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X-RAY DIFFRACTION STUDY OF THE ATOMIC STRUCTURE OF STILLWELLITE CeBO[SiO$_4$]

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Stillwellite CeBO[SiO$_4$] has a hexagonal cell with parameters a = 6.85, c = 6.70 A, Z = 3. The space group is P3$_1$. The structure is characterized by columns of Si tetrahedra and Ce nine-pointed figures alternating along the z axis. The columns are interlayed by helical chains of BO$_4$ tetrahedra extending in the same direction.

The rare-earth borosilicate stillwellite was first found in Australia in 1955. Earlier authors [1, 2] established the trigonal crystal system and also determined the lattice parameters and space group of the mineral.

For the present full investigation we used Soviet samples of stillwellite put at our disposal by V. D. Dusmatov and A. F. Efimov.

Using an RKOP camera and isometric grains of diameter about 0.2 mm, we determined the Laue class ($\bar{3}$m) and hexagonal cell parameters a = 6.85 ± 0.03, c = 6.70 ± 0.03 A (V = 272.3 A^3), in agreement with the earlier results [2]. The chemical composition of the samples studied corresponded to the empirical formula REBSiO$_5$, where RE is predominantly Ce and La; hence, with a slight idealization of the composition, the formula of stillwellite took the form CeBSiO$_5$. On the basis of this formula and the experimental density value of ρ = 4.70 g/cm^3, we obtained the value of Z = 2.97 ≈ 3. The law governing the systematic extinction of the reflections on the layer-line patterns (KFOR camera) – only those 00l reflections with l = 3n were present – led to the space group P3$_1$21 (or the enantiomorphic P3$_2$21). The fact that the structure was noncentrosymmetric was in accordance with the strong piezoeffect of the stillwellite crystal. We note that our space group differs from that proposed earlier (P3$_1$12 in [2]) in respect to the mutual orientation of the 2 axis and the edge of the cell. Here we must point out that later, after full study of the structure, it was concluded that stillwellite had a lower true symmetry, described by the group C_3^2 = P3$_1$ (or P3$_2$), being a subgroup of P3$_1$21. These groups are characterized by the same laws of extinction, but P3$_1$ corresponds to another Laue class, $\bar{3}$.

The main experimental material (hk0 and 0kl patterns) was obtained with both photographic and ionization-gage recording of the intensities. In the latter case we used a URS-50I diffractometer adapted for the study of single crystals (Geiger counter). Measurement of the "photographic" intensities was carried out by the standard method, by comparing with a scale of photographic densities; the "diffractometer" measurements were based on the area of the peaks, introducing a correction for the nonlinearity of the counter. In both cases the values of F^2 were calculated with due allowance for the kinematic and polarization factors; only for the intensities of the reflections in the hk0 zone obtained in the diffractometer were additional corrections for absorption (spherical sample) introduced. Analysis of the structure was carried out in parallel on the basis of the I(hk$l$) values obtained by the two methods; very similar results were obtained. The final results were based on the diffractometer intensities.

In the group P3$_1$21 the multiplicity of points in the general-position complex is 6, and for the special position is 3 (two-fold axes) [3]. Since the qualitative and quantitative composition of the stillwellite cell gave no grounds for the existence of isomorphic relations between the cations in the structure, we may conclude that all the cations and at least three O atoms should lie on two-fold axes.

The determination of the coarse model of the structure was made easier by the presence of the "heavy" Ce atoms. The coordinates of the latter were obtained from p(xy) and p(yz) Patterson projections plotted from 88 independent hk0 and 358 $0kl$ reflections respectively. The p(xy) projection (in agreement with the number of Ce atoms in the cell, namely, three) contains six strong (x, 2x) peaks arranged on the long diagonals of the hexagonal cell. This arrangement of the Patterson maxima corresponded to positioning of the Ce atoms on the short diagonals (edges) of the cell and represented one of the three-fold complexes ($x0^1/_3$ or $x0^5/_6$) of the $P3_121$ group [3]. Subsequently, for convenience, the origin of coordinates of the cell was moved by z/6 in height (as compared with the standard) to the level of one of the Ce atoms, thus giving this the coordinates x00. In addition to the peaks indicated, corresponding to the Ce–Ce vectors, some comparatively weak maxima (which could not, however, be associated with the Ce–Si vectors) were found in p(xy).

