

## Crystal chemistry of lead aluminosilicate hollandite: A new high-pressure synthetic phase with octahedral Si

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### ABSTRACT

Single crystals of lead aluminosilicate hollandite, with composition  $Pb_{0.8}Al_{1.6}Si_{2.4}O_8$ , have been synthesized at 16.5 GPa and 1450 °C. Crystals are tetragonal [space group  $I4$ ,  $Z = 2$ ,  $a = 9.414(3)$ ,  $c = 2.750(3)$  Å,  $V = 243.7(3)$  Å<sup>3</sup>]. Si and Al are disordered on the octahedral site. Pb is best modeled by two atom sites, one on the fourfold axis and the other split, lying off the fourfold axis. This feature was predicted by Post and Burnham (1986) but not previously observed.

### INTRODUCTION

Hollandite-type compounds possess a general chemical formula  $A_xB_8O_{16}$ , where A represents large mono- or divalent cations with  $x \leq 2$ , and B represents smaller, two- to five-valent cations. The basic structure accommodates a large variety of chemical species, with reported  $A = Ag, Ba, Cl, Cs, K, Na, Pb, Rb, Sr,$  and  $Tl$ , and  $B = Al, Co, Cr, Cu, Fe, Ga, Ge, In, Mg, Mn, Ni, Sb, Sc, Si, Sn, Ti,$  and  $Zn$ , forming some 30 different end-member compositions (Pentlinghaus, 1978).

The crystal structure of hollandite,  $BaMn_8O_{16}$ , was first solved by Byström and Byström (1950). They showed that the ideal structure has tetragonal symmetry,  $I4/m$ , with B cations octahedrally coordinated to O atoms and forming an edge- and corner-sharing framework structure with two types of one-dimensional channels that are  $1 \times 1$  and  $2 \times 2$  octahedra wide (Fig. 1). The large A-type cations occupy the  $2 \times 2$  channels and are ideally located at the intersection of the mirror and the fourfold axis of rotation, i.e., at the Wyckoff position  $2b$ ,  $(0,0,1/2)$ . They are coordinated with eight O atoms, all at equal bond lengths, located at the corners of a rectangular prism.

The unit-cell volume is completely dependent on the B-O bond length (Post et al., 1982; Cheary, 1986), and consequently the size of the channels is independent of the size of the A cation. Cheary (1986) suggested that if the channel cation is too small for the size of the tunnel, then  $x < 2$  and the tunnel cation tends to occupy a position along the fourfold axis but offset from the mirror. The amount of offset is correlated with the number of vacancies in the tunnel. Diffuse streaks in X-ray and electron diffraction patterns indicate that vacancies are probably ordered (Beyeler, 1976). The resulting superlattice periodicities along the  $c$  axis are commensurate or incom-

mensurate, depending on the number of vacancies. Beyeler (1976) suggested that the ordering is due to tunnel cation-cation electrostatic interactions that force the vacancies to be positioned at regular intervals. On the other hand, Post et al. (1982) argued that the displacement of the tunnel cations is a function of their size and that smaller cations tend to be displaced from the special position because they prefer to be closer to the nearest coordinating O atoms. Larger cations remain on the special positions. Using energy-structure modeling, Post and Burnham (1986) demonstrated that the positions of the tunnel cations are a function of the positions of the octahedral cations with differing valences, and they showed that tunnel cations must occupy a variety of different positions because no structures have been found with ordering of the octahedral cations. Furthermore, their calculations reveal that there is no reason for the tunnel cation to be constrained to occupy a position along the fourfold axis.

Post et al. (1982) also showed that the symmetry depends on the ratio of the average ionic radius of B to that of A. When  $r_B/r_A > 0.48$  the tunnel cations are too small for the tunnel, and so the octahedra tilt, the tunnel walls distort, and the symmetry is reduced to monoclinic,  $I2/m$ . An additional symmetry dependence was demonstrated by Kudo et al. (1990), who transformed a tetragonal cryptomelane to monoclinic symmetry by increasing the tunnel-site cation occupancy.

