*Canadian Mineralogist*
Volume. 31, pp. 147-152 (1993)

# THE CRYSTAL STRUCTURE OF STILLWELLITE

PETER C. BURNS, FRANK C. HAWTHORNE AND DANIEL J. MACDONALD

*Department of Geological Sciences, The University of Manitoba, Winnipeg, Manitoba R3T 2N2*

GIANCARLO DELLA VENTURA AND GIAN CARLO PARODI

*Dipartimento di Scienze della Terra, Sezione mineralogico-cristallografica, Universit di Roma "La Sapienza",*
*P. Aldo Moro 5, 00185 Roma, Italy*

## ABSTRACT

Stillwellite, $X[BO(SiO_4)]$, where $X$ represents Ce and La (dominant), with lesser Pr, Nd and Th, is trigonal, $a$ 6.841(2), $c$ 6.702(2) Å, $V$ 271.7(2) Å$^3$, $Z = 3$, space group $P3_1$; its structure has been refined by least-squares methods to an $R$ index of 2.7% using 1003 observed $[F > 5\sigma(F)]$ reflections. Stillwellite contains helical chains of $(BO_4)$ tetrahedra polymerized by sharing corners. These chains are decorated by $(SiO_4)$ tetrahedra that share two corners with adjacent $(BO_4)$ tetrahedra. Large, irregular 9-coordinate *REE* sites link the polyhedral chains. Stillwellite most likely has $P3_121$ symmetry at high temperatures and undergoes a ferroelectric phase-transition to $P3_1$ upon cooling.

*Keywords*: stillwellite, crystal structure, phase transition, chemical composition, rare-earth elements, Vetralla, Vico Volcano, Italy.

## SOMMAIRE

La stillwellite, $X[BO(SiO_4)]$, où $X$ représente surtout Ce et La, avec Pr, Nd et Th accessoires, est trigonale, $a$ 6.841(2), $c$ 6.702(2) Å, $V$ 271.7(2) Å$^3$, $Z$ = 3, groupe spatial $P3_1$. Sa structure a été affinée en utilisant 1003 réflexions observées $[F > 5\sigma(F)]$, par moindres carrés, jusqu'à un résidu de 2.7%. La stillwellite contient des chaînes hélicoïdales de tétraèdres $BO_4$ articulés par partage de sommets. Ces chaînes sont décorées de tétraèdres $SiO_4$ qui partagent deux sommets avec les tétraèdres $BO_4$ voisins. Des sites plus spacieux et irréguliers, à coordinence 9, contiennent les atomes de terres rares et servent à joindre les chaînes de polyèdres. La stillwellite aurait une symétrie $P3_121$ à température élevée, et adopterait ls symétrie $P3_1$ au cours de son refroidissement, suite à une transition ferroélectrique.

(Traduit par la Rédaction)

*Mots-clés*: stillwellite, structure cristalline, polymorphisme, composition chimique, terre rares, Vetralla, volcan Vico, Italie.

## INTRODUCTION

Stillwellite, $X[BO(SiO_4)]$ with $X$ representing the rare-earth elements (*REE*), dominantly cerium and lanthanum, was originally described from Queensland, Australia (McAndrew & Scott 1955). The crystal structure of stillwellite was solved by Voronkov & Pyatenko (1967) using Patterson projections and refined with data collected with photographic techniques. A recent find of stillwellite provided the opportunity and impetus to more accurately characterize the structure and chemistry of this mineral.

The stillwellite occurs in a porous holocrystalline ejectum collected on the western border of the volcano Vico, near Vetralla, north of Rome. Such ejecta are common in some pyroclastic units of the Vico volcanic complex. The host rock is a block of syenitic appearance (maximum dimension about 2 m), dominantly composed of sanidine with minor clinopyroxene, magnetite, sodalite and titanite. In interstices and vugs between the large sanidine crystals, euhedral crystals of ekanite, thorite, zircon, hellandite and stillwellite occur. Individual crystals of stillwellite are pale pink and transparent, with a maximum dimension of 0.5 mm.