The side projection p(yz) contained more information, for we were able to obtain not only the coordinates of the Ce and Si but also twelve of the fifteen oxygen atoms. Thus, the Ce and Si atoms lay almost exactly on a single vertical and were separated by distances of c/2, which explains the absence of peaks corresponding to the Ce–Si vectors on the p(xy) plot.

The next stage consisted of plotting electron-density syntheses σ (xy) and σ (yz) from the amplitudes F(hk0) and F($0kl$), the phases of which were determined on the basis of the Ce and Si coordinates. Even at the stage of the first approximation, the σ (xy) projection was distinguished by great clarity and contained peaks corresponding to all the atoms in the cell, including boron. The position of the latter agreed satisfactorily with the character of the Patterson maxima in the p(xy) plot. Further approximation in the σ (xy) projection, allowing for the light atoms, led to a refinement of the horizontal coordinates, with a good value of the R factor. Figure 1 gives the σ (xy) projection in contours, while Fig. 3 represents a comparison between the experimental and calculated values of F(hk0).

The structural plan obtained on the basis of the $P3_121$ group enabled us to fix the main details of the spatial distribution of the atoms. The two systems of general-position oxygen atoms (2 × 6), clearly revealed on the syntheses, formed tetrahedra around the Si atoms. The remaining three O and three B atoms were grouped around the 3_1 axis, projecting along the z direction into horizontal 2 axes, in agreement with the proposed single-parameter position of these atoms. Clearly, the maxima corresponding to the 3(O + B) group must lie in the σ (yz) projection at the levels of the two-fold axes with respect to z.

The Ce and Si atoms were clearly located in the side projection, together with the twelve O atoms which had been reliably located in the p(yz) synthesis. In addition to this, the projection also contained a series of smaller peaks, among which were both true maxima corresponding to missing O and B atoms and also "phantoms." However, these additional peaks lay in a general and not a special position, and their number was twice as great as the number of atoms to be determined. Nor did the position change at the next stage of refinement, when the twelve O atoms with known coordinates were taken into account. The most probable explanation

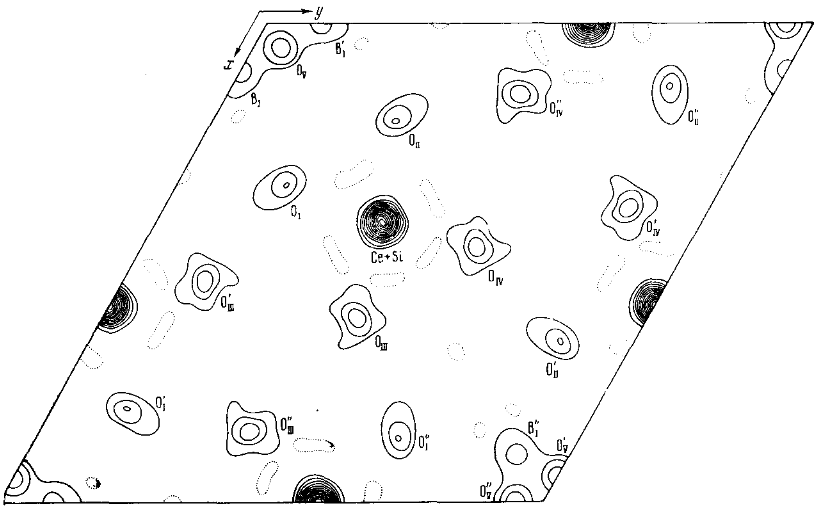

Fig. 1. Electron-density projection $\sigma(x, y)$. Contours drawn every 9 electrons/A^2 for light atoms and 30 electrons /A^2 for Ce + Si.

