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A New Barium-Manganese (III) Oxide $BaMn_3O_5(OH)$: Preparation and Structure Determination

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Single crystals of a new barium–manganese oxide were grown under hydrothermal conditions at 600°C and 0.2 GPa. The chemical composition determined by X-ray analysis is $BaMn_3O_5(OH)$. The compound crystallizes in the orthorhombic system (space group *Immm*) with a basic cell of $a = 19.355(3)$ Å, $b = 4.531(1)$ Å, $c = 2.791(1)$ Å, and $Z = 2$. The structure exposes a supercell with twice the volume of the basic cell and monoclinic symmetry ($a = 19.554(3)$ Å, $b = 4.531(1)$ Å, $c = 5.581(1)$ Å, $\beta = 98.20(1)°$, $Z = 4$, space group $C2/m$). The crystal structure was determined by the Patterson method and refined to $R = 0.038$ based on 1184 independent reflections. The structure consists of ribbons composed of four parallel chains of edge-sharing MnO_6 octahedra running along [001] and parallel to the (010) plane. The two outer chains of the ribbon are complete. One out of two Mn ions is missing in the two inner chains. In these octahedra the corner-sharing oxygens are replaced by Ba. The MnO_6 octahedra are highly distorted and indicate the trivalent state of Mn. Valence balance at the site and large temperature factors are clear evidence of a replacement of one of seven independent oxygens by OH.

INTRODUCTION

Intensive work has been done on the preparation and the structure determination of Ba–Mn oxides, including compounds of $BaMnO_2$, $BaMn_2O_3$, Ba_2MnO_3, and Ba_2MnO_4 (1–5). The valence states of the Mn ions in these compounds were Mn^{2+} or Mn^{4+}. Exceptionally intensive studies were performed on $BaMnO_3$ because this compound exhibits a number of polymorphs depending on the preparation methods. For example, Negas and Roth (6) reported 15-, 8-, 6-, 10-, and 4-layer (*L*) polymorphs prepared from the thermal decomposition of the 2*L* layer phase, leading to oxygen-deficient $BaMnO_{3-x}$. All these studies employed solid-state reactions under dry conditions.

Hydrothermal preparation of inorganic material proofed to be a powerful technique for the synthesis of new compounds, which are often obtained in metastable form. Sometimes suitable crystals for X-ray diffraction studies were grown. There are only few examples for the preparation of Ba–Mn oxides grown under hydrothermal conditions (7–9), all of which dealt with the $BaMnO_3$ polymorphs. For instance, Christensen and Ollivier (8) obtained the 9*L* phase by hydrothermal method.

Recently we reported on the preparation and crystal structure of $BaMn_2O_3(OH)_2$ in this journal (10). The valence state of all Mn ions was trivalent and the compound contained oxygens and also hydroxyl groups (OH). The compound was quite different from other barium–manganese oxides in the valence state and the existence of OH. Here we describe the preparation and crystal structure of another new compound in the Ba–Mn–O–OH system, namely $BaMn_3O_5(OH)$.

EXPERIMENTAL

Synthesis of Single Crystals

A conventional test tube type autoclave was used for the hydrothermal preparation. A mixture of $Ba(OH)_2 \cdot 8H_2O$ (100 mg) and γ-MnO(OH) (10 mg) was inserted into a silver capsule with 0.3 ml of distilled water and the

