

cal properties is explained by the substantial difference between the properties of the  $\alpha$  and  $\beta$  solid solutions at the boundaries of the transitional region, and the quite considerable change in properties in the region of the  $\alpha$  solid solutions — a faster occupation of the first kind of spaces by the cations and a faster release of those of the second kind than predicted by the statistical model.

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## Crystal structure of traskite

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The solution of the crystal structure of traskite completes the crystal-chemical study of the Californian group of new barium minerals discovered by Alfors et al.<sup>1</sup> The brownish-red crystals of this mineral, with its glassy luster, are represented by fine nonisometric grains up to 0.3 mm in size with a conchoidal fracture. According to ref. 1 the most fully developed faces are those of the pinacoid {0001} and prism {10 $\bar{1}$ 0}, more rarely the {11 $\bar{2}$ 2}, {41 $\bar{5}$ 2}, and {61 $\bar{7}$ 1}. The parameters of the hexagonal lattice are  $a = 17.88 \text{ \AA}$ ,  $c = 12.30 \text{ \AA}$ ;  $\rho_{\text{meas}} = 3.71 \text{ g/cm}^3$ ; possible Fedorov groups include P6/mmm, P6mm, P622, P6m2, P6 $\bar{2}$ m. For the x-ray diffraction study of traskite we used a nonisometric fragment ( $0.1 \times 0.1 \times 0.2 \text{ mm}$ ); in the first stage of the work, involving the verification and refinement of the lattice parameters and Fedorov group (which were determined from powder diffraction patterns in ref. 1), we recorded x-ray oscillation photographs and

layer-line scans. The lattice constants and the hexagonal symmetry of traskite were confirmed, but the x-ray rotation photograph taken along the c axis contained "inbuilt" diffuse lines, which formally doubled the period (to  $24.6 \text{ \AA}$ ). Thus the traskite structure may be classified among the group of OD structures<sup>2</sup> characterized by the presence of disordered structural blocks. The OD character of the traskite structure is evidently determined by the rotation of its structural elements around the z axis through angles equal to multiples of  $60^\circ$  (possibly  $30^\circ$ ).

The structural solution was carried out within the framework of a hexagonal lattice having parameters  $a = 17.89(1)$ ,  $c = 12.33(1)$  (single-crystal automatic "Syntex" P1 diffractometer),  $\rho_{\text{calc}} = 3.52$ ,  $Z = 1$  assuming the Fedorov group P6m2. The experimental material for the structural solution (422 independent nonzero reflections)

TABLE 1. Coordinates of the Basis Atoms in the Structure of Traskite

Atoms	x/a	y/b	z/c	Multiplicity of the position	Atoms	x/a	y/b	z/c	Multiplicity of the position
Ba <sub>1</sub>	-0.2207	0.2207	0.243	6	O <sub>6</sub>	0.571	-0.571	0	3
Ba <sub>2</sub>	0.4222	-0.4222	0.500	3	O <sub>7</sub>	0.472	0.095	0.179	12
Ba <sub>3</sub>	0.3515	0.3618	0	6	O <sub>8</sub>	0.387	-0.387	0.136	6
Ba <sub>4</sub>	0.5694	-0.5694	0.500	3	O <sub>9</sub>	0.447	-0.447	0	3
Ba <sub>5</sub>	0.2034	-0.2034	0.238	6	O <sub>10</sub>	0.377	0.466	0.185	12
A	2/3	1/3	0.271	2	O <sub>11</sub>	0.617	-0.617	0.172	6
B	1/3	2/3	0.240	2	Cl <sub>1</sub>	0.185	-0.185	0	3
C	1/3	2/3	0	1	Cl <sub>2</sub>	0.791	-0.791	0	3
D	0.4007	0.4062	0.297	12	OH <sub>1</sub>	0.289	0.302	0.214	12
Si <sub>1</sub>	0.569	-0.569	0.139	6	OH <sub>2</sub>	0.285	-0.285	0.388	6
Si <sub>2</sub>	0.440	-0.440	0.128	6	OH <sub>3</sub>	0.715	-0.715	0.382	6
Si <sub>3</sub>	0.092	0.358	0.500	6	(O, OH) <sub>4</sub>	0.509	-0.509	0.361	6
Si <sub>4</sub>	0.736	0.098	0.500	6	(H <sub>2</sub> O) <sub>1</sub>	0.878	-0.878	0.246	6
O <sub>1</sub>	0.318	0.418	0.395	12	(H <sub>2</sub> O) <sub>2</sub>	0.088	-0.088	0	3
O <sub>2</sub>	0.272	0.267	0.500	6	(H <sub>2</sub> O) <sub>3</sub>	0.864	-0.864	0	3
O <sub>3</sub>	0.833	-0.833	0.500	3	(H <sub>2</sub> O) <sub>4</sub>	0	0	0.500	1
O <sub>4</sub>	0.169	-0.169	0.500	3	(H <sub>2</sub> O) <sub>5</sub>	0	0	0	1
O <sub>5</sub>	0.403	0.311	0.385	12					

