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The crystal structure of hollandite

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Abstract

The crystal structure of hollandite from Gowari Wadhona, India has been refined. Chemical formula determined by EPMA and moisture counter is $(Ba_{0.75}K_{0.38})_{1.13}(Mn_{7.85}Fe_{0.15})_8O_{16}\cdot 0.41H_2O$. The structure is monoclinic, $I2/m$, and cell constants are a=10.006(3)Å, b=2.866(1)Å, c=9.746(2)Å, β=91.17(3)°. Each atom exists on a mirror plane (y=0, or 0.50). Manganese atom is in octahedral coordination. MnO_6 octahedra are distorted and manganese atoms shift to unshared oxygens. The tunnel site is occupied by Ba^{2+}, K^+ and H_2O. These cations and molecules do not show continuous distribution along the tunnel but only one single peak is observed. This mineral gives an X-ray powder pattern different from that of tetragonal hollandite. The relationship between the site occupancies of tunnel cations and the powder diffraction intensities is discussed. As the occupancy of tunnel site increase, the intensity ratio of I(200)+I(002) to I(301)+I($\bar{1}$03) decreases.

Introduction

Hollandite group of minerals are characterized by tunnels in their structures. Their general formula is described as $A_XMn_8O_{16}$. They are named depending on the species of A-cations. Cryptomelane, coronadite and manjiroite have the same structure as hollandite and contain large cations such as K^+, Pb^{2+}, Na^+ respectively. Byström and Byström (1950) analysed the structure of hollandite from Swedish manganese ores, on the basis of tetragonal cell. The MnO_6 octahedra in hollandite share edges and form double chains. These chains share corners with neighboring double chains to form a framework structure containing large tunnels. Generally Ba^{2+} ion and H_2O molecule occupy the tunnel site of hollandite structure. Hollandite is sometimes slightly distorted from tetragonal symmetry to monoclinic. Post *et al.* (1982) reported the structure of monoclinic hollandite having chemical formula $(Ba_{0.75}Pb_{0.16}Na_{0.10}K_{0.04})(Mn,Fe,Al)_8(O,OH)_{16}$, and interpreted the monoclinic structure as a result of Mn and O atom deviations from ideal positions of tetragonal hollandite. H_2O molecules in hollandite occupy the tunnel sites and behave as zeolitic water (Gruner, 1943). Hollandite of fine powder easily release water by heating. But single crystal X-ray diffraction experiments of hollandite which has little water is difficult because it does not release the water on heating.

In this paper, the crystal structure of monoclinic hollandite which contains a significant amount of K^+ was determined, and the factors affecting the change of tetragonal to monoclinic symmetry are discussed. Comparison of monoclinic and tetragonal structures and behavior of H_2O molecules in hollandite are also discussed based on the results of X-ray powder diffraction experiments.

Experiment

The crystal specimen of hollandite from Gowari Wadhona (India) was used in this study. The specimen contains Ba^{2+} and K^+ as tunnel cations. Composition analysis of hollandite was made on the JEOL JCMA-733 electron microprobe analyzer. The mean value of five analytical data are as follows. BaO=13.42, K_2O=2.08, MnO_2=79.13, Fe_2O_3=1.71 (wt%). Water content was measured by the DuPont moisture evolution analyzer 902H. The specimen was kept at 750°C for 1 hour in N_2 atmosphere and the released moisture was counted. The mean of two analytical data is 0.85 wt%.

An X-ray powder diffraction pattern of this mineral was studied in order to make crystallographic characterization of the specimen. The results and experimental conditions are given in Table 1 and Table 2. These diffraction peaks were indexed based on a body centered lattice. Most of the strong diffraction peaks were observed as doublets or quadruplets because of a monoclinic symmetry which is deformed from tetragonal one. For example, diffraction peak of tetragonal hollandite which is indexed (200) is splitted to (200) and (002) in monoclinic, likewise (101) to (101) and $(\bar{1}01)$, (301) to $(\bar{3}01)$, (301), (103) and $(\bar{1}03)$ and so on. So it is easy to distinguish monoclinic hollandite from tetragonal hollandite by X-ray powder diffraction pattern.