## EXPERIMENTAL METHODS

### *X-ray analysis*

The stillwellite crystal selected for study was ground to a sphere and mounted on a Nicolet R3m automated four-circle diffractometer. Twenty-five reflections were centered using graphite-monochromated Mo*K*α X radiation. The cell dimensions (Table 1) were derived from

TABLE 1. MISCELLANEOUS INFORMATION FOR STILLWELLITE

| | | | |
|---|---|---|---|
| $a$ (Å) | 6.841(2) | Crystal Size (mm) | 0.26x0.26x0.26 |
| $c$ (Å) | 6.702(2) | Total Ref. | 1067 |
| $V$ (Å$^3$) | 271.7(2) | $\|F_o\| \geq 5\sigma(F)$ | 1003 |
| F(000) | 351 | Final $R$(obs.) | 2.7% |
| | | Final $wR$(obs.) | 3.3% |
| Space Group | $P3_1$ | | |
| Unit Cell Contents | | $3\{X[BO(SiO_4)]\}$, X = Ce,La | |

$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$

$wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma F_o^2]^{½}$, w=1

TABLE 2. CHEMICAL COMPOSITION** OF STILLWELLITE

| Point | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| $SiO_2$ | 22.06 | 22.62 | 22.55 | 22.54 |
| $UO_2$ | 0.22 | 0.07 | 0.08 | 0.25 |
| $ThO_2$ | 5.41 | 3.82 | 4.78 | 5.02 |
| $Pr_2O_3$ | 1.82 | 1.97 | 1.65 | 1.99 |
| $La_2O_3$ | 19.12 | 19.42 | 21.54 | 19.45 |
| $Nd_2O_3$ | 5.36 | 5.48 | 4.24 | 5.07 |
| $Ce_2O_3$ | 30.82 | 31.69 | 30.86 | 31.92 |
| $Sm_2O_3$ | 0.34 | 0.38 | 0.22 | 0.34 |
| $Y_2O_3$ | 0.28 | 0.20 | 0.13 | 0.26 |
| CaO | 0.34 | 0.28 | 0.29 | 0.28 |
| $B_2O_3$* | 13.46 | 13.46 | 13.46 | 13.46 |
| Total | 99.26 | 99.41 | 99.82 | 100.57 |

+1: $(Ce_{0.50}La_{0.31}Nd_{0.08}Th_{0.05}Pr_{0.03}Ca_{0.02}Sm_{0.01})B_{1.02}O(Si_{.97}O_4)$
2: $(Ce_{0.51}La_{0.31}Nd_{0.09}Th_{0.04}Pr_{0.03}Ca_{0.01}Sm_{0.01})B_{1.01}O(Si_{.99}O_4)$
3: $(Ce_{0.49}La_{0.35}Nd_{0.07}Th_{0.05}Pr_{0.03}Ca_{0.01})B_{1.01}O(Si_{.98}O_4)$
4: $(Ce_{0.51}La_{0.31}Nd_{0.08}Th_{0.05}Pr_{0.03}Ca_{0.01}Sm_{0.01}Y_{0.01})B_{1.01}O(Si_{.98}O_4)$

* $B_2O_3$ calculated from stoichiometry ** electron-microprobe data + formula recalculated on the basis of 5 oxygen atoms; $Na_2O$, FeO, MgO, $TiO_2$, $Nb_2O_5$, $Al_2O_3$, $Ta_2O_5$, SrO not detected.

the setting angles of twenty-five automatically aligned reflections by least-squares methods. A total of 1067 reflections were measured (3° < 2θ < 60°), with index ranges $0 \leq h \leq 10$, $0 \leq k \leq 12$, $-9 \leq l \leq 9$. Two standard reflections were measured every fifty reflections; no significant changes in their intensities occurred during data collection. Application of an empirical absorption-correction based on 396 psi-scan reflections reduced $R$ (azimuthal) from 5.01% to 1.95%. The data were then corrected for Lorentz, polarization and background effects, and reduced to structure factors; of the 1067 reflections measured, 1003 were classed as observed [$F \geq 5\sigma(F)$].

