

The Crystal Structure of $K_2Cr_8O_{16}$: The Hollandite-Type Full Cationic Occupation in a Tunnel

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The crystal structure of K–Cr oxide of hollandite type synthesized under high pressure and high temperature was determined by the single crystal X-ray diffraction method. The compound crystallizes with the tetragonal symmetry of the space group $I4/m$, the cell parameters $a = 9.7627(4)$ and $c = 2.9347(6)$ Å, and $Z = 1$. The structure refinement based on 572 unique reflections ($2\theta < 100^\circ$) converged to $R = 0.0296$. The experiment confirmed that the chemical composition was stoichiometric, $K_2Cr_8O_{16}$, in which the tunnel sites were fully occupied by K ions without displacement from the special position ($2b$). The result suggests that the high pressure induces a high cation occupancy in the tunnel and opens a way to control the occupancy and some physical properties related to tunnel cations. © 1996 Academic Press, Inc.

INTRODUCTION

The crystal structure of the mineral hollandite was originally determined by Byström and Byström (1). The crystal system is either tetragonal ($I4/m$) or pseudotetragonal (monoclinic, $I2/m$). It is constructed by a framework of MnO_6 octahedra and has a 2×2 tunnel consisting of four double strings of edge-sharing MnO_6 octahedra. The tunnel accommodates large cations such as Ba^{2+} , Pb^{2+} , Na^+ , and K^+ ions. As the distance between tunnel sites (~ 2.9 Å) was very short for large cations such as Ba–Ba in the tunnel, Byström and Byström (2) also proposed a model of cation arrangement to avoid short interatomic distances between tunnel cations. After these reports intense struc-

tural studies of hollandite-type compounds have focused on the complex cation arrangements in the tunnel, and on physical properties related to the tunnel framework and the distribution of tunnel cations.

Hollandite compounds are represented by the general formula $A_xB_8O_{16}$, where A represents large tunnel ions such as K, Na, Ba, Sr, Rb, and Cs, and B represents cations in an oxygen-octahedron such as Mn, Ti, Al, Cr, V, and Si.

Extensive studies have been done on the synthesis and structure determination of hollandite compounds motivated from applicational interests such as one-dimensional ionic conductor through the tunnel (3–6), the immobilization of radio active waste (7–12), from the structural interest of cation arrangements in the tunnel (13–17), and the interest in earth science as the phase constituting the earth's mantle (18, 19).

Most of the previous studies dealt with the hollandite compounds of partially occupied tunnels ($x < 2.0$) to report an elongated electron density distribution on the tunnel cations. Some of those reports stated that the elongated distribution was direct evidence of the displacement of tunnel cations. In many cases, however, the result was shown in a “multi-atoms” model in which some of the cations were assigned at the special position and others at the sites displaced along the tunnel from the special ones (5, 14, 15, 22–24), or in giving large anisotropic temperature factors (U_{33} in $I4/m$) in a tunnel direction (13, 21).

There is one exceptional case of natural hollandite (Ba, K)_{1.13}(Mn, Fe)₈O₁₆·0.41H₂O reported by Miura (25) in which the tunnel cations do not show any displacement from the special position in spite of their partial occupancy ($1 < x < 2$).

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Endo *et al.* (26) synthesized a compound, $\text{K}_2\text{Cr}_8\text{O}_{16}$, under high pressure and reported the crystal structure. Two models, $\text{KCr}_8\text{O}_{16}$ and $\text{K}_2\text{Cr}_8\text{O}_{16}$, were examined for assessing the chemical composition and the latter composition yielded a better R factor (0.058). They concluded that the composition was represented more reasonably by $\text{K}_2\text{Cr}_8\text{O}_{16}$ than by $\text{KCr}_8\text{O}_{16}$.

