Crystal structure of cymrite

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A space group of $P2_1$ and a = 5.33, b = 36.6, c = 7.67 Å and β = 90° have been established for cymrite $BaAl_2Si_2O_8 \cdot H_2O$. The cymrite layer of the structure consists of blocks alternating through b/2 which are displaced in the positive and negative directions along the z axis. In addition, successive blocks are distinguished by a "stepwise" displacement of the atoms along the x axis.

An x-ray structural study of cymrite from the Baikal region showed that it may be considered as a hydrated form of α-celsian having the chemical formula[1] $BaSi_2Al_2O_8 \cdot H_2O$. In ref. 1 the structure of cymrite was established by a hexagonal approach and the presence of secondary reflections (satellites) on the x-ray patterns was not explained. After a new find of cymrite in Alaska[2] the symmetry of cymrite was established as orthorhombic. Analysis of the intensities of both the primary and secondary reflections enabled us to identify the distortions in the structure giving rise to the satellites on the x-ray diffraction pattern. Their presence is caused by displacements of the Ba atoms along the x axis, the magnitude and direction of which depend on the y coordinates. From the projection of hk0 the convergence between the experimental and calculated structural factors was reduced to R = 18%, while from the three-dimensional data R = 23.5%. Attempts to improve the agreement between the structural factors were unsuccessful.

A structural study of single crystals of cymrite found recently in California was more successful. A detailed analysis of the intensities for hk1, hk2, etc. scans showed only one plane of symmetry, perpendicular to the b axis. A quite clear distinction from Alaskan cymrite was established for h0l, h1l scans because no planes of symmetry were detected for these sections of the reciprocal lattice. From these data it follows that cymrite has a monoclinic symmetry and that the crystals studied previously were triplets (the specimen from the Baikal region) and twins (the specimen from Alaska).

The unit-cell parameters of Californian cymrite are: a = 5.33, b = 36.6, c = 7.67 Å, β = 90°. The geometry of the x-ray diffraction patterns is such that each hk$l$ reflection having k = 4n is accompanied by satellites having indices hk ± 1l and sometimes hk ±2l. The satellites are absent for the 0k0 reflection, which indicates extinctions of the 0k0 reflections having k = 2n ± 1. Under these conditions groups of $P2_1/a$ and $P2_1$ symmetry are possible. Since we were unable to arrange the atoms from the previously established structural model of cymrite in the first group, the structure of the mineral was refined within the scope of space group $P2_1$, taking into account that the extinctions of the h0l reflections having h = 2n ± 1 are caused by the pseudohexagonal nature of the structure.

The experimental data were corrected for the LP factor of the reflection intensities from 0kl, hk0-hk4 scans, obtained with a KFOR goniometer with Mo radiation from a single crystal of size 0.1-0.2 mm. Intensities were estimated by means of the "blackening spots."

The atomic coordinates determined for Alaskan cymrite were taken as the initial coordinates. An appreciable improvement in the convergence between the calculated and experimental structural factors is obtained when Ba is displaced from the origin along the x axis. The least-squares method was used initially to refine the x and y coordinates of the atoms from the intensities of the hk0 zones (R_{hk0} = 9.3%). The same method, but for the whole hk$l$ block, was used to refine the coordinates of Ba and Si to R = 17.7%. However, refinement of the coordinates of the O atoms did not lower the values of R_{hkl}. For this reason their coordinates were taken from a three-dimensional synthesis and subsequently adjusted by the method of least squares. This leads to R_{hk0} = 8.3%, R_{0kl} = 15.0%, and R_{hkl} = 16.7%. Since the value of R_{0kl} exceeded R_{hk0} substantially the z coordinates of O and the H_2O molecules were first refined (initially by the least-squares method for the 0kl zone), and then the variants were counted in which the z coordinates of each O were varied by intervals of 0.01 Å in the higher and lower directions until there was an improvement in R_{0kl}. The final coordinates of the atoms are shown in Table 1 (R_{0kl} = 11%, R_{hk0} = 8.3%, R_{hkl} = 13.5%) and the interatomic distances calculated from them are presented in Table 2.