### *Chemical composition*

The crystal of stillwellite used for collection of X-ray data was mounted in epoxy, ground, polished and carbon coated. Electron-microprobe analyses were done using a Cameca SX50 electron microprobe in the wavelength-dispersion mode, with operating conditions of 15 kV, 20 nA and a beam size of 5 μm. The following standards were used for the analyses: microlite (Na, Ca, Ta), $FeNb_2O_6$ (Fe), olivine (Mg), titanite (Ti), $MnNb_2O_6$ (Nb), kyanite (Al), diopside (Si), strontianite (Sr), $UO_2$ (U), $ThO_2$ (Th), *REE* glass (Pr, Nd, Sm), monazite (La, Ce), and synthetic garnet (Y). Count times were 60 s for Pr, La, Nd, Ce, Sm and Y, and 10 s for the other elements. Analyses for Nd, La, Ce, Sm and Y were done using the $L\alpha$ lines. There is no line interference with the La, Ce and Y $L\alpha$ lines, but the Sm$L\alpha$ line overlaps with the Ce$L\beta_2$ and Pr$L\beta_3$ lines. A correction was calculated for Sm but was insignificant owing to the low concentrations of Ce and Pr. The Ce$L\beta$ line falls near the Nd$L\alpha$ line, but examination of the spectra showed that they do not overlap. As the La$L\beta$ line interferes with the Pr$L\alpha$ line, analyses for Pr were done using the $L\beta$ line, which shows no interference. Analyses were done at four points in the crystal and show it to be essentially homogeneous (Table 2). The analyses indicate that the *REE* site contains Ce and La, with lesser amounts of Nd, Th and Pr.

## STRUCTURE REFINEMENT

All calculations were done using the Siemens SHELXTL PC software. The space group $P3_1$ given by Voronkov & Pyatenko (1967) was verified by examination of systematic extinctions and the successful refinement of the structure. Scattering factors for neutral atoms together with anomalous dispersion coefficients were taken from Cromer & Mann (1968) and Cromer & Liberman (1970). Least-squares refinement with starting parameters taken from Voronkov & Pyatenko (1967) and an isotropic displacement model converged to an $R$ index of 3.6%. Conversion to an anisotropic displacement model, together with the refinement of all parameters, converged to an $R$ index of 3.3% and a $wR$ index of 3.9%. A model with weighted structure-factors and an isotropic extinction-correction was tried but did not lead to an improvement in the results of the refinement. The results given here are a significant improvement over those reported by Voronkov & Pyatenko (1967), $R_{hk0}$ = 9.2% and $R_{0kl}$ = 12.8%.

Examination of the displacement parameters for each atom showed the values obtained at the O3 site to be several times larger than those obtained at the other oxygen positions. A difference-Fourier map, calculated with an empty O3 position, shows that the site is split into two maxima separated by about 1 Å (Fig. 1). The O3 site was modeled as two independent sites, with the two sites refining to a separation of 0.94(2) Å and having occupancies of 0.55(2) and 0.45(2), respectively. The split-site model gave an $R$ index of 2.7%, a $wR$ index of 3.3% and a goodness-of-fit of 1.7 for 1003 independent observed reflections, and resulted in reasonable displacement-parameters for all sites. Considerable disorder at the boron site also is suggested by large displacement-parameters, but split-site models did not significantly improve the refinement.

