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Hydrothermal Synthesis and Structure Determination of a New Manganese (III) Oxide, $BaMn_2O_3(OH)_2$

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A single crystal of a new manganese (III) oxide containing Ba ion was grown under the hydrothermal condition of 240°C and 3.3 MPa. The chemical composition of the crystal was determined to be $BaMn_2O_3(OH)_2$. It is orthorhombic: $a = 11.585(4)$ Å, $b = 4.1200(9)$ Å, $c = 4.390(1)$ Å, $Z = 2$, probable space group *Cm2m*. The structure was determined using the X-ray data of 915 independent reflections and refined to $R = 0.044$. It is composed of a framework of MnO_6 octahedra which form zigzag chains in the *b*-axis direction with Ba ions in large cavities between the chains. The structure is characterized by the fcc stacking composed of BaO_5 layers in which Mn ions occupy the interlayer octahedral sites. The chemical composition and the lattice sites indicate that Mn ions are trivalent and hydrogen atoms are present for charge compensation. It is the first example of a Ba–Mn oxide containing solely Mn^{3+} ions.

Introduction

The Ba–Mn–O system exhibits a variety of crystalline phases corresponding to differing molar ratios of Ba to Mn and the oxidation states of Mn ions. Extensive work has been carried out to elucidate the structures and the phase relations of the Ba–Mn–O system where the oxidation states of Mn ions are mostly +2 or +4; that is, where the products of the Ba–Mn oxides generally contain Mn^{2+} or Mn^{4+}. $BaMnO_2$ (*1*), $BaMn_2O_3$ (*2*), and Ba_2MnO_3 (*3*) are the oxides of Mn^{2+}, and $BaMnO_3$ (*4*) and Ba_2MnO_4 (*1*) are those of Mn^{4+} for different molar ratios of Ba to Mn. Among those oxides, $BaMnO_3$ has been investigated to a great extent because of the existence of many polymorphs depending on the preparation methods and subsequent heat treatment. The structure of $BaMnO_3$ is basically characterized by the stacking modes of closed-packed layers of BaO_3. Mn^{4+} ions are located on the interlayer octahedral sites to form MnO_6 octahedra. In this regard the construction of $BaMnO_3$ structure is considered to be similar to that of the perovskite structure (*4, 5*). The polymorphs of $BaMnO_3$ are made of different stacking modes of the closed-packed lay-

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ers. Negas and Roth (*6*) reported 15-, 8-, 6-, 10-, and 4-layer (L) polymorphs which were formed as a result of the successive thermal decomposition of 2L $BaMnO_3$ above 1150°C leading to oxygen-deficient $BaMnO_{3-x}$. They claimed that the amount of Mn^{3+} ions plays an important role in deciding the type of stacking modes. As for the Ba–Mn oxides containing Mn^{3+} ions, the above-mentioned $BaMnO_{3-x}$ may be a single example. It has mixed valences of Mn ions and may be written as $Ba(Mn^{3+}_{2x}Mn^{4+}_{1-2x})O_{3-x}$ where the value of x reaches 0.3 (*6, 7*). There are no oxides in the Ba–Mn–O system containing solely Mn^{3+} ions.

Solid-state reaction has been mainly employed in the synthesis of Ba–Mn oxides and resulted in the oxides of Mn^{2+} or Mn^{4+} as described above. We may expect to obtain new compounds from aqueous solutions under hydrothermal conditions. There are only a few papers dealing with the hydrothermal synthesis of Ba–Mn oxides (*8–10*). For instance, Christensen and Ollivier (*9*) obtained 9L phase of $BaMnO_3$ using the hydrothermal technique. However, Ba–Mn oxides with manganese oxidation states of less than four have not been reported to be prepared by the hydrothermal method.

In the present work, the hydrothermal method was employed to prepare new compounds of the Ba–Mn–O system, especially those containing Mn^{3+} ions. A single crystal was obtained with the composition of $Ba Mn_2O_3(OH)_2$ indicating a new hydrated Ba–Mn oxide. This paper deals with the structure determination of the new crystal and shows that Mn ions in the new crystal are trivalent.