Okada *et al.* (27) synthesized three hollandite-type compounds of $\text{Rb}_2\text{Cr}_8\text{O}_{16}$, $\text{K}_2\text{Cr}_2\text{V}_6\text{O}_{16}$, and $\text{K}_2\text{V}_8\text{O}_{16}$ under high P - T conditions for the measurements of magnetization and electric resistivity. They performed no chemical analysis for these compounds but performed an X-ray structure analysis on one of these hollandites, $\text{Rb}_2\text{Cr}_8\text{O}_{16}$, that suggested that the composition must be close to $\text{Rb}_2\text{Cr}_8\text{O}_{16}$.

These studies suggested that hollandites which were synthesized under high pressure might have high contents of tunnel cations. In this study the crystal structure of the $\text{K}_2\text{Cr}_8\text{O}_{16}$ hollandite is reexamined in order to clarify the cation arrangement and occupancy in the tunnel in terms of high pressure synthesis. This is the first report that has confirmed a hollandite-type compound having a tunnel which is effectively filled with cations without elongation in their electron density distribution.

EXPERIMENTAL

Sample Preparation

The sample is one of specimens, which was synthesized by Endo *et al.* (26) under high temperature–pressure conditions. That is, the mixture of starting materials, $\text{K}_2\text{Cr}_2\text{O}_7$ and Cr_2O_3 in the molar ratio of 3:2, was charged in a gold capsule and treated in the pressure range from 5.5 to 6.5 GPa and the temperature range from 1100 to 1250°C for 30 min. The product was quenched to room temperature and the black single crystals of $\text{K}_2\text{Cr}_8\text{O}_{16}$ hollandite were obtained in the reaction product as shown in Fig. 1.

Single Crystal X-Ray Study

Weissenberg camera works revealed that the crystal was tetragonal and the reflections of $h + k + l = \text{odd}$ were absent, which yielded three candidates for the space group; $I4$, $\bar{I}4$, and $I4/m$. All the reflections observed were sharp without super or diffuse ones.

A single crystal of $0.15 \times 0.025 \times 0.025 \text{ mm}^3$ in size was mounted on a Rigaku AFC5S four-circle diffractometer for the intensity data collection. The intensity data were collected under the conditions of a scanning speed of $5^\circ/\text{min}$ and a scanning width of $\Delta\omega = (1.10 + 0.30 \tan \theta)^\circ$. Three standard reflections were measured after every 150 data collection, which maintained consistency throughout the experiment. The data corrections were made for Lorentz and polarization factors on all the reflections. The empirical correction for absorption effects was also made

by the Furnas method around the c axis (28). The crystal data and experimental conditions are listed in Table 1.

Structure Refinement

The structure refinement started from the parameters reported by Yamamoto *et al.* (20), assuming the centrosymmetric space group $I4/m$. In the preliminary stage of refinement, 1238 nonequivalent reflections merged from 8482 reflections ($2\theta < 120^\circ$) were used. The low intensity or high 2θ data resulted in a poor R factor. The intensity data were, therefore, limited to 572 reflections of $2\theta < 100^\circ$, $F_o > 3\sigma$ and $F_o > 3.0$.

The chemical composition started from $\text{K}_2\text{Cr}_8\text{O}_{16}$ and the K ion was fixed at the special position (2b). After the successive cycles of refinement for positions and isotropic temperature factors of Cr and O ions, the R and R_w factors converged to 0.062 and 0.063, respectively. At this stage temperature factors of all the atoms were converted to anisotropic ones and the refinement procedure continued to converge to $R = 0.0328$ and $R_w = 0.0378$.

Estimation of Chemical Composition

In order to clarify the cation occupancy and the chemical composition of the hollandite, it was analyzed by an electron microprobe analyzer (HITACHI S550 scanning microscope equipped with KEVEX energy dispersive spectrometer). The result is 80.65% Cr_2O_3 (total Cr expressed as Cr_2O_3) and 11.93% K_2O . This means the K cation number is 1.91 per 8 Cr, so that the analysis suggests the chemical composition $\text{K}_{1.91}\text{Cr}_8\text{O}_{16}$ instead of $\text{K}_2\text{Cr}_8\text{O}_{16}$ (Cr_2O_3 , 81.05% and K_2O , 12.56%). The analytical error could allow the upper K content to 1.96 per 8 Cr. Thus, the probe analysis indicates almost a full occupancy with deficiency of only a few percent.