A single crystal specimen of rectangular shape with 0.1 x 0.15 x 0.1 mm in size was selected for structural analysis. Cell dimensions were determined using 14 high-angle reflections measured on a Rigaku AFC-5UD diffractometer with Mok_α radiation (λ=0.71069 Å) monochromatized by pyrolytic graphite. The results are summarized in Table 3. Intensity data were collected on the above diffractometer. The scan range was $2.5° < 2\theta < 90°$. Effects of Lorentz and polarization factors were corrected in data collection procedure, and only the structure factors larger than $3\delta(Fo)$ were used for structure refinement. Absorption correction was not made. As reflections with $h+k+l=2n+1$ were not observed and center of symmetry was detected by Wilson's statistics program, RSWS-3 (Sakurai, 1967), $I2/m$ was assumed as the space group. Geometrical deformation from the tetragonal structure is rather small (the length of a- and c axes are nearly equal and β is nearly 90 degrees). The reason for assuming a body-centered space group $I2/m$ instead of $C2/m$ is for the convenience of comparison between the present monoclinic structure and the conventional tetragonal one.

TABLE 1. Powder diffraction data for hollandite

d(Å)	I	h	k	l	
7.02	8	-1	0	1	
6.88	7	1	0	1	
4.99	16	2	0	0	
4.85	25	0	0	2	
3.51	18	-2	0	2	
3.44	22	2	0	2	
3.16	37	-3	0	1	
3.12	100	3	0	1	
3.09	89	-1	0	3	
3.06	42	1	0	3	
2.747	2	1	1	0	, 0 1 1
2.498	11	4	0	0	
2.433	8	0	0	4	
2.398	27	-1	1	2	, 2 1 1 , 1 1 2
2.347	3	-3	0	3	
2.301	1	3	0	3	
2.241	5	-4	0	2	
2.204	35	4	0	2	,-2 0 4
2.168	18	2	0	4	, 3 1 0
2.145	11	0	1	3	
1.991	2	-3	1	2	
1.963	11	-5	0	1	, 2 1 3
1.920	2	-1	0	5	
1.905	3	1	0	5	
1.853	9	-4	1	1	
1.843	5	4	1	1	
1.826	6	-1	1	4	
1.817	12	1	1	4	
1.765	4	-4	0	4	
1.726	3	4	0	4	
1.696	8	-3	0	5	
1.688	3	5	0	3	
1.666	21	6	0	0	
1.623	21	5	1	0	
1.561	3	-5	1	2	
1.545	18	5	1	2	
1.542	20	-2	1	5	
1.536	4	2	1	5	
1.409	2	7	0	1	
1.394	1	1	1	6	
1.371	15	-5	1	4	
1.349	2	5	1	4	
1.344	7	4	1	5	

TABLE 2. Experimental conditions for powder data

Diffractometer	Rigaku SC-7
Radiation	Cuk$_\alpha$
Voltage	35 KV
Current	20 mA
Monochromator	Graphite
Slit	D.S. 1° S.S. 1° R.S. 0.3mm
Scan speed	1° /min
Chart Speed	1 cm/min
Time Constant	2
Chart Full Scale	1000 cps

TABLE 3. Crystal data for hollandite

Formula	:	$(Ba_{0.75}K_{0.19})_{0.94}(Mn_{7.82}Fe_{0.18})_8O_{16}\cdot 0.41H_2O$		
Space Group	:	I2/m		
Cell dimensions	:	a	10.006 (3)	Å
		b	2.866 (1)	Å
		c	9.746 (2)	Å
		β	91.17 (3)	°
		V	279.4 (1)	Å^3
Z	:	1		
$D_{calc.}$	:	4.83	g/cm^3	

Standard deviations are given in parentheses.

Structure refinement

Refinement was carried out using full matrix least-square program, RSFLS-4 (Sakurai, 1967). Neutral atomic scattering factors used in calculation were taken from the International Tables for X-ray Crystallography Vol. IV (1974). Tetragonal structure solved by Byström and Byström (1950) was taken as a starting model for the least-squares refinement. The relationship between tetragonal and monoclinic cells are as follows.

a(tet)=c(mon) b(tet)=a(mon) c(tet)=b(mon)

As Fe and H_2O contents are very low, these atoms were neglected in the starting model. All atoms occupy special positions. Mn and O are in (m). Ba and K ions were assumed to occupy the same positions (b) statistically with the population ratio 0.75:0.38. Thus, the chemical formula for the starting model becomes $(Ba_{0.75}K_{0.38})_{1.13}Mn_8O_{16}$. Refinement was started with isotropic temperature factors using 492 reflections. When the R factor was reduced to 8.8%, anisotropic temperature factors were applied. 1350 independent reflections were used for the final stage of structure-refinement. The final R factor after 7 cycles with 42 parameters, including anisotropic temperature factors, reduced to 5.0%. The atomic coordinates and anisotropic temperature factors are given in Table 4. The interatomic distances and angles are given in Table 5. After the refinement, a difference-Fourier synthesis was performed using the program RSSFR-5 (Sakurai, 1967).