Experimental

Synthesis of Single Crystal

A single crystal of a Ba–Mn mixed oxide was synthesized by using a conventional Morley-type autoclave. Typical experimental conditions are as follows. After a mixture of γ-MnO(OH) (1 g) and $Ba(OH)_2 \cdot 8H_2O$ (16 g) was inserted in a Teflon capsule (100 cm^3 in capacity) with 50 ml of distilled water, the suspension was treated at 240°C under 3.3 MPa for 72 hr followed by quenching to room temperature. A black precipitate with crystals of flat-rod shapes was obtained as shown in Fig. 1. The size of the crystals is up to 1 mm long, 0.3 mm wide, and 0.01 mm thick. The density of the compound is 5.2 g/cm^3, measured by the pycnometer method. The chemical composition of the crystal was determined by the following methods. A molar ratio of Ba to Mn was analyzed by an electron probe microanalyzer (EPMA) and the amount of Ba was obtained by an inductively coupled argon plasma atomic emission spectrometer (ICPA). The hydrogen content was obtained using a Perkin–Elmer Model 240 elemental analyzer. The chemical composition was thus determined as $BaMn_2O_3(OH)_2$.

Single-Crystal X-ray Study

Weissenberg camera work revealed that the crystal was orthorhombic and the reflections with $h + k$ = odd were absent, which gave four space groups of *Cmm*2, *Cm*2*m* (this is not a standard symbol, but converted from the standard symbol of *Amm*2 for coincidence with the other three notations), *C*222, and *Cmmm* (*11*).

A rod-shaped specimen of 0.50 × 0.01 mm in size was mounted on a Rigaku-5UD four-circle diffractometer. All the intensity data in reciprocal space with $2\theta < 120°$ were collected, at room temperature, using monochromatized Mo$K\alpha$ radiation. The 2θ-ω scan technique was used for data collection under the conditions of scanning speed, 2°/min, and scanning width, $\Delta\omega = (1.0 + 0.5 \tan\theta)°$. The corrections were made for Lorentz and polarization factors for all the collected data of 5932 reflections. An absorption correction was not made,

