

Fig. 1. The layer of  $[\text{Ca}.6\text{CO}(\text{NH}_2)_2]^{2+}$  cations, parallel to the  $bc$  plane, with the adjacent layers of bromide anions. Dot-dashed lines show the tessellation of  $\text{Br}^-$ , dotted lines denote hydrogen bonds. One urea molecule from the upper layer, drawn in heavier lines, is added to show the complete environment of the  $\text{Br}^-$  ions.

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## Refinement of the Crystal Structure of Brewsterite, $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Al}_4\text{Si}_{12}\text{O}_{32} \cdot 10\text{H}_2\text{O}$

BY J. L. SCHLENKER, J. J. PLUTH AND J. V. SMITH

*Department of the Geophysical Sciences, University of Chicago, Chicago, Illinois 60637, USA*

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**Abstract.** Brewsterite, composition derived from electron microprobe analysis:  $(\text{K}_{0.01}\text{Ba}_{0.24}\text{Sr}_{0.71})_2\text{Al}_{4.1}\text{Si}_{11.9}\text{O}_{32} \cdot n\text{H}_2\text{O}$ ,  $a = 6.793$  (2),  $b = 17.573$  (6),  $c = 7.759$  (2) Å,  $\beta = 94.54$  (3)°,  $P2_1/m$ , has a full occupancy of two cation and ten water sites. The Sr, Ba atom is bonded to five water molecules at 2.63–2.83 Å and four framework O atoms at 2.83 and 2.89 Å. Pairs

of water molecules at 2.98 or 3.07 Å alternate with Sr, Ba along  $a$  and  $c$  to form a two-dimensional system of intersecting chains. Distances between water molecules and framework O atoms range upwards from 2.90 Å. Hydrogen bonding is likely but no unique model is apparent. Tetrahedral distances indicate ~0.3 Al in site  $T(A)$ , ~0.4 Al in  $T(B)$  and  $T(C)$ , and ~0 Al

in  $T(D)$ . The perturbation of an individual  $T-O$  distance from the mean of its host tetrahedron [ $\Delta(T-O)$ ] correlates with  $\sec(T-O-T)$  as  $\Delta(T-O) = -0.072 - 0.057 \sec(T-O-T)$ , correlation coefficient 0.75, in accord with extended Hückel molecular-orbital theory. The coefficient 0.057 is smaller than the value 0.132 for dehydrated H-mordenite, in accord with theoretical expectation for the greater mean electronegativity of tetrahedral cations in mordenite than in brewsterite.

**Introduction.** The crystal structure of brewsterite, originally determined by Perrotta & Smith (1964), was refined to provide data for testing models on the crystal chemistry of zeolites.

Electron microprobe analysis yielded the composition  $K_{0.02}Ba_{0.48}Sr_{1.42}Al_{4.12}Si_{11.95}O_{32} \cdot nH_2O$ . This does not give an exact valence balance, probably because of unquantifiable errors in the correction factors referred to feldspar standards (ARL microprobe, *GLAB* program), and the formula  $(K_{0.02}Ba_{0.50}Sr_{1.48})Al_{4.0}Si_{12.0}O_{32} \cdot 10H_2O$  may be the best approximation to the chemical composition.

A cleavage fragment ( $0.3 \times 0.08 \times 0.2$  mm along **a**, **b** and **c** respectively) was mounted with the **b** axis oriented on a Picker FACS-1 diffractometer, and 7299 diffractions (maximum  $2\theta$   $55^\circ$ ; Mo  $K\alpha$ ;  $\theta-2\theta$  scan at  $2^\circ \text{ min}^{-1}$ ) from two octants yielded 2505 averaged diffractions in  $P2_1/m$ , stronger than  $3\sigma(F^2)$ . After correction for absorption ( $\mu = 31 \text{ cm}^{-1}$ ) and  $L_p$  factors, equivalent diffractions were averaged with the expressions given in Rinaldi, Pluth & Smith (1975). Refinement with the Ibers *NUCLS* program utilized half-ionized scattering factors and anomalous-

scattering corrections (Ibers & Hamilton, 1974) weighted according to the electron microprobe analysis. The final  $R$  and  $R_w$  are 0.046 and 0.059 respectively.

