THE CRYSTAL STRUCTURE OF RAMSAITE

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Abstract

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THE CRYSTAL STRUCTURE OF RAMSAITE

$Na_2Ti_2Si_2O_9 = Na_2Ti_2O_3[Si_2O_6]$

The structure of this Na titanosilicate* was solved in 1942 ([1,2]) on the basis of the principles of closest packing ([3]) and became one of the classic examples of the application of the latter to the interpretation of the structures of ionic compounds ([4]) with such a large (for that time) number of parameters—22. In connection with the last two circumstances, and in order to refine it with the use of modern computing techniques, an independent structure determination was desirable; for this structure the discrepancy factor, calculated from independent coordinates ([1,2]), was 36.59%, i.e., a value quite promising in present-day X-ray structure analysis.

Table 1

Coordinates of the basis atoms in the structure of ramsaite $Na_2Ti_2O_3[Si_2O_6]$

Atoms	x/a	y/b	z/c
Ti	0.169 (0.163)	0.652 (0.651)	0.631 (0.635)*
Si	0.026 (0.023)	0.158 (0.153)	0.206 (0.19)
Na	0.155 (0.152)	0.066 (0.045)	0.643 (0.65)
O_1	0.25 (0.25)	0 (0)	0.014 (0.02)
O_2	0.072 (0.072)	0.515 (0.492)	0.741 (0.76)
O_3	0.064 (0.067)	0.266 (0.23)	0.449 (0.44)
O_4	0.274 (0.263)	0.182 (0.175)	0.443 (0.45)
O_5	0.085 (−0.09)	0.569 (0.617)	0.292 (0.31)

* The coordinates from ([1,2]) are given in parentheses.

For the X-ray structural investigation, isometric light-brown single crystals of Khibiny ramsaite with dimensions $0.10 \times 0.10 \times 0.15$ mm^3 were selected. The parameters of the primitive orthorhombic cell (rotation photographs and refinement on a diffractometer by the single-crystal method): $a = 14.518 \pm 0.003$, $b = 8.976 \pm 0.003$, $c = 5.081 \pm 0.005$ Å agree with those determined earlier.

Figure 1

Figure 1: Figure 1

In the structure determination, 7 layer-line sweep photographs were used (Weissenberg photographs, Mo radiation) about the c and b axes: ($hk0 \div hk4$ ($\max \sin\theta/\lambda = 0.924$ Å^{-1}), $h0l - h1l$ ($\max \sin\theta/\lambda = 0.905$ Å^{-1}). The extinction rules unambiguously confirmed the space group indicated in ([1,2]), $D_{2h}^{14} = Pnca$, with 8-fold general positions and 4-fold special positions. In the former one may expect three octets of Na, Ti, and Si atoms, as well as 32 O atoms, and only 4 O atoms in special positions. Reflection intensities were estimated by the marking method standard in our laboratories, with a blackening step of $\sqrt[4]{2}$. Films taken with multiple exposures were used for estimating strong reflections. No absorption correction was introduced.

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* Ramsaite, a rare Na titanosilicate, was discovered by A. E. Fersman ([5]) in nepheline syenites in association with field spar, aegirine, eudialyte, etc. Optically negative. $2V$ from 33 to 40°. $N_o = 2.02$, $N_m = 2.01$, $N_p = 1.92$, $N_o - N_p = 0.10$. Dispersion very strong. Hardness 6. Cleavage very perfect on (100) and less perfect along the prism (210). Specific gravity 3.38–3.43. Chemical analyses agree very well with the formula $Na_2Ti_2Si_2O_9$.

In accordance with the previously calculated "heaviness criterion"

$$r = \left(\sum f_T^2 / \sum f^2\right)^{1/2} = 1$$

the structure was determined by the "heavy-atom" method.

The main attention was given to the Patterson projection uv along the short edge c (5.08 Å), and therefore with the smallest number of overlaps.

Fig. 1. Structures idealized according to the strictly maintained principle of closest packing:
a—pyroxene-diopside with 4 layers, alternately composed of Ca, Mg octahedra and pyroxene chains $[Si_2O_6]_\infty$, doubly oriented with respect to the packing axis; *b*—ramsayite with 6 layers, divided into two-story sections with Na and Ti cations in octahedra and single-story sections with pyroxene chains (of two orientations) $[Si_2O_6]_\infty$.