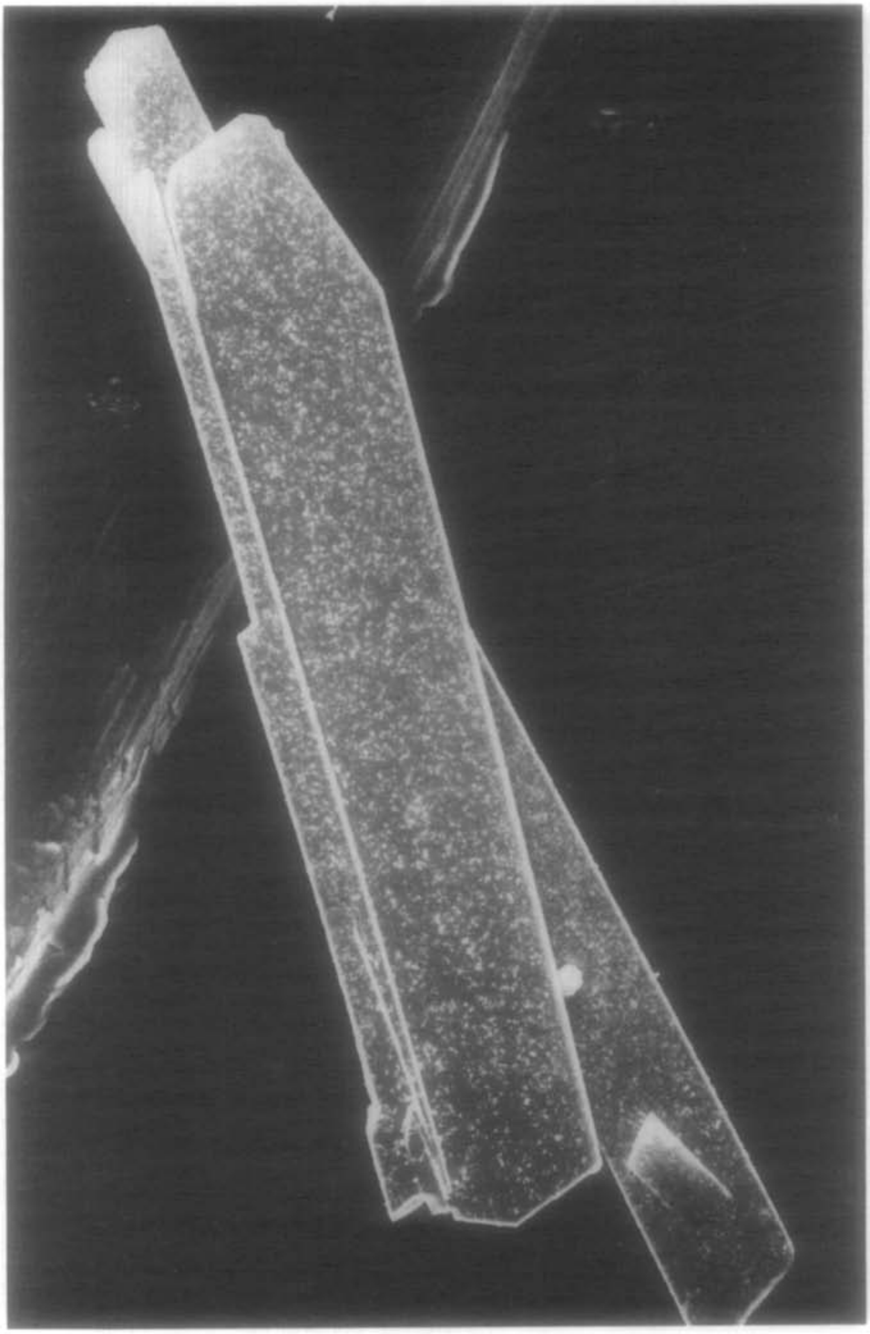

FIG. 1. The scanning electron microscopic image of single crystals of $BaMn_2O_3(OH)_2$. The flat rod-like crystal is about 0.5 mm long.

TABLE I

CRYSTAL DATA AND EXPERIMENTAL CONDITIONS FOR $BaMn_2O_3(OH)_2$

Crystal data		Experimental conditions	
Cell dimensions		Crystal size (mm^3)	0.5 × 0.1 × 0.01
a (Å)	11.585(4)	Radiation	Mo$K\alpha$ X-ray
b (Å)	4.1200(9)	Monochromator	Graphite
c (Å)	4.390(1)	Scanning speed	2°/min
V (Å^3)	209.55(9)	Scanning width ($\Delta\omega$)	$(1.0 + 0.5 \tan\theta)°$
Space group	*Cm*2*m*	Max. value of 2θ	120°
	(*Cmm*2, *C*222, *Cmmm*)	Collected reflections	5932
Chemical formula	$BaMn_2O_3(OH)_2$	Used reflections	915 (5781)
D_{calc} (g/cm^3)	5.18	Diffractometer	Rigaku-5UD
D_{obs} (g/cm^3)	5.2	R value	0.044
Z	2	Weighted R value	0.040
μ (Mo$K\alpha$) (cm^{-1})	155.7		

but the Furnas method was applied to the intensity data for the approximate correction of absorption effect (*12*). The discrepancy factor R_{eq} between equivalent reflections was 0.049. The equivalent reflections were averaged and the independent 915 data were obtained from 5781 reflections for $F_o > 3\sigma$, which were used for the structure analysis. The cell parameters were determined from 11 reflections of high 2θ value ($51° < 2\theta < 87°$). The crystal data and experimental conditions are summarized in Table I.

Initial Model and Structure Refinement

An initial model of the structure was deduced from a Patterson map synthesized by the intensity data using the program FOURIER (*13*). The model was determined by considering that one Mn and six oxygen atoms form a MnO_6 octahedron and Ba ion occupies a large cavity in the structure. The chemical composition of the compound was $BaMn_2O_3(OH)_2$, and thus the formular unit of $BaMn_2O_5$ was taken in the single-crystal X-ray study. There were two formula units in the unit cell. There was one crystallographic position for both Mn and Ba ions and three independent ones for oxygen ions. Assuming a centrosymmetric space group *Cmmm*, the structure was refined according to the RFINE4 computer program (*14*) modified by Horiuchi (*15*). The function minimized in the refinements was $\Sigma 1/\sigma^2(s|F_o|-|F_c|)^2$, where σ is the standard error in the counting statistics and s is the scale factor. Neutral atom scattering factors and dispersion corrections for Ba, Mn, and O atoms were taken from "International Tables for X-ray Crystallography" (*16*). Ba ion was fixed at the origin of the unit cell. After the pilot search, values of the isotropic temperature factors of Ba and Mn were started from 0.5 Å^2 in contrast with a large value of 1.2 Å^2 for three oxygen atoms. The atomic position of Mn was refined after the determination of scale factor. Then, the positions of three oxygen atoms were refined. The isotropic temperature factors were refined in the order of Ba, Ba and Mn, and then all the atoms. At this stage the discrepancy factors of R and R_w were reduced to 0.067 and 0.050, respectively. Site occupancies of cations were refined and showed no departure from full occupancy.

