_{obs}$. With this weighting, the weighted R factor decreased to 6.3%; however, the con-
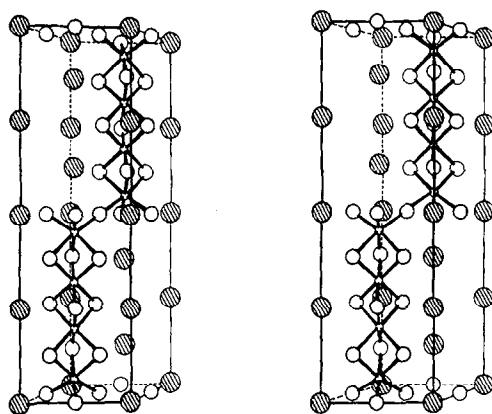

FIG. 1. Stereo view of unit cell of $Ba_8Mn_8O_{24}$. Ba atoms are shown as striped circles, O atoms as large open circles, and Mn atoms as small open circles.

ventional R was higher (8.1%) and, more importantly, the parameter errors were larger, so the unit weight results are the ones reported. Interatom distances and bond angles are shown in Table III. All the above calculations were carried out with X-ray system (7). A stereoscopic illustration of the unit cell contents (Fig. 1) and an illustration of the manganese environment (Fig. 2) were prepared with Johnson's program ORTEP (8).

Discussion

The detailed investigation of the $BaMnO_{3-x}$ system by Negas and Roth revealed the following succession of phases with increasing temperature:

TABLE III

INTERATOMIC DISTANCES AND ANGLES $Ba_8Mn_8O_{24}$

Distances (Å)

Ba(1)–O(1)	2.833 (1)	Mn(2)–O(2)	1.880 (19)
Ba(1)–O(3)	2.893 (15)	Mn(2)–O(3)	1.901 (15)
Ba(2)–O(2)	2.839 (30)	O(1)–O(1)	2.831 (1)
Ba(2)–O(3)	3.063 (16)	O(1)–O(3)	2.715 (16)
Ba(3)–O(1)	2.913 (3)	O(2)–O(2)	2.501 (24)
Ba(3)–O(2)	2.916 (15)	O(2)O(3)	2.841 (23)
Ba(3)–O(3)	2.845 (7)	Mn(1)–Mn(2)	2.507 (11)
Mn(1)–O(1)	1.904 (4)	Mn(2)–Mn(2)	2.404 (11)
Mn(1)–O(3)	1.907 (15)		

Angles (°)

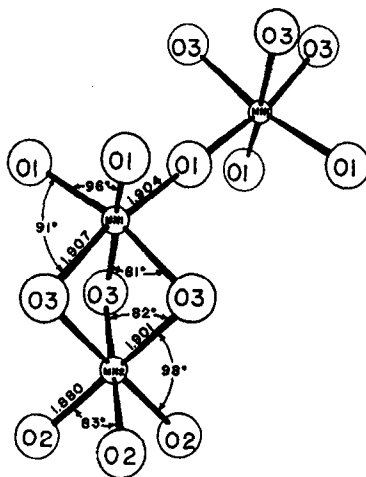|	
O(1)–Mn(1)–O(1)	96.11 (26)
O(1)–Mn(1)–O(3)	90.89 (27)
O(3)–Mn(1)–O(3)	81.17 (56)
O(2)–Mn(2)–(O2)	83.48 (68)
O(2)–Mn(2)–O(3)	97.51 (40)
O(3)–Mn(2)–O(3)	81.52 (56)
Mn(1)– O(1)–Mn(1)	180 (7)
Mn(1)– O(3)–Mn(2)	82.37 (49)
Mn(2)– O(2)–Mn(2)	79.53 (96)

FIG. 2. Portion of structure showing a pair of face-sharing octahedra linked to another octahedron by corner sharing.

2L (continuous strings of face-sharing octahedra); 15L (strings of 5 face-sharing octahedra linked to each other by corner sharing); 8L (strings of 4); 6L (alternating strings of 4 and 2); 10L (alternating strings of 3 and 2) and 4L (pairs of face-sharing octahedra only). The six-layer modification is interesting, because, of the two possible six-layer stacking arrangements, only the hexagonal $BaTiO_3$ arrangement had been reported before. A 9L modification (strings of 3) has been prepared by Chamberland, Sleight, and Weiher at elevated pressures (3) and, stabilized by as little as 5 mole % ruthenium, by Donohue, Katz, and Ward (4), or 10 mole % $SrMnO_3$ by Negas (9). The possibilities for varying string lengths of face-sharing octahedra are obviously particularly rich in this system.

"Pseudo-eight-layer" structures have been reported among rhenium containing complex metal oxides by Longo, Katz, and Ward (10). In these cases weak reflections indicated actual cells which were larger in the a direction by a factor of $\sqrt{3}$ and in the c direction by a factor of 3. A comparison of observed and calculated intensities for the pseudo-cell suggested a stacking sequence of the (Zhdanov notation) 44 type. The present study is thus different in that it not only deals with a true 8L structure but also with an 8L arrangement exhibiting the maximum amount of face-sharing.

The Mn–Mn bond length of 2.404 Å is short, suggestive of metal–metal interactions, and similar to the same distance reported for the 2L $BaMnO_3$ structure (11). The Mn–O bond distances, shown in Table III, were compared to those calculated with the Shannon–Prewitt radii (12) and are reasonably consistent with expected values for the coordination numbers involved and the +4 oxidation state for manganese. Negas and Roth report an oxygen deficiency in the eight-layer structure, one sample having a composition $BaMnO_{2.959}$; however, we were not in a position to carry out a meaningful

analysis for the mixture of phases we had available. The argument that a reduced oxidation state for Mn (below +4) plays a role in the phases which have shorter face-sharing sequences remains a plausible one. For the 8L arrangement, and, *a fortiori*, for the 15L and 2L phases, anion deficiency need not be large, and indeed is very small as shown by Negas (2, 9).

Acknowledgments

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