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## The Structure and Chemistry of a Barium Titanate Hollandite-Type Phase

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### Abstract

The crystal structure of a synthetic hollandite phase  $(\text{Ba}_{0.98}\text{Ca}_{0.03}\text{Zr}_{0.02})(\text{Al}_{1.10}\text{Ni}_{0.48}\text{Ti}_{6.4})\text{O}_{16}$  has been refined by the full-matrix least-squares method using 624 three-dimensional reflections to a final  $R$  value of 0.059 for the 22 variables involved. The data were collected on a four-circle diffractometer using graphite-monochromated Mo  $K\alpha$  radiation. The structure is tetragonal, space group  $I4/m$  with cell dimensions  $a = 10.039$  (1),  $c = 2.943$  (1) Å, and  $Z = 2$ . Refinement of the structure with the large  $A$  cations on the  $2(b)$  site  $(0,0,\frac{1}{2})$  resulted in an unacceptably high residual. This atom was displaced to site  $4(e)$   $(0,0,\pm z)$  with  $z = 0.3845$  (7), as indicated by the difference electron density map, and refinement proceeded satisfactorily.

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There are now two  $A$ –O(1) bond distances, four each of 2.787 (3) and 3.126 (3) Å. The O(1) atoms form a cage-like framework around the  $4(e)$  site which effectively immobilizes large  $A$  atoms such as Cs, K, Rb and Ba. Results of solid-state preparations of  $\text{Ba}_x\text{Al}_{2x}\text{Ti}_{8-2x}\text{O}_{16}$  show a large range of  $x$ , varying from 0.3–1.2.

### Introduction

$\text{BaAl}_2\text{Ti}_6\text{O}_{16}$  (ideal formula) is the most abundant phase used in SYNROC, a synthetic rock developed for nuclear-waste immobilization (Ringwood, 1978). This synthetic phase possesses the tetragonal hollandite structure and is capable of a large number of

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substitutions of cations with different radii and charges. Ringwood, Kesson, Ware, Hibberson & Major (1979a) have shown, through accelerated leaching tests, that this compound is extremely stable and strongly resists attack by aqueous sodium chloride solutions at elevated pressures and temperatures.

The crystal structure of natural hollandite,  $\text{BaMn}_8\text{O}_{16}$ , was first studied by Byström & Byström (1950). They found the structure to consist of an octahedral framework forming large channels parallel to the  $c$  axis. It is within these channels that large cations can reside, thus stabilizing the structure (Bayer & Hoffman, 1966). Dryden & Wadsley (1958) successfully synthesized a non-stoichiometric phase  $\text{Ba}_x(\text{Ti}_{8-x}\text{Mg}_x)\text{O}_{16}$  possessing this tetragonal hollandite structure. These workers found that the hollandite structure was able to accommodate a range of compositions with  $x$  varying from 0.6–1.14. The range for the hollandite lattice was studied further by Bayer & Hoffman (1966). They showed the large cations  $\text{Cs}^+$ ,  $\text{K}^+$  and  $\text{Rb}^+$  and many smaller ions could combine to form the tetragonal hollandite-type structure.

Although the main features in all previous structural analyses of the tetragonal hollandite have never been in doubt, a refinement using modern methods has been desirable. Both previous structure determinations resulted in high  $R$  values and neither individual temperature factors nor final difference electron density maps appear to have been calculated. Recently, Cadée & Verschoor (1978) synthesized several compounds with hollandite stoichiometry. A single-crystal analysis showed that these phases have a small monoclinic distortion of the tetragonal lattice. In the course of the structure solution the  $A$  cation position was moved from the expected special position  $2(b)$  (0,0,0) to special position  $4(e)$  (0, $\pm y$ ,0), decreasing the coordination number to 10.

In view of the important potential application of this phase for the immobilization of radioactive elements in high-level nuclear wastes and the need for a fundamental understanding of its properties and behaviour, a detailed crystal structure analysis of the SYNROC hollandite-type phase was carried out.

