# CRYSTAL STRUCTURE OF NaSmSiO$_{4}$

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## Abstract

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A. V. CHICHAGOV, V. V. ILYUKHIN, Academician N. V. BELOV

# CRYSTAL STRUCTURE OF $NaSmSiO_4$

Na, Sm orthosilicate was synthesized in the system $Na_2O$–$Sm_2O_3$–$SiO_2$–$H_2O$ by hydrothermal crystallization from a 30% NaOH solution at 450° and a pressure of ~1000 atm ([1]). X-ray analysis of single crystals revealed a tetragonal body-centered cell with parameters $a = 11.8$ and $c = 5.45$ Å. The diffraction symbol $4/ml$—/— corresponds to three Fedorov groups $I4/m$, $I4$, and $I\bar{4}$. The experimentally determined density is $\rho = 4.7$. Recalculation from chemical analysis (analyst V. S. Bykova): $Na_2O$ 13.38; $Sm_2O_3$ 66.7; $SiO_2$ 20.23; $K_2O$ 0.13; $\Sigma = 100.44$ wt.% according to ([2], [3]) leads to the material composition of the indicated cell $Na_8Sm_8Si_8O_{32}$ ($Z = 8$ formula units of $NaSmSiO_4$).

A three-dimensional set of X-ray intensities from a single-crystal fragment measuring $0.2 \times 0.2 \times 0.3$ mm comprised 536 nonzero reflections from layer-line scans $hk0$, $hk1$, $hk2$, $hk3$, $hk4$ ($\max \sin\vartheta/\lambda = 0.92$; $MoK_\alpha$ radiation, Weissenberg goniometer). Reduction to a common scale was carried out using reflections of the side zone $h0l$. The intensity was estimated visually on a double scale of blackenings with a step $\sqrt[4]{2}$. The scale was obtained by simultaneous fixation of two reflections from the crystal under study with different vertical coordinates $x$ (i.e., with different $\sin\vartheta/\lambda$), but with the same horizontal coordinate $z$ in the coordinate system of the Weissenberg photograph. The initial reflections were chosen so that the first of them was an unresolved doublet $K_{\alpha_1} + K_{\alpha_2}$, and the second was "semi-resolved." The coupling coefficient between them was found with the aid of a third scale.

The $x$- and $y$-coordinates of the heavy Sm atom were determined from the Patterson projection $p(uv)$, and then a series of calculations of ordinary and difference Fourier syntheses with the plane group $I4$ revealed the $x$- and $y$-coordinates of the remaining atoms ($R_{hk0} = 0.10$). Nevertheless, exact localization of the positions of all atoms in the projection even along the short period 5.45 Å was impossible because of overlaps of the electron densities of three pairs of atoms (Na–O; Sm–O; O–O), which required analysis of the three-dimensional structural material.

The Patterson function $P(uvw)$ gives the $x$-, $y$-, $z$-coordinates of Sm, and the arrangement of the Sm–Sm vectors excludes a fourth-order inversion axis and hence the Fedorov group $I\bar{4}$. A Fourier synthesis $\rho(xyz)$ according to the Sm coordinates, calculated in the three-dimensional group $I4$ (with an unrecorded origin on the fourfold axis, i.e., $z_{\mathrm{Sm}} = 0$), reveals mirror planes perpendicular to the fourfold axis; moreover, all atoms are concentrated in them except for two O atoms that are related by these $m$. Calculation of $\rho(xyz)$ from the coordinates of all atoms within this same group does not change the character of the picture. Thus the origin of coordinates is fixed, and we nevertheless arrive at the centrosymmetric group $C_{4h}^5 = I4/m$*.

The final atomic coordinates were obtained by the method of successive approximations with alternating calculations of ordinary and difference (but now three-dimensional) Fourier syntheses. $R_{hkl} = 0.16$. The introduction of an isotropic thermal correction ($B = -0.37$ Å$^2$) and refinement of the coefficients $K$ and $K_L$ bringing the array of reflections to an absolute scale reduce the $R$-factor to 0.14*.