Table 1 shows positional and displacement parameters, and Table 2 the interatomic distances calculated with the *ORFFE* program (Busing, Martin & Levy, 1964).\*

**Discussion.** Brewsterite (group 7 zeolite; Breck, 1974) is a framework silicate which can be decomposed mathematically into  $T_{10}O_{20}$  chains along **a**. These are connected into sheets by single four-rings, and the sheets are linked by bridging oxygens across mirror planes to give the framework (Fig. 1). A two-dimensional channel system is formed by the intersection of channels along **a** and **c**. The Sr, Ba atoms, located between the sheets at the intersection of the channels, are surrounded by five  $H_2O$  at 2.63–2.83 Å and four framework O atoms at 2.83 and 2.89 Å (Fig. 2). The irregular coordination polyhedron is approximated by a capped trigonal prism modified by adding three apices in the horizontal plane with consequent change of each vertical face into four triangular faces. Addition of three more apices in the horizontal plane would give the polyhedron in hexagonal close packing. The next nearest neighbour to Sr, Ba is O(9) at 3.18 Å.

A two-dimensional system of alternating Sr, Ba and water molecules occurs along **a** and **c**. Down **c**, the chain consists of Sr, Ba– $W(4)$ – $W(1)$ –Sr, Ba with

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32677 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

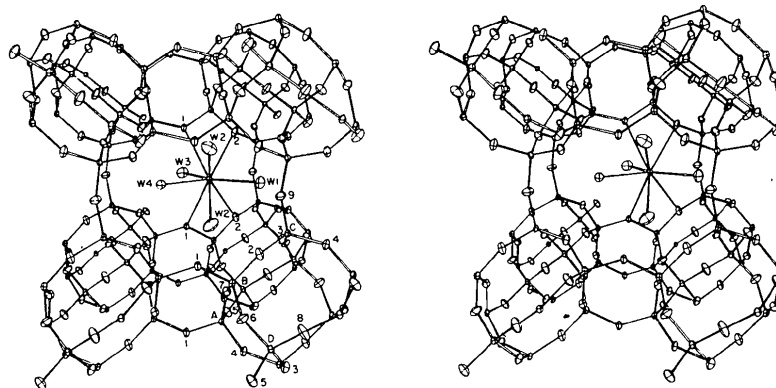
Table 1. Atomic coordinates ( $\times 10^4$ ) and thermal parameters ( $\times 10^4$ )

The anisotropic temperature factor is in the form  $\exp\left(-\sum_{j=1}^3 \sum_{i=1}^3 \beta_{ij} h_i h_j\right)$