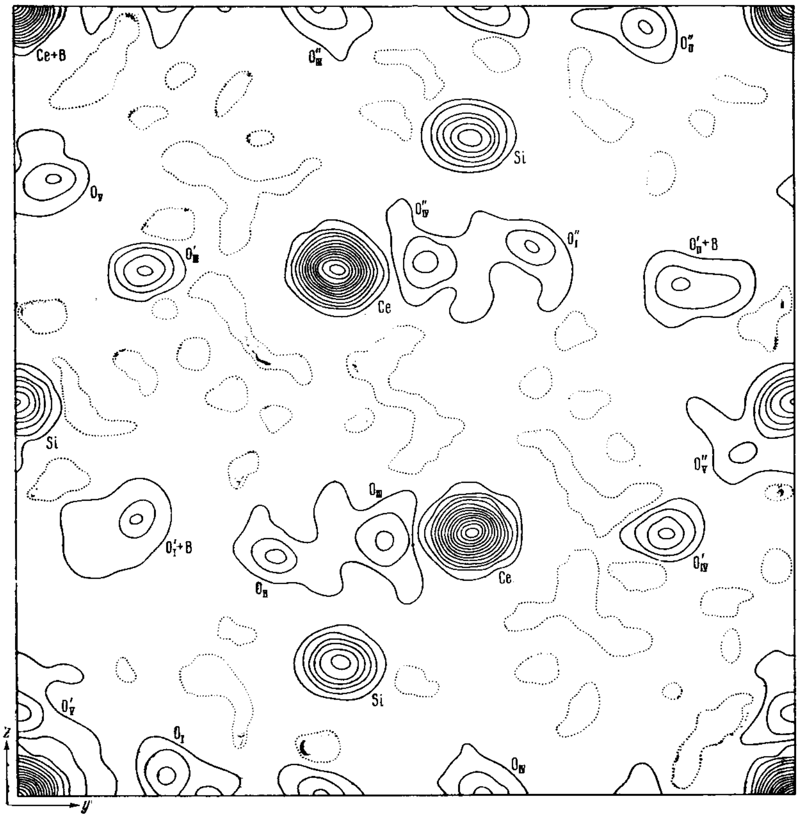

Fig. 2. Electron-density projection σ(y, z). Contours drawn every 8.5 electrons/A^2 for light atoms and 18 electrons/A^2 for Ce.

of this contradiction lies in the assumption that the symmetry of the structure determined in the early stages was higher than the true symmetry of the mineral.

The search for the final model by means of crystal-chemical analysis led to contradiction with the group P3$_1$21. It was found impossible to obtain interatomic distances B−O and O−O agreeing with the standard values for the known horizontal coordinates of the atoms and any coordination of the boron (triangular or tetrahedral) within the bounds of this group. It was also noted that the most probable form of the B polyhedron was the tetrahedron, since in the case of triangular coordination of boron there would be too great an excess of positive valence $(+{}^2/_3)$ on the oxygen atoms linking the B triangle with the Si tetrahedron (and the inevitability of such a connection between the B and Si polyhedra was well established). The four-fold coordination of boron (later fully justified) was also indirectly supported by the low double refraction of stillwellite (about 0.009) and also by a direct study of the infrared spectra of this mineral carried out by I. I. Plyusnin. The analysis finally led to the necessity

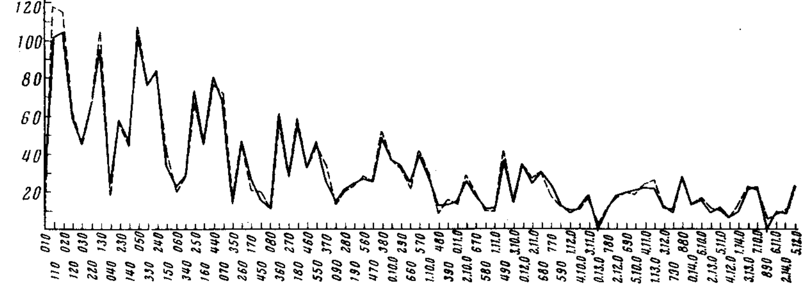

Fig. 3. Comparison between experimental (continuous lines) and calculated (broken lines) values of F(hk0).