The xy and yz projections of the structure of cymrite are presented in Figs. 1 and 2. The average cation–anion distance r = 1.675 Å over all the tetrahedra corresponds to that expected for tetrahedra having the composition $Si_{0.5}Al_{0.5}$, if we assume[3] that r(Si–O) = 1.61 Å and r(Al–O) = 1.75 Å. The average cation–anion distances for the majority of the tetrahedra are 1.67 ± 0.01 Å, which indicates a virtually disordered distribution of Si and Al through these tetrahedra with a slight predominance of Si atoms in them. Exceptions are the tetrahedra T_1 and T_3 (Figs. 1 and 2) stretched along the a chain, which are more enriched in Al and for which $r_1 = r_3$ = 1.70 Å; consequently, their composition is approximately $Si_{0.4}Al_{0.6}$ and the remainder $Si_{0.6}Al_{0.4}$ (r = 1.67 Å) with variations from $Si_{0.65}Al_{0.35}$ (r = 1.66 Å) to $Si_{0.5}Al_{0.5}$ (r = 1.68 Å). The average distances from the two tetrahedral cations to the common basal O are presented[1] in Fig. 1.

A characteristic peculiarity of the cymrite layer is that the tetrahedra are developed about the normals to their bases, which form a clearly defined pseudoditrigonal pattern. Here the direction of rotation of the tetrahedra in the upper lattices (odd numbers) is opposite to that of the tetrahedra in the lower lattices (even numbers) (Fig. 1), while the angles of rotation of the tetrahedra in the upper lattices from zero to b/2 along y (α = 12°30') are markedly larger than those in the tetrahedra of the lower lattices (α = 5°48'). Since the structure in the second half of the unit cell is reversed by the axis 2_1, each individual layer consists of blocks alternating along the y axis which differ in the shape of the six loops of the upper

TABLE 1. Atomic Coordinates in the Structure of Cymrite

Atom	x	y	z	Atom	x	y	z
Ba$_1$	−0.0249	−0.0015	0.0083	O$_{11}$	0.294	0.002	0.218
Ba$_2$	0.5267	0.1235	0.0083	O$_{12}$	0.218	0.050	−0.221
Ba$_3$	0.0292	0.2485	0.0083	O$_{13}$	0.766	0.062	0.185
Ba$_4$	0.5267	0.3735	−0.0083	O$_{14}$	0.750	0.064	−0.171
T$_1$	0.506	0.0416	0.280	O$_{15}$	−0.0416	0.125	0.225
T$_2$	0.510	0.0416	−0.270	O$_{16}$	0.036	0.125	−0.180
T$_3$	0.0092	0.083	0.304	O$_{17}$	0.311	0.178	0.230
T$_4$	0.0204	0.083	−0.265	O$_{18}$	0.770	0.186	−0.180
T$_5$	0.0292	0.167	0.302	O$_{19}$	0.811	0.196	0.230
T$_6$	0.0283	0.167	−0.268	O$_{20}$	0.270	0.189	−0.180
T$_7$	0.529	0.208	0.302	O$_{21}$	0.453	0.250	0.230
T$_8$	0.527	0.208	−0.260	O$_{22}$	0.527	0.250	−0.185
T$_9$	0.535	0.292	0.292	O$_{23}$	0.811	0.304	0.233
T$_{10}$	0.528	0.292	−0.265	O$_{24}$	0.269	0.311	−0.174
T$_{11}$	0.0308	0.333	0.302	O$_{25}$	0.324	0.324	0.240
T$_{12}$	0.0308	0.333	−0.260	O$_{26}$	0.770	0.314	−0.180
T$_{13}$	0.0304	0.417	0.300	O$_{27}$	−0.047	0.375	0.230
T$_{14}$	0.0204	0.417	−0.265	O$_{28}$	0.025	0.375	−0.184
T$_{15}$	0.521	0.458	0.302	O$_{29}$	0.307	0.431	0.226
T$_{16}$	0.521	0.458	−0.267	O$_{30}$	0.770	0.436	−0.180
O$_1$	0.516	0.0416	0.506	O$_{31}$	0.805	0.444	0.225
O$_2$	0.0158	0.0835	0.522	O$_{32}$	0.267	0.439	−0.179
O$_3$	0.0375	0.167	0.514	H$_2$O(1)	−0.025	−0.002	0.387
O$_4$	0.525	0.210	0.516	H$_2$O(2)	0.527	0.124	0.387
O$_5$	0.536	0.290	0.516	H$_2$O(3)	0.029	0.248	0.387
O$_6$	0.0258	0.333	0.516	H$_2$O(4)	0.527	0.374	−0.387
O$_7$	0.0204	0.416	0.520	H$_2$O(5)	−0.025	0.006	0.624
O$_8$	0.510	0.458	0.516	H$_2$O(6)	0.527	0.131	0.624
O$_9$	0.474	0	0.194	H$_2$O(7)	0.029	0.256	0.624
O$_{10}$	0.544	−0.0006	−0.222	H$_2$O(8)	0.527	0.382	−0.624