Discussion

A. Chemical component

Nanbu and Tanida (1964, 1980) pointed out that there are two types of hollandite, hydrous and anhydrous. Hydrous hollandite contains high H_2O (about 5%) and low Fe_2O_3 and belongs to tetragonal system. It is reported as a primary mineral from hydrothermal deposits or as oxidation products of other manganese oxide minerals. The anhydrous hollandite contains less than 1% H_2O and more than 10% Fe_2O_3, and belongs to monoclinic system. It occurs in metamorphosed manganese deposits. However, hollandite from Gowari Wadhona shows low Fe_2O_3 content and low H_2O content. Therefore high Fe_2O_3 content is not a typical feature of anhydrous hollandite. In this point of view, hollandite and cryptomelane are very similar.

TABLE 4. Atomic coordinates and temperature factors for hollandite

	Ba	Mn(1)	Mn(2)	O(1)	O(2)	O(3)	O(4)
X	0.0	0.16405(6)	0.35185(6)	0.2056(3)	0.1580(3)	0.1548(3)	0.5418(3)
Y	0.5	0.0	0.0	0.0	0.0	0.0	0.0
Z	0.0	0.34692(6)	0.83170(6)	0.1495(4)	0.8019(3)	0.5431(3)	0.8231(4)
β_{11}	0.00257(7)	0.00122(4)	0.00101(4)	0.0015(2)	0.0019(2)	0.0028(2)	0.0015(2)
β_{22}	0.0701(14)	0.0102(4)	0.0098(4)	0.0164(22)	0.0164(23)	0.0148(23)	0.0158(23)
β_{33}	0.00279(8)	0.00143(4)	0.00167(4)	0.0035(3)	0.0026(2)	0.0023(2)	0.0036(3)
β_{12}	0.0	0.0	0.0	0.0	0.0	0.0	0.0
β_{13}	0.00027(5)	0.00041(3)	0.00012(3)	0.0002(2)	0.0003(2)	0.0003(2)	0.0003(2)
β_{23}	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Standard deviations are given in parentheses.
The β's are defined by the general temperature factors
$\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2kl\beta_{23}+2lh\beta_{13}+2hk\beta_{12})]$

TABLE 5. Interatomic distances and angles

	distance(Å)	angles(°)		distance(Å)	angles(°)
Mn(1)-O octahedron			Mn(2)-O octahedron		
Mn(1) -O(1)‴	1.938(2)x2		Mn(2) -O(2)‴	1.938(2)x2	
Mn(1) -O(1)	1.977(4)		Mn(2) -O(2)	1.955(3)	
Mn(1) -O(3)	1.916(3)		Mn(2) -O(4)	1.904(3)	
Mn(1) -O(4)′	1.895(2)x2		Mn(2) -O(3)‴	1.884(2)x2	
O(1) -O(1)‴	2.571(4)x2**		O(2) -O(2)‴	2.557(4)x2**	
O(1) -O(4)′	2.778(4)x2		O(2) -O(3)‴	2.779(4)x2	
O(3) -O(4)′	2.798(4)x2		O(4) -O(3)‴	2.780(4)x2	
O(3) -O(1)″	2.763(4)x2		O(4) -O(2)‴	2.727(4)x2	
O(1) ″-O(4)′	2.536(4)x2**		O(2)‴-O(3)‴	2.522(5)x2**	
O(1)‴-O(1)‴*	2.866(1)(=b)		O(2)‴-O(2)‴*	2.866(1)(=b)	
O(4)′ -O(4)′*	2.866(1)(=b)		O(3)‴-O(3)‴*	2.866(1)(=b)	
O(1)‴-Mn(1)-O(1)‴*		95.39(10)	O(2)‴-Mn(2)-O(2)‴*		95.39(10)
O(4)′ -Mn(1)-O(4)′*		98.25(10)	O(3)‴-Mn(2)-O(3)‴*		98.96(11)
O(1)‴-Mn(1)-O(4)′		82.85 (9)x2	O(3)‴-Mn(2)-O(2)‴		82.55(11)x2
O(1) -Mn(1)-O(1)‴		82.12(12)x2	O(2) -Mn(2)-O(2)‴		82.14(11)x2
O(1) -Mn(1)-O(4)		91.66(12)x2	O(2) -Mn(2)-O(3)‴		91.78(12)x2
O(3) -Mn(1)-O(1)‴		91.60(13)x2	O(4) -Mn(2)-O(2)‴		90.45(12)x2
O(3) -Mn(1)-O(4)′		94.47(13)x2	O(4) -Mn(2)-O(3)‴		95.39(12)x2
Tunnel Site					
Ba′-O(1)′	2.878(3)x4				
Ba′-O(2)′	2.899(3)x4				
O(1)′ -O(2)′	3.411(5)x4				
O(1)′ -O(2)‴	3.679(4)x4				
O(1)‴-Ba′-O(2)‴		72.37(9)x4			
O(1)′ -Ba′-O(2)‴		79.07(8)x4			
O(1)′ -O(2)‴-O(1)″		89.45(11)x4			
O(2)′ -O(1)‴-O(2)″		90.51(10)x4			