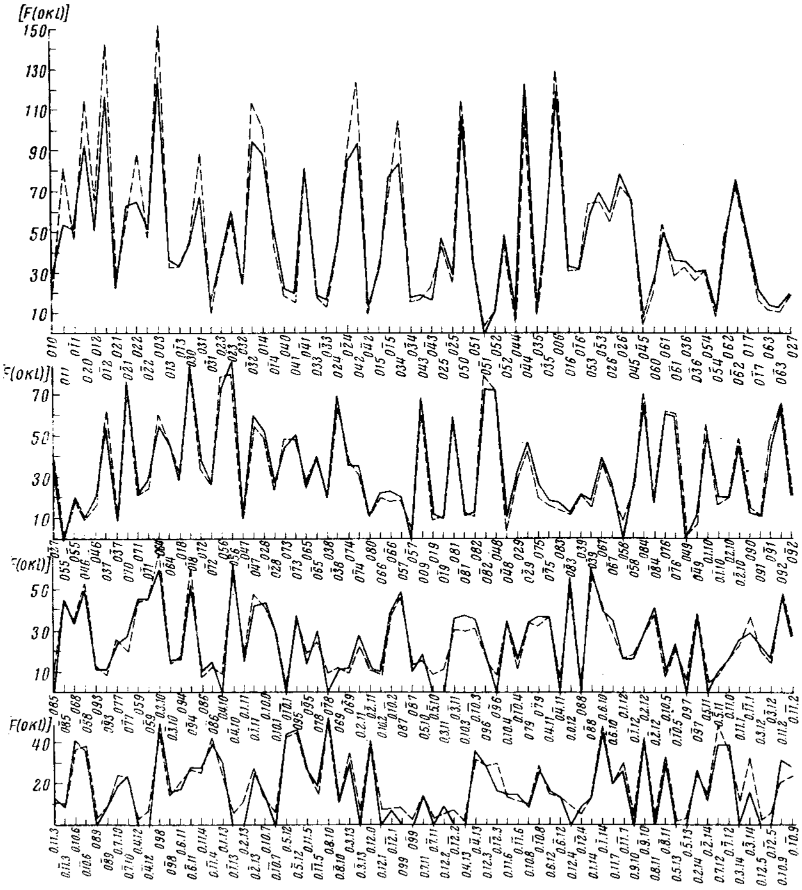

Fig. 4. Comparison between the experimental (continuous line) and calculated (broken line) values of F(0k*l*).

of displacing the O atoms not connected to the Si some distance along the z axis from the levels (2-axes), dictated by the space group $P3_121$. In estimating the extent of the displacement Δz, we used the additional σ (yz) electron-density peaks corresponding to the horizontal coordinates of the missing oxygen atoms, which were stably repeated on all subsequent syntheses. This identification of the peaks in question with O atoms inevitably led to the vanishing of the two-fold axes and to a reduction in the symmetry of the structure to $P3_1$. The use of the coordinates thus established for the construction of electron-density projection σ (yz) on the basis of the plane group p1 led to the development of a noncentrosymmetric projection, the substantial removal of false maxima, and a considerable fall in the R factor. In this projection the B atoms were not resolved, since they overlapped other atoms in the structure. In order to locate the B atoms and also confirm the final form of the structure as a whole, we plotted Patterson and Fourier difference syntheses, with the subtraction of contributions from all the known atoms, including two of the three Ce atoms (in the p synthesis) and all the fixed atoms (in the Fourier synthesis). Both functions gave closely coinciding z coordinates for the B atoms. Figure 2 gives the final form of the σ (yz) projection, and Fig. 4 gives a comparison between the calculated and experimental values of F(0k*l*). The final values of the R factors ($\sin\vartheta/\lambda \leq 1.32$) were:

$$R_{hk0} = 9.2\%, \quad R_{0kl} = 12.8\%.$$

Thus we have found that the true symmetry group of stillwellite is $P3_1$, with a marked $P3_121$ pseudosymmetry, i.e., within the limits of experimental accuracy, not only the Ce^{3+} and Si^{4+} cations but also twelve of the fifteen oxygen atoms obey the pseudogroup cited. Furthermore, even the remaining O and B atoms appear to have a higher symmetry, namely, 3m, in the xy projection. The reduction in the symmetry of the structure only appears by virtue of the vertical coordinates of these latter atoms. It is precisely this which makes the

TABLE 1. Coordinates of the Basic Atoms in the Structure of Stillwellite

Atoms	x	y	z	Atoms	x	y	z
Ce	0.587	0	0	O_{II}	0.195	0.339	0.310
Si	0.585	0	0.500	O_{III}	0.613	0.464	0.320
B	0.113	0	0.973	O_{IV}	0.464	0.614	0.014
O_I	0.339	0.194	0.023	O_V	0.051	0.051	0.781

final stage in the analysis of the structure so difficult, even more so because the contribution of the 3(O + B) group to the scattering is so small, some 11% of the total scattering power of the cell. It thus becomes quite understandable why the true Laue class of stillwellite ($\bar{3}$) tends to be masked out. Table 1 gives the coordinates of the basic atoms in the structure (group P3_1).