was obtained in the same diffractometer [Mo radiation, graphite monochromator,  $(2\theta-\theta)$  method, variable scan rate of 6-24° per minute,  $0 \leq h \leq k \leq l \leq 16$ ]. Conversion of the intensities into  $|F_{hkl}|$  and all subsequent calculations were carried out in the Moscow University Computing Center, using a BESM-4M computer and the "Kristall" program.<sup>3</sup> No absorption correction was introduced.

From the three-dimensional Patterson function we found the coordinates of the 24 barium atoms, giving  $R_{hkl} = 40\%$ . The rest of the atoms were revealed by a series of cycles of successive approximations. The coordinates of the heavy Ba, Fe, and Ti were refined by the method of least squares, but the coordinates of the light Si, Cl, and O atoms were hardly refined at all owing to the insufficient number of reflections in the experimental set (the heavy and medium atoms of the structure were arranged on the principle of hexagonal holohedry). The final R factor was  $R_{hkl} = 0.12$ . The coordinates of the base atoms and the interatomic distances are respectively given in Tables 1 and 2.

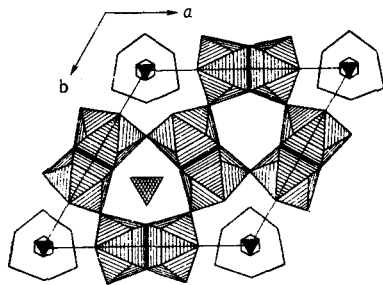


Fig. 1. Stage of the structure at the level  $z = 0$ . The shading shows the skeletal layer of  $Ba_3$  polyhedra. The cellular shading indicates the top of a trigonal Ca prism. The hexagons around the origin of coordinates are water rings.

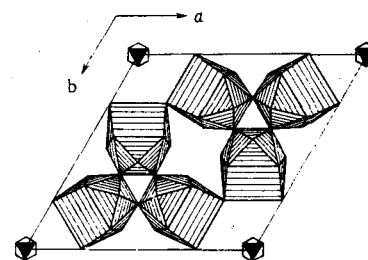


Fig. 2. Stage of the structure at the level  $z = 0.25$ . Almost identical  $Ba_4$  and  $Ba_5$  polyhedra may be seen.

The basis of the structure is formed by a tubular construction of barium polyhedra. Three stages of this structure (in projection along the  $c$  axis) are illustrated by means of similar Ba ten-vertex polyhedra at each level in Figs. 1-3. The stage at the zero level ( $z = 0$ ) in Fig. 1 contains  $Ba_3$  polyhedra, each of which may be visualized in the form of a tetragonal prism with two caps (hemi-octahedra) on neighboring faces. The polyhedra, paired along a common edge, create ditrigonal rings around  $\bar{6}$  axes in the center of the cell, the core of these rings being a trigonal Ca prism connected to the Ba framework vertically (along the  $c$  direction) by standing diorthogroups (Fig. 4). The stage with  $z = 0.25$  (Fig. 2) is complicated by tetrahedral prisms with centered opposite faces. The cavities of this stage are filled with octahedra of three kinds. The most skeletal layer is at a level of  $z = 0.50$  (Fig. 3). The large polyhedra of this layer - almost regular pentagonal prisms - are coupled to one another along the vertical edges, and form cavities (around the  $\bar{6}$  axis), in which rings with the composition  $[Si_{12}O_{36}]$  are situated (Fig. 4).