Standard deviations are given in parentheses.

Symmetry code			
′	1/2+x,	1/2+y,	1/2+z
″	-y,	y,	-z
‴	1/2-x,	1/2+y,	1/2-z
*	x,	-1+y,	z

**shared edges.

B. *General descriptions of structure*

The structure of monoclinic hollandite is basically similar to tetragonal hollandite (Byström and Byström, 1950). There are eight MnO_6 octahedra in a unit cell (Fig. 1). Each octahedron shares an edge to form a double chain. Each double chain shares corner to form a framework structure. There is a cavity in the framework of MnO_6 octahedron and A-cation occupies this cavity. In the specimen used in this experi-

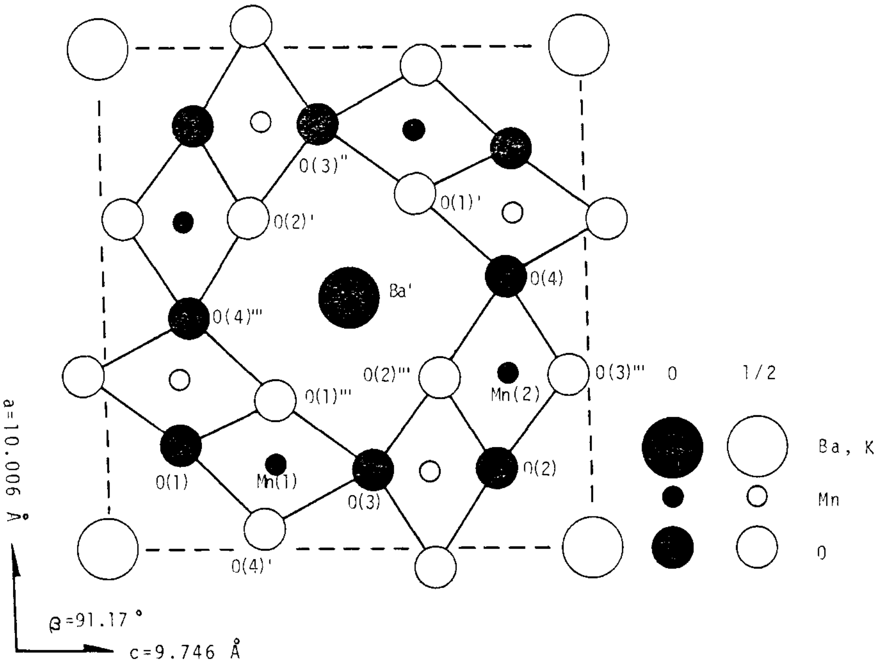

FIG. 1. The structure of hollandite.

ment, the ionic radii ratio of Mn to A-cation is 0.49. Here, the A-cations are Ba^{2+} and K^{+}. H_2O molecules also occupy this cavity. Every ion exists on a mirror plane, i.e. the y-coordinates are 0.0 or 0.5. The framework structure is distorted to monoclinic symmetry. The cell constants and the atomic coordinates are in good agreement to those from Sweden. However, there is a wide variations in species of the tunnel cations between the present one and that reported by Post *et al.* (1982). Thus, the present data clearly indicate that the distortion of the framework structure does not depend on the ionic species of the A-cations. Also, it's dependence on the mean radii of the A-cation is not definite.