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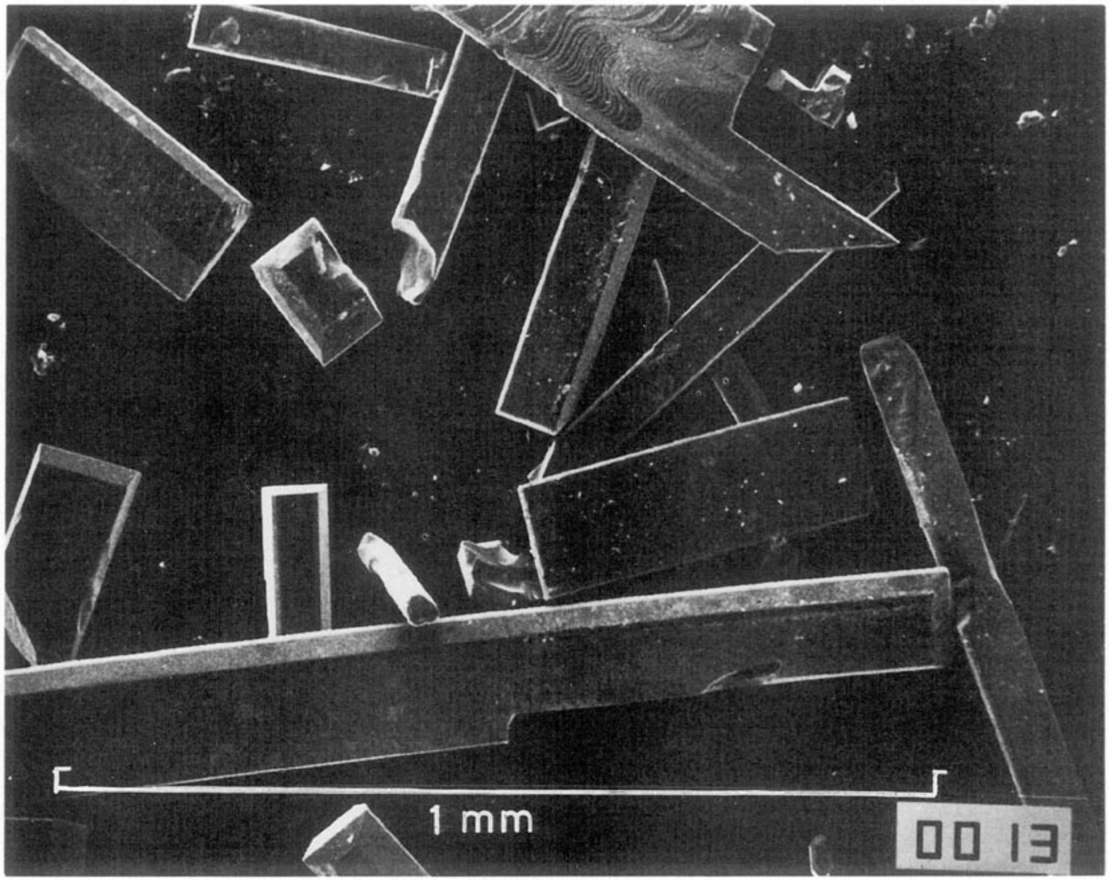

FIG. 1. Scanning electron microscope image of single crystals of $BaMn_3O_5(OH)$. The white line at the bottom of the photograph is 1 mm long. The flat surface of the crystals is (100).

suspension was heated to 600°C and 0.2 GPa for 48 hr. The reaction product was quenched to room temperature. Black single crystals of flat-rod shape were obtained in the precipitate as shown in Fig. 1. The size of the crystals is up to 4 mm long, 0.8 mm wide, and 0.1 mm thick. The molar ratio Ba : Mn was determined to be roughly 1 : 3 by the electron probe microanalysis.

X-Ray Diffraction

Rod-shaped crystals were mounted along the *c* axis and examined on a Weissenberg camera. Oscillation photographs exhibited strong reflections in layers with 1 = even and comparatively weak reflections in odd layers. In the Weissenberg photographs of l = even the crystal showed the basic structure with orthorhombic symmetry, but close inspection of the photographs of l = odd revealed the monoclinic superstructure. Furthermore, different intensity ratios for those reflections in different samples indicated twinning with (100) as common plane for the individual twins.

Intensities for the structure determination were collected on a STOE-STADI4 automatic four circle diffractometer with Mo*Kα* radiation monochromatized by a pyrolytic graphite. A rod-shaped crystal of size $0.50 \times 0.075 \times 0.055$ mm^3 was used for all measurements. The final lattice constants (Table 1) were determined from the 2θ values of 56 reflections in the range 67.6–69.7 degrees (temperature 297°K). The intensities of 4413 reflections ($-31 \leq h \leq 31$, $-7 \leq k \leq 7$, and $-9 \leq l \leq 9$; many reflections were measured twice) were measured with a scan ratio $2\theta : \omega$ of 1 : 1. The average measuring time per reflection was 60 sec with an average scan width of one degree. Three standard reflections (−511, 311, and 3 − 11), monitored every 3 hr showed consistency throughout the data collection.