This is the first time a plane ring of such a configuration has been encountered. In contrast to the corrugated

TABLE 2. Interatomic Distances in the Structure of Traskite, Å

Ba-polyhedra					
$Ba_1-(OH)_3$	2.63	$Ba_2-(OH)_2$	$2.76 \times 4$	$Ba_3-O_{10}$	$2.84 \times 2$
-O <sub>7</sub>	$2.69 \times 2$	-O <sub>1</sub>	$2.83 \times 4$	-O <sub>8</sub>	2.96
-O <sub>5</sub>	$2.70 \times 2$	-(O, OH) <sub>4</sub>	$3.20 \times 2$	-O <sub>7</sub>	$3.00 \times 2$
-Cl <sub>2</sub>	3.02			-(OH) <sub>1</sub>	$3.22 \times 2$
-(H <sub>2</sub> O) <sub>1</sub>	3.06			-Cl <sub>1</sub>	3.06
-O <sub>11</sub>	$3.16 \times 2$			-O <sub>8</sub>	3.49
-O <sub>3</sub>	3.42			-Cl <sub>2</sub>	3.49
$Ba_4-(O, OH)_4$	$2.54 \times 2$			$Ba_5-O_1$	$2.76 \times 2$
-(OH) <sub>3</sub>	$2.99 \times 4$			-O <sub>10</sub>	$2.82 \times 2$
-O <sub>5</sub>	$3.02 \times 4$			-Cl <sub>1</sub>	2.99
				-(OH) <sub>2</sub>	3.14
				-(OH) <sub>1</sub>	$3.32 \times 2$
				-O <sub>8</sub>	$3.51 \times 2$
Si-tetrahedra					
$A-O_{11}$	$1.96 \times 3$	$B-O_8$	$2.10 \times 3$	$C-O_8$	$2.36 \times 6$
-(OH) <sub>3</sub>	$2.03 \times 3$	-(OH) <sub>2</sub>	$2.36 \times 3$	$O_8-O_8$	$2.88 \times 6$
$O_{11}-O_{11}$	2.67	$O_8-O_8$	2.88	$O_8-O_8$	$3.37 \times 3$
$(OH)_3-(OH)_3$	2.60	$(OH)_2-(OH)_2$	2.60		
$O_{11}-OH_3$	3.00	$O_8-(OH)_2$	3.22		
				$D-O_{10}$	1.92
				-(O, OH) <sub>4</sub>	1.93
				-O <sub>1</sub>	2.00
				-O <sub>5</sub>	2.04
				-O <sub>7</sub>	2.17
				-(OH) <sub>1</sub>	2.20
				O-O	2.51-3.07
$Si_1-O_{11}$	1.55	$Si_2-O_9$	1.59	$Si_3-O_4$	1.59
-O <sub>7</sub>	$1.57 \times 2$	-O <sub>10</sub>	$1.64 \times 2$	-O <sub>1</sub>	$1.64 \times 2$
-O <sub>6</sub>	1.72	-O <sub>8</sub>	1.65	-O <sub>2</sub>	1.69
$O_{11}-O_7$	$2.55 \times 2$	$O_9-O_9$	2.51	$O_4-O_1$	$2.65 \times 2$
-O <sub>6</sub>	2.56	-O <sub>10</sub>	$2.69 \times 2$	-O <sub>2</sub>	2.71
$O_7-O_6$	$2.69 \times 2$	$O_{10}-O_8$	$2.66 \times 2$	$O_1-O_1$	2.59
-O <sub>7</sub>	2.71	-O <sub>10</sub>	2.81	-O <sub>2</sub>	$2.73 \times 2$
				$Si_4-O_3$	1.55
				-O <sub>5</sub>	$1.63 \times 2$
				-O <sub>2</sub>	1.64
				$O_3-O_2$	2.54
				-O <sub>5</sub>	$2.65 \times 2$
				$O_5-O_2$	$2.51 \times 2$
				-O <sub>5</sub>	2.84