At this stage two cases of occupancy refinements were performed based on the X-ray intensity data. In the first case all the parameters including a scale factor, 6 positional parameters, and 14 thermal parameters were again refined successively fixing the composition at $\text{K}_2\text{Cr}_8\text{O}_{16}$. After the procedure the occupancy of the tunnel cation K was refined to $R = 0.0320$ and $R_w = 0.0370$ yielding the composition $\text{K}_{1.99(1)}\text{Cr}_8\text{O}_{16}$. Then, all the parameters were refined in the same way as mentioned above except the composition was fixed at $\text{K}_{1.91}\text{Cr}_8\text{O}_{16}$. The discrepancy factors of R and R_w were improved to $R = 0.0305$ and $R_w = 0.0362$. At the final stage all the parameters were refined simultaneously including the occupancy of the tunnel cation. The factors were further improved to $R = 0.0296$ and $R_w = 0.0356$ with the composition of $\text{K}_{1.96(1)}\text{Cr}_8\text{O}_{16}$. This composition is equivalent to the tunnel occupancy of 98%. Indeed the tunnel might have a few vacant sites, but taking into account the discrepancy factors R and R_w of about 3%, it is effectively concluded that the tunnel is fully occupied by tunnel cations. Hereafter the composition is represented

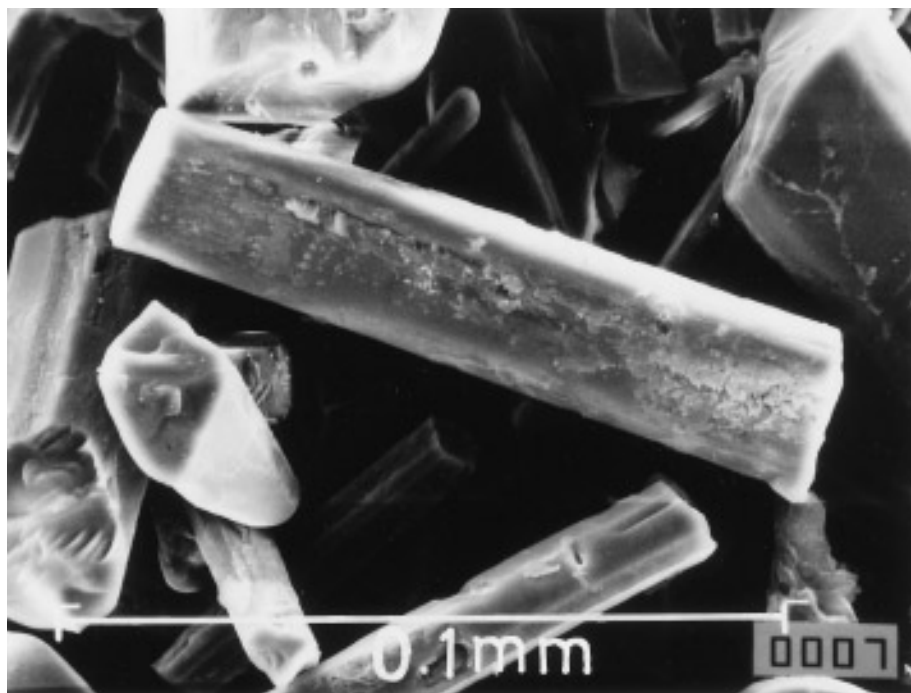


FIG. 1. Scanning electron micrograph of $K_2Cr_8O_{16}$ hollandite crystals.