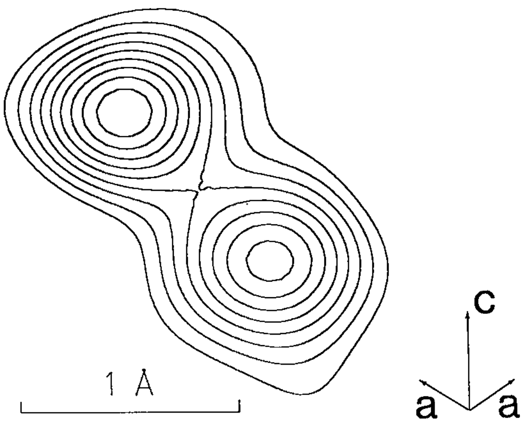

FIG. 1. Difference-Fourier map around the O3 site in stillwellite.

Final positional parameters are given in Table 3, anisotropic displacement-parameters in Table 4, selected interatomic bond-distances and angles in Tables 5 and 6, and a bond-valence analysis in Table 7. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI National Research Council of Canada, Ottawa, Ontario K1A 0S2.

TABLE 3. ATOMIC PARAMETERS FOR STILLWELLITE

| | x | y | z | *$U_{equiv.}$ |
|---|---|---|---|---|
| X | 0.41184(6) | -0.00016(7) | 0 | 42(1) |
| Si | 0.4167(3) | 0.0001(4) | -0.5008(19) | 26(7) |
| B | -0.1104(18) | 0.0005(24) | 0.0060(26) | 163(34) |
| 01 | 0.1416(13) | -0.3961(12) | -0.0042(9) | 85(20) |
| 02 | 0.5340(14) | 0.3949(12) | 0.0038(9) | 86(21) |
| 03A | -0.0037(20) | 0.0562(20) | -0.7825(16) | +62(25) |
| 03B | 0.0543(25) | -0.0012(24) | 0.1194(20) | +62(25) |
| 04 | 0.6571(12) | -0.1945(12) | 0.0214(10) | 57(19) |
| 05 | 0.8493(12) | 0.1936(11) | -0.0242(11) | 62(20) |

*$U_{equiv.} = U_{equiv.} x10^4$

+ the displacement factors of 03A and 03B were constrained to be equivalent.

TABLE 4. ANISOTROPIC THERMAL PARAMETERS FOR STILLWELLITE

| | *$U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| X | 50(2) | 40(2) | 33(1) | 20(1) | -2(1) | -2(1) |
| Si | 31(9) | 40(8) | 9(6) | 20(8) | 0(8) | -4(6) |
| B+ | 41(36) | 174(44) | 333(51) | 97(36) | 132(40) | 209(41) |
| 01 | 114(28) | 72(25) | 51(22) | 33(23) | -11(22) | -17(19) |
| 02 | 149(30) | 58(24) | 51(22) | 50(23) | -3(22) | -23(19) |
| 03A | 84(36) | 63(31) | 28(22) | 28(26) | 17(27) | 19(27) |
| 03B | 84(36) | 63(31) | 28(22) | 28(26) | 17(27) | 19(27) |
| 04 | 60(24) | 49(23) | 56(24) | 22(20) | -13(20) | 18(20) |
| 05 | 75(27) | 29(22) | 78(25) | 24(22) | 36(22) | 39(20) |

*$U_{ij} = U_{ij}*10^4$

+ non-positive definite.

TABLE 5. SELECTED BOND-DISTANCES (Å) FOR STILLWELLITE

| | | | |
|---|---|---|---|
| X-01 | 2.397(6) | Si-01b | 1.59(1) |
| X-02 | 2.397(8) | Si-02f | 1.59(1) |
| X-03Aa | 2.552(7) | Si-04g | 1.65(1) |
| X-03B | 2.57(2) | Si-05e | 1.656(9) |
| X-04 | 2.61(1) | <Si-O> | 1.622 |
| X-05 | 2.603(8) | | |
| X-01b | 2.551(6) | B-03Ai | 1.56(2) |
| X-02c | 2.549(6) | B-03Aa | 1.41(2) |
| X-04d | 2.717(7) | B-03B | 1.36(2) |
| X-05e | 2.738(6) | B-03Bj | 1.61(2) |
| *<X-O> | 2.569 | B-04h | 1.48(1) |
| | | B-05h | 1.49(2) |
| | | *<B-O> | 1.485 |