Space Group Determination

The outline of the crystal structure was obtained by the above treatment, but the

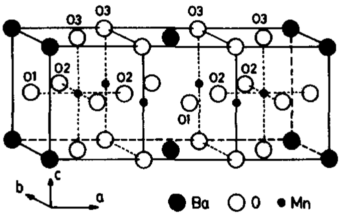

FIG. 2. A perspective view of the crystal structure of $BaMn_2O_3(OH)_2$. A unit cell is shown in the figure.

space group remained undetermined. It should be determined from one centrosymmetric group (*Cmmm*) and three asymmetric ones (*C*222, *Cm*2*m*, and *Cmm*2). The refinements were continued for the four space groups by changing isotropic temperature factors to anisotropic ones. The discrepancy factors of R and R_w were found to be reduced for each space group; 0.050 and 0.041 (19 variables) for *Cmmm*, 0.047 and 0.041 (25 variables) for *Cmm*2, and 0.044 and 0.040 (25 variables) for *Cm*2*m*, respectively. The refinement for *C*222 diverged in refining the nondiagonal terms of the temperature factors, so the discrepancy factors remained at 0.050 and 0.042 for R and R_w, respectively. Thus, *Cm*2*m* gives the smallest values of R and R_w as compared with those for other groups. Also, we found in a preliminary experiment that although very small, the crystal possibly showed the sign of piezoelectric effect, which yielded an asymmetric group. Accounting for all these factors, the space group *Cm*2*m* is the most probable, but the other three members still remain candidates.

Results and Discussion

Crystal Structure of $BaMn_2O_3(OH)_2$

The crystal structure determined is illustrated in Fig. 2. Final atomic coordinates and temperature factors obtained under the *Cm*2*m* space group are listed in Table II.

TABLE II

FINAL ATOMIC COORDINATES AND TEMPERATURE FACTORS FOR $BaMn_2O_3(OH)_2$

Atom	Position	x	y	z	$B_{eq}/Å^2$
Ba	2a	0.0	0.0	0.0	0.54
Mn	4e	0.33887(8)	−0.0080(5)	0.5	0.44
O(1)	2b	0.5	0.00(1)	0.5	0.93
O(2)	4e	0.1738(5)	−0.021(3)	0.5	0.95
O(3)	4*d*	0.3354(6)	−0.001(6)	0.0	1.97

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba	0.00095(2)	0.0066(2)	0.0085(2)	0.0	0.0	0.0
Mn	0.00068(4)	0.0064(3)	0.0067(3)	0.0000(3)	0.0	0.0
O(1)	0.0008(3)	0.022(3)	0.012(2)	0.0	0.0	0.0
O(2)	0.0010(2)	0.022(3)	0.011(2)	0.0006(9)	0.0	0.0
O(3)	0.0015(3)	0.014(3)	0.053(4)	0.003(2)	0.0	0.0

Note. B_{eq}: Equivalent isotropic temperature factors computed according to the relation $B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}(a_i \cdot a_j)$.

The interatomic distances and angles of the MnO_6 octahedron and the BaO_{12} polyhedron are listed in Table III, which were calculated by the program UMBADTEA (*17*).