### Experimental

The crystals were synthesized from a mixture of SYNROC-A components (Ringwood, Kesson, Ware, Hibberson & Major, 1979a,b). These components were sealed in a Ni capsule and pressurized to 0.5 GPa in a piston-cylinder apparatus (Boyd & England, 1960). The temperature was increased to 1573 K, held for one hour, and then slowly lowered at  $3 \text{ K min}^{-1}$  to 1423 K, and then at  $30 \text{ K min}^{-1}$  to room temperature. After removing the charge, the large hollandite-type crystals ( $\sim 0.5 \times 0.5 \times 1 \text{ mm}$ ) were easily visible amongst the

Table 1. *Electron-microprobe analyses and calculated atomic contents*

	1*	2	3	4	5
TiO <sub>2</sub>	68.	81.	62.	77.	70.
Al <sub>2</sub> O <sub>3</sub>	7.5	11.2	13.1	13.7	12.4
FeO	<0.1				
NiO	4.7				
BaO	20.	7.	25.	9.	18.
CaO	0.2				
ZrO <sub>2</sub>	0.3				
Total	100.7	99.2	100.1	99.7	100.4
Ti <sup>4+</sup>	6.40	6.75	5.91	6.45	6.48
Al <sup>3+</sup>	1.10	1.46	1.96	1.8	1.42
Fe <sup>2+</sup>	—				
Ni <sup>2+</sup>	0.48				
Ba <sup>2+</sup>	0.98	0.3	1.2	0.39	0.9
Ca <sup>2+</sup>	0.03				
Zr <sup>4+</sup>	0.02				
O <sup>2-</sup>	16.00	16.00	16.00	16.00	16.00

\* Analysis of crystal used in structure determination.

other phases. The crystals are acicular, cleaving along the long dimension, *i.e.* parallel to the  $c$  axis. They are birefringent, exhibiting a brilliant green colour when viewed with transmitted light. Some crystals are also pleochroic. Most of the crystals examined showed twinning and/or multiple fragments. Splitting of reflections was apparent on zero- or upper-level Weissenberg photographs. It was not until a very small fragment ( $< 100 \mu\text{m}$ ) was chosen that the splitting disappeared.

Powder samples of the hollandite phase with differing stoichiometries ranging from  $\text{Ba}_{0.6}\text{Al}_{1.2}\text{Ti}_{6.8}\text{O}_{16}$  to  $\text{Ba}_{1.6}\text{Al}_{3.2}\text{Ti}_{4.8}\text{O}_{16}$  were also prepared.  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Al}(\text{NO}_3)_3$  and  $\text{TiO}_2$  (anatase) were thoroughly mixed in the desired ratios in an agate mortar. The mixture was sintered in air at 1273 K for 1 h to decompose the nitrates. The resulting mixture was reground and sealed in a Pt capsule. The sample was then reacted under *solidus* conditions at 0.5 GPa pressure and 1673 K temperature for 0.5 h in a piston-cylinder apparatus. The products were examined by electron-microprobe and powder X-ray techniques. The electron-microprobe analyses were carried out by Mr N. Ware and are presented in Table 1.

### Crystal structure analysis

Several crystals were mounted on quartz glass fibres and preliminary Weissenberg ( $\text{Cu } K\alpha/\text{Mo } K\alpha$  radiation) and precession ( $\text{Mo } K\alpha$  radiation) photographs were taken. Exposure of the  $hk(0-2)$  and  $h(0-1)l$  layers, respectively, showed a tetragonal cell with Laue symmetry  $4/m$  and revealed systematic absences for reflections of the type  $h + k + l = 2n + 1$ , confirming the space group as  $I4/m$ ,  $I\bar{4}$ , or  $I4$ . Long-exposure rotation photographs ( $> 100 \text{ h}$ ) taken with the  $c$  axis as the rotation axis showed extra diffuse spectra between the Bragg layer lines. Reflections at 2

Table 2. Crystal data for  $(\text{Ba}_{0.98}\text{Ca}_{0.03}\text{Zr}_{0.02})\text{-}(\text{Al}_{1.10}\text{Ni}_{0.48}\text{Ti}_{6.4})\text{O}_{16}$ 

Tetragonal, $I4/m (C_{4h}^2, \text{No. } 87)$	
$a = 10.039 (1) \text{ \AA}$	$c = 2.943 (1) \text{ \AA}$
$V = 296.6 (1) \text{ \AA}^3$	$Z = 2$
$D_c = 4.23 \text{ Mg m}^{-3}$	$\mu(\text{Mo } K\alpha) = 8.466 \text{ mm}^{-1}$