TABLE 1
Crystal Data and Experimental Conditions for
 $K_2Cr_8O_{16}$ Hollandite

Crystal data	
Crystal system	Tetragonal
Space group	$I4/m$
Cell dimensions (\AA)	$a = 9.7627(4)$ $b = 9.7627(4)$ $c = 2.9347(6)$
Volume (\AA^3)	279.70(6)
Z	1
Chemical formula	$K_2Cr_8O_{16}$
D_{calc} (g/cm^3)	4.45
$\mu(\text{MoK}\alpha)$ (cm^{-1})	86.1
$F(000)$	358.0
Experimental conditions	
Crystal size (mm^3)	$0.15 \times 0.025 \times 0.025$
Radiation	MoK α X-ray ($\lambda = 0.7107 \text{\AA}$)
Monochromator	Graphite
Scanning speed	$5^\circ/\text{min}$.
Scanning mode	$2\theta - \omega$
Scanning width	$\Delta\omega = (1.10 + 0.30 \tan \theta)^\circ$
Collected reflections ($2\theta < 120^\circ$)	8482
Unique reflections ($2\theta < 100^\circ$)	881
Used unique reflections ($2\theta < 100^\circ$, $F_o > 3\sigma$, $F_o > 3.0$)	572
R factor	0.0296
R_w factor	0.0356
R_{int} factor	0.0675

by $K_2Cr_8O_{16}$ under the allowance of a few percent of K deficiency.

The final $F_o - F_c$ tables are available as supplementary material.² The function $\sum w(s|F_o| - |F_c|)^2$ was minimized in the refinement, where s is the scale factor and w is the weight which was fixed at unity. Neutral atomic scattering factors for K, Cr, and O were taken from the ‘‘International Tables for X-Ray Crystallography’’ (29). The computer program RADY (30) was used for the refinement.

At the last stage D-Fourier maps were synthesized by the program FRAXY (31), which showed no significant residual electron density all over the structure.

RESULTS AND DISCUSSION

Chemical Composition

Final atomic coordinates, site occupancies, and temperature factors for K–Cr hollandite are listed in Table 2. The final occupancies for cations were confirmed to yield effectively a full occupancy as mentioned above. The crystals synthesized by Endo *et al.* (28) are, therefore, of the hollandite type with the stoichiometric composition $K_2Cr_8O_{16}$ as shown in Fig. 2.

Valence States of Cr Ions

In $A_xB_8O_{16}$ -type hollandites octahedral B cations are originally tetravalent, but some have a reduced valence depending on the valence state and content x of A cations.

TABLE 2
Final Atomic Coordinates and Temperature Factors for
 $K_2Cr_8O_{16}$ Hollandite

Atom	Position	Occup.	x	y	z	B_{eq} (\AA^2) ^a
K	2b	1.0	0.0	0.0	0.5	1.33
Cr	8h	1.0	0.34813(5)	0.16496(5)	0.0	0.34
O(1)	8h	1.0	0.1536(2)	0.2013(2)	0.0	0.44
O(2)	8h	1.0	0.5398(2)	0.1633(2)	0.0	0.48

Anisotropic temperature factors ($\times 10^{-4}$) ^b							
	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}	U_{eq}/U_{iso}
K	200(5)	200(5)	104(6)	0	0	0	168
Cr	41(1)	44(1)	45(1)	6(1)	0	0	44
O(1)	52(6)	51(6)	64(7)	-4(5)	0	0	55
O(2)	44(6)	88(7)	52(6)	4(5)	0	0	61

^a The B_{eq} are defined by $B_{eq} = 4/3 \sum_i \sum_j \beta_{ij} a_i a_j$.

^b The anisotropic temperature factor is defined by $U = \exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$ and $U_{eq} = 1/3 \sum_i U_{ii}$.