The amount of the twin was determined in the following way: At layers with the index 1 = even the reflection *hkl* of the main crystal and the reflection $-(h + l)kl$ of the twin are superimposed. At layers with the index 1 = odd the reflection *hkl* of the twin occurs at the lattice point $-(h + l)kl$ of the main crystal, which is systematically absent (*C* centering). Therefore, the twin ratio can be obtained from the comparison of the intensities of the

TABLE 1
Crystal Data and Experimental Conditions for $BaMn_3O_5(OH)$ at Room Temperature

Crystal data		Experimental conditions	
Basic structure		Crystal size (mm^3)	0.50 × 0.075 × 0.055
Cell dimensions		Radiation	(Mo$K\alpha$) = 0.71069Å
a_b (Å)	19.355(3)	Monochromator	Graphite
b_b (Å)	4.531(1)	Scanning speed	≈ 60 sec/Refl.
c_b (Å)	2.791(1)	Scanning width	≈ 1°
V_b (Å^3)	244.9(1)	Max. value of 2θ	70°
Space group *Immm*		Collected reflections	4413
(*I*222, $I2_12_12_1$, *Imm*2)		Unique reflections	1192
Z_b	2	Used reflections	1184
Superstructure		Diffractometer	STOE STADI 4
Cell dimensions		R_{eq}	0.025
a_s (Å)	19.554(3)	R	0.038
b_s (Å)	4.531(1)	R_w	0.038
c_s (Å)	5.581(1)		
β_s(°)	98.20(1)		
V_s (Å^3)	489.8(2)		
Space group *C*2/*m*			
(*C*2, *Cm*)			
Z_s	4		
Chemical formula	$BaMn_3O_5(OH)$		
D_{calc}	5.42		
μ(MoK_α) (cm^{-1})	151.6		

reflection *hkl* (belonging to the main crystal) and $-(h + l)kl$ (belonging to the twin). From the measurement of six high intensity reflections and their twin equivalents we found that our specimen contained only 3.2% of the twin.

The intensities of the superimposed reflections at 1 = even were reduced according to the such determined twin ratio (this assumes orthorhombic symmetry for the 1 = even reflections, which was already observed in Weissenberg photographs and was confirmed by inspection of the measured intensities).

The data were corrected for Lorentz and polarization effects and a numerical absorption correction was applied. All crystallographic calculations were carried out with the program package SHELX76 (11). Averaging symmetry equivalent reflections yielded 1192 independent reflections with an internal consistency factor of $R_{eq} = 0.025$. Eight reflections have been omitted from the calculations: three weak reflections ($F < 2\sigma(F)$) and five very strong reflections at low 2θ with high extinction. The experimental conditions and crystal data are summarized in Table 1.

TABLE 2
Positional ($\times 10^{-4}$) and Thermal ($\times 10^{-4}$ Å^2) Parameters for $BaMn_3O_5(OH)$

Atom	x/a	z/c	U_{11}	U_{22}	U_{33}	U_{13}	U_{eq}
Ba	4251.8(2)	2125(1)	61(2)	64(2)	53(2)	8(1)	59
Mn(1)	2088(1)	8551(2)	34(4)	56(4)	43(5)	4(3)	44
Mn(2)	645(1)	2823(2)	23(4)	51(4)	50(5)	2(3)	42
Mn(3)	2113(1)	3551(2)	29(4)	54(4)	28(5)	4(3)	37
O(1)	2781(3)	1353(10)	52(20)	74(19)	56(24)	7(16)	60
O(2)	2757(3)	6436(11)	30(20)	106(21)	161(29)	3(18)	100
O(3)	1403(3)	792(10)	21(19)	133(22)	50(23)	9(16)	68
O(4)	1403(3)	5605(10)	32(20)	122(22)	78(25)	−4(17)	79
O(5)	4281(3)	7139(12)	137(28)	127(26)	214(36)	27(24)	159
O(6)	0	0	80(32)	160(34)	63(35)	−14(25)	103
O(7)	0	5000	98(32)	130(32)	75(36)	47(26)	97

Note. The parameters y/b, U_{12} and U_{23} are zero due to space group symmetry (Special position 4*i* of space group *C*2/*m*). E.s.d.'s (in parentheses) in units of the last digit.