$\times c$  as found for  $\text{BaFeMn}_7\text{O}_{16}$  (Mukherjee, 1964),  $3 \times c$  for  $\text{Ba}_{0.65}\text{Ru}_{2.7}\text{Cr}_{1.3}\text{O}_8$  (Cadée & Prodan, 1979) or  $2 \times a$  and  $c$  for redledgeite  $(\text{Mg,Ca,OH,H}_2\text{O}) \leq 2(\text{Ti}_{6.0}\text{-Cr}_{1.5}\text{Si}_{0.5})_8\text{O}_{16}$  (Strunz, 1963) and  $(\text{K,Ba})(\text{AlTi})_8\text{O}_{16}$  (Bayer & Hoffman, 1966) were not present.

The crystal chosen for data collection was irregular in shape with approximate dimensions  $0.100 \times 0.060 \times 0.025 \text{ mm}$  (elongated in the  $c$  direction). The crystal was mounted on to a computer-controlled fully automatic Picker FACS-1 four-circle diffractometer, with the  $c$  axis approximately parallel to the  $\phi$  axis of the diffractometer. Unit-cell dimensions and crystal-orientation matrix were obtained by least-squares refinement of the setting angles of twelve carefully centred reflections having  $2\theta$  values between  $50$  and  $60^\circ$ , using  $\text{Mo } K\alpha_1$  radiation ( $\lambda = 0.70926 \text{ \AA}$ ) reflected from a graphite-crystal monochromator. Crystal data are given in Table 2.

Intensity data were measured by the  $\theta$ - $2\theta$  continuous-scan technique with a scan speed of  $2^\circ \text{ min}^{-1}$  ( $2\theta$ ) and range from  $0.8^\circ$  below the  $K\alpha_1$  to  $0.8^\circ$  above the  $K\alpha_2$  peak for the reflection concerned. Stationary background counts of 20s duration were made at each extreme of the scan range and were assumed to vary linearly between these extremes. Three standard reflections had no significant variations in intensity throughout the course of the experiment. Intensities were collected for reflections having  $2\theta$  values between  $3$  and  $120^\circ$  and spanning one unique octant of reciprocal space. Of the 1248 reflections measured (excluding standards), 734 (59%) for which  $I > 3\sigma(I)$  were accepted as being significantly above background. After sorting and averaging, only the 624 unique reflections were used in subsequent calculations. These were reduced to  $F$  values in the usual way and corrected for absorption effects. The statistical discrepancy value for this data set  $R_s (= \sum \sigma / \sum |F_o|)$ , where  $\sigma$  is the error contribution to  $|F_o|$  from counting statistics alone) is  $0.040$ . Transmission factors for  $F_o$ , calculated by the analytical method of de Meulenaer & Tompa (1965), varied from  $0.825$  to  $0.903$ . Extinction effects were not observed as there were no intense low-angle reflections; consequently, no correction was made for these effects.

### Structure solution and refinement

Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974).

Two composite curves were calculated using the Al/Ni ratio and the Ca/Zr composition obtained from probe results (see analysis 1, Table 1).

The refinement was carried out using the full-matrix least-squares program *SFLS* (Prewitt, 1966) which minimizes the function  $\sum w(|F_o| - k|F_c|)^2$ , where  $k$  is an overall scale factor and  $w$  is the weight of an observation taken as unity in the initial stages and later as  $w(hkl) = 1/\sigma_2$  where  $\sigma_2 = \{\sigma_1^2 + 0.25[0.03(F_o)]^2\}^{1/2}$ .

Initial atomic coordinates from Byström & Byström (1950) were used in the refinement in space group  $I4/m$ . After several cycles of refinement, the discrepancy factor  $R$  (where  $R = \sum ||F_o| - k|F_c|| / \sum |F_o|$ ) remained at  $0.20$  with little shift from the initial atomic coordinates. Interestingly, both previous structural analyses (Byström & Byström, 1950; Dryden & Wadsley, 1958) reported high  $R$  values, of  $0.19$  and  $0.21$  respectively, at the completion of the structure solution.