With 6 independent atoms, 5 of which occupy 8-fold special positions and one (O) a 16-fold general position in the space group $I4/m$, the structure is described by 13 parameters. The coordinates of the basis atoms and interatomic distances are given in Tables 1 and 2.

**Table 1**

**Coordinates of the basis atoms of NaSm silicate**

| Atoms | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| Na | 0.410 | 0.106 | 0.500 |
| Sm | 0.185 | 0.117 | 0.000 |
| Si | 0.102 | 0.249 | 0.500 |
| $O_1$ | 0.044 | 0.200 | 0.258 |
| $O_2$ | 0.389 | 0.110 | 0.000 |
| $O_3$ | 0.237 | 0.201 | 0.500 |

The main architectural feature of the structure is the quadrilateral rings of heavy Sm polyhedra located at two levels of the $I$-cell (Fig. 1), joined to one another by vertical edges. Translationally identical (along the 4-fold axis) rings are articulated by the vertices of the polyhedra in such a way that "shaft" columns with a square cross section (3.5 × 3.5 Å) are formed, with vertical walls paved by tiles–rectangular faces of Sm polyhedra (Fig. 2). The ring at the vertex of the cell is joined to the central inclined edges of two adjoining polyhedra, which along the screw axis $2_1$ form a twisted (cask-like) column (Fig. 3). In the cavities between the shafts, at two levels around the axis $4_2$, Na semipolyhedra are situated, also connected to one another by edges. In

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* A test for the piezoelectric effect, carried out at the Faculty of Physics of Moscow University, gave a negative result.

addition, the Na semipolyhedron has two common faces with two neighboring Sm polyhedra in the ring and a pair of common edges with Sm polyhedra in the column.

**Table 2**

**Interatomic distances in the structure of $NaSmSiO_4$, Å**

| Sm eight-vertex polyhedron | | Na semipolyhedron | | Si orthotetrahedron | |
|---|---|---|---|---|---|
| $Sm{-}O_1$ (2) | 2.34 | $Na{-}O_1^2$ (2) | 2.74 | $Si{-}O_1$ (2) | 1.59 |
| $Sm{-}O_1^1$ (2) | 2.37 | $Na{-}O_3$ (2) | 2.74 | $Si{-}O_3^1$ | 1.66 |
| $Sm{-}O_3$ | 2.41 | $Na{-}O_4$ | 2.33 | $Si{-}O_4$ | 1.69 |
| $Sm{-}O_4^1$ | 2.34 | $Na{-}O_3^2$ | 2.56 | $(Si{-}O)_{av}$ | 1.64 |
| $Sm{-}O_4$ (2) | 2.96 | $Na{-}O_3^3$ | 2.36 | $O_1{-}O_2^1$ | 2.64 |
| $O_1{-}O_2$ (2) | 2.81 ** | $O_1^2{-}O_2^2$ | 2.81 | $O_1{-}O_3^1$ (2) | 2.72 |
| $O_1{-}O_1^1$ (2) | 3.44 | $O_1^2{-}O_4$ (2) | 3.17 | $O_1{-}O_4$ (2) | 2.64 |
| $O_1{-}O_4^1$ (2) | 3.17 | $O_1^2{-}O_3^3$ (2) | 3.21 | $O_3{-}O_4^1$ | 2.68 |
| $O_1^1{-}O_3$ (2) | 3.21 | $O_3^2{-}O_4$ | 4.10 | $(O{-}O)_{av}$ | 2.67 |
| $O_1^1{-}O_4$ (2) | 3.21 | $O_3^2{-}O_3^3$ | 3.68 | | |
| $O_2{-}O_4$ (2) | 3.44 | $O_3^2{-}O_3$ (4) | 3.77 | | |
| $O_3{-}O_4^1$ (2) | 2.98 *** | $O_3{-}O_1^2$ (2) | 2.72 | | |
| $O_3{-}O_4^1$ | 2.68 * | $O_3{-}O_4$ | 3.44 | | |
| $O_1{-}O_4$ (2) | 2.64 * | | | | |

**Note.** Shared edges of the Sm eight-vertex polyhedron: *—with the Si orthotetrahedron; **—in the Sm ring; ***—in the Sm column.