In the case of $K_2Cr_8O_{16}$ three quarters of Cr ions are tetravalent and one quarter should be trivalent. The Cr–O distances range from 1.871 to 1.965 Å with the mean length of 1.927 Å as listed in Table 3. The distance 1.927 Å is shorter than the sum of ionic radii of Cr^{3+} and O^{2-} (2.015 Å) and of Cr^{4+} and O^{2-} (1.95 Å), respectively. Such a short distance is commonly observed in hollandite structures. The mean Mn–O distance 1.913 Å is shorter than the sum of ionic radii of Mn^{3+} and O^{2-} (2.05 Å) and of Mn^{4+} and O^{2-} (1.94 Å) in $Rb_{1.5}Mn_8O_{16}$ hollandite (20). This is also true in the cases of Ti–O in $CsTi_8O_{16}$ and V–O in $Ba_{1.09}V_8O_{16}$ (15, 24). It can be supported that Cr ions are

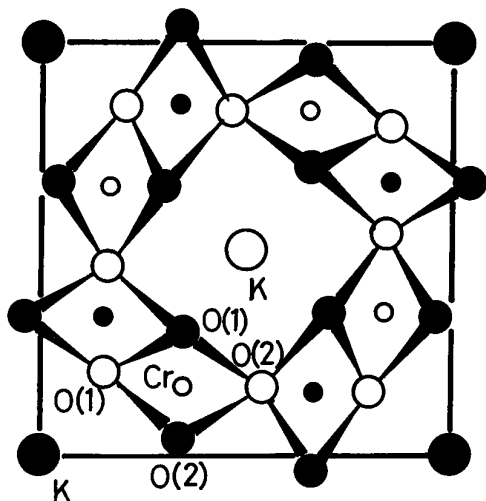


FIG. 2. The structure of $K_2Cr_8O_{16}$ hollandite projected on (001). Open circles denote atoms at $z = 0.0$ and solid circles at $z = 0.5$.

TABLE 3
Interatomic Distances (\AA) and Angles ($^\circ$) of
the CrO_6 Octahedron and the KO_{12} Polyhedron
for $K_2Cr_8O_{16}$ Hollandite

Atom	Distance	Angle
CrO ₆ octahedron		
Cr–O(1)	1.932(2)	
Cr–O(1) ⁱ	1.965(1) × 2	
Cr–O(2) ⁱⁱ	1.913(1) × 2	
Cr–O(2)	1.871(2)	
Mean	1.927(1)	
O(1)–O(1) ⁱ	2.570(2)** × 2	82.51(7)
O(1) ⁱ –O(1) ^{is*}	2.9347(6)	96.63(9)
O(1)–O(2) ⁱⁱ	2.799(2) × 2	93.45(7)
O(1) ⁱ –O(2)	2.733(2) × 2	90.85(7)
O(1) ⁱ –O(2) ⁱⁱ	2.530(3)** × 2	81.46(6)
O(2)–O(2) ⁱⁱ	2.744(2) × 2	93.0(1)
O(2) ⁱⁱ –O(2) ^{ii*}	2.9347(6)	100.20(9)
Mean	2.743(1)	89.95(2)
KO ₁₂ polyhedron		
K–O(1)	2.874(2) × 8	
K–O(2)	3.311(2) × 4	
Mean	3.020(1)	
O(1)–O(1)*	2.9347(6) × 4	61.40(4)
O(1)–O(1) ⁱⁱⁱ	3.495(3) × 8	74.89(2)
O(1)–O(2) ⁱⁱ	2.799(2) × 8	53.25(4)
O(1)–O(2) ⁱ	2.733(2) × 8	51.87(4)
Mean	2.998(1)	60.20(1)

Symmetry code; i $1/2 - x, 1/2 - y, 1/2 + z$
 ii $1/2 - y, -1/2 + x, 1/2 + z$
 iii $-y, x, z$
 * $x, y, 1 + z$
 ** Shared edge

tetravalent and trivalent in $K_2Cr_8O_{16}$. The small B_{eq} (0.34 Å²) of the Cr ion indicates that Cr^{3+} and Cr^{4+} ions occupy approximately the same position in spite of different valence states.