At this stage, a three-dimensional Fourier map was calculated for the unique portion of the unit cell, using the phases calculated from the least-squares refinement. This clearly showed an elongated region of electron density on the  $c$  axis at the Ba position on  $(0,0,\frac{1}{2})$ . A second difference Fourier map was calculated using only phases derived from the Ti and the two O positions. This again showed a region of electron density elongated along the  $c$  axis and centred on  $(0,0,\frac{1}{2})$ ; however, we could now resolve two peaks, which were symmetrically related at  $(0,0,\pm z)$ . These  $4(e)$  positions, rather than  $2(b)$  sites, were assigned to the Ba atom which was then allocated an occupancy such that the contribution to the scattering was maintained at  $0.98$  Ba atoms per cell. Refinement using this model reduced the value of  $R$  to  $0.11$  using isotropic temperature factors and  $0.062$  with the introduction of anisotropic temperature factors.

Occupancies for Ba and Ti and for the composites Al/Ni, Ca/Zr were refined separately. Although the occupancies changed only slightly, the  $R$  value decreased to  $0.059$  and the weighted value  $R_w$  to  $0.058$  {where  $R_w = [\sum w(|F_o| - k|F_c|)^2 / \sum w|F_o|^2]^{1/2}$ }. An

Table 3. Final atomic coordinates and thermal parameters for  $\text{BaAl}_2\text{Ti}_6\text{O}_{16}$  with *e.s.d.*'s in parentheses

	Site	$x$	$y$	$z$	$B_{\text{eq}} (\text{Å}^2)$
A	4(e)	0.0	0.0	0.3845 (7)	2.18
B	8(h)	0.3512 (1)	0.1673 (1)	0.0	0.65
O(1)	8(h)	0.1539 (3)	0.2018 (3)	0.0	0.63
O(2)	8(h)	0.5410 (3)	0.1658 (3)	0.0	0.74
		$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$
A		0.015 (1)	0.015 (1)	0.054 (2)	0.0
B		0.010 (1)	0.010 (1)	0.006 (1)	0.0
O(1)		0.011 (1)	0.009 (1)	0.004 (1)	-0.002 (2)
O(2)		0.011 (2)	0.010 (1)	0.008 (1)	-0.001 (2)

$U_{13} = U_{23} = 0.0$ , from symmetry constraints.

Table 4. *Interatomic distances (Å) and angles (°) of BaAl<sub>2</sub>Ti<sub>6</sub>O<sub>16</sub> with e.s.d.'s in parentheses*

A—O(1)	2.787 (3) 4×	O(1)—A—O(1)	132.1 (1)
A—O(1)	3.126 (3) 4×		80.51 (4)
A—O(2)	3.397 (3) 4×		59.38 (5)
A—A	3.623 (4) 1×		168.5 (1)
	2.943 (1) 1×		103.61 (2)
	2.263 (4) 1×		109.2 (1)
			70.37 (4)
B—O(2)	1.905 (3) 1×	O(2)—B—O(2)	94.7 (1)
B—O(2)	1.950 (2) 2×		98.0 (1)
B—O(1)	1.974 (2) 2×	O(2)—B—O(1)	91.8 (1)
B—O(1)	2.011 (3) 1×		107.5 (1)
B—B	2.943 (1)		82.4 (1)
		O(2)—B—O(1)	173.4 (1)
			91.5 (1)
		O(1)—B—O(1)	96.4 (1)
			81.9 (1)

analysis of  $w(|F_o| - |F_c|)^2$  vs  $F_o$  and  $\sin \theta/\lambda$  showed no systematic trends, indicating an adequate weighting scheme. The standard deviation of an observation of unit weight was 1.45.

A difference Fourier map calculated at this stage showed residuals at (0,0,0.31) of  $4 e \text{ \AA}^{-3}$ , which is about  $3 e \text{ \AA}^{-3}$  above general background, and (0,0, $\frac{1}{2}$ ) of  $2.2 e \text{ \AA}^{-3}$ . Other refinements in space group *I4* resulted in increased *R* values with retention of the mirror symmetry especially about  $(h,k,\frac{1}{2})$ . This suggests *I4/m* as the correct space group. Final atomic parameters are presented in Table 3.\* Bond lengths and angles are shown in Table 4.