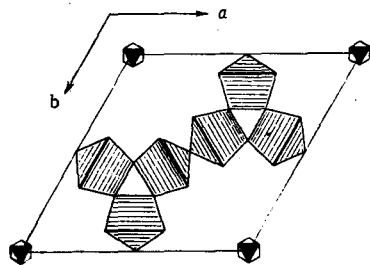


Fig. 3. Stage of the structure at the level  $z = 0.50$ . Layer of almost regular pentagonal  $Ba_2$  and  $Ba_4$  prisms connected to one another by common edges.

twelve-membered ring<sup>4</sup> in  $Na_5YSi_4O_{12}$  the  $[Si_{12}O_{36}]$  ring in traskite is highly symmetrical: To an excellent degree of approximation the symmetry is  $12/mmm$ . Thus the tubular barium framework of traskite is cemented by a discontinuous silicon-oxygen coupling: the large spaces around the origin of coordinates by  $[Si_{12}O_{36}]$  rings, the smaller ones around the three-fold axes by  $[Si_2O_7]$  groups (Fig. 4).

Traskite is similar to the Californian silicate muirite  $Ba_3(Ca, Ba)(Ca, Ti, Mn)_4(OH)_8[Si_8O_{24}](Cl, OH)_8$ , which is also anomalous as regards barium content.<sup>5</sup> As in the case of muirite<sup>5</sup> we notice the zeolite-like appearance of the traskite structure: At the level  $z = 0$  there is a ring of  $H_2O(OH, F)$  atoms around the  $\bar{6}$  axis. Water molecules lie in the center of this ring and that of its silicon-oxygen counterpart.

By analogy with muirite, traskite is a complex system of variable composition



where A, B, C, D are different crystal-chemical positions which are occupied by Ti, Fe, Mn, Ca, Sr, Mg, Al atoms according to the chemical analysis presented in ref. 1; the results of this analysis, recalculated to allow for 3.5% Cl, are given below (wt. %):

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	FeO	MnO	MgO
27.30	0.45	5.71	4.46	1.35	0.32

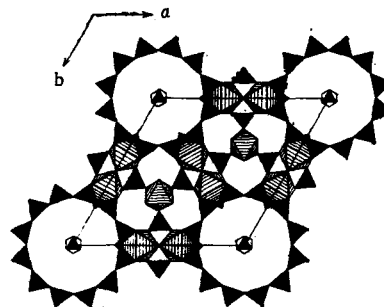


Fig. 4. "Small-cation" coupling of the structure. Shown in black is the island silicon-oxygen motif: twelve-membered rings around the origin of coordinates and vertical  $Si_2O_7$  groups around  $\bar{6}$  axes in the middle of the cell. The shaded octahedra are filled with cations of groups A, B, and D.

CaO	K <sub>2</sub> O	BaO	SrO	Cl	H <sub>2</sub> O	$\Sigma$
0.89	0.05	53.50	0.35	3.50	2.52	100%

Position A (octahedron) is probably occupied by Fe and Ti atoms with distances Fe-O 1.96-2.03 Å, position B (octahedron) by Fe and Mn atoms (Fe-O 2.10-2.36 Å) position C (trigonal prism) by Ca and Sr (Ca-O 2.36 Å), position D (octahedron) by Ti, Fe, Mg, Al (Ti-O 1.92-2.20 Å). Thus the Ti, Fe, Mn, Ca, Mg cations only occupy the cavities of the broad three-dimensional framework which the barium polyhedra create.

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