Cation Arrangements in the Tunnel

The electron density distribution of the K ion at the special position was examined by synthesizing a Fourier section passing through the K atom as shown in Fig. 3. It exhibits an isotropic electron density distribution around the K ion with a normal value of B_{eq} (1.33 Å²), showing no elongation along the c axis. This result indicates that K ions are fixed at the special position and take no position displaced from the special one, although the tunnel cations in most of the hollandites showed an elongated electron density distribution (e.g., 23). It is notable that the compound has the stoichiometric composition $K_2Cr_8O_{16}$ with the tunnel fully occupied by K cations and the tunnel cations are fixed at the special position (2b).

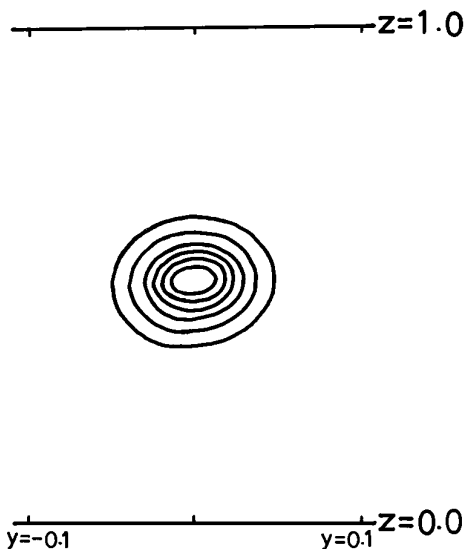


FIG. 3. The electron density distribution of tunnel cation, K. The map is parallel to the plane of (100) at $x = 0.0$. The contour starts from $10 \text{ e}/\text{\AA}^3$ at the interval of $20 \text{ e}/\text{\AA}^3$.

There are a few studies that report the cation arrangement with the stoichiometric or nearly stoichiometric composition $A_xB_8O_{16}$ ($x \sim 2.0$), which suggest two ways to synthesize the compound with a high content of tunnel cations. One is to synthesize the compound under the condition of extremely high content of the tunnel cation. Wilhelm and Hoppe (32) prepared a hollandite-type single crystal of KRu_4O_8 for the X-ray study, sintering the mixture of K_2O and RuO_2 with the ratio of $K : Ru = 8 : 1$ under the condition of $700\text{--}800^\circ\text{C}$ for 15 days. This is an extremely K rich condition. The crystal structure was determined by the single crystal X-ray diffraction method and it revealed that the tunnel was fully occupied by K ions with the occupancy of 1.024. In the experiment the structure was refined to $R = 0.0312$ with isotropic temperature factors to each atom; the factor for the K ion was reported to be 1.56 \AA^2 , which is larger than in the present study for $K_2Cr_8O_{16}$ (1.33 \AA^2). However no anisotropic temperature factor was introduced so the displacement of tunnel cations is unknown.

Another way to give a high occupation to the tunnel is to prepare the compound under high pressure. Although there have been numerous works for hollandite compounds synthesized under ambient pressure, only a few studies have dealt with the compounds synthesized under high pressure.

The hollandite compound $K_2Mo_8O_{16}$ was synthesized under hydrothermal conditions of $500\text{--}700^\circ\text{C}$ and 0.3 GPa by Toradi and Calabrese (33). The single crystal X-ray analysis revealed that the structure contained Mo_4O_{16} clusters and the chemical composition was $K_{1.92}Mo_8O_{16}$, close to the stoichiometric composition. In this case the pressure was not high enough for preferential occupation of K cations to tun-

nel sites, but taking into account the high mobility of ions under the hydrothermal condition and the K rich condition of the K^+/Mo^{6+} ratio larger than 2.0 in the synthesis, even low pressure might induce high cation content.