TABLE 3

Interatomic Distances (Å) and Angles (°) for $BaMn_3O_5(OH)$. E.S.D.'s: 0.006 Å or 0.2°, Respectively

Barium–oxygen distances			
Ba–O(1)	2.847	Ba–O(5)′	2.839
Ba–O(5)	2.794	Ba–O(5)″	2.793
The following distances occur twice:			
Ba–O(3)	2.972	Ba–O(6)	3.029
Ba–O(4)	2.974	Ba–O(7)	3.030
$Mn(1)O_6$ octahedron			
Mn(1)–O(1)	1.918	Mn(1)–O(3)	1.960
Mn(1)–O(2)	1.883	Mn(1)–O(4)	1.968
Mn(1)–O(1)	2.280 (twice)		
O(1)–Mn(1)–O(2)	92.3	O(2)–Mn(1)–O(3)	179.2
O(1)–Mn(1)–O(3)	86.9	O(2)–Mn(1)–O(4)	85.8
O(1)–Mn(1)–O(4)	178.0	O(3)–Mn(1)–O(4)	95.0
O(1)–Mn(1)–O(1)	167.2		
The following angles occur twice:			
O(1)–Mn(1)–O(1)	85.2	O(1)–Mn(1)–O(3)	94.0
O(1)–Mn(1)–O(2)	86.0	O(1)–Mn(1)–O(4)	94.6
$Mn(2)O_6$ octahedron			
Mn(2)–O(3)	1.991	Mn(2)–O(6)	1.873
Mn(2)–O(4)	1.989	Mn(2)–O(7)	1.872
Mn(2)–O(5)	2.270 (twice)		
O(3)–Mn(2)–O(4)	85.0	O(4)–Mn(2)–O(6)	174.2
O(3)–Mn(2)–O(6)	89.3	O(4)–Mn(2)–O(7)	89.4
O(3)–Mn(2)–O(7)	174.3	O(6)–Mn(2)–O(7)	96.4
O(5)–Mn(2)–O(5)	172.8		
The following angles occur twice:			
O(5)–Mn(2)–O(3)	87.4	O(5)–Mn(2)–O(6)	92.4
O(5)–Mn(2)–O(4)	87.3	O(5)–Mn(2)–O(7)	92.4
$Mn(3)O_6$ octahedron			
Mn(3)–O(1)	1.917	Mn(3)–O(3)	1.921
Mn(3)–O(2)	1.898	Mn(3)–O(4)	1.922
Mn(3)–O(2)	2.280 (twice)		
O(1)–Mn(3)–O(2)	96.5	O(2)–Mn(3)–O(3)	175.5
O(1)–Mn(3)–O(3)	88.1	O(2)–Mn(3)–O(4)	86.7
O(1)–Mn(3)–O(4)	176.9	O(3)–Mn(3)–O(4)	88.8
O(2)–Mn(3)–O(2)	167.2		
The following angles occur twice:			
O(2)–Mn(3)–O(1)	85.2	O(2)–Mn(3)–O(3)	94.0
O(2)–Mn(3)–O(2)	86.4	O(2)–Mn(3)–O(4)	95.1

The structure was solved in space group *C*2/*m* by Patterson and subsequent Fourier methods. The Ba atom was placed at position 4*i* and refined to $R = 0.51$. Fourier analysis revealed three further 4*i* positions of equal height which were attributed to Mn ions and refined to $R = 0.25$. All oxygen atoms were located in a Fourier map. The structure was then refined to $R = 0.038$ including anisotropic temperature factors. The refinement was carried out in the centrosymmetric space group *C*2/*m*. Refinement in space group *C*2 produced no significant improvement of the reliability factor. Final atomic coordinates and thermal displacement factors are listed in Table 2, interatomic distances and angles in Table 3.