and lower tetrahedral lattices. The boundary between the blocks occurs at the chain of T_1 and T_3 tetrahedra (Fig. 1); the z coordinates of the basal O atoms differ greatly in each block (Fig. 2). Whereas the z coordinates of the basal O atoms in the first block (up to b/2 along the y axis) vary from 0.22 to 0.24, in the following block the corresponding coordinates are 0.17-0.19. The "break" in the blocks along the z axis occurs at the basal O atoms common to the tetrahedra T_1, T_3 and T_2, T_4 (Fig. 2).

Let us consider in more detail the nature of the distortions in the lattices in the first block of the layer. It is known that on passing from the hexagonal pattern of a tetrahedral lattice having a parameter b_t to a ditrigonal pattern the b parameter of the lattice (where $b = b_t \cos \alpha$) decreases with an increase in the angle α. Since in the cymrite layer being considered the b parameters for the upper and lower lattices are the same, while the α angles are different, the linear dimensions of the upper lattice in the ab plane should be greater in the absence of rotation of the tetrahedra (the angle α is increased) than the dimensions of the lower lattice. In fact, it follows from Table 2 that the average edge length of the bases for all the tetrahedrons is 2.73 Å for the upper tetrahedral lattice and 2.68 Å for the lower. Here, the edge lengths of the bases of the tetrahedra (the average for each) in the upper lattice increase regularly along the y axis from the T_3 tetrahedra (2.69 Å) to the T_9-T_{11} tetrahedra (2.76 Å) and decrease to the $T_{15}-T_2$ tetrahedra (2.70 Å) (Fig. 2).

On the other hand, for the lower lattices of the block the edge length of the base is shortened in the same direction from the T_4 tetrahedron (2.75 Å) to the T_8-T_{12} tetrahedra (2.66 Å) and then these values increase for the $T_{16}-T_1$ tetrahedra (2.69; 2.70 Å). Since for the majority of the tetrahedra the r values are close to each other and, consequently, also close to the average edge length over the tetrahedron,[4] the data presented indicate that the tetrahedra of the upper lattice are flattened along the c axis (relative to their true geometrical shape), while the tetra-

hedra of the lower lattice are greatly elongated. Furthermore, the z coordinates of the basal O atoms of the upper lattice along the y axis from O_{11} to O_{10} (Fig. 2) first increase from 0.225 (O_{11}) to 0.240 (O_{25}) (the flattening of the tetrahedra is increased) and then decrease to 0.222 (O_{10}) (the flattening of the tetrahedra is decreased). The z coordinates of the apical and basal O atoms (Table 1) also confirm the relationships noted for the degree of stretching and flattening of the tetrahedra along the z axis for the lattices of the tetrahedra in the first block of the layer.

Thus, in each block of the cymrite layer lattices of different linear dimensions in the tetrahedra are joined and their commensurability is achieved by the different angle of rotation of the two lattices and also by a certain twisting of the upper lattice (having a large parameter b_t) relative to the lower one. The stresses which may arise in such a connection are "stripped," due to the successive rotation of the blocks by the 2_1 axis which, moreover, ensures that the layer is plane-parallel on the whole.