The *ANUCRYS Structure Determination Package* (Whimp, Taylor, McLaughlin & Kelly, 1977), as implemented on the Univac 1100/42 computer at the Australian National University, was used throughout the structure solution.

### Discussion

The structure determined from this study (Fig. 1)† consists of a framework of  $BO_6$  octahedra similar to that reported by Byström & Byström (1950) and Dryden & Wadsley (1958), forming channels running parallel to the *c* axis.

These authors placed the large *A* atoms on the special position 2(*b*) (0,0, $\frac{1}{2}$ ) within the channels. In our present study we have shown that the *A* atoms are incorrectly located on this site. The correct position for

\* A list of structure factors and a stereoview have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35235 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† A stereoview of the structure with the *z* axis vertical has been deposited. See previous footnote.

these cations is on special position 4(*e*) at (0,0, $\pm z$ ) with  $z = 0.3845$  (7), the mirror symmetry being preserved by partial occupancy of the two new sites. This positional shift for the *A* cation was also found from an X-ray study of a monoclinic hollandite by Cadée & Verschoor (1978) and a small shift (22%  $\times c$ ) was proposed for the tetragonal hollandite  $K_{1.54}Mg_{0.77}Ti_{7.23}O_{16}$  by Beyeler (1976) from an analysis of the supplementary diffuse spectra. The *A* atom in this position is enclosed by eight O(1) atoms, four at 2.787 Å and four at 3.126 Å. Four more O(2) atoms surround the *A* cation in the  $z = \frac{1}{2}$  plane; however, these lie at a greater distance of 3.397 Å.

The coordination of the *A* cation is thus considered to be essentially eightfold, although the four O(2) atoms will exert a small attractive force since they occupy spaces between the O(1) framework in a different plane.

For the *A* atoms to move along these channels involves passing through the square-planar arrangement of O(1) atoms above or below the 4(*e*) site. The size of the window defined by this oxygen framework and through which the Ba ions would have to pass is much smaller (half the diagonal distance across the window is 2.55 Å) than the sum of the Ba and O ionic radii (2.82 Å, Shannon & Prewitt, 1969). This cage-like arrangement of the O(1) and O(2) atoms around the *A* cations effectively immobilizes the large radwaste elements such as Ba, Cs and Rb. The effectiveness of these obstructions to *A*-cation movement through the tunnels has been conclusively shown by the intensive leaching tests of Ringwood *et al.* (1979a). The apparent ready diffusion of the *A* atoms from unit cell to unit cell proposed by Beyeler (1976) and Dryden & Wadsley (1958) on the basis of a.c. dielectric-constant measurements can be interpreted more reasonably as the movement of atoms from one equivalent 4(*e*) site to the other across the mirror at (0,0, $\frac{1}{2}$ ), within the O(1) framework. This is consistent with the results of Bernasconi, Beyeler & Strässler (1979) who found the value for the d.c. conductivity of  $K_{1.54}Mg_{0.77}Ti_{7.23}O_{16}$  to be negligible [ $< 10^{-7} (\Omega m)^{-1}$ ].

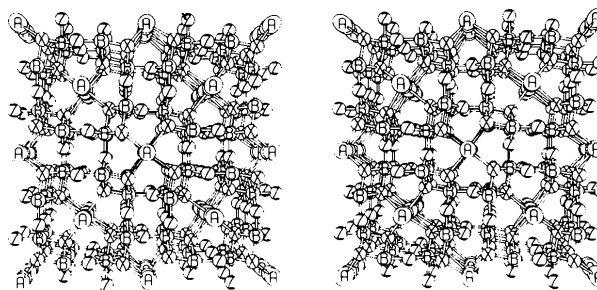


Fig. 1. Stereoscopic drawing (ORTEP II, Johnson, 1976) of  $BaAl_2Ti_6O_{16}$  viewed down the fourfold axis. *A* ≡ Ba, Ca, Zr; *B* ≡ Ti, Al, Ni; *X* ≡ O(1); *Z* ≡ O(2).