RESULTS AND DISCUSSION

Oxidation State of Mn and Chemical Composition

Since the compound was synthesized under hydrothermal conditions the chemical composition may vary as a function of the valence state of manganese and the possible existence of OH anions. Infrared spectroscopy (IR) clearly indicated the presence of hydroxyl groups.

The following assumptions lead to the oxidation state of Mn: Three different MnO_6 octahedra are present in the structure: $Mn(1)O_6$, $Mn(2)O_6$, and $Mn(3)O_6$; the mean Mn–O distances are listed in Table 3. The mean Mn–O distances of these MnO_6 octahedra are 2.048, 2.044, and 2.036 Å, respectively, fairly larger than the sum (1.940 Å) of the ionic radii of Mn^{4+} and O^{2-} and smaller than the sum (2.230 Å) of those of Mn^{2+} and O^{2-} but in good agreement to the sum (2.045 Å) of the radii of Mn^{3+} and O^{2-}. The unequal values of the Mn–O distances and O–Mn–O angles in Table 3 indicate that the MnO_6 octahedra are highly distorted, which is characteristic of the Jahn–Teller effect of Mn^{3+} ions. The small values (0.0044, 0.0042, and 0.0037 Å^2 for Mn(1), Mn(2), and Mn(3), respectively) of the isotropic temperature factors of Mn ions also suggest that the Mn ions are in a single oxidation state. Therefore, it is concluded that all three Mn of Mn(1), Mn(2), and Mn(3) are Mn^{3+} and the site occupation is not a mixture of Mn^{2+} and Mn^{4+}. The chemical composition is therefore $BaMn_3O_5(OH)$.

Crystal Structure of $BaMn_3O_5(OH)$

The crystal structure of $BaMn_3O_5(OH)$ is displayed in Figs. 2–4. In Fig. 2 the basic and supercells are shown. The *c* axis of the supercell is double the *c* axis of the basic cell. Supercells and basic cells have a common *b* axis. The *a* axis of the supercell is the diagonal of the *a* and *c* axes and the angle β is given by $\tan \beta = -a(\text{basic})/c(\text{basic})$.

The structure consists basically of a framework of MnO_6 octahedra. These units are interconnected by edge sharing to form ribbons of four adjacent chains (Fig. 3). Chains and ribbons are running in *c* direction, with the plane of the ribbon parallel to the *a*–*c* plane. The two outer chains of the ribbon consist only of complete MnO_6 octahedra. The octahedra of the inner chains are different: The central Mn position is vacant in every second octahedron and the oxygens connecting these octahedra in *b* direction are replaced by barium, thus forming empty Ba_2O_4 octahedra.

Neighboring ribbons are, however, translated by a step of half the height of the octahedra ($= b/2$) and shifted by a distance of half an octahedron in the direction of the chain (Figs. 3 and 4). This shift of the ribbons along *c* explains the angle of $\beta \cong 100°$ in the monoclinic cell. The

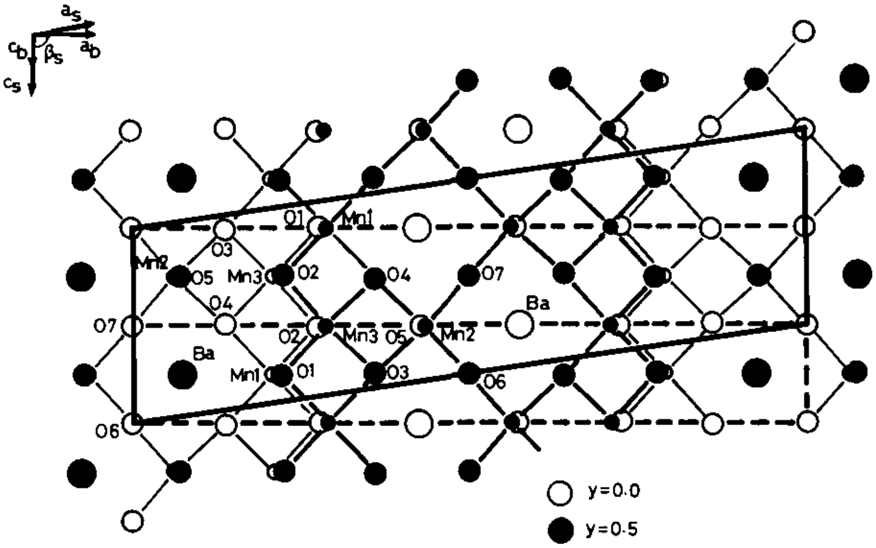

FIG. 2. The crystal structure of $BaMn_3O_5(OH)$ viewed down along the *b*-axis. The basic cell is indicated by the broken line and the supercell by the solid line.