As may be seen from Fig. 2, the Ba atoms in each block are displaced markedly from the average positions, the displacement in the adjacent blocks taking place in the opposite directions along the x axis. The absolute displacement of all the Ba atoms is approximately the same (Table 1). In accordance with the results in ref. 2, the appearance of satellites among the hk0 reflections on the x-ray diffraction patterns of cymrite is caused by the "stepwise" displacement of the atoms, chiefly Ba, along the x axis with a change in the direction of the displacement through each b/2 along the y axis.

Likewise the appearance of satellites along the y* axis for the 0kl scans is due to the stepwise displacement of the atoms in each block along the z axis. Since it is the O and Si atoms, but not Ba, which are most strongly displaced along the z axis, the satellites on the 0kl section have a markedly lower intensity than the satellites on the hk0 section.

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TABLE 2. Interatomic Distances (Å) in the Structure of Cymrite

T_1-O_1	1.73	T_5-O_3	1.63	T_9-O_5	1.72	$T_{13}-O_7$	1.69
T_1-O_9	1.68	T_5-O_{19}	1.67	T_9-O_{23}	1.60	$T_{13}-O_{29}$	1.66
T_1-O_{11}	1.66	T_5-O_{17}	1.65	T_9-O_{25}	1.68	$T_{13}-O_{31}$	1.66
T_1-O_{13}	1.74	T_5-O_{15}	1.70	T_9-O_{21}	1.68	$T_{13}-O_{27}$	1.69
Cp.	1.70	Cp.	1.66	Cp.	1.67	Cp.	1.67
Av.(calc)	1.73	Av.(calc)	1.67	Av.(calc)	1.67	Av.(calc.)	1.67
T_2-O_1	1.72	T_6-O_3	1.67	$T_{10}-O_5$	1.68	$T_{14}-O_7$	1.65
T_2-O_{10}	1.61	T_6-O_{18}	1.69	$T_{10}-O_{26}$	1.66	$T_{14}-O_{32}$	1.68
T_2-O_{12}	1.63	T_6-O_{20}	1.66	$T_{10}-O_{24}$	1.70	$T_{14}-O_{30}$	1.64
T_2-O_{14}	1.70	T_6-O_{16}	1.69	$T_{10}-O_{22}$	1.67	$T_{14}-O_{28}$	1.67
Cp.	1.66	Cp.	1.68	Cp.	1.68	Cp.	1.66
Av.(calc.)	1.67	Av.(calc.)	1.68	Av.(calc.)	1.67	Av.(calc.)	1.67
T_3-O_2	1.67	T_7-O_4	1.64	$T_{11}-O_6$	1.64	$T_{15}-O_8$	1.64
T_3-O_{11}	1.71	T_7-O_{19}	1.66	$T_{11}-O_{23}$	1.67	$T_{15}-O_{29}$	1.62
T_3-O_{13}	1.77	T_7-O_{17}	1.70	$T_{11}-O_{25}$	1.67	$T_{15}-O_{31}$	1.70
T_3-O_{15}	1.67	T_7-O_{21}	1.69	$T_{11}-O_{27}$	1.69	$T_{15}-O_{10}$	1.68
Cp.	1.70	Cp.	1.67	Cp.	1.67	Cp.	1.66
Av.(calc.)	1.71	Av.(calc.)	1.67	Av.(calc.)	1.67	Av.(calc.)	1.68
T_4-O_2	1.63	T_8-O_4	1.72	$T_{12}-O_6$	1.72	$T_{16}-O_8$	1.66
T_4-O_{12}	1.65	T_8-O_{18}	1.65	$T_{12}-O_{26}$	1.67	$T_{16}-O_{32}$	1.66
T_4-O_{14}	1.76	T_8-O_{20}	1.66	$T_{12}-O_{24}$	1.64	$T_{16}-O_{30}$	1.70
T_4-O_{16}	1.67	T_8-O_{22}	1.65	$T_{12}-O_{28}$	1.65	$T_{16}-O_9$	1.65
Cp.	1.68	Cp.	1.67	Cp.	1.67	Cp.	1.67
Av.(calc.)	1.64	Av.(calc.)	1.67	Av.(calc.)	1.67	Av.(calc.)	1.68
T_1 tetrahedron		T_4 tetrahedron		T_7 tetrahedron		T_{10} tetrahedron	
O_1-O_9	2.85	O_2-O_{12}	2.60	O_4-O_{17}	2.74	O_5-O_{22}	2.73
O_1-O_{13}	2.90	O_2-O_{14}	2.88	O_4-O_{19}	2.72	O_5-O_{24}	2.88