The atoms Ti, Si, Na, and four kinds of O were successively localized; the fifth O atom is in a special position.

The x, y-coordinates were refined by successive approximations with alternating constructions of electron-density projections and calculation of the factor R at each stage. Starting from the x, y coordinates and elementary crystal-chemical

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

considerations, it was not difficult to locate the atoms Ti, Si, Na, O in the Patterson projection uv, and in the side projection xz.

Fig. 2. Ramsayite. Axonometry of the ideal structure consisting of Na, Ti octahedra and Si chains.

Fig. 3. Na semi-octahedron in ramsayite. Under the quadrangular lid, the triangular base common to an analogous Na semi-octahedron located one story lower is indicated by a dotted line.

The coordinates x, y, z, averaged over two projections, were refined by the least-squares method on the basis of a three-dimensional set of intensities.

(526 independent and nonzero reflections from the layer lines $hk0 \div hk4$). All calculations were carried out at the Computing Center of Moscow University on the M-20 electronic computer, using the programs of B. L. Tarnopol' skii and V. I. Andrianov [6].

The final coordinates of the basis atoms of ramsayite (22 parameters) are given in Table 1. The discrepancy factor for these coordinates for all nonzero reflections was

Table 2

Interatomic distances in the structure of ramsayite $Na_2Ti_2O_3[Si_2O_6]$ **(in angstroms)**

Si tetra-hedra		Ti octa-hedra		Na poly-hedra	
$Si—O_3$	1.68	$Ti—O_1$	1.88	$Na—O_3$	2.55
$Si—O'_3$	1.60	$Ti—O_2$	1.94	$Na—O'_4$	2.26
$Si—O'_2$	1.69	$Ti—O_4$	1.85	$Na—O'_2$	2.53
$Si—O'_5$	1.60	$Ti—O'_5$	2.16	$Na—O'_1$	2.45
$O_3—O'_3$	2.64	$Ti—O'_4$	1.95	$Na—O''_4$	2.64
$O_3—O'_2$	2.71	$Ti—O''_5$	2.16	$Na—O'_5$	2.43
$O_3—O'_5$	2.64	$O_1—O'_2$	2.83	$Na—O'_3$	2.43
$O'_3—O'_2$	2.68	$O_1—O_4$	2.79	$O_3—O'_4$	4.06
$O'_3—O'_5$	2.61	$O_1—O'_5$	3.04	$O_3—O'_1$	3.40
$O'_2—O'_5$	2.79	$O_1—O'_4$	2.86	$O_3—O'_5$	3.66
		$O'_2—O_4$	2.87	$O_3—O''_3$	2.64
		$O'_2—O'_5$	2.73	$O'_4—O'_1$	3.42

Si tetrahedra		Ti octahedra		Na polyhedra	
		O'_2—O''_5	2.81	O'_4—O''_4	3.29
		O_4—O'_4	2.89	O'_4—O'_3	3.12
		O_4—O''_5	2.55	O'_2—O''_4	2.87
		O'_5—O'_4	2.55	O'_2—O'_5	3.20
		O'_5—O''_5	2.99	O'_2—O'_3	2.72
		O'_4—O''_5	2.74	O'_1—O''_4	3.42
				O'_1—O'_5	3.04
				O''_4—O'_5	2.74

Mean distances:

Si tetrahedra		Ti octahedra		Na polyhedra	
Si—O	1.64	Ti—O	1.99	Na—O	2.47
O—O	2.68	O—O	2.81	O—O	3.20

Shortest distance: Na—Na 3.01

In the metachain the angle Si—O—Si = 139°42′.

R^{hkl} = 12.80% (overall temperature correction B = 0.13). With a satisfactory valence balance, the interatomic distances agree well with those previously established in silicates.

The structure of ramsayite has much in common with the structure of the pyroxene diopside, $CaMg[Si_2O_6]$ [3,7,8]. In both, the basis may be regarded as layers, perpendicular to the a axis, of cation polyhedra: Na and Ti in ramsayite, Ca and Mg in diopside (Figs. 1 and 2).