link between adjacent ribbons constitutes the key for the formation of twins: The combined shift and translation is possible in two different directions. The three-dimensional structure is obtained by a superposition of ribbons by corner-sharing in the *b* direction. As seen along *b* (Fig. 3), the structure may be considered as a packing of MnO_6 octahedra with channels parallel to [010] in which the Ba atoms are located.

The crystal structure may also be described as a close packed arrangement of oxygen atoms. One out of seven O atoms is replaced by a barium in a characteristic way. The central interstitials of the octahedra are occupied by Mn if all corners are oxygen atoms. The central position is empty if one of the atoms at the corner is a barium. Therefore each barium is surrounded by 12 oxygen atoms at a mean Ba–O distance of 2.94 Å in a cuboctahedron.

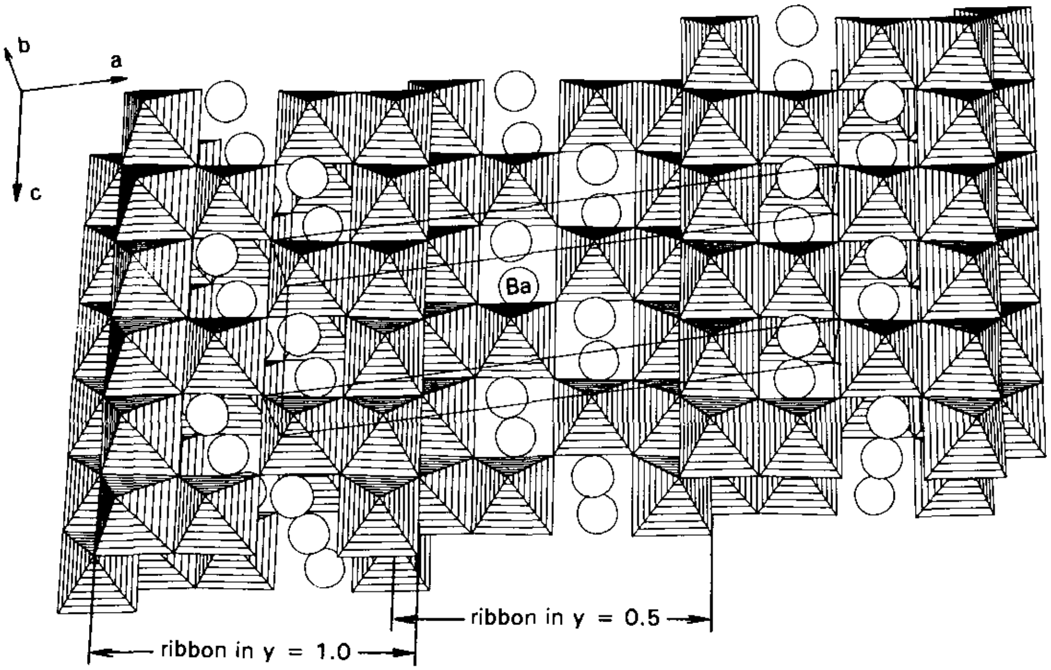

FIG. 3. Chains of octahedra running along *c* in forms of ribbons built by four chains.

