

A Single Crystal Study of Eight-Layer Barium Manganese Oxide, BaMnO₃

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A single crystal study of hydrothermally prepared eight-layer BaMnO₃ has been carried out which confirms the (Zhdanov notation) 121121 layer stacking scheme for the BaO₃ layers. The MnO₆ 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 AO₃ 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 ABO₃ structure.

The hydrothermal reaction between Ba(OH)₂·8H₂O and MnO₂ 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 SrMnO₃ 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 Ba₈Mn₈O₂₄^a SPACE GROUP P6₃/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 10⁴.

^b U₁₁ = U₂₂ = 2U₁₂ and U₁₃ = U₂₃ = 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

0+0L	2 153* 16	18 292 -222	11 467 -421	6 340 320	4 1949 1877	1 273* 271	18 282* -22	15 308* -152	1 315 269
6 478 441	3 1290 -1076	4 3137 3291	12 1127 1193	8 1546 1526	5 1185 1129	2 273* -15	20 287* 219	16 322 178	2 291* 16
8 2647 3206	5 1835 1728	21 297* -236	15 541 517	10 348 -556	6 223 -192	3 353 420	22 763 794	3 391 354	4 1160 1166
10 282 -348	6 201 -136	22 888 933	16 295* -5	12 318 -337	7 1359 1320	4 1356 1383		2.5+L	5 776 -771
12 376 -369	7 2165 2124	23 313* -72	17 300* -217	14 221* -67	8 1055 975	5 853 -864			6 297* -131
14 519 -257	8 1597 1530		18 256* -240	10 292 232	9 1137 -1089	6 280* -345		0 2407 2395	7 1012 -993
16 5160 3367	9 1480 -1563	0+4L	17 549 -597	20 368 243	11 618 -524	8 744 804	0 237* -58	1 296* 67	8 738 824
18 244* -21	10 289 256		18 318* 229	22 934 948	12 1567 1462	9 906 987	2 232* 2	3 378 365	9 860 832
20 262* 230	11 1041 -963	0 215* 286		24 830 787	13 630 856	10 293* 185	3 493 408	4 299* 121	10 311 223
22 831 881	12 2313 2461	1 434 427	0 2927 2861	1+2L	15 415 -371	11 405 454	4 888 1749	5 301* -151	11 634 392
24 1272 1181	13 899 870	2 220* 62	2 288* 105	3 289* -30	16 271* 13	12 1147 1265	5 1013 -985	6 335 276	12 1003 1084
0+1L	14 225* 217	3 702 682	1 288* -12	4 291* 106	17 685 -824	13 516 -521	6 241* -125	7 305* -92	
2 110* -1	15 223* -144	4 2020 2188	2 288* 105	5 300 24	18 286* 132	14 311* 35	7 1085 -1040	8 907 861	3+6L
3 685 594	16 274 295	5 1161 -1206	3 289* -30	6 329 313	19 293* -501	15 324 190	8 829 787	9 311* 34	0 1895 1905
4 2324 2499	17 801 -774	6 229* -72	4 291* 106	7 174* 8	20 911 877		9 968 894	10 311* -301	0 1895 1905
5 1524 -1540	18 320 165	7 1433 -1495	5 300 24	8 1292 1331	21 619 568		10 311 193	11 318* 166	3+7L
6 251 -260	19 565 -572	8 1153 1122	6 329 313	7 297* 17	5 1371 -1239		11 508 419		
7 1585 -1714	20 1331 1261	9 1159 1170	7 297* 17	8 1381 1267	6 274 -249	1+4L	0 307* -35	12 1532 1592	2+6L
8 1237 1253	21 785 641	10 333 295	8 1292 1331	9 1459 1321	7 1780 -1636		1 307* -1555	13 405 -398	0 329* 205
9 1402 1381	22 291* -275	11 708 696	9 303* -6	10 346 311	8 1381 1267	0 3380 3171	2 307* -8	14 277* 115	0 381* 77
10 342 305	23 891 888	12 1815 1869	10 322 -191	11 605 548	9 303* -6	0 3380 3171	3 308* -736	15 391 448	0 381* 77
11 680 589	24 554 489	13 706 -687	11 391 -30	12 1601 1644	10 322 -191	0 3380 3171	4 1245 1298	16 289* 27	0 2552 2442
12 1861 1984	25 623 -319	14 275 177	12 360 -172	13 701 -682	11 605 548	0 3380 3171	5 749 736	17 491 466	0 358* 237
13 773 -796	0+3L	15 276* 343	13 701 -682	14 237* 36	12 1601 1644	0 3380 3171	6 313* -89	18 302* 105	4+5L
14 213* 109	0 4165 3941	16 300 217	14 237* 36	15 370 391	13 701 -682	0 3380 3171	7 817 822	19 317 220	2+8L
15 532 556	1 185* 80	17 669 650	15 370 391	16 252* 176	14 237* 36	0 3380 3171	8 245* 107	20 840 855	0 348* 24
16 254 68	2 1474 8	18 2544 181	16 252* 176	17 722 717	15 370 391	0 3380 3171	9 327 324	1+7L	0 1697 1686
17 763 718	3 292 487	19 438 435	17 722 717	18 268* 217	16 252* 176	0 3380 3171	10 2000 2106	2+4L	4+6L
18 254 177	4 210* 180	20 1133 1040	18 268* 217	19 340 317	17 722 717	0 3380 3171	11 304 115	3+5L	0 387 146
19 263 313	5 292 -210	0+5L	19 340 317	20 868 844	18 268* 217	0 3380 3171	12 273* -238	4+8L	0 479L
20 1055 984	6 447 456	0 279* 281	20 868 844	21 879 -582	19 340 317	0 3380 3171	13 278* 81	5+9L	0 1358 1439
21 766 -652	7 203* -88	0 1511 1572	21 879 -582	22 339 -632	20 868 844	0 3380 3171	14 283* -37	6+10L	0 1760 1847
22 363 -488	8 1312 1347	0 1911 1972	22 339 -632	23 770 -689	21 879 -582	0 3380 3171	15 289* 61	7+11L	5+6L
23 735 -661	9 218 34	0 10+L	23 770 -689	24 325 431	22 339 -632	0 3380 3171	16 1889 1968	8+12L	0 2166 2052
24 485 -499	10 477 -475	0 383* 209	24 325 431	0 218* -8	23 770 -689	0 3380 3171	17 301* 3	9+13L	0 1760 1847
25 622 539	11 240 296	0 1+L	0 218* -8	1 239 -197	24 325 431	0 3380 3171	18 304* -174	10+14L	5+6L
0 603 438	12 314 -471	0 218* -8	1 239 -197	2 147 -20	0 10+L	0 3380 3171	19 314* 76	11+15L	0 283* 170
1 768 -663	13 238* -101	0 170 -20	2 147 -20	3 545 -506	0 3380 3171	0 3380 3171	20 207* -24	12+16L	
	14 251 -28	0 170 154	3 545 -506				0 330 144	13 255* -110	
	15 2261 2259	0 170 154					14 2561 164	14 303* 164	
	16 266* -11	0 170 154					15 303* 164	0 291* 225	