Si orthotetrahedra are closely associated with Sm polyhedra, having with three of them simultaneously three common edges. Their intergrowth is clearly visible in Fig. 3, where one of the three such shared edges is indicated. The $[SiO_4]^{4-}$ tetrahedron also has a pair of common edges with two Na polyhedra.

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

The question of the form of the Sm polyhedra and, consequently, of the coordination of Sm, as is usual for large cations, is decided in two ways. If one limits

* Absorption was not taken into account.

the coordination sphere of samarium only six O at distances of 2.34-2.41 Å, the coordination polyhedron is a trigonal prism (c.n. = 6).

**Fig. 1.** Structure of $NaSmSiO_4$. Projection on *xy*

In this case the four-membered rings of Sm prisms will not form a continuous three-dimensional spatial connection, but will be joined to one another by Si orthotetrahedra, which in this respect have only one common edge with the Sm polyhedron and two with Na polyhedra. The connection of the latter with the Sm polyhedron will also change; now each Na semi-octahedron retains only two faces in common with the end faces of two neighboring Sm prisms in the ring. If, however, in addition to the first sphere, two more O atoms at distances of 2.96 Å are included in the coordination of samarium, then at c.n. $= 6 + 2$ an 8-vertex polyhedron is obtained; this is the aforementioned trigonal prism, one rectangular face of which just forms one of the walls of the column, while semioctahedra develop on the other two.

In most descriptions of structures with large cations, this broad concept of coordination is used. In the present case, an essential consideration is that for the middle subgroup TR (Sm—Ho) c.n. $= 8 = 6 + 2$ seems more logical than c.n. $= 6$, characteristic of the subgroup including Y, Er—Yb ([1,5]). We note that the distance 2.96 Å is not unusual for TR at c.n. = 8, in particular, a similar distance was encountered in Ce-kainosite ([4]). The two groups of distances clearly

**Fig. 2.** Structure of $NaSmSiO_4$. Two translationally identical four-membered rings of Sm eight-vertex polyhedra, around which Si orthotetrahedra are arranged

**Fig. 3.** Helical column of Sm eight-vertex polyhedra. The triad of edges common to the Si orthotetrahedron is highlighted.

Figure 3

Figure 3: Figure 3

illustrate Pauling' s rule on the shortening of shared edges in polyhedra with multivalent cations and the "adaptation" of the large TR-polyhedron to the $[SiO_4]^{4-}$-tetrahedron (Table 2). The valence balance in this variant also appears more satisfactory (Table 3).

The presence of columnar channels in the structure gives it a zeolitic character, and it would seem natural to find water molecules in them. Indeed, both in planar and in three-dimensional Fourier syntheses at the origin of coordinates (i.e., at the center of the ring of Sm-polyhedra), an electron-density peak is recorded with a strength approximately equal to oxygen. Placing an O atom in this position (with multiplicity 2) leads to a decrease of $R_{hkl}$ by 0.3%. However, chemical-analysis data do not reveal the presence of water, the content of which in this position should be no less than 1.5%. Consequently, in order to clarify whether water is present in the channels, or whether these positions are also occupied by random $Na^+$ and $OH^-$, or $K^+$ and $OH^-$ (chemical analysis shows a small excess of sodium and records an insignificant amount of potassium), a special study is required, which will probably connect these facts into a single whole.

**Table 3**

**Valence balance in the structure of** $NaSmSiO_4$

| Anion | Cation: Sm | Cation: Na | Cation: Si | $\Sigma = \omega_i/n_i$ |
|---|---|---|---|---|
| $O_1$ | 6/8 (6/6)* | 1/7 | 1 | 1.9 (2.14) |
| $O_2$ | 3/8 (3/6) | 4/7 | 1 | 1.94 (2.07) |
| $O_3$ | 9/8 (3/6) | 1/7 | 1 | 2.17 (1.64) |

* In parentheses are given the valence strengths falling on one O atom for coordination number Sm equal to 6.

Moscow State University
named after M. V. Lomonosov

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

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