The crystal structure shown in Fig. 2 presents a new type of Ba–Mn mixed oxide. The main framework is composed of MnO_6 octahedra which are joined together by sharing edges to form a zigzag chain in the *b* direction. These chains are linked to-

TABLE III

INTERATOMIC DISTANCES (Å) AND ANGLES (°) OF MnO_6 OCTAHEDRON AND BaO_{12} POLYHEDRON

Atom	Distance	Atom	Distance	Angle
		MnO_6 Octahedron		
Mn–O(1)	1.867(1)	O(1)–O(2)	2.95(3)	95(1)
Mn–O(2)	1.913(6)	O(1)–O(2)	2.82(3)	93(1)
Mn–O(2)	2.12(1)	O(1)–O(3)	2.907(4) ×2	91.0(2) ×2
Mn–O(2)	2.01(1)	O(2)–O(2)	2.712(7) ×2	84.4(3) ×2
Mn–O(3)	2.1956(6) ×2	O(2)–O(3)	2.886(6) ×2	89.0(2) ×2
		O(2)–O(3)	3.07(2) ×2	90.6(7) ×2
		O(2)–O(3)	2.96(2) ×2	89.2(7) ×2
Mean	2.050(6)	Mean	2.90(2)	89.7(6)
		BaO_{12} Polyhedron		
Ba–O(1)	3.01(3) ×2	O(1)–O(2)	2.82(3) ×4	56.1(4) ×4
Ba–O(1)	3.01(3) ×2	O(1)–O(2)	2.95(3) ×4	58.9(4) ×4
Ba–O(2)	2.890(4) ×4	O(1)–O(3)	2.907(4) ×8	59.8(4) ×8
Ba–O(3)	2.81(2) ×2	O(2)–O(3)	2.96(2) ×4	61.3(3) ×4
Ba–O(3)	2.80(2) ×2	O(2)–O(3)	3.07(2) ×4	64.0(3) ×4
Mean	2.90(2)	Mean	2.94(2)	60.0(5)

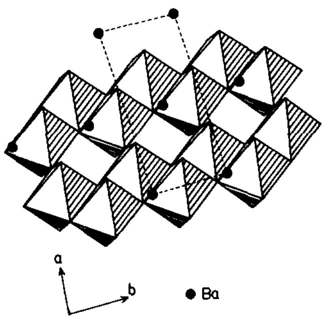

FIG. 3. A sheet of MnO_6 octahedra in the *a–b* plane. The dashed line indicates unit cell.

gether by sharing corners to form a sheet in the *a–b* plane as shown in Fig. 3. The sheets are stacked in the *c* direction by sharing corners of the octahedra to form a three-dimensional framework. A large cavity appears between the sheets, which accommodates a Ba ion coordinated by 12 oxygen atoms. The crystal has a flat-rod shape as shown in Fig. 1. The rod direction coincides with the *b* direction, implying that the elongation of the crystal occurs in the direction of the structural zigzag chain. The flat plate in crystal shape coincides with the structural sheet in the *a–b* plane and they often show a cleavage to split each other into thinner plates.

From the viewpoint of the stacking mode of Ba and O, the unit cell is constructed of three fcc lattices made of Ba and O, connected along the *a* axis as shown in Fig. 2. So the Ba–O lattice can be regarded as the cubic closed-packed stacking of the layers with the composition of BaO_5. Figure 4 visualizes the layer of BaO_5 which corresponds to (311) plane of the original cell. The relationship between the original cell and the stacking mode of BaO_5 layers is depicted in Fig. 5a. It is seen that the unit cell contains nine layers as numbered from 1 to 9 in Fig. 5a. Figure 5b presents a view of the stacking, where the above-mentioned chain of edge-sharing octahedra is seen to run diagonally and to connect to the neighboring chains by sharing corners. It is noted that the interlayer octahedral sites are fully occupied by Mn ions. The outline of the $BaMn_2O_3(OH)_2$ structure described above exhibits a strong analogy with that of 2L $BaMnO_3$ in that the lattice composed of Ba and O is regarded as a closed-packed stacking and Mn ions occupy the interlayer octahedral sites to form MnO_6 octahedra.