* The sites 03A and 03B were given the weights 0.55 and 0.45, respectively, when calculating mean bond-distances.

a = -x+y-1, -x, z+2/3
b = -x+y, -x, z+2/3-1
c = 1-y, x-y+1, z+1/3
d = -y, x-y, z+1/3
e = -x+y, -x+1, z+2/3-1
f = -y+1, x-y, z+1/3-1
g = -y, x-y, z+1/3-1
h = x-y, y, z
i = x, y, z+1
j = -x+y-1, -x, z+2/3-1

TABLE 6. SELECTED BOND-ANGLES (°) AND LENGTHS OF POLYHEDRAL EDGES (Å) FOR STILLWELLITE

| | | | |
|---|---|---|---|
| 01-X-03Aa | 78.6(4) | 01-03Aa | 3.14(1) |
| 01-X-03B | 78.8(4) | 01-03B | 3.16(2) |
| 01-X-04 | 75.8(3) | 01-04 | 3.08(1) |
| 01-X-01b | 74.6(3) | 01-01b | 3.00(1) |
| 01-X-04d | 67.7(2) | 01-04d | 2.86(1) |
| 02-X-03Aa | 78.3(3) | 02-03Aa | 3.13(2) |
| 02-X-03b | 78.2(4) | 02-03b | 3.13(1) |
| 02-X-05 | 76.3(3) | 02-05 | 3.09(2) |
| 02-X-02c | 75.3(3) | 02-02c | 3.02(1) |
| 02-X-05e | 67.3(2) | 02-05e | 2.86(1) |
| 03Aa-X-01b | 92.3(2) | 03B-04d | 2.32(2) |
| 03Aa-X-04d | 85.6(3) | 04-05 | 2.32(1) |
| 03Aa-X-05e | 52.6(3) | 04-01b | 2.743(9) |
| 03B-X-02C | 92.3(4) | 04-02c | 2.50(1) |
| 03B-X-04d | 52.0(4) | 05-01b | 2.507(9) |
| 03B-X-05e | 86.2(3) | 05-02c | 2.86(1) |
| 04-X-05 | 52.8(2) | 01-05e | 3.26(1) |
| 04-X-01b | 67.2(2) | 01-04d | 3.26(1) |
| 04-X-02c | 78.3(3) | <O-O>X | 2.90 |
| 04-X-04d | 97.6(3) | | |
| 05-X-01b | 78.4(2) | | |
| 05-X-02c | 67.4(2) | | |
| 05-X-05e | 97.0(3) | | |
| 01-X-05e | 56.5(1) | | |
| 02-X-04d | 56.6(2) | | |
| <O-X-O> | 74.5 | | |
| | | | |
| 01b-Si-02f | 119.2(5) | 01b-02f | 2.74(1) |
| 01b-Si-04g | 115.3(4) | 01b-04g | 2.743(9) |
| 01b-Si-05e | 101.0(8) | 01b-05e | 2.507(9) |
| 02f-Si-04g | 100.9(8) | 02f-04g | 2.50(1) |
| 02f-Si-05e | 115.5(5) | 02f-05e | 2.74(1) |
| 04g-Si-05e | 104.6(4) | 04g-05e | 2.62(1) |
| <O-Si-O> | 109.4 | <O-O>Si | 2.64 |
| | | | |
| 03Ai-B-04h | 109.0(1.1) | 03Ai-04h | 2.48(1) |
| 03Aa-B-04h | 123.2(1.3) | 03Aa-04h | 2.54(2) |
| 04h-B-05h | 102.5(1.0) | 04h-05h | 2.62(2) |
| 03Ai-B-05h | 100.7(1.1) | 03Ai-05h | 2.35(2) |
| 03Aa-B-05h | 115.6(1.1) | 03Aa-05h | 2.45(1) |
| 03Ai-B-03Aa | 103.6(9) | 03Ai-03Aa | 2.332(5) |
| <O-B-O> | 109.1 | <O-O>B | 2.46 |
| | | | |
| 03B-B-04h | 118.2(1.3) | 03B-04h | 2.44(2) |
| 03Bj-B-04h | 97.1(1.0) | 03Bj-04h | 2.32(2) |
| 04h-B-05h | 102.5(1.0) | 04h-05h | 2.62(2) |
| 03B-B-05h | 127.0(1.2) | 03B-05h | 2.56(2) |
| 03Bj-B-05h | 104.5(1.1) | 03Bj-05h | 2.45(1) |
| 03B-B-03Bj | 102.6(1.1) | 03B-03Bj | 2.327(8) |
| <O-B-O> | 108.7 | <O-O>B | 2.45 |

