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Abstract

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S. M. SKSHAT (Poland), V. I. SIMONOV, Academician N. V. BELOV

CRYSTAL STRUCTURE OF SYNTHETIC Na,Sc-SILICATE

$Na_3Sc[Si_2O_7]$

The structure of the only known natural scandium silicate, $Sc_2[Si_2O_7]$, has until now attracted attention because of the rarity in it of configurations of the radical $[Si_2O_7]$ (^{1}). As a rule, the diorthogroup is inscribed in a (pseudo)trigonal prism, one or two edges of which are elongated, being conjugated with polyhedra around large cations, with two (or one) shortened edges, which is determined by an Si—O—Si angle usually of the order of 140–150°. In thortveitite the Si tetrahedra are turned with respect to one another exactly or almost exactly by 180° (the bridging O at the center of inversion) (^{2}). The six outer O atoms form a trigonal antiprism, i.e., an elongated octahedron. In the structure of thortveitite, layers of corundum type built of Sc octahedra are interleaved with layers of isolated elongated octahedra with the diorthogroups inscribed in them, and these octahedra in their layers center, above and below, rings of Sc octahedra (carbonate motif, (^{3})). To some extent the exceptional position of the natural Sc silicate makes the synthesis and structural analysis of other Sc silicates, in particular diorthosilicates, especially interesting.

At the Institute of Crystallography of the Academy of Sciences of the USSR, in the laboratory of hydrothermal synthesis, well-formed transparent single crystals with a distinct rhombic habit were obtained in the system $Na_2O—Sc_2O_3—SiO_2—H_2O$. An X-ray spectral test (V. V. Lider) established a large amount of Sc in these crystals. A detailed chemical analysis of the crystals was kindly performed by V. S. Bykova, and its recalculation led to the simple formula $Na_3Sc[Si_2O_7]$, which is obtained from the formula of thortveitite after replacement of half of the Sc^{3+} atoms by $3Na^{1+}$.

An X-ray diffraction examination confirmed the rhombic symmetry of the crystals, with dimensions of the primitive unit cell $a = 5.354 \pm 0.003$, $b = 9.347 \pm 0.004$, $c = 13.089 \pm 0.004$ Å. Taking the specific gravity 2.840 g/cm^3, we obtain for the number of formula units in the indicated cell $4 \times Na_3Sc[Si_2O_7]$. The diffraction experimental material (Mo radiation, equi-inclination Weissenberg goniometer) gave the layer-line photographs $0kl$–$5kl$, $h0l$–$h1l$, and $hk0$. Intensities were estimated visually on a $\sqrt[4]{2}$ scale of blackenings. Analysis of the systematic extinctions led to the X-ray group $mmm\,Pbn-$, to which two Fedorov groups correspond: $D_{2h}^{16} = Pbnm$ and $C_{2v}^{9} = Pbn2_1$. A test for the piezoelectric effect (Department of Crystal Physics, Moscow State University) gave a negative result. The statistics of the intensities $0kl$ led to a hypercentric distribution (^{4}), which could be due to special positions of Sc within the holohedral rhombic group. Both arguments were in favor of the common centrosymmetric group D_{2h}^{16}—in particular, in its "mineralogical" aspect, $Pbnm$. It formed the basis for the structure determination and was confirmed by the final results. Within this group Sc and at least one Na and one O must be located in special fourfold (centers of symmetry or mirror planes) positions.

A three-dimensional Patterson synthesis was constructed from 541 independent reflections, different from zero, from the layer-line photographs $0kl$–$5kl$. This same array

was used in the determination and refinement of the structure. Analysis of the interatomic-vector function indicated the placement of the Sc cations ($Z = 21$) at centers of symmetry and made it possible to localize the Si atom ($Z = 14$) in a general position. The use of Sc in a special position for superposition synthesis would have led to the appearance of exaggerated symmetry. Therefore, as the key for constructing the three-dimensional minimization function, the centrosymmetric vector Si—Si was chosen. Fourier inversion of the function $M_2(\mathbf{r})$ gave the signs for calculating the corresponding superposition synthesis (^{5,6}), which confirmed the placement of Sc and Si and revealed the positions of two kinds of Na: eightfold in general positions, and fourfold in special positions (on the mirror planes m).