Because it accommodates many chemical species, the hollandite structure has been considered as a host for high-level radioactive wastes along with perovskite and zirconolite in the synthetic titanate ceramic Synroc (Ringwood et al., 1979; Smith and Lumpkin, 1993). The role of the hollandite structure is to immobilize the Ba, Cs, and Rb isotopes. In surprising dichotomy, Beyeler (1976)

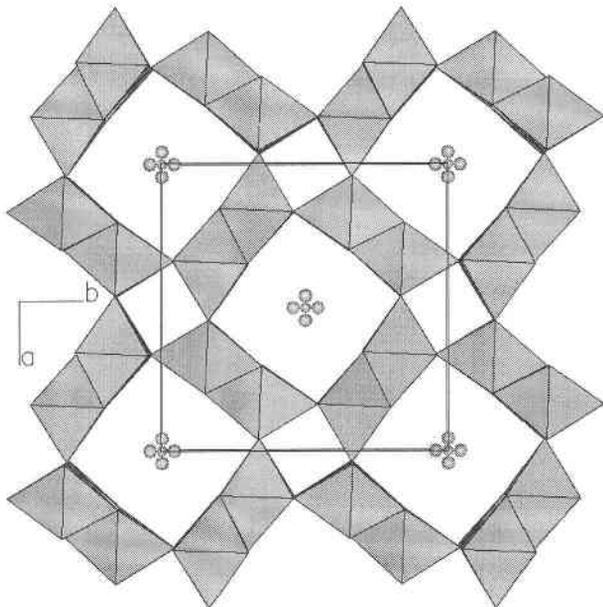


Fig. 1. A representation of the crystal structure of lead aluminosilicate hollandite viewed down the  $c$  axis. The  $(\text{Al,Si})\text{O}_6$  polyhedra are represented as solid octahedra, with the O atoms at the corners and the Al and Si atoms at the centers. The Pb atoms are shown as spheres, with Pb2 on the fourfold axis and Pb1 on a split site located off the fourfold axis. In the idealized hollandite structure, the A cation is located on the fourfold axis. The unit cell is indicated by the solid lines.

demonstrated that, because of its channel vacancies, the hollandite structure behaves as a classic example of a one-dimensional electrochemical superionic conductor.

Ringwood et al. (1967) transformed sanidine at 900 °C and 12 GPa into the hollandite structure, with Al and Si randomly occupying the octahedral sites. This was the first oxide structure identified with both Al and Si displaying sixfold coordination and only the second, after stishovite, with  $^{60}\text{Si}$ . They postulated that because feldspars are the most abundant minerals in the Earth's crust, it is possible that the hollandite structure, with  $^{60}\text{Si}$  and  $^{60}\text{Al}$ , may be a common phase within the transition zone of the mantle. Subsequently, Reid and Ringwood (1969) systematically examined feldspar structure-type materials to identify others that would transform to the hollandite structure at high pressures. They were able to synthesize  $\text{Sr}_x\text{Al}_{2x}\text{Si}_{4-2x}\text{O}_8$  and  $\text{Ba}_x\text{Al}_{2x}\text{Si}_{4-2x}\text{O}_8$ ,  $x \approx 0.75$ , with the hollandite structure but failed with the Na-, Ca-, and Rb-rich feldspars. Yamada et al. (1984) determined the structure of the  $\text{KAlSi}_3\text{O}_8$  phase by X-ray powder diffraction methods, and Zhang et al. (1993) reported the structure obtained from a single crystal as a function of pressure.