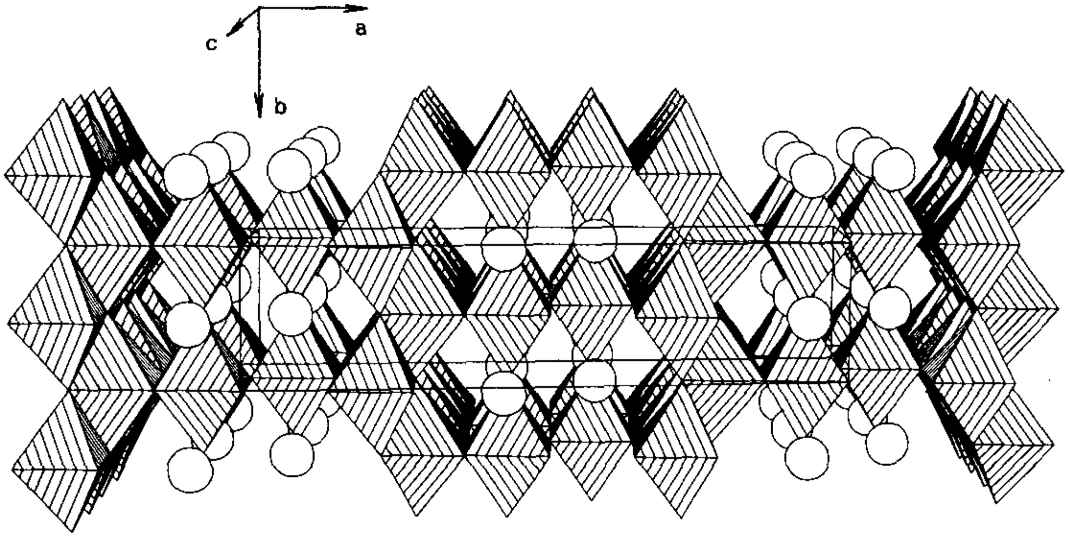

FIG. 4. The atomic arrangement viewed down [001].

The BaO_{12} cuboctahedra are connected by common square faces in *b* direction directly and *c* direction alternating between chains.

Possible Location of Hydrogen Atom

As IR measurement and chemical composition of the compound indicated the presence of hydroxyl group, the possible location of the hydrogen atom was deduced from the following considerations: Pauling's valence balance rule for ionic crystals (12) yields a bond strength for O(1), O(2), O(3), O(4), O(5), O(6), and O(7) of 13/6. 12/6, 11/6, 11/6, 9/6, 10/6, and 10/6, respectively. The lowest value is observed for O(5) which at the same time exhibits the highest isotropic temperature factor (see Table 2). As seen in Fig. 2 the oxygen O(5) is surrounded by two Mn(2) ions in *b* direction and three Ba ions. No cation is observed on the side opposite to Ba along the *a* direction. It is therefore assumed that the hydrogen is located around O(5) at the side opposite to Ba along the *a* direction.

Crystal Shape and Linkage of MnO_6 Octahedra

The single crystals usually have a flat-rod shape with the elongation along the *c* direction and the flat surface as (100), as shown in Fig. 1. The outer chains of the above described ribbons consist completely of MnO_6 octahedra. Each of these chains is connected by sharing edges to two other such chains from neighboring ribbons. In this way corrugated sheets in the *b* direction are formed, which consist only of MnO_6 octahedra (see Fig. 4). The plane of these sheets is parallel to (100), the flat surface of the crystals. The long direction of the crystal (Fig. 1) coincides with the *c* direction, the direction of the ribbons in the structure.

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REFERENCES

1. A. Hardy, *Acta Crystallogr.* **15,** 179 (1962).
2. L. Katz and R. Ward, *Inorg. Chem.* **3,** 205 (1964).
3. M. Mansmann, *Z. Anorg. Allg. Chem.* **339,** 52 (1965).
4. K. Sander and Hk. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **451,** 35 (1979).
5. K. Sander and Hk. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **478,** 52 (1981).
6. T. Negas and R. S. Roth, *J. Solid State Chem.* **3,** 323 (1971).
7. B. L. Chamberland, A. W. Sleight and J. F. Weiher, *J. Solid State Chem.* **1,** 506 (1970).
8. A. N. Christensen and G. Ollivier, *J. Solid State Chem.* **4,** 131 (1972).
9. A. P. Pottoff, B. L. Chamberland, and L. Katz, *J. Solid State Chem.* **8,** 234 (1973).
10. O. Tamada, N. Yamamoto and Y. Oka, *J. Solid State Chem.* **74,** 401 (1988).
11. G. Sheldrick, "SHELX76, Program for Crystal Structure Determination." University of Cambridge, 1976.
12. L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, New York (1960).