O_1-O_{11}	2.74	O_2-O_{16}	2.80	O_4-O_{21}	2.67	O_5-O_{26}	2.79
O_9-O_{13}	2.77	$O_{12}-O_{16}$	2.95	$O_{19}-O_{17}$	2.75	$O_{22}-O_{24}$	2.64
O_9-O_{11}	2.83	$O_{12}-O_{14}$	2.58	$O_{19}-O_{21}$	2.76	$O_{22}-O_{26}$	2.69
$O_{11}-O_{13}$	2.55	$O_{14}-O_{16}$	2.72	$O_{17}-O_{21}$	2.76	$O_{24}-O_{26}$	2.67
Cp.	2.78	Cp.	2.76	Cp.	2.73	Cp.	2.73
T_2 tetrahedron		T_5 tetrahedron		T_8 tetrahedron		T_{11} tetrahedron	
O_1-O_{10}	2.61	O_3-O_{15}	2.74	O_4-O_{20}	2.81	O_6-O_{23}	2.68
O_1-O_{12}	2.65	O_3-O_{17}	2.65	O_4-O_{18}	2.81	O_6-O_{25}	2.67
O_1-O_{14}	2.89	O_3-O_{19}	2.71	O_4-O_{22}	2.73	O_6-O_{27}	2.71
$O_{10}-O_{12}$	2.55	$O_{15}-O_{17}$	2.71	$O_{18}-O_{20}$	2.67	$O_{25}-O_{23}$	2.83
$O_{10}-O_{14}$	2.63	$O_{15}-O_{19}$	2.73	$O_{20}-O_{22}$	2.63	$O_{25}-O_{27}$	2.73
$O_{12}-O_{14}$	2.91	$O_{19}-O_{17}$	2.75	$O_{22}-O_{18}$	2.69	$O_{23}-O_{27}$	2.73
Cp.	2.71	Cp.	2.71	Cp.	2.72	Cp.	2.72
T_3 tetrahedron		T_6 tetrahedron		T_9 tetrahedron		T_{12} tetrahedron	
O_2-O_{13}	3.01	O_3-O_{16}	2.81	O_5-O_{21}	2.68	O_6-O_{24}	2.83
O_2-O_{11}	2.79	O_3-O_{20}	2.77	O_5-O_{23}	2.66	O_6-O_{26}	2.79
O_2-O_{15}	2.76	O_3-O_{18}	2.83	O_5-O_{25}	2.71	O_6-O_{28}	2.77
$O_{11}-O_{13}$	2.85	$O_{16}-O_{20}$	2.67	$O_{23}-O_{21}$	2.76	$O_{26}-O_{24}$	2.66
$O_{13}-O_{15}$	2.56	$O_{16}-O_{18}$	2.66	$O_{23}-O_{25}$	2.70	$O_{26}-O_{24}$	2.63
$O_{11}-O_{15}$	2.65	$O_{18}-O_{20}$	2.67	$O_{21}-O_{25}$	2.81	$O_{24}-O_{28}$	2.70
Cp.	2.77	Cp.	2.74	Cp.	2.72	Cp.	2.73
T_{13} tetrahedron		T_{14} tetrahedron		T_{15} tetrahedron		T_{16} tetrahedron	
O_7-O_{27}	2.71	O_7-O_{28}	2.73	O_8-O_{29}	2.67	O_8-O_{30}	2.83
O_7-O_{29}	2.78	O_7-O_{30}	2.76	O_8-O_{31}	2.78	O_8-O_{32}	2.76
O_7-O_{31}	2.74	O_7-O_{32}	2.79	O_8-O_{10}	2.74	O_8-O_9	2.71
$O_{29}-O_{27}$	2.80	$O_{28}-O_{30}$	2.69	$O_{31}-O_{29}$	2.70	$O_{32}-O_{30}$	2.68
$O_{29}-O_{31}$	2.72	$O_{30}-O_{32}$	2.65	$O_{31}-O_{10}$	2.78	$O_{32}-O_9$	2.64
$O_{31}-O_{27}$	2.66	$O_{28}-O_{32}$	2.63	$O_{29}-O_{10}$	2.64	O_9-O_{30}	2.70
Cp.	2.73	Cp.	2.70	Cp.	2.72	Cp.	2.73
Ba_1-O_9	3.03	Ba_2-O_{11}	2.78	Ba_3-O_{19}	2.83	Ba_4-O_{32}	3.08
Ba_1-O_9'	3.02	Ba_2-O_{12}	3.63	Ba_3-O_{26}	3.13	Ba_4-O_{29}	3.02
Ba_1-O_{10}	2.90	Ba_2-O_{13}	2.88	Ba_3-O_{18}	3.05	Ba_4-O_{30}	2.95
Ba_1-O_{10}'	3.51	Ba_2-O_{14}	2.85	Ba_3-O_{23}	2.92	Ba_4-O_{31}	3.49
Ba_1-O_{11}	3.58	Ba_2-O_{19}	3.51	Ba_3-O_{17}	3.45	Ba_4-O_{26}	2.87
Ba_1-O_{12}	2.90	Ba_2-O_{18}	3.01	Ba_3-O_{24}	2.98	Ba_4-O_{23}	3.60
Ba_1-O_{13}	2.93	Ba_2-O_{17}	2.87	Ba_3-O_{20}	2.92	Ba_4-O_{24}	2.97
Ba_1-O_{14}	3.03	Ba_2-O_{20}	3.13	Ba_3-O_{25}	3.66	Ba_4-O_{25}	2.85
Ba_1-O_{32}	2.86	Ba_2-O_{15}	2.84	Ba_3-O_{21}	2.83	Ba_4-O_{23}	3.00
Ba_1-O_{29}	3.42	Ba_2-O_{15}'	3.46	Ba_3-O_{21}'	3.51	Ba_4-O_{28}'	2.98
Ba_1-O_{30}	2.98	Ba_2-O_{16}	2.99	Ba_3-O_{22}	3.04	Ba_4-O_{27}	2.92
Ba_1-O_{31}	2.94	Ba_2-O_{18}'	3.08	Ba_3-O_{22}'	3.06	Ba_4-O_{27}'	3.56