C. MnO_6 octahedra

Manganese atoms are in octahedral coordination. There are two MnO_6 octahedra which are symmetrically independent in a unit cell. These octahedra are distorted from the ideal shape. The O-O bond lengths (Table 5) vary from 2.526(4) to 2.866(1) Å and the shared octahedral edges are obviously shorter than unshared edges in both octahedra. The Mn-O bond lengths vary from 1.895(2) to 1.977(4) Å and from 1.884(2) to 1.955(3) Å in the $Mn(1)O_6$ and $Mn(2)O_6$ octahedra, respectively. Mn atoms do not exist at the center of MnO_6 octahedra, but shift towards the unshared edges. These features are common to the both octahedra $Mn(1)O_6$ and $Mn(2)O_6$. The variance of the octahedral angles $\delta\theta(\mathrm{oct})^2=\sum_{i=1}^{12}(\theta_i-90^\circ)^2/11$ is a measure of distortion for octahedra (Robinson *et al.*, 1971). $\delta\theta(\mathrm{oct})^2$'s of $Mn(1)O_6$ and $Mn(2)O_6$ are 34.0 and 30.0, respectively. As $\delta\theta(\mathrm{oct})^2$ of tetragonal cryptomelane from Tirodi mine, India is 35.4 (Miura, unpublished), the distortion of octahedra is not a main reason for the distortion of the framework structure.

D. *Tunnel site*

Ba^{2+} and K^+ occupy the tunnel site. These cations are surrounded by eight oxgen atoms. Four oxgen atoms are on a mirror plane at y=0.5 and the remaining four oxgens are on a mirror plane at y=-0.5, which is symmetrically equivalent. Minimum and maximum distances are 2.878(3)Å and 2.899(3)Å for Ba-O, 3.411(5)Å and 3.679(4)Å for O-O of the coordination polyhedron. Thus, oxygen atoms form rectangle configuration (Table 5). Fig. 2 shows electron density of tunnel cations. Tunnel runs along b. Ba^{2+} and K^+ ions occupy the special position (0,0.5,0), and are observed as a high electron density. Post *et al.* (1982) reported that 20% of Ba^{2+} and Pb^{2+} shifts from (0,0,0) to (0,0.21,0), which corresponds to a shift from (0,0.5,0) to (0,0.71,0) in the present coordinate system. However an extra-electron distribution is not obtained in the tunnel of this structure, and only one single peak is observed. Although small residual densities were observed along the b-axis on difference-Fourier map, further refinements with additional partial atoms failed to reduce the R factors, indicating that most of A-cations occupy only one special position.

E. *Water molecules in tunnel*

Anhydrous hollandite contains about 1 wt% of water molecules in it's structure. It is reported that water molecules behave with a zeolitic feature in tunnel site (Gruner, 1943). It was difficult to determine the positions of water molecules from the single crystal X-ray data. But there is a strong correlation between powder diffraction intensities and tunnel site occupancies as shown in Fig. 3. The calculated results based on the atomic coordinates of hollandite from Gowari Wadhona with each tunnel site occupancies are also shown. The vertical axis indicates the intensity ratio of $I(200)+I(002)$ to $I(301)+I(\bar{1}03)$ in a powder diffraction profiles. The horizontal axis is tunnel site occupancy. Generally, as the occupancy of A-cation in tunnel site increases, the intensity ratio $I(200)+I(002)/I(301)+I(\bar{1}03)$ decreases. When hollandite from Gowari Wadhona is heated upto 500°C, water is released from it's structure, and an increase of the intensity ratio is observed. These features are in good agreement with the calculated results and indicate that water molecules also occupy the tunnel site.