TABLE 7. BOND-VALENCE* ANALYSIS FOR STILLWELLITE

| | O1 | O2 | O3A+ | O3B+ | O4 | O5 | Σ |
|---|---|---|---|---|---|---|---|
| X[a] | 0.54<br>0.34 | 0.54<br>0.34 | 0.19 | 0.15 | 0.29<br>0.21 | 0.29<br>0.20 | 3.09 |
| Si | 1.12 | 1.12 | | | 0.95 | 0.93 | 4.12 |
| B | | | 0.33<br>0.49 | 0.46<br>0.23 | 0.74 | 0.72 | 2.97 |
| Σ | 2.00 | 2.00 | 1.01 | 0.84 | 2.19 | 2.14 | |

* Bond-valence parameters from Brown (1981).
+ The bond-valence parameters for the O3A and O3B sites adjusted for their partial occupancies.
[a] The bond-valence parameters for the X site are an average of the Ce and La parameters calculated using the microprobe data to determine relative amounts.

## DESCRIPTION OF THE STRUCTURE

Boron is coordinated by four atoms of oxygen in a tetrahedral arrangement. This is somewhat disguised in Table 5 because the positional disorder of the O3 oxygen results in six bond distances (rather than the normal four). However, O3A and O3B cannot be occupied simultaneously, and any *local* configuration involves only four of these six positions. Let us consider the local configuration in which O3Ai is occupied. In this case, the O3B position cannot be occupied. For the O3Aa and O3Bj positions (Table 5), there is no resulting restriction; either could be occupied. However, if the O3Aa position is occupied, the local mean bond-length (to O3Ai, O3Aa, O4b and O5h) is 1.485 Å, the same as the grand mean distance. Similarly, the local mean bond-length if O3B is occupied also is 1.485 Å, whereas the alternative possible configurations involve a difference of 0.025 Å in the mean tetrahedral bond-length, with no obvious explanation for this. Consequently, it seems reasonable that the local configurations involve either both O3A atoms (in Table 5) or both O3B atoms. The mean distances of 1.485 Å are in line with observed mean $^{[4]}$B–O distances in other structures, and with the sums of the relevant ionic radii (1.38 + 0.11 = 1.49 Å; Shannon 1976).

The $(BO_4)$ tetrahedra polymerize by sharing corners to form a helical chain extending along the *z* axis (Fig. 2). The periphery of the chain is decorated by $(SiO_4)$ tetrahedra that share two corners with adjacent $(BO_4)$ tetrahedra and have two ôfreeö vertices. The resultant $[BSiO_5]$ chain is the fundamental building block of the structure that is repeated by the lattice translations to form a hexagonal columnar array (Fig. 3). Linkage between $[BSiO_5]$ chains is provided by the interstitial *REE*s. The latter are coordinated by nine oxygen atoms, the bond lengths ranging from 2.397 to 2.738 Å, with a mean value of 2.569 Å (Table 5), and the occupancy is dominated by Ce and La, with minor Nd, Pr and Th.