Let us consider the probable reasons for the distortions observed in the structure of cymrite. Basically, it would appear, the displacements of Ba are associated with a certain ordering in the distribution of Si and Al. As has already been mentioned, the T_1 and T_3 tetrahedra are distinguished by a maximum Al content and, consequently, their common basal O atoms are the most undersaturated by positive valences.[2] This applies particularly to the O_{13} atom having the greatest increased distance from the nuclei of T_1 and T_3 (1.75 Å). The O_{14} atom would also appear to be highly undersaturated because the average distance from O_{14} to the nuclei of T_2 and T_4 is equal to 1.73 Å. For these reasons the Ba_2 atom is displaced along the x axis, converging from O_{13} and O_{14} (Fig. 1). Furthermore, such a displacement is favored by the relatively high valency unsaturation of the O_{15} anion, from which the dis-

tance to the nuclei of T_3 and T_5 is equal to 1.69 Å. The Ba_1 atom also tends to converge from O_{13} and O_{14} and is displaced along the x axis in the direction opposite to the displacement of Ba_2 (Fig. 1). The displacement of Ba_1 and Ba_2 along the y axis scarcely occurs at all here. It would seem that if the Ba_1 and Ba_2 atoms move in opposition to each other along a straight line joining their centers this would also give rise to a stronger electrostatic repulsion between them. The relatively high unsaturation of O_{21} and O_{27} (Fig. 1) favors the displacement of Ba_3 and Ba_4 in the same direction as Ba_2 along the x axis. Furthermore, with a unidirectional displacement of the Ba atoms they become uniformly distributed in the ab plane in each block through the hexagonal arrangement.