Abriel *et al.* (13) reported three new compounds of the hollandite structure $K_2V_8O_{16}$, $K_{1.8}V_8O_{16}$, and $Tl_{1.74}V_8O_{16}$, which were synthesized under the temperature range $750\text{--}1000^\circ\text{C}$ and the pressure 2.5–3.5 GPa. All these high pressure compounds have relatively high contents of tunnel cations. They pointed out the relationship between the cation occupation and the U_{33} -coefficient of anisotropic temperature factor. The compounds with lower content of tunnel cations, $K_{1.8}V_8O_{16}$ and $Tl_{1.74}V_8O_{16}$, showed U_{33} values, 0.26 and 0.252, respectively, higher than the value 0.122 for $K_2V_8O_{16}$. This result indicates that in the former two compounds some of the tunnel sites are vacant and the tunnel cations have some room which allows the cation displacement toward the vacant site, yielding higher U_{33} values. But even in $K_2V_8O_{16}$ the tunnel cation showed some displacement, as seen by the value of U_{33} (0.122) being much higher than U_{11} (0.026). They reported the site occupancy of $98.4 \pm 1.6\%$ in $K_2V_8O_{16}$, yielding that the tunnel had a nearly full occupancy but there still remained a small number of vacant sites. The occupancy of 98.4% is the same as that in the present study. The cation displacement occurs in $K_2V_8O_{16}$ but is not observed in $K_2Cr_8O_{16}$. Usually the occupancy tends to exhibit a higher value when the least squares method starts from the stoichiometric composition $A_2B_8O_{16}$, as in the first trial in this study (the occupancy of 0.995(5) instead of 0.980(5)). It is probable that the occupancy might be lower in $K_2V_8O_{16}$.

In the present study the compound is synthesized under a higher pressure range (5.5–6.5 GPa) and exhibits effectively a full occupancy of tunnel sites. The tunnel cation K exhibits no displacement from the special position, which is clarified by the values of U_{11} (0.0198) and U_{33} (0.0103). This result suggests that the high pressure induces the preferential cation occupation in the tunnel sites. This is the first example to report the cation arrangement without displacement under the full tunnel occupation.

$Rb_2Cr_8O_{16}$ was synthesized at 1200°C and 7 GPa, and $K_2Cr_2V_6O_{16}$ and $K_2V_8O_{16}$ at 1200°C and 3 GPa by Okada *et al.* (26) as mentioned above. These conditions are similar to those used in the present study. The structure analysis for $Rb_2Cr_8O_{16}$ with a fixed x converged to an R value of 0.068. The small R value suggested that the composition was $Rb_2Cr_8O_{16}$ or close to it. There is no chemical analysis or X-ray analysis to determine the chemical composition (analysis for site occupancy) for these compounds, but it is probable that these compounds have a full cation occupation in the tunnel without cation displacement.

Ringwood *et al.* (18) synthesized a hollandite $K_2(AlSi_3)_2O_{16}$ under 12 GPa and Yamada *et al.* (19) also did under a pressure higher than 14 GPa. The pressures are

much higher than those in the present study, so the tunnel might have a full K occupancy. As the structure analyses were done only by the powder X-ray diffraction method, the experiments did not confirm the full occupancy and the cation displacement in the tunnel.

All these reports including the present study suggest that the high pressure induces a high cation occupation in the tunnel as well as the high ratio of tunnel cation in starting materials. The above reports lead to the general conclusion that the high pressure synthesis of the hollandite compound results in a full occupancy of large cations in the tunnel by the pressure effect pumping up cations into the tunnel (in other words the tunnel would be broken down by the pressure compression if the tunnel had vacant sites), and the full occupancy gives no allowance for tunnel cations to displace from the tunnel site and results in the regular occupation of cations at the special position.

It is of no doubt that the occupancy and arrangement of cations in the tunnel have a profound effect on the physical properties of hollandite compounds such as one dimensional ionic conductivity or immobilization of tunnel cations. The above conclusion opens a way to control the tunnel occupation and cation arrangement by the pressure effect, and, consequently, physical properties related to tunnel cations.

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