In the stillwellite structure, only four of the five crystallographically independent O atoms are linked with Si atoms, so that the formula of the mineral becomes $CeBO[SiO_4]$. The main elements of the structure, in addition to the Si tetrahedra, are BO_4 tetrahedra and Ce polyhedra; the latter have an irregular form with nine vertices. The main architectural detail of the structure is a series of infinite vertical columns formed by Si tetrahedra set on edge; these alternate along the z axis with large Ce polyhedra (Fig. 5). One polyhedron of each type corresponds to the c period of the cell. The columns are interconnected by 3_1 axes in such a way that the Ce polyhedra touch along common edges. This arrangement of the columns produces tortuous vertical channels in which are inscribed infinite helical chains of B tetrahedra. Analogous chains were found earlier in the structure of boric anhydrides, B_2O_3, which has the same symmetry, P3_1 [4]. Each B tetrahedron of the chain is connected by its free vertices with two Si tetrahedra and has two common edges with the Ce polyhedra of the two neighboring columns (Figs. 5 and 6).

It is well known that typical representatives of the "second chapter" of the crystal chemistry of silicates [5] include structures with octahedral coordination of large cations (Na, Ca, RE). As the cation-anion distances increase, the edges of the corresponding octahedra (3.6 to 3.8 A) prove to be "incommensurable" with the edges of the Si tetrahedra (2.6 to 2.7 A); in other words, the edges of the octahedron around the cation with the larger radius (about 1 A) cannot take on a value of the order of 2.6 to 2.7 A without considerable energy losses, leading to a reduction in the stability of the structure. Clearly, an increase in the coordination number of the cation is accompanied by a general tendency toward the shortening of the edges of the corresponding polyhedron, some of these edges being commensurable with the edges of the tetrahedra, as indeed we find in the stillwellite structure. Moreover, individual elements of the structure may be considered from the point of view of both the "first" and "second" chapter of crystal chemistry [5]; the shortest edges of the Ce polyhedron (Fig. 5) are at the same time the edges of the Si (2.55 and 2.56 A) and B (2.33 and 2.36 A) tetrahedra, while one of the long ones (3.59 A) is closed by the B diortho group.

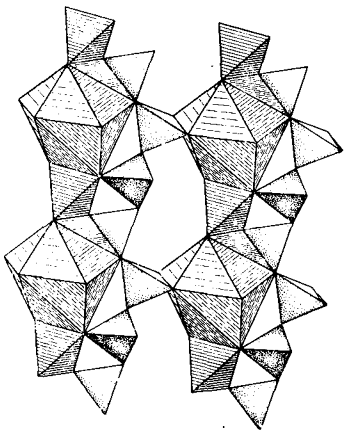

Fig. 5. Fragment of the structure of stillwellite: two translationally identical columns and chains of B tetrahedra.

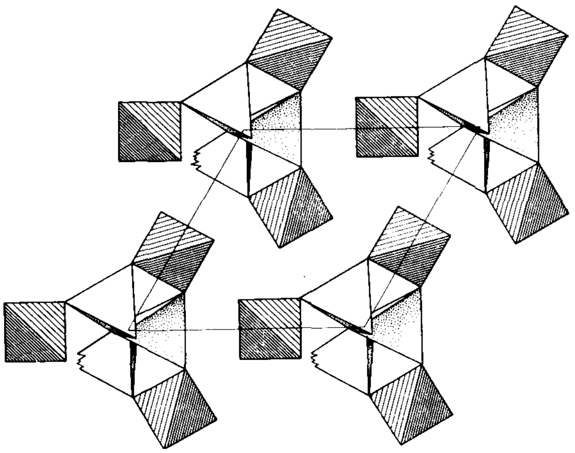

Fig. 6. Motif of BO_4 and SiO_4 tetrahedra in the (x, y) projection.

TABLE 2. Local Balance of Valences in the Structure of Stillwellite (Mean Interatomic Distances, in A, Shown in Brackets)

Anion	Cation				Anion	Cation			
	Ce^{+3}	Si^{+4}	B^{+3}	Σ		Ce^{+3}	Si^{+4}	B^{+3}	Σ
O_I	$2\times\frac{1}{3}$ (2.68)	1 (1.64)	$\frac{3}{4}$ (1.49)	$2+\frac{5}{12}$	O_{III}	$2\times\frac{1}{3}$ (2.49)	1 (1.60)	—	$2-\frac{1}{3}$
O_{II}	$2\times\frac{1}{3}$ (2.68)	1 (1.64)	$\frac{3}{4}$ (1.45)	$2+\frac{5}{12}$	O_{IV}	$2\times\frac{1}{3}$ (2.49)	1 (1.60)	—	$2-\frac{1}{3}$
					O_V	$\frac{1}{3}$ (2.59)	—	$2\times\frac{3}{4}$ (1.46)	$2-\frac{1}{6}$