Table 1

Coordinates and temperature factors of the basic atoms of the structure
$Na_3Sc[Si_2O_7]$

Atoms	x/a	y/b	z/c	B
Sc	0	0	0	0.77
Si	0.512	0.176	0.131	0.86
Na_1	0.017	0.021	0.250	1.82
Na_2	0.015	0.347	0.093	1.92
O_1	0.442	0.122	0.250	1.15
O_2	0.479	0.347	0.118	1.19
O_3	0.320	0.090	0.062	1.32
O_4	0.800	0.127	0.107	1.21

In the electron-density synthesis, constructed using signs determined by the cation positions, all the basic atoms of the structure were localized. Refinement of the atomic coordinates and their isotropic individual parameters of thermal vibrations was carried out by the least-squares method using programs ([7]). The final values of these parameters, corresponding to $R = 11.3\%$, are given in Table 1. The small scatter of the constants B for atoms of the same kind and their natural increase from Sc to Na indicate that the values obtained are sufficiently reasonable, although the specimen used in the experiment was not assigned a spherical shape and X-ray absorption was not taken into account.

Fig. 1. $Na_3Sc[Si_2O_7]$. Projection *bc*. Sc octahedra and Si_2O_7 diortho groups are shown; Na positions are indicated by circles.

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In accordance with the gross chemical formula, the new Sc silicate proved to be a diorthosilicate with the usual prismatic configuration of the $[Si_2O_7]$ group. The two tetrahedra of this group are connected to one another by a mirror plane of symmetry, and among the lateral edges of the enclosing $[Si_2O_7]$ quasitrigonal prism two are short and one is long (O_2—O_2' 3.44, O_4—O_4' 3.73, O_3—O_3' 4.93 Å), which naturally corresponds to the Si–O_1–Si angle reduced to 136°.

In describing the structure—the structural motif of the phase $Na_3Sc[Si_2O_7]$—it is convenient to proceed from the very close correspondence of the parameters of its cell to the

parameters of a series of layered silicates: vermiculite, nontromite, sanbornite (even $b : a = 1.74$, i.e., almost exactly $\sqrt{3}$, as is characteristic of the usual (pseudo-) "orthohexagonal" basis of layered minerals). And indeed, in Fig. 1, perpendicular to the axis $c = 13.089$ Å, two centers stand out (as we now call the central layers of three-story packets in micas) made up of Sc octahedra, broken up in a single closest oxygen packing (according to the anticorundum–carbonate motif). The two Sc octahedra falling on the centered orthohexagonal rectangle in the Na, Sc phase are translationally nonequivalent and in projection look in different directions, as if connected by the glide plane b, normal to the short axis a (Fig. 2). The pair Sc_2 is one third of Mg_6 in the orthohexagonal basis of phlogopite; the remaining 2/3 of the cations are given by the Na_2 cations in a general position, although not in octahedra. Twice (relative to Sc) the number of Si atoms is used for two rings on both sides of the Sc layer. The silicate rings here are broken into separate Si tetrahedra, each connected by its base with three Sc octahedra (each Sc octahedron on the two sides of the layer is connected with six different Si tetrahedra). Further, however, there is repeated what recalls the structural features of astrophyllite and lamprophyllite, namely: the fourth vertices of the Si tetrahedra from the rings of neighboring packets are joined in the mirror plane between the packets, and thus diorthogroups $[Si_2O_7]$ are formed. In the same mirror planes, alternating with the bridging O_1, the cations Na_1 are located, i.e., the situation existing in bafertisite, astrophyllite, and lamprophyllite is repeated. Writing the formula of Na, Sc-diorthosilicate in the form $Na^{I}Na_2^{II}Sc[Si_2O_7]$, we can identify it with the content of the packet, dividing the 7th O atom and Na^{I} into two halves on different sides of the packet:

Fig. 2. $Na_3Sc[Si_2O_7]$. Orthohexagonal arrangement of Sc octahedra in projection *ab* and their connection with $[Si_2O_7]$ groups

$$Na^{I}_{0.5+0.5}Na^{II}_{2}Sc\,[Si_2O_6O_{0.5+0.5}].$$

Table 2

Interatomic distances (Å) in the structure of $Na_3Sc[Si_2O_7]$

Sc-octahedron	Si-tetrahedron	Na_1-polyhedron
Sc $-O_2$ 2.11	Si $-O_1$ 1.68	Na_1 $-O_2$ (×2) 2.37
Sc $-O_3$ 2.07	Si $-O_2$ 1.62	Na_1 $-O_4$ (×2) 2.42
Sc $-O_4$ 2.13	Si $-O_3$ 1.59	Na_1 $-O_1$ (×1) 2.46
	Si $-O_4$ 1.64	Na_2**-tetrahedron**
O_2 $-O_3$ 2.87	O_1 $-O_2$ 2.73	Na_2 $-O_2$ 2.51
O_2 $-O_4$ 2.88	O_1 $-O_3$ 2.56	Na_2 $-O_3$ 2.36
O_3 $-O_4$ 2.87	O_1 $-O_4$ 2.68	Na_2 $-O_3$ 2.47
O_2 $-O'_3$ 3.03	O_2 $-O_3$ 2.65	Na_2 $-O_4$ 2.36
O_2 $-O'_4$ 3.11	O_2 $-O_4$ 2.68	
O_3 $-O'_4$ 3.07	O_3 $-O_4$ 2.66	

The principal interatomic distances are given in Table 2. With a normally elongated distance from Si to the bridging O_1, there are no other anomalies in the geometry of the Si tetrahedron. (Mean Si–O = 1.63 Å.) In the centrosymmetric Sc octahedron, the elongation along one of its (pseudo)

···of the three-fold axes, namely the one parallel to *c*, can be associated with the $[Si_2O_7]$ groups elongated in the same direction. With six equatorial edges of length 3.03-3.11 Å, two polar faces of the Sc octahedron are bounded by edges (triangles $O_2O_3O_4$) of 2.87-2.88 Å. This reduction in size may be regarded as the cause or consequence of the fact that these faces simultaneously (Pauling' s rule) serve as the bases of trigonal prisms around Na_1, located on the mirror plane between two Sc atoms. Of the six vertices of this prism, only four—two O_2 and two O_4—are in direct contact with Na_1 (2.37 and 2.42 Å), while two O_3 are 3.02 Å away and fall out of the active coordination. The polyhedron around Na_1 is completed by the bridging O_1 from the diorthogroup, situated with it in the mirror plane (2.46 Å). The displacement of two O_3 from Na_1 by 3.02 Å is "necessary," for otherwise the Na_1 heptahedron would have not only two faces in common with the Sc octahedra, but also two edges in common with both tetrahedra of the diorthogroup. Thus, the active coordination of Na_1 is limited to a pentaverticon—an almost tetragonal flattened pyramid.

The Na_2 cations in the general position, as is evident from Table 2, have four nearest neighbors at distances of 2.36-2.57 Å; the fifth (O'_2) is 2.89 Å away. A strongly distorted coordination tetrahedron around Na_2 is characteristic of Na in those synthetic (silicate) phases of it that are obtained from highly alkaline media ([8], [9]).

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Nicolas Copernicus University
Toruń, Poland

Moscow State University
named after M. V. Lomonosov

Institute of Crystallography
Academy of Sciences of the USSR

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