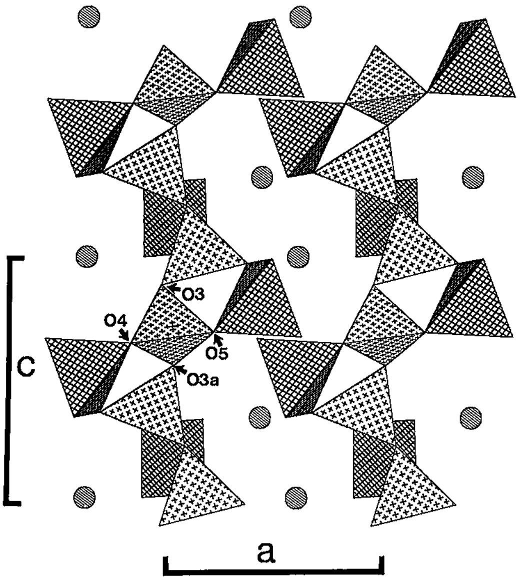

FIG. 2. A polyhedral representation of the crystal structure of stillwellite projected along [100]; $(BO_4)$ tetrahedra are denoted by + symbols, $(SiO_4)$ tetrahedra, by cross-hatching, and the *X* position, by hatched circles.

After this manuscript had gone through the review process, Callegari *et al.* (1992) published a refinement of stillwellite from the same locality. The numerical results of the two studies are very similar, although the details of the refinement procedure (specifically the handling of the twinning and domain structure) are somewhat different. However, the discussions of the domain structure and twinning are equivalent, and do suggest the presence of a phase transition as discussed below.

## A PROPOSED PHASE-TRANSITION IN STILLWELLITE

An intriguing result of this refinement is the extremely prominent splitting of the O3 position (Fig. 1); an explanation of this is required. The structure of stillwellite was originally solved in the space group $P3_1$ (Voronkov & Pyatenko 1967), and was successfully refined here with the same symmetry. However, inspection of Figure 3 shows that the structure is approximately compatible with 2-fold axes along [100], [010] and $[\overline{11}0]$ and passing through the $(BO_4)$ tetrahedra. This additional pseudosymmetry also is apparent in the atomic coordinates of Table 3 and the bond lengths of Table 5. The structure of stillwellite is approximately compatible with $P3_121$ symmetry, and ideal coordinates are given in Table 8. However, refinement of the structure in this space group results in a physically unrealistic structure,

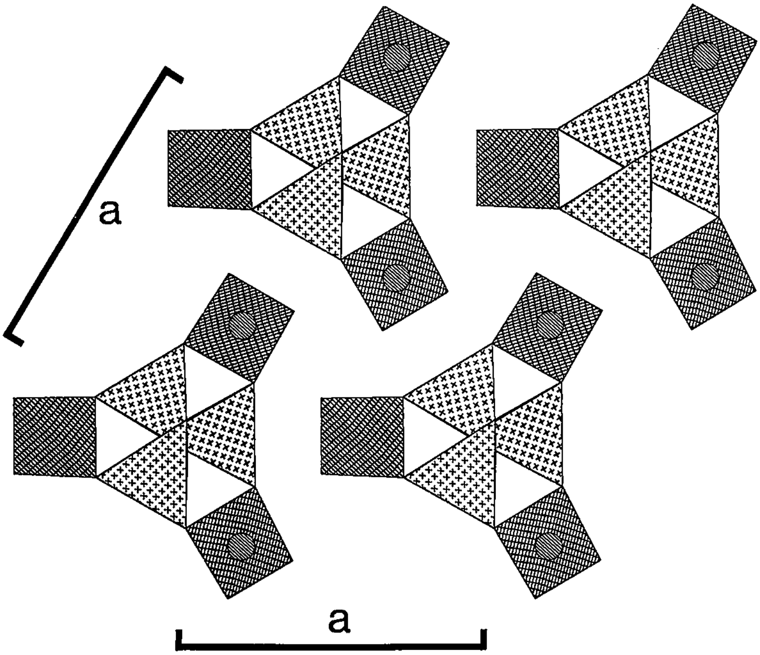

FIG. 3. A polyhedral representation of the crystal structure of stillwellite down [001]; legend as in Figure 2.

with the O2 displacement parameter 10 times greater than expected.