Madon et al. (1989) reported that their synthesis of  $(\text{Ca}_{0.5}\text{Mg}_{0.5})\text{Al}_2\text{Si}_2\text{O}_8$  at 50 GPa and laser-induced high temperatures exhibited an X-ray powder diffraction pattern consistent with hollandite. Liu (1978) reported the synthesis of  $\text{NaAlSi}_3\text{O}_8$  hollandite at 21–24 GPa from jadeite and stishovite. Above 24 GPa the  $\text{NaAlSi}_3\text{O}_8$  hol-

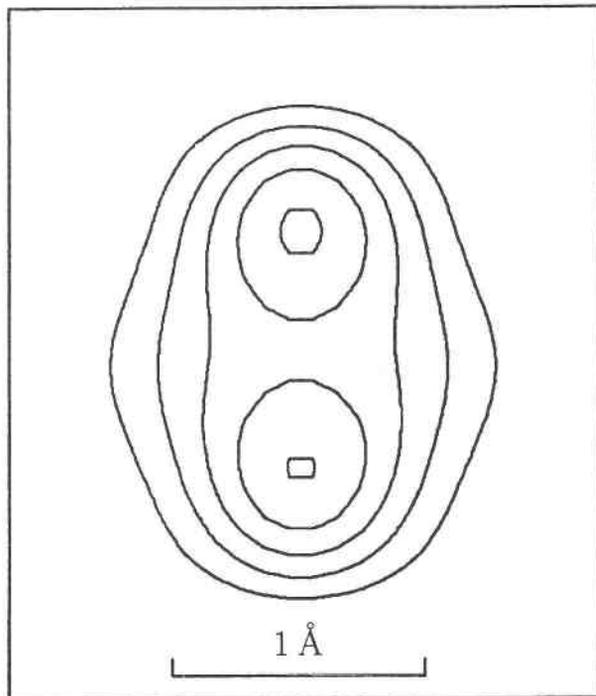


Fig. 2. A difference-Fourier map of the lead aluminosilicate hollandite structure viewed along the  $b$  axis with Pb removed from the model. The  $c$  axis is vertical. The contour lines are at  $20 \text{ e}/\text{\AA}^3$  intervals. In the idealized hollandite structure, the A cation is located in the center of the map, but in our study the Pb atoms are at nonequivalent split sites as indicated.

landite transforms to the calcium ferrite structure. In this paper we report the structure of yet another aluminosilicate phase with the hollandite structure,  $\text{Pb}_{0.8}\text{Al}_{1.6}\text{Si}_{2.4}\text{O}_8$ .

#### EXPERIMENTAL METHODS

In his study of the high-pressure stability fields of pyroxenes and their transformations to garnet, Gasparik (1989) synthesized an unknown purple phase to which he assigned a composition of  $\text{PbAl}_2\text{Si}_3\text{O}_{10}$  on the basis of microprobe analysis. The unknown phase was created in the split-sphere, cubic anvil apparatus (USSA-2000, SUNY expt. 520) from a starting mixture of synthetic jadeite, orthoenstatite, and orthopyroxene of composition  $\text{En}_{44}\text{Py}_{56}$  at 1450 °C and 16.5 GPa for 7.3 h with a Pb flux.

We obtained an irregularly shaped crystal of this unknown phase (approximately  $15 \times 15 \times 35 \mu\text{m}$  in size), mounted it on a Rigaku AFC-5R diffractometer operated at 45 kV and 180 mA with monochromatic  $\text{MoK}\alpha$  radiation ( $\lambda = 0.7093 \text{ \AA}$ ), and centered a set of 15 reflections in the region  $18^\circ < 2\theta < 27^\circ$ . Cell parameters were refined to values of  $a = 9.414(3)$  and  $c = 2.750(3) \text{ \AA}$ , with a unit-cell volume of  $243.7(3) \text{ \AA}^3$ , based on a tetragonal body-centered lattice. Unconstrained cell parameters deviate from tetragonal symmetry by less than one standard deviation. The cell parameters and intensity distribution of the reflections indicate a hollandite structure type. This