Type	x	y	z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	
T(A)	4(f)	3218 (2)	812 (1)	8224 (2)	54 (3)	13 (1)	29 (2)	1 (1)	2 (2)	–0 (1)
T(B)	4(f)	4054 (2)	566 (1)	2108 (2)	68 (3)	12 (1)	36 (2)	1 (1)	5 (2)	1 (1)
T(C)	4(f)	5553 (2)	1582 (1)	5336 (2)	64 (3)	11 (1)	31 (2)	2 (1)	7 (2)	2 (1)
T(D)	4(f)	9087 (2)	528 (1)	6410 (2)	50 (3)	10 (1)	36 (2)	2 (1)	0 (2)	–1 (1)
O(1)	4(f)	3501 (6)	1059 (2)	283 (4)	122 (10)	18 (1)	37 (6)	–3 (3)	9 (6)	–2 (2)
O(2)	4(f)	4218 (6)	1240 (2)	3607 (5)	104 (10)	29 (2)	62 (6)	8 (3)	9 (6)	–13 (3)
O(3)	4(f)	7825 (6)	1211 (2)	5454 (5)	96 (9)	19 (1)	71 (6)	13 (3)	12 (6)	9 (2)
O(4)	4(f)	4500 (6)	1408 (2)	7150 (5)	117 (10)	21 (1)	54 (6)	1 (3)	29 (6)	6 (2)
O(5)	4(f)	850 (6)	920 (2)	7615 (5)	81 (9)	25 (2)	97 (7)	22 (3)	–22 (6)	–20 (3)
O(6)	4(f)	2228 (6)	9966 (2)	2388 (6)	139 (11)	22 (2)	128 (8)	–12 (3)	22 (7)	21 (3)
O(7)	4(f)	3851 (6)	9921 (2)	7952 (5)	94 (9)	16 (1)	74 (6)	6 (3)	5 (6)	–4 (2)
O(8)	2(c)	0	0	5000	189 (18)	30 (3)	96 (11)	29 (5)	–15 (11)	–30 (4)
O(9)	2(e)	5718 (10)	2500	4994 (8)	204 (18)	14 (2)	134 (12)		89 (12)	
Sr, Ba	2(e)	2501 (1)	2500	1780 (1)	80 (1)	9 (1)	42 (1)		5 (1)	
H <sub>2</sub> O(1)	2(e)	598 (12)	2500	4699 (9)	256 (23)	40 (3)	123 (14)		63 (14)	
H <sub>2</sub> O(2)	4(f)	9286 (9)	1474 (4)	1518 (8)	234 (17)	45 (3)	299 (16)	7 (5)	79 (13)	35 (5)
H <sub>2</sub> O(3)	2(e)	5996 (11)	2500	241 (11)	185 (20)	37 (3)	224 (19)		67 (15)	
H <sub>2</sub> O(4)	2(e)	665 (13)	2500	8660 (9)	395 (28)	22 (2)	112 (13)		–17 (15)	

Table 2. Selected bond lengths (Å) and angles (°)