Oxidation State of Mn and Position of Hydrogen Atoms

The chemical composition of $BaMn_2O_3(OH)_2$ gives the average oxidation state of Mn as three. But it still remains unknown whether the ions in the crystal are a mixture of Mn^{2+} and Mn^{4+} or only Mn^{3+}. The valence state of Mn is determined as follows. The Mn–O distances of MnO_6 octahedron are listed in Table III. The mean Mn–O distance is 2.050 Å, which is fairly larger than the summation (1.940 Å) of ionic radii of Mn^{4+} and O^{2-} and smaller than the summation (2.230 Å) of those of Mn^{2+} and O^{2+}, but very close to the summation (2.045 Å) of those of Mn^{3+} and O^{2-}. The unequal values of the Mn–O distances and O–Mn–O angles in Table III indicate that the MnO_6 octahedra is highly distorted, which may be due to the Jahn–Teller effect of the Mn^{3+} ions. The small value (0.44 Å^2) of the isotropic temperature factor of Mn suggests that the Mn ions are in a single oxidation

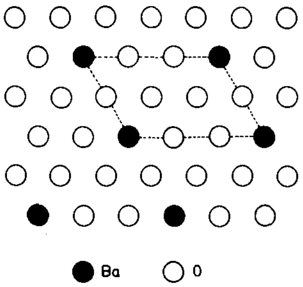

FIG. 4. A closed-packed layer of BaO_5. The dashed line indicates BaO_5 unit.

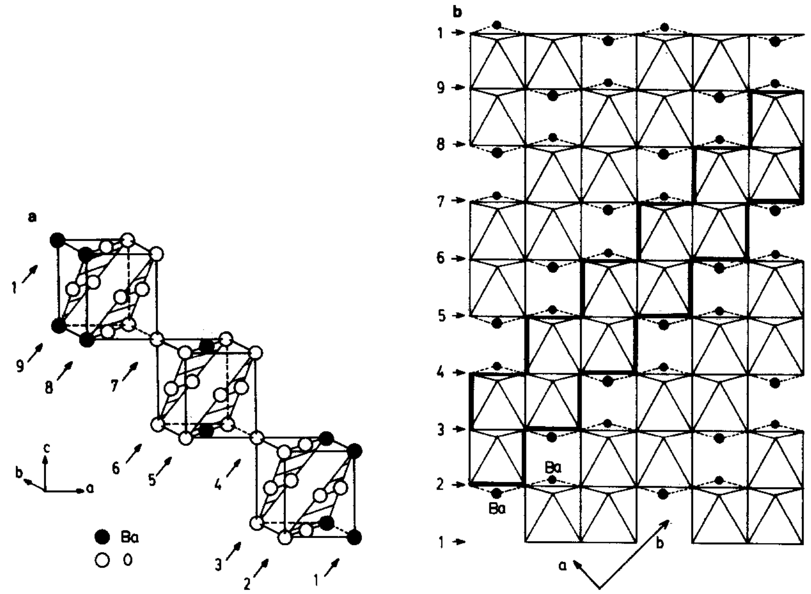

FIG. 5. (a) The relationship between the unit cell and the stacking of BaO_5 layers. BaO_5 layers are numbered from 1 to 9 and Mn atoms are omitted for clarity. (b) A view of the stacking of BaO_5 layers. Oxygen atoms are represented by O_6 octahedra. One of the chains of MnO_6 octahedra is shown by thick lines.

state. Therefore, it is concluded from the crystal data that the Mn is not a mixture of Mn^{2+} and Mn^{4+} but is Mn^{3+}.

The formula adopted for the unit cell is $BaMn_2O_5$ and thus we have to replace two oxygen atoms with two OH molecules in order to have the chemical composition $BaMn_2O_3(OH)_2$. Unfortunately the positions of the hydrogen atom could not be observed in the electron density map and they were determined by the following procedure. The Pauling's valence balance rule for ionic crystal (*18*) was employed to estimate the contributions of plus charges to the oxygen atoms from the neighboring cations. They were $10/6e$ for O(1) and O(2) and $8/6e$ for O(3), indicating that O(3) appreciably lacks plus charge contribution. Also the isotropic temperature factor B for O(3) (1.97 Å^2) shows a clear contrast to those for O(1) and O(2) (0.93 and 0.95 Å^2, respectively). It is, therefore, suggested that the hydrogen atom is attached to O(3) oxygen for charge compensation.

In conclusion, $BaMn_2O_3(OH)_2$ is a new Ba–Mn mixed oxide containing solely Mn^{3+} ion. The structure is constructed of the fcc stacking of closed-packed BaO_5 layers with Mn ions on the interlayer octahedral sites. Thus, the compound can be grouped into the Ba–Mn mixed oxides from the viewpoint of this structural feature, even though it contains two OH molecules in the chemical formula. Hydrogen atoms are incorporated in the crystal just for charge compensation.

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