The magnitude of  $U_{33}$  for the  $A$  cation is very much larger than for the other atoms. Little mention of this unusually high value has been made elsewhere in the literature, although Cadée & Verschoor (1978) found a high value for the barium  $U_{22}$  in the monoclinic  $\text{Ba}_{0.7}\text{Sn}_{2.6}\text{Cr}_{1.4}\text{O}_8$  hollandite phase, and Fournès, Vlasse & Saux (1977) also reported a large isotropic  $B$  parameter for Tl in the hollandite-type structure  $\text{TlV}_5\text{S}_8$ . This large anisotropic thermal motion, together with the high residual at  $(0,0,0.31)$  and  $(0,0,\frac{1}{2})$  obtained from the difference Fourier map, indicates additional positional disorder such that the refined site is the most probable over a range.

The Al, Ni and Ti atoms are coordinated by six O atoms at the corners of distorted octahedra. These atoms are distributed randomly over the special position  $8(h)$ . This site is capable of accommodating a large range of elements varying both in size and charge (for examples see Cadée & Verschoor, 1978; Bayer & Hoffman, 1966; Ringwood *et al.*, 1979*a*). These substitutions are reflected in the cell volume, being smallest for the aluminium–silicon cation combination ( $V = 236.3 \text{ \AA}^3$ , Reid & Ringwood, 1969) and increasing for combinations of cations with larger ionic radii, *e.g.* titanium–gallium hollandite [ $298.9 (2) \text{ \AA}^3$ , Cadée & Verschoor, 1978]. To accommodate cation combinations with very large ionic radii, *e.g.* tin and indium [ $V = 353.5 (2) \text{ \AA}^3$ ], the hollandite structure distorts slightly, lowering the symmetry to monoclinic. The volume change from the smallest to the largest hollandite compound cited above represents almost a 50% increase with the symmetry change occurring between 290 and  $300 \text{ \AA}^3$ .

Endo, Kume, Kinomura & Koizumi (1976) report a monoclinic hollandite structure for the phase  $\text{K}_2\text{Cr}_8\text{O}_{16}$ . Conversion of the lattice parameters of this phase from  $C2/m$  ( $a = 13.820$ ,  $b = 2.941$ ,  $c = 9.772 \text{ \AA}$ ,  $\beta = 135^\circ$ ) to  $I2/m$  results in the cell edges  $a = c = 9.772 \text{ \AA}$  and  $\beta = 90^\circ$ . This suggests a tetragonal hollandite structure, as could be expected from the small ionic radii of  $\text{Cr}^{3+}$  and  $\text{Cr}^{4+}$  and small volume ( $280.8 \text{ \AA}^3$ ).

Each O(1) atom is coordinated to two  $A$  atoms and three octahedral metal atoms. The O(2) atoms are coordinated to three octahedral metal atoms only.

As mentioned previously, a long-exposure rotation photograph showed bands of diffuse scattering between the layer lines. This phenomenon has also been reported by various other investigators. Beyeler (1976) showed that the diffuse scattering arises only from the Ba ions in the tunnels and has modelled it on the basis of cation ordering within the channels. In our present case the diffuse planes are situated at approximately 0.33 of a reciprocal-lattice cell from the Bragg planes along the  $c$  direction.

At 50% occupancy only one  $A$  site in four need be occupied, that is, one in every two unit cells (Fig. 2*a*). However, at higher Ba concentrations adjacent cells

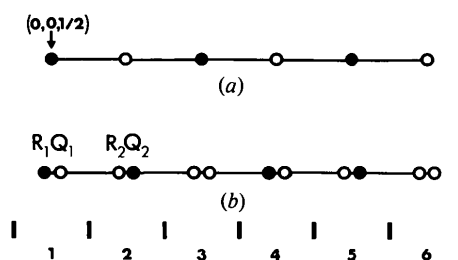


Fig. 2. A schematic diagram of channels showing six unit cells parallel to  $c$  (a) at 50% Ba occupancy, (b) at higher occupancies. ● = occupied site, ○ = vacant site.