$T(A)-O(1)$	1.652 (4)	$T(B)-O(1)$	1.677 (4)	Cation coordination			
$T(A)-O(4)$	1.634 (4)	$T(B)-O(2)$	1.657 (4)	$Sr-W(4)$	2.634 (7)	$Sr-W(1)$	2.695 (7)
$T(A)-O(5)$	1.651 (4)	$T(B)-O(6)$	1.656 (4)	$Sr-W(3)$	2.740 (7)	$2Sr-W(2)$	2.827 (6)
$T(A)-O(7)$	1.642 (4)	$T(B)-O(7)$	1.664 (4)	$Sr-O(2)$	2.831 (4)	$2Sr-O(1)$	2.889 (4)
Average	1.645	Average	1.664	Water coordination			
$T(C)-O(2)$	1.671 (4)	$T(D)-O(3)$	1.620 (4)	$2W(1)-O(3)$	3.032 (6)	$O(3)-W(1)-O(3)$	96.6 (3)
$T(C)-O(3)$	1.671 (4)	$T(D)-O(5)$	1.614 (4)	$W(1)-W(4)$	3.070 (10)	$2W(4)-W(1)-O(3)$	76.5 (2)
$T(C)-O(4)$	1.656 (4)	$T(D)-O(6)$	1.598 (4)	$W(2)-W(3)$	2.980 (9)	$2Sr-W(1)-O(3)$	120.6 (2)
$T(C)-O(9)$	1.640 (2)	$T(D)-O(8)$	1.597 (1)	$W(2)-O(6)$	3.355 (7)	$Sr-W(1)-W(4)$	150.6 (4)
Average	1.660	Average	1.607	$W(2)-O(7)$	3.295 (7)	$W(3)-W(2)-O(6)$	164.6 (3)
$O(1)-T(A)-O(4)$	107.4 (2)	$O(1)-T(B)-O(2)$	102.8 (2)	$W(2)-O(7)$	3.607 (12)	$W(3)-W(2)-O(7)$	90.9 (2)
$O(1)-T(A)-O(5)$	106.4 (2)	$O(1)-T(B)-O(6)$	108.7 (2)	$W(2)-W(2)$		$W(3)-W(2)-Sr$	101.1 (2)
$O(1)-T(A)-O(7)$	111.3 (2)	$O(1)-T(B)-O(7)$	112.1 (2)	$2W(3)-W(2)$	2.980 (9)	$O(6)-W(2)-O(7)$	76.6 (2)
$O(4)-T(A)-O(5)$	109.1 (2)	$O(2)-T(B)-O(6)$	111.9 (2)	$W(3)-O(4)$	3.175 (8)	$O(6)-W(2)-Sr$	92.6 (2)
$O(4)-T(A)-O(7)$	113.0 (2)	$O(2)-T(B)-O(7)$	112.1 (2)	$2W(4)-O(5)$	2.898 (5)	$O(7)-W(2)-Sr$	165.7 (2)
$O(5)-T(A)-O(7)$	109.4 (2)	$O(6)-T(B)-O(7)$	109.1 (2)	$W(4)-W(1)$	3.070 (10)	$W(2)-W(3)-W(2)$	74.5 (3)
$O(5)-T(A)-O(9)$	110.1 (2)	$O(3)-T(D)-O(5)$	106.9 (2)			$2W(2)-W(3)-O(4)$	143.5 (3)
$O(2)-T(C)-O(4)$	111.9 (2)	$O(3)-T(D)-O(6)$	111.7 (2)			$2W(2)-W(3)-O(4)$	94.1 (2)
$O(2)-T(C)-O(9)$	105.3 (3)	$O(3)-T(D)-O(8)$	109.7 (2)			$2W(2)-W(3)-Sr$	120.5 (2)
$O(3)-T(C)-O(4)$	109.9 (2)	$O(5)-T(D)-O(6)$	108.5 (2)			$2O(4)-W(3)-Sr$	95.3 (2)
$O(3)-T(C)-O(9)$	108.5 (3)	$O(5)-T(D)-O(8)$	109.5 (2)			$O(5)-W(4)-O(5)$	146.7 (3)
$O(4)-T(C)-O(9)$	111.0 (3)	$O(6)-T(D)-O(8)$	110.5 (2)			$2W(1)-W(4)-O(5)$	73.6 (2)
$T(A)-O(1)-T(B)$	133.0 (3)	$T(D)-O(6)-T(B)$	151.9 (3)			$2Sr-W(4)-O(5)$	103.3 (2)
$T(B)-O(2)-T(C)$	145.4 (3)	$T(A)-O(7)-T(B)$	136.7 (3)			$Sr-W(4)-W(1)$	152.7 (4)
$T(D)-O(3)-T(C)$	140.1 (3)	$T(D)-O(8)-T(D)$	180.				
$T(A)-O(4)-T(C)$	146.7 (3)	$T(C)-O(9)-T(C)$	159.2 (4)				
$T(D)-O(5)-T(A)$	141.1 (3)						

Fig. 1. Stereoplot of crystal structure of brewsterite viewed down *a*, drawn with the *ORTEP* program (Johnson, 1965). Displacement ellipsoids at 30% probability level.

distances 2.63, 3.07 and 2.70 Å. Down *a*, the chain bifurcates to give Sr,Ba—two  $W(2)-W(3)-Sr,Ba$  with distances 2.83, 2.98 and 2.74 Å. The water molecules lie at 2.90 to 3.35 Å from framework O atoms. Hydrogen bonding is likely but no unique model is apparent.

The mean  $T-O$  distances [ $T(A)$  1.645,  $T(B)$  1.664,  $T(C)$  1.660,  $T(D)$  1.607 Å] indicate 0.3 Al in  $T(A)$ , ~0.4 Al in  $T(B)$  and  $T(C)$  and ~0.0 Al in  $T(D)$  when referred to reference values of ~1.60–1.61 Å for Si–O and ~1.74–1.75 Å for Al–O in frameworks (Smith, 1974).