Each layer consists of infinite zigzags along c (brucite-type chains) of Ti octahedra, incrusted with Na polyhedra, in ramsayite, and of Mg octahedra, incrusted with Ca polyhedra, in diopside [3]. But in the latter the cation layers are one-story, whereas in ramsayite they are doubled, connected by the glide plane n. According to the principle of closest anion (O) packing, octahedral coordination was assumed [1,2] for Na and Ca; however, because of their larger sizes both Ca and Na acquire additional neighbors (approach other O atoms), the Ca atoms two (coordination number 8), and the Na atoms one (coordination number 7, Fig. 3). As a result of the increase in coordination number, the discrete cation chains in the layer coalesce (Fig. 4).

Neighboring packets (one-story in diopside, two-story in ramsayite) along the a axis are linked to one another by the silico-oxygen metachains $[Si_2O_6]_\infty$, extending along c in strict agreement with the principal Mg zigzags in diopside and Ti zigzags in ramsayite. In light of the notion that silico-oxygen radicals

Fig. 4. Ramsayite, real structure. Two levels are shown: the upper one with silico-oxygen pyroxene chains of tetrahedra; the lower one with regular Ti octahedra and seven-vertex polyhedra around Na. Four-cornered caps are visible in the latter. The triangular faces were indicated in the preceding figure.

Figure 4: Fig. 4. Ramsayite, real structure. Two levels are shown: the upper one with silico-oxygen pyroxene chains of tetrahedra; the lower one with regular Ti octahedra and seven-vertex polyhedra around Na. Four-cornered caps are visible in the latter. The triangular faces were indicated in the preceding figure.

are passively adapted to the architecture of the more important other structural details [7], it is curious that $c = 5.25$ Å in diopside and $c = 5.08$ Å in ramsayite. In the former the cation zigzags are made up of the larger Mg octahedra, in the latter of the smaller Ti octahedra. In both structures, for the period b there are two metachains with opposite orientation (bases–apices) along the axis of (quasi-) closest packing a. It is not difficult to see, between the approaching tetrahedra of neighboring chains, an "empty" oxygen octahedron, at the center of which (the inversion center) the origin of the coordinates has been taken.

If this story is regarded as the zero one in a six-layer closest packing

(Fig. 4), then the next levels with metachains will be the third and the sixth. In pyroxene-diopside with four-layer packing (Fig. 1), the $[Si_2O_6]_\infty$ chains fill all even levels.

Along the x axis, at a height of $0.25a$, there pass parallel twofold screw axes, which through common vertices connect chains of octahedra and superpose Na polyhedra on one another; this forces the Na atoms to move away from the common face (coordinate $x = 0.155$ instead of 0.167, and versus 0.169 for the Ti atom) and makes these common faces triangular, whereas the opposite faces are quadrilaterals (the second rule of ionic structures). In the diopside structure both basal faces are quadrilaterals[9]. Owing to the displacement away from the common vertical, the Na–Na distance becomes equal to 3.01 Å, instead of 2.42 Å, corresponding to the ideal packing of octahedra.

Fig. 4. Ramsayite, real structure. Two levels are shown: the upper one with silico-oxygen pyroxene chains of tetrahedra; the lower one with regular Ti octahedra and seven-vertex polyhedra around Na. Four-cornered caps are visible in the latter. The triangular faces were indicated in the preceding figure.

The triad of O atoms common to two Na atoms ($O_1 + 2O_5$) is that third (of 9 in the formula) of the oxygen atoms which do not participate in the silico-oxygen radical of ramsayite, and the formula of the latter, in expanded form, becomes $Na_2Ti_2O_3[Si_2O_6]$, where the metasilicate type of the radical is emphasized, with a more than orthosilicate ratio $Si : O = 1 : 4\frac{1}{2}$ in the gross formula.

In the ideal structure of ramsayite (slightly distorted in the real one), the

single possible 6-layer centrosymmetric closest packing[3] is well expressed: $|ABCACB| = |\quad\quad|$..., as against $|\ \ |$... in the ordinary hexagonal, $|\quad|$... in the cubic, and $|\quad\ \ |$... in the topaz packing. Other representatives of this packing are carborundum II and the corresponding modification of wurtzite ZnS.

Perfect cleavage along (100) corresponds to the decomposition of the structure into layers; the less perfect cleavage along (210) is analogous to the pyroxene (110) cleavage according to the pseudotetragonal prism that isolates the $[Si_2O_6]_\infty$ chain.

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Note: Figure translations are in progress. See original paper for figures.