BAOTITE – A MINERAL WITH [Si_4O_{12}] METASILICATE RINGS

V. I. Simonov

Institute of Crystallography of the Academy of Sciences, USSR

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The crystal structure of baotite (space group $I4_1/a$, dimensions of the unit cell: a = 19.68, c = 5.88 A) has been established by the method of minimalization of Patterson projections. The final atomic coordinates resulted from several computings of signs of hkl alternating with Fourier syntheses. Baotite is a new example of a ring silicate with a tetragonal radical [Si_4O_{12}]. The detailed formula of baotite is $Ba_4(Ti, Nb)_8ClO_{16}[Si_4O_{12}]$. The ring radicals [$Si_4O_{12}$] are on the 4-fold inversion axes, and (Ti, Nb)-octahedra are around 4-fold screw axes in columns analogous to those in the structure of rutile.

Recently in China a new silicate mineral, baotite, was discovered by the Soviet mineralogist Semenov and the Chinese scientist Hung Weng-hsing [1]. Two chemical analyses carried out by T. A. Kapitonova and A. V. Bykova led to the following formula for baotite: $Ba(Ti, Nb)_2SiO_7$ plus some Cl, approximately equal to one atom to four atoms of Si. The tetragonal cell of baotite (bipyramidal symmetry class) has the parameters: a = 19.68, c = 5.88 A. Its space group $C_{4h}^6 = I\,4_1/a$ is determined uniquely from the systematic extinctions of reflections. The central cell contains 16 formula units of the composition described above.

The determination of the crystal structure of baotite is facilitated by its high symmetry and by the presence of the heavy Ba atom (Z = 56). The horizontal glide planes of symmetry shorten by twofold the parameters $\underline{a}$ and $\underline{b}$ on the projection $\sigma(x, y)$. The planar symmetry group of this projection is p4. Its independent unit is $^1/_{16}$ of the content of the body-centered baotite cell. On the projection of interatomic vectors p(x, y) it was possible to localize Ba. The Patterson peak corresponding to the vectors between the Ba atoms is linked with the second degree operation of the fourfold axis, and it serves as a basis for the construction of the (minimum) Buerger M-function [2]. The elementary operation of rotation about the fourfold axis allows one to obtain $M_4(x, y)$ from $M_2(x, y)$ which gives the base plane of the model of baotite. A more precise structure is obtained by alternate calculation of the sign of the structure amplitudes and projections of the electron densities. The final value of the reliability factor, calculated from all 164 values (Mo-radiation) of the structure amplitudes hk0 with $F_E \neq 0$ is equal to 15.3% with a maximum value of $\vartheta/\lambda = 1.02$. In F_C an isotropic temperature factor was introduced with Ba = 0.65 A.

In Fig. 1 is given a sketch of the baotite structure, all the cation polyhedra, except Ba, being shown. It is noticed that the fourfold metasilicate rings [Si_4O_{12}] are strung along the $\bar{4}$ axis. A similar ring was proposed by Ito [3] for the borosilicate axinite, but without strict proof. Strunz discussed the possibility of similar rings in neptunite [4], but the structure of this mineral still awaits a solution.

The geometrically analogous metaphosphate ring [P_4O_{12}] characterizes Al-metaphosphate $Al_4[P_4O_{12}]_3$ [5].

Between each pair of translationally identical rings [Si_4O_{12}] of baotite large cavities are formed in which the large Cl atoms are distributed at the general points of the fourfold inversion axis. Thus the solution of the structure elucidates the role and quantity of Cl (the absence of defects being assumed) in the mineral. The oxygen atoms of the silicate radical which form the vertical edges of the tetrahedra are simultaneously the

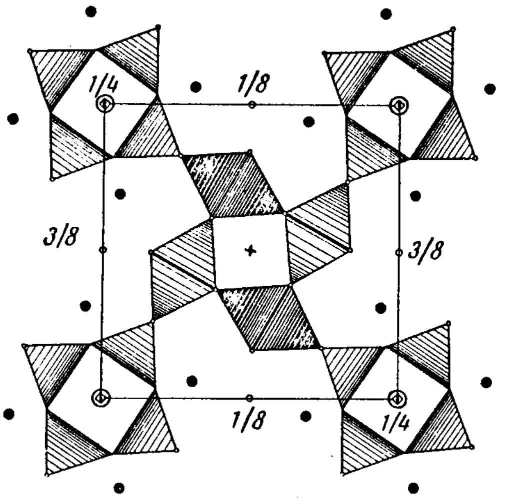

Fig. 1. Diagram of the structure of baotite. $^1/_4$ of the cell is shown. Ba) dark circles, Cl) light circles on the $\bar{4}$ axes.

The Horizontal Coordinates of the Basic Atoms of Baotite (along the a and b axes). Origian of Coordinates on the Fourfold Inversion Axis

Type of atom	x	y
Ba	0.153	0.029
$(Ti, Nb)_{I, II}$	0.137	0.220
Si	0,064	0,093
Cl	0.000	0.000
O_I	0,092	0,015
$O_{II, III}$	0,090	0.128
$O_{IV, V}$	0.195	0.184
$O_{VI, VII}$	0.081	0,244

apices of two (Ti, Nb)-octahedra. The central part of Fig. 1 (in which is shown one fourth of the whole tetragonal cell) is occupied by a pattern looking as if it had been excised from the rutile structure [1]. Four infinite vertical columns of (Ti, Nb)-octahedra, which are connected together by common horizontal edges, are close around the fourth-order screw axis (4_1) and form a continuous square tube. It will be noticed that the period (2.96 A) along the axis of the tube is equal to one octahedron,whereas in baotite (5.88 A) it is equal to two. This is a result of the different types of fourfold axes lying along the tube: 4_2 in rutile, 4_1 or 4_3 in baotite.

Expansion of the chemical formula of baotite to correspond to the crystal structure gives the formula $Ba_4(Ti, Nb)_8ClO_{16}[Si_4O_{12}]$. Four of these units (180 atoms) occur in the unit cell of the mineral. The Cl takes the parameter-less point in the special position of the $\bar{4}$ axis. The metasilicate rings $[Si_4O_{12}]$ lie in the plane perpendicular to this axis and level with its second special position. The peripheral O atoms of the silicate rings enter the (Ti, Nb)-octahedra and determine their vertical coordinates. The Ba atoms are placed in the large gaps in the structure at about the same height as the Cl.

The values of the horizontal coordinates of the basic atoms of baotite, obtained from the σ (x, y) projection are cited in the table. In the σ (x, y) projection the atoms Ba, Si, Cl and O_I are not overlapped by other atoms. The remaining atoms of the structure are distributed in pairs along the $\underline{z}$ axis quite exactly one above the other, and in the table their horizontal coordinates are given the same value, though this is not required by symmetry. Exact fixing of all the individual coordinates of the basic atoms is hampered by the large value of the period $\underline{a}$. The weighted projections along the c-axis constructed from reflections of any one of the layer lines are useless, because the distance between overlapping atoms is close to a half-period along Z.

The infinite colums of (Ti, Nb)-octahedra play a determining role in baotite. The length of the edges of these octahedra cause the structure to obey the rules of the "first chapter of silicate crystal chemistry" [7]. The one story $[Si_4O_{12}]$ rings are a consequence of the "commensurable" nature of the edges of the Si-tetrahedra and the edges of the (Ti, Nb)-octahedra.

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