**TABLE 1.** A summary of the refinement results for lead aluminosilicate hollandite

No. obs.	830
No. unrej. obs. ( $F_o > 4\sigma_{F_o}$ )	433
$R_{int}$	0.058
$R_w$	0.045
Space group	$I4$
$a$ (Å)	9.414(3)
$c$ (Å)	2.750(3)
$V$ (Å <sup>3</sup> )	243.7(3)

requires that the composition of the crystal should be rewritten as  $Pb_{0.8}Al_{1.6}Si_{2.4}O_8$  with 20% vacancy in the tunnels. To check if the vacancies show positional order we searched for superstructure reflections by recording slow continuous scans from 0 0 0.15 to 0 0 3, but no peaks other than the strong 0 0 2 were found. Therefore, even if the vacancies along a given channel are periodic, their positions cannot be correlated between neighboring tunnels.

A hemisphere of intensity data was measured to  $2\theta = 60^\circ$  [ $(\sin \theta)/\lambda = 0.70$ ] using profiles from  $\omega$  step scans. The intensities were converted to structure factors, and an absorption correction was applied using the shape of the crystal and a mass absorption coefficient of  $288.3 \text{ cm}^{-1}$  (modified after Burnham, 1966). Additional absorption corrections were made during refinement of the structure using the analytical function of Katayama (1986). Neutral atomic scattering factors (Doyle and Turner, 1968) as well as real and imaginary anomalous dispersion corrections were used to model the electron distribution. The structure was initially refined in space group  $I4/m$  using a revised version of RFINE4 (Finger and Prince, 1975) and starting parameters from  $KAlSi_3O_8$  hollandite (Zhang et al., 1993) with Pb occupying the special position  $2b$  at  $(0,0,1/2)$ . The best fit to this model gave an unsatisfactory value of 20% for the  $R$  factor and a value  $B_{Pb} > 10 \text{ \AA}^2$  for the isotropic displacement factor of Pb.

We then constructed a difference-Fourier map with Pb removed from the model (Fig. 2). This figure indicates that Pb appears to occupy a split site along the fourfold axis. Refining this model, we located Pb at  $(0,0,1/2 \pm 0.14)$ , a displacement of  $0.385 \text{ \AA}$  from the special position, with  $B_{Pb} = 6.3 \text{ \AA}^2$ , and improved the  $R$  factor to 11%. However, an isotropic displacement factor this large still signifies positional disorder. Therefore, the symmetry was lowered to  $I4$ , and the split Pb site was refined as two nonequivalent atoms with  $B_{Pb}$  constrained to be the same for both sites. This model refined to an occupancy of 0.62

**TABLE 2.** A summary of the refined atomic parameters for lead aluminosilicate hollandite

Atom	$x$	$y$	$z$	$B_{eq}$ (Å <sup>2</sup> )	Occupancy
Pb1	0.0435(5)	0.0	0.4146(28)	1.5(1)	0.466(7)
Pb2	0.0	0.0	0.7179(28)	1.5(1)	0.334(7)
Si,Al	0.3510(4)	0.1638(4)	0.0	0.61(6)	0.6,0.4
O1	0.1546(6)	0.2016(7)	0.0	0.4(1)	1.0
O2	0.5418(6)	0.1641(7)	0.0	0.4(1)	1.0

**TABLE 3.** A summary of the bond lengths (Å) for lead aluminosilicate hollandite

(Si,Al)-O1	1.883(7)
(Si,Al)-O1 × 2	1.871(5)
(Si,Al)-O2	1.796(6)
(Si,Al)-O2 × 2	1.797(4)
Mean (Si,Al)-O	1.836(1)
Pb1-O1	2.449(7)
Pb1-O1	2.700(8)
Pb1-O1	2.957(8)
Pb1-O1	2.895(7)
Pb1-O1	2.374(8)
Pb1-O1	2.632(8)
Pb1-O2	2.791(8)
Mean Pb1-O	2.685(3)
Pb2-O1 × 4	2.514(7)