Individual  $T-O$  distances can be examined in terms

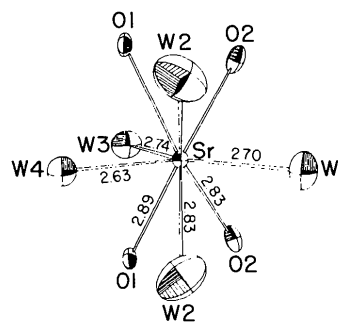


Fig. 2. Coordination of Sr, Ba atom. Displacement ellipsoids at 50% probability level.

of models of ionic bonding and of predictions from molecular-orbital theory. Because the Sr,Ba atom is close to only O(1) and O(2) of the eight types of framework O atoms, simple ionic theory would suggest that  $T-O$  distances to O(1) and O(2) should be longer than those to the other framework O atoms, and this is true for three out of four pertinent distances in Table 2 [ $\Delta(T-O)$ : O(1) +0.007 and +0.013; O(2) +0.011 and -0.007 Å, where  $\Delta(T-O)$  is the deviation of an individual mean  $T-O$  distance from the mean of its host tetrahedron].

Extended Hückel molecular-orbital (EHMO) calculations (reviewed by Gibbs, Meagher, Smith & Pluth, 1977) applied to  $T_5O_{16}$  clusters isolated mathematically from tetrahedral frameworks lead to a negative linear correlation between  $\Delta(T-O)$  and  $\sec(T-O-T)$  as shown by Tossell & Gibbs (1975). For dehydrated H-mordenite, Gibbs, Meagher, Smith & Pluth (1977) found that  $\Delta(T-O) = -0.152 - 0.132 \sec(T-O-T)$  with correlation coefficient 0.94. For brewsterite (Fig. 3), the corresponding relations are: (all oxygens)  $\Delta(T-O) = -0.072 - 0.057 \sec(T-O-T)$ ; [omitting O(1) and O(2)]  $\Delta(T-O) = -0.076 - 0.060 \sec(T-O-T)$ .

The correlation coefficients for brewsterite (0.751

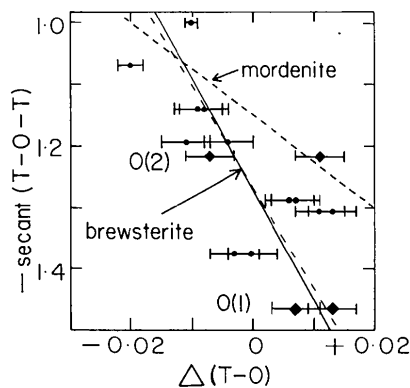


Fig. 3. Relation between  $\Delta(T-O)$  and  $-\sec(T-O-T)$  for H-mordenite and brewsterite [solid line, all data; dashed line, O(1) and O(2) omitted]. Data points and error bars are for brewsterite [diamonds for O(1) and O(2)].

and 0.745, respectively) are much worse than those for mordenite. EHMO theory predicts that the coefficient for the  $-\sec(T-O-T)$  term should increase with the electronegativity of the tetrahedral ion, and the relative coefficients for mordenite and brewsterite agree with this prediction. Thus mordenite contains a higher fraction of the more electronegative ion  $Si^{4+}$  than  $Al^{3+}$  and has a larger coefficient for the  $-\sec(T-O-T)$  term (Si/Al: mordenite, 5.2; brewsterite, 2.9), irrespective of whether O(1) and O(2) of brewsterite are considered. Unfortunately, the correlation coefficients for brewsterite are too low for this agreement to be convincing, and further structure analyses of ion-exchanged varieties of brewsterite, both hydrated and dehydrated, are planned to test the effect of cation type and position on the framework geometry.

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