TABLE 3. Interatomic Distances and Valence Angles in the Stillwellite Structure

Interatomic distances, A				Valence angles	
		Si tetrahedron			
Si — O_I	1.64	O_I — O_{II}	2.58	O_I — Si — O_{II}	104°
Si — O_{II}	1.64	O_I — O_{IV}	2.56	O_I — Si — O_{III}	114°
Si — O_{III}	1.60	O_I — O_{III}	2.73	O_I — Si — O_{IV}	104°
Si — O_{IV}	1.60	O_{II} — O_{III}	2.55	O_{II} — Si — O_{III}	104°
		O_{II} — O_{IV}	2.72	O_{II} — Si — O_{IV}	114°
		O_{III} — O_{IV}	2.71	O_{III} — Si — O_{IV}	116°
		B tetrahedron			
B — O_I	1.49	O_I — O_V	2.36	O_I — B — O_{II}'	105°
B — O_{II}''	1.45	O_I — O_V'	2.39	O_I — B — O_V	107°
B — O_V	1.45	O_{II}'' — O_V	2.46	O_I — B — O_V'	108°
B — O_V'	1.47	O_{II}'' — O_V'	2.49	O_{II}'' — B — O_V	116°
		O_V — O_V'	2.31	O_{II}'' — B — O_V'	117°
		O_I — O_{II}''	2.33	O_V — B — O_V'	105°
		Ce polyhedron			
Ce — O_I	2.73	O_I — O_V	2.36 (1)		
Ce — O_{II}	2.72	O_{II} — O_V	3.59 (1)		
Ce — O_I''	2.63	O_I — O_{III}'	2.91 (2)		
Ce — O_{II}'	2.64	O_I — O_I''	4.05 (2)		
Ce — O_{III}	2.63	O_I — O_{IV}	2.56 (2)		
Ce — O_{IV}	2.62	O_I — O_{IV}'	3.92 (2)		
Ce — O_{III}'	2.35	O_{IV} — O_I''	3.34 (2)		
Ce — O_{IV}'	2.36	O_{IV} — O_{II}'	2.92 (2)		
Ce — O_V	2.59	O_{IV} — O_{IV}'	2.95 (2)		
		O_{III}' — O_V	3.16 (1)		
		O_{IV}' — O_V	3.10 (1)		
		O_{III}' — O_I''	3.08 (2)		
		O_I'' — O_{II}'	2.33 (1)		

Here we must note that, in our earlier communication [6], the "bridge" O atom of this arbitrarily separated diortho group was included in the coordination sphere of the Ce atom. However, the corresponding excessive Ce—O distance (3.36 A), obtained from the final coordinates on the basis of the true group $P3_1$, compels us to acknowledge that this operation was unjustified.

Although formally the balance of valences in the structure is satisfactory and the deviations are no greater than the classical 25%, we must pass one comment on this. There is now a considerable amount of crystal-chemical data indicating that a deficit in the sum of the valence forces converging at an anion is usually compensated by a shortening of the corresponding interatomic distances, while an excess is accompanied by a corresponding increase. It follows from Tables 2 and 3 that in this respect the case of stillwellite is no exception.

The structural peculiarities of stillwellite are in good agreement with its low birefringence and the absence of cleavage, while the polar character of the structure (group $P3_1$) agrees with the piezoactivity of the material.

The closest structural relative of stillwellite, $Ce[SiO_4] \cdot BO$, is the mineral rhabdophanite, $Ce[PO_4] \cdot nH_2O$ (n = 0-1). The structure of the latter [7] is based on analogous columns of eight-vertexed Ce figures and PO_4 tetrahedra, while H_2O molecules lie in the channels of the structure. In the structure of rhabdophanite, the Ce–P columns pass exactly through the middle of the horizontal edges of the cell, satisfying the requirements of a 6_2 axis. In the case of stillwellite, the B–O forces cause the "rhabdophanite" six-groups to be replaced by three-groups of Ce–Si columns, and it is this which results in the reduction of symmetry in the mineral from $P6_222$ to $P3_1$.

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