The displacement of the Ba_2 atom to O_{15} leads to its

Fig. 1. Projection of the structure of cymrite along the z axis.

Fig. 2. Projection of the structure of cymrite along the x axis.

removal from O_{11} to O_{17} for the upper lattice of tetrahedra in the lower layer. Simultaneously Ba_2 approaches from O_{14} and O_{18} and is removed from O_{16} for the lower lattice of the upper layer (Fig. 1). For the equation $R_{pd}(Ba_2-O_{11}) = R_{pd}(Ba_2-O_{15}) = R_{pd}(Ba_2-O_{17})$ and $R_{pd}(Ba_2-O_{14}) = R_{pd}(Ba_2-O_{16}) = R_{pd}(Ba_2-O_{18})$ (here R_{pd} is the projection of the Ba−O distance on the ab plane) to be satisfied in the projection on the ab plane, a larger angle of rotation of the tetrahedra is necessary for the upper lattice than for the lower. Analogous conditions should also be fulfilled for the ligands in the environment of Ba_3, Ba_4, and Ba_1' (Fig. 1). Thus, the displacement of the Ba atoms along the x axis determines the necessity for a difference in the angles of rotation for the two lattices of the tetrahedra, which is achieved by their flattening and elongation along the z axis.

It is seen from Fig. 1 that the distances from the centers of the Ba atoms projected on the ab plane to the three closest basal O atoms of the upper lattice in the first block are less than the corresponding distance to the three closest basal O atoms of the lower lattice (e.g., the distances from the Ba_3 projection points to O_{19}, O_{21}, O_{23} and to O_{20}, O_{22}, O_{24}). Since the average Ba−O distance for a given coordination environment of Ba is virtually a constant quantity an increased distance along the z axis from the Ba atoms to the plane of the basal O atoms should correspond to a shorter distance from the center of a loop to the three closest basal O atoms in the ab plane and vice versa. For this reason the distance along the z axis from the basal O atoms of the upper lattice of the tetrahedra to the closest Ba atoms ($z_{Ba} = 0$) exceeds the corresponding

distance from the plane of the basal O atoms of the lower lattice to the Ba atoms for $z_{Ba} = 1$ (Fig. 2).

Thus, the different rotation of the tetrahedra in the upper and lower lattices leads to a stepwise displacement of the successive blocks in a layer in the positive and negative directions along the z axis, with a period of $b/2$.

As may be seen from Fig. 1, the coordination environment of the Ba atoms approaches an octahedral arrangement. The averages of the six shortest Ba−O lengths for Ba_1, Ba_2, Ba_3, and Ba_4 are equal to 2.92, 2.90, 2.92, and 2.93 Å respectively. However, owing to the small angle of rotation of the tetrahedra in the lower lattice and the opposing displacements of Ba_1 and Ba_2 along the x axis, three comparatively short Ba−O distances, equal to 3.01-3.08 Å on the average (Table 2) are still fixed for each Ba atom and then for each Ba atom the coordination number may be considered as 9 with an average Ba−O distance of 2.95 Å.

Experimentally we have established eight positions, labeled on Fig. 2, in which four water molecules are distributed statistically, each at a distance of ~3 Å from the nearest basal O atoms and we may refer to hydrogen bonds.

The relationships established in the distortion of the structure of cymrite can be simulated, having constructed a model on the basis of an average Ba−O distance of 2.92 Å, the angles of rotation of the tetrahedra of the upper ($\alpha = 12°30'$) and lower ($\alpha = 5°48'$) lattices, and a space group $P2_1$ for the anionic structure.

These data are sufficient to calculate the coordinates of the Ba and O atoms and to obtain the stepwise displacement of these atoms along the x axis automatically, as well as the ordering in the distribution of Si and Al. Table 2 shows the calculated average cation−anion distances for all the tetrahedra, which agree well with the experimental data.

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[1]The basal O atoms form the bases of the tetrahedra in the plane of the cymrite layer.

[2]The average distance from a given basal O to the two nearest nuclei of tetrahedral cations can be taken conditionally as a measure of the relative valency unsaturation of this O atom by tetrahedral cations: To a first approximation, the greater this distance, the greater is the unsaturation of the anions.

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