It seems reasonable to propose that stillwellite has $P3_121$ symmetry at higher temperatures; the small amount of deviation from this symmetry suggests that stillwellite crystallizes in the space group $P3_121$ and inverts to $P3_1$ on cooling. According to the classification of Aizu (1969), this is a ferroic transition. Inspection of the tables of Stokes & Hatch (1988) shows this to be a pure ferroelectric transition, characterized by the onset of spontaneous dielectric polarization components. The origin of the O3 atomic positional disorder is now apparent. The transition involves a loss of the 2-fold axis along the $x$ axis, and this allows the O3–O3 edge of the $(BO_4)$ polyhedron to move away from the vertical. This involves a tilting of the $(BO_4)$ tetrahedron, which can occur upward or downward with regard to the $z$ axis. Both possibilities occur, giving rise to the disordered O3 anion (if averaged over the whole crystal). There are two possibilities in this regard: (i) the tilting is totally disordered over the whole crystal; (ii) the tiltings are cooperative over considerable volumes, giving rise to a domain structure in the crystal; in view of the size of the displacement, the latter seems more likely.

TABLE 8. ATOMIC COORDINATES FOR $P3_121$ PHASE OF $(REE)BSiO_5$

| | | x | y | z |
|---|---|---|---|---|
| REE | 3a | 0.412 | 0 | 1/3 |
| Si | 3b | 0.412 | 0 | 5/6 |
| B | 3a | -0.110 | 0 | 1/3 |
| O1' | 6c | 0.396 | 0.537 | 0.662 |
| O2' | 3 | -0.026 | 0 | 5/6 |
| O3' | 6c | 0.149 | 0.346 | 0.021 |

O1' - O1 + O2 in Table 3
O2' - O3A + O3B in Table 3
O3' = O4 + O5 in Table 3

## ACKNOWLEDGEMENTS

The Natural Sciences and Engineering Research Council of Canada supported this work in the form of postgraduate scholarships to PCB and DJM, and operating, major equipment and infrastructure grants to FCH. Mr. S. Fiori is acknowledged for supplying the samples studied.

## REFERENCES

AIZU, K. (1969): Possible species of ôferroelasticö crystals and of simultaneously ferroelectric and ferroelastic crystals. *J. Phys. Soc. Jap.* **27**, 387-396.

BROWN, I.D. (1981): The bond valence method: an empirical approach to chemical structure and bonding. *In* Structure and Bonding in Crystals II (M. O'Keeffe & A. Navrotsky, eds.). Academic Press, New York (1-30).

CALLEGARI, A., GIUSEPPETTI, G., MAZZI, F. & TADINI, C. (1992): The refinement of the crystal structure of stillwellite: RE[$BSiO_5$]. *Neues Jahrb. Mineral. Monatsh.*, 49-57.

CROMER, D.T. & LIBERMAN, D. (1970): Relativistic calculation of anomalous scattering factors for X rays. *J. Chem. Phys.* **53**, 1891-1898.

______ & MANN, J.B. (1968): X-ray scattering factors computed from numerical Hartree–Fock wave functions. *Acta Crystallogr.* **A24**, 321-324.

MCANDREW, J. & SCOTT, T.R. (1955): Stillwellite, a new rare-earth mineral from Queensland. *Nature* **176**(4480), 509-510.

SHANNON, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **A32**, 751-767.

STOKES, D.M. & HATCH, H.T. (1988): *Isotropy Subgroups of the 230 Crystallographic Space Groups.* World Scientific, London, U.K.

VORONKOV, A.A. & PYATENKO, YU.A. (1967): X-ray diffraction study of the atomic structure of stillwellite CeBO[$SiO_4$]. *Sov. Phys. Crystallogr.* **12**, 214-220.

*Received November 13, 1991, revised manuscript accepted March 11, 1992.*