will sometimes be occupied (Fig. 2*b*). Even at concentrations lower than 50% there is a probability that this will occur, assuming a random growth distribution of occupied and unoccupied cells. Since the original  $A$  site on  $(0,0,\frac{1}{2})$  has now been split into two sites, the problem of the close separation of  $A$  atoms in adjacent unit cells ( $2.943 \text{ \AA}$  apart in the original model) can now be more readily accommodated. If an  $A$  atom resides in site  $R_1$  (Fig. 2*b*), then the probability of finding an  $A$  atom at  $Q_1$  will be zero due to size constraints. The probability of finding atoms in both  $Q_1$  and  $R_2$  will be negligible, again due to charge and size constraints [ $Q_1 - R_2 = 2.263 (4) \text{ \AA}$ ], and at positions  $R_1$  and  $R_2$ , *i.e.* one unit cell apart, the probability will be the same as the original model. Occupied sites  $R_1$  and  $Q_2$  will be the most favoured when adjacent cells are occupied on the basis of both steric [ $R_1 - Q_2 = 3.623 (4) \text{ \AA}$ ] and electrostatic considerations. The displacements of the  $A$  ions from their idealized sites can therefore be attributed to the mutual steric and electrostatic repulsion which occurs when adjacent cells are occupied. Using the constraint that only sites whose distance is greater than and equal to  $R_1 - Q_2$  are occupied, then variable repeat distances are attainable, *i.e.* the stoichiometry of the crystal varies along the channels. It is only by examining the diffuse scattering that the true ordering/disordering pattern of the  $A$  atoms will become known. Optical-modelling experiments for such a purpose are currently being undertaken.

The maximum composition of the large univalent cations  $\text{Rb}^+$  and  $\text{K}^+$  in these channels corresponds to full occupancy (Bayer & Hoffman, 1966). Although these cations are somewhat larger than  $\text{Ba}^{2+}$ , the repulsive force has decreased, thus enabling these atoms to be stable on sites at one unit-cell distance apart. This implies a possibility that, at full or near-full occupancy, the univalent cations could conceivably be placed on special position 2(*b*)  $(0,0,\frac{1}{2})$  as found for  $\text{K}_2\text{Cr}_8\text{O}_{16}$  (Endo *et al.*, 1976). On the other hand, Beyeler (1976) has proposed a shift from the  $(0,0,\frac{1}{2})$  position for  $\text{K}^+$  in  $\text{K}_{1.54}\text{Mg}_{0.77}\text{Ti}_{7.23}\text{O}_{16}$  hollandite, although in this structure the  $A$  site is only partially occupied. In the case of  $\text{Cs}^+$ , Bayer & Hoffman (1966)

produced only non-stoichiometric phases of  $Cs_xAl_xTi_{8-x}O_{16}$ . They concluded that the ionic radius of  $Cs^+$  is too large for every unit cell to be occupied. Ringwood *et al.* (1979a) have shown Cs to readily replace Ba in  $BaAl_2Ti_6O_{16}$  hollandite, forming an extensive solid-solution series.

The microprobe analyses of the Ba-hollandite show the Ba composition to extend over a wide range with  $x$  varying from 0.3 to 1.2, in agreement with Dryden & Wadsley (1958). This upper Ba composition is also within the theoretical maximum value of  $x$  ( $= 1.33$ ) using the model in Fig. 2(b) and assuming that during growth there was always a Ba atom available to occupy a vacant site and that only steric and charge constraints prevented it from doing so.

These formulae, however, do not follow the general stoichiometry of  $A_x(B_{2x}Ti_{8-2x})O_{16}$ , although each individual charge gave homogeneous analyses. Furthermore, the X-ray powder photographs showed typical hollandite-type patterns. Interpretation of these analyses is made difficult by the overlap of the Ba  $La$  and Ti  $K\alpha$  lines, resulting in large errors ( $\pm$  several percent) for the weight percent of these elements. Thus, the compositions presented here should only be used as a guideline, and are not necessarily inconsistent with hollandite stoichiometry.

Both X-ray photographs and microprobe analyses confirmed the presence of additional phases of rutile,  $Al_2TiO_5$ , and a Ba,Ti aluminate co-existing with Ba-hollandite.

The Na analogue of this series,  $Na_x(Al_yTi_{8-y})O_{16}$ , behaves differently from the other large cations, in forming the  $Na_xTiO_2$ -type structure (Bayer & Hoffman, 1965). Although a small amount of Na has been reported to substitute in the  $A$  cation site (see *e.g.* Norrish, 1951) the application of a large amount of pressure is needed to stabilize this cation in the hollandite-type structure (Ringwood, Reid & Wadsley, 1967).

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