for Pb1 at  $(0,0,0.33)$  and 0.20 for Pb2 at  $(0,0,0.65)$ , with  $B_{Pb} = 5.9 \text{ \AA}^2$ . The  $z$  coordinate of the octahedral cation was fixed at 0.0 to establish an origin, and the  $z$  coordinates of the O atoms were refined to 0.0 within one standard deviation. The  $R$  factor improved to 10%. Next, the  $x$  and  $y$  coordinates of the Pb atoms were allowed to vary from 0.0 so that Pb was no longer constrained to lie on the fourfold symmetry axis. The  $x$  and  $y$  coordinates of Pb2 did not deviate from the symmetry axis, however Pb1 shifted  $0.4 \text{ \AA}$  along the  $x$  direction. Furthermore,  $B_{Pb}$  assumed a reasonable value of  $1.5 \text{ \AA}^2$ , and the  $R$  factor dropped to 4.5%. Because this  $R$  factor was less than  $R_{int} = 5.8\%$ , further processing of the data would be statistically meaningless, and so the refinement was halted at this point. The details of the refinement are summarized in Tables 1 and 2, and calculated bond lengths are listed in Table 3. Observed and calculated structure factors are listed in Table 4.<sup>1</sup>

## RESULTS

The ratio  $r_B/r_A$  for this structure is 0.35. This is less than the critical value of 0.48 determined by Post et al. (1982) to correlate with the reduction in symmetry to  $I2/m$ , and it is consistent with the observed symmetry. Ordering of cations in the octahedral B site has never been observed in any hollandite structure, including lead aluminosilicate hollandite. The B site consists of 40% Al and 60% Si with an average bond length of  $1.836 \text{ \AA}$ , consistent with a predicted bond length of  $1.840 \text{ \AA}$ , on the basis of an Si-O bond length of  $1.775 \text{ \AA}$  in stishovite (Ross et al., 1990) and a  $(Al_{0.25}Si_{0.75})$ -O bond length of  $1.816 \text{ \AA}$  in  $KAlSi_3O_8$  hollandite (Zhang et al., 1993). The octahedra are distorted, with edge-sharing dimensions ( $2.42$ – $2.44 \text{ \AA}$ ) shorter than nonedge-sharing dimensions ( $2.63$ – $2.66 \text{ \AA}$ ), as is usual for edge-sharing polyhedra.

The most important structural feature of this study is the distribution of Pb atoms, in particular that the refined position of the Pb1 atom is off the fourfold axis. This

<sup>1</sup> A copy of Table 4 may be ordered as Document AM-95-597 from the Business Office, Mineralogical Society of America, 1015 Eighteenth Street NW, Suite 601, Washington, DC 20036. Please remit \$5.00 in advance for the microfiche.

feature has not been previously observed in a hollandite structure, and the observation confirms the prediction of the Post and Burnham (1986) study that was based on the model that the A cation is displaced from the special position to shorten its closest A-O bond lengths. However, the displacement could also be a consequence of Pb-Pb repulsions. The Pb-Pb separation in FCC Pb metal is 3.5 Å, a value that is 0.75 Å longer than the *c*-cell edge in this study. If the occupancy of Pb were 1.0, then the Pb-Pb separation in this study would be 2.750 Å. With the displacement of the Pb atom from the special position, Pb-Pb separation may increase to 2.86 Å, and with an occupancy of 0.8, the Pb-Pb separation approaches 3.58 Å, a value that is similar to that in Pb metal.

It is not clear why Pb<sup>2+</sup> would occupy a position along the fourfold axis; however, the refinement results strongly support this. It is possible that Pb is quite disordered and actually occupies many positions. Furthermore, electron lone-pair effects are often significant for Pb atoms. However, the occupancy of the Pb atom and the Si-Al ratio are similar to those observed by Reid and Ringwood (1969) for Sr- and Ba-rich hollandite, and so it may be assumed that the crystal chemistry of these structures is similar. If their crystal chemistry is similar, then the lone-pair effects of Pb could be clarified through single-crystal structural studies of Sr- and Ba-rich hollandite.

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