^a The columns are I, 10|F_o|, 10|F_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 $F_{\text{obs}} < 35.0$. The scheme was: $w = 1/\sigma^2$ with $\sigma = 35.0/F_{\text{obs}}$. With this weighting, the weighted R factor decreased to 6.3%; however, the con-

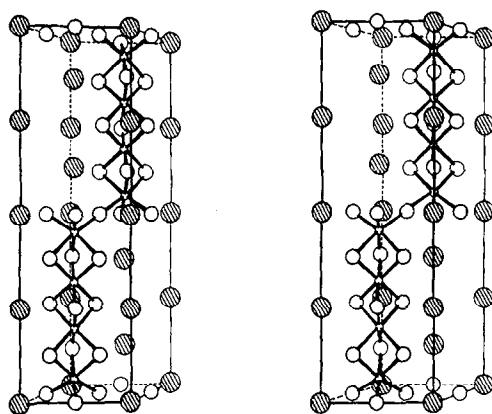


FIG. 1. Stereo view of unit cell of $\text{Ba}_8\text{Mn}_6\text{O}_{24}$. Ba atoms are shown as striped circles, O atoms as large open circles, and Mn atoms as small open circles.

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 $\text{Ba}_8\text{Mn}_6\text{O}_{24}$

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)–O(2)	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)		

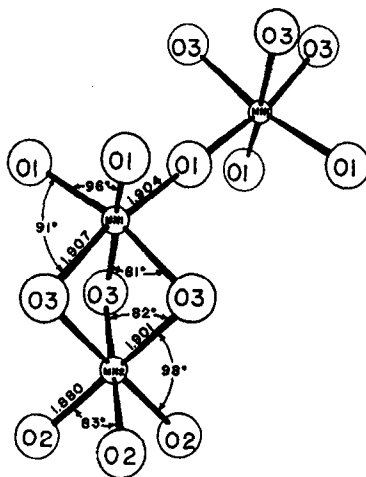


FIG. 2. Portion of structure showing a pair of face-sharing octahedra linked to another octahedron by corner sharing.

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 $\text{BaMnO}_{2.959}$; 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).

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