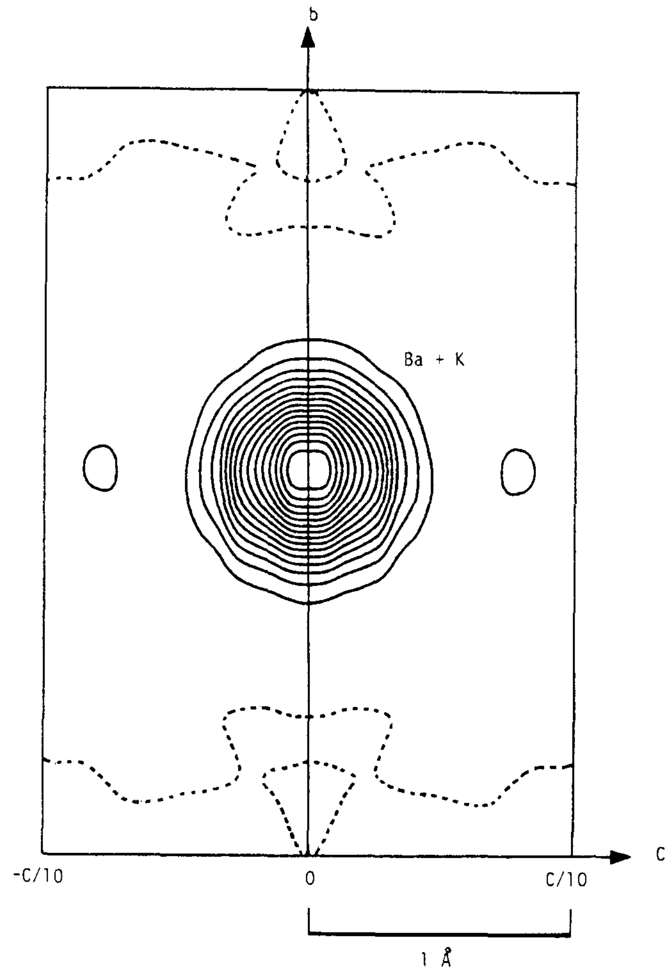

FIG. 2. Electron density section parallel to (100), x=0.
Contours are at intervals of 10 e/Å^3, the zero contours being broken.

Conclusion

The anhydrous hollandite from Gowari Wadhona, shows that the MnO_6 octahedra form a tunnel structure, but the framework is distorted to a monoclinic symmetry. The distortion does not depend on the species of cations or molecules in the tunnel site as previously reported by Post *et al.* (1982). Ba^{2+} and K^+ ions as well as H_2O molecules occupy the special positions which are located at the tunnel center and do not

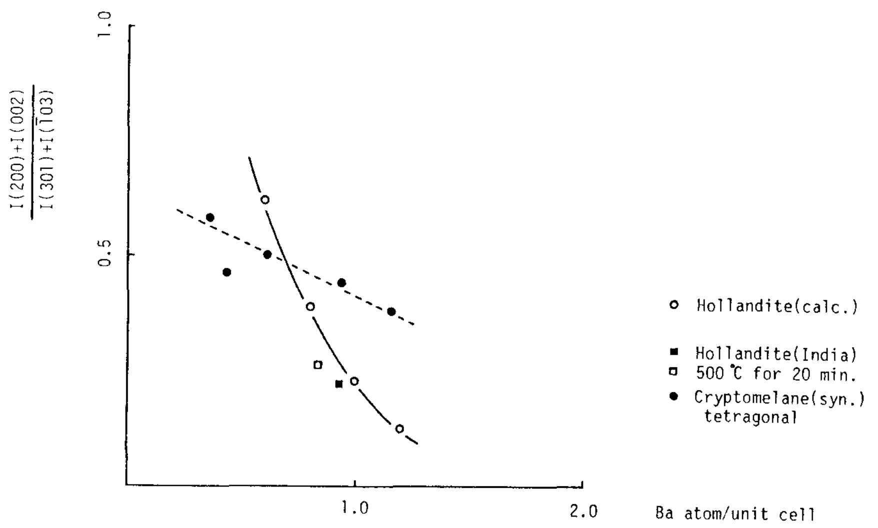

FIG. 3. The relationship between intensity ratio I(200)+I(002)/I(301)+I($\bar{1}$03) and cation occupancy in tunnel. Each data are normalized in terms of number of electron.

show continuous distribution along the tunnel. The occupancy of A-cation in the tunnel site affects the X-ray diffraction profile. As the occupancy increases the intensity ratio of I(200)+I(002) to I(301)+I($\bar{1}$03) decreases. When hollandite is heated, increase of the intensity ratio is observed. These data indicate that water molecules also occupy the tunnel site.

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