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Abstract

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CRYSTAL STRUCTURE OF SYNTHETIC Na-ZINCOSILICATE Na_2ZnSiO_4

Sodium zincosilicates are of interest because of their particular feature—when activated by Mn, they luminesce in the yellow and green regions of the spectrum. In nature Na–Zn silicates have not been found; samples were obtained in the laboratory of hydrothermal synthesis of the Institute of Crystallography, Academy of Sciences of the USSR, during a study of crystallization in the system Na_2O–ZnO–SiO_2–H_2O ([1]). The synthesis was carried out in steel autoclaves lined with titanium, with a filling coefficient of 68-80%. In the temperature interval 350-550° (with a gradient of 0.5 deg/cm, with $T_{\text{lower}} > T_{\text{upper}}$) at varying NaOH concentration (1-25 wt.% and higher), 7 individual Na–Zn-silicate phases were isolated, 6 of which were obtained for the first time. The simplest in composition was the phase designated by the authors ([1], [2]) as phase D of the indicated composition Na_2ZnSiO_4.

The chemical composition of phase D (analyst V. S. Bykova) is as follows (wt.%):

Na_2O	SiO_2	ZnO	H_2O	Σ
28.00	28.35	39.74	3.30	99.39

The phase crystallized under conditions of high alkalinity (NaOH concentration > 25 wt.%) with the ratio in the initial charge $ZnO : SiO_2 = 1 : 1$; $Na_2O : (ZnO + SiO_2) = 2 : 1$.

Biaxial crystals of phase D ($n_g = 1.663$; $n_m = 1.655$; $n_p = 1.640$), when activated by Mn, luminesce in the green part of the spectrum under ultraviolet excitation. In addition to bright luminescence, the crystals are characterized by a strong piezoelectric effect. The specific gravity is 3.4, with hardness 4.0. The fingerprint characteristic (interplanar spacings from the powder X-ray pattern) is given in Table 1.

Table 1

Interplanar spacings of Na_2ZnSiO_4 (Fe radiation)

I	d/n	I	d/n	I	d/n	I	d/n
8	4.39	4	2.90	5	2.16	6	1.67
8	4.27	7	2.85	4	2.00	8	1.61
2	3.86	8	2.74	6	1.97	10	1.50
2	3.35	8	2.64	6	1.89	7	1.47
2	3.27	10	2.59	5	1.78	7	1.46
9	2.98	7	2.43	6	1.76	6	1.42
						8	1.37

As a result of X-ray analysis of single-crystal fragments measuring $0.2 \times 0.3 \times 0.2$ mm^3, the monoclinicity of phase D was established, with cell $a = 8.75$, $b = 5.48$, $c = 5.33$ Å at $\beta = 127°$. The Fedorov group is $C_s^2 = Pa$. The material content of this cell is $Z = 2$ units of Na_2ZnSiO_4. It was convenient to replace the morphological cell by an almost rectangular one ($a' = a + c$), with $a' = 7.02$, $b = b'$, $c = c'$; $\beta = 90°20'$. $C_s^2 = Pn$. The experimental X-ray diffraction material gave three zero-level reciprocal-lattice layers along the axes a', b', c. (Mo—K_α radiation, $\max \sin\vartheta/\lambda =$

$= 1$ Å). The intensities were estimated visually, from blackening marks with a step of $\sqrt[4]{2}$. The Patterson syntheses $p(xz)$ and $p(yz)$ agreed well with each other and made it possible to locate the heavier Zn and, after it, Si. The subsequent interpretation was carried out by the method of successive approximations using electron-density syntheses. The atomic coordinates listed in Table 2 were obtained at the following achieved discrepancy factors with isotropic temperature corrections:

R_{0kl}	B_{0kl}	R_{hk0}	B_{hk0}	R_{h0l}	B_{h0l}
0.15	0.4	0.16	0.7	0.18	was not introduced

With 8 independent atoms the structure is determined by 22 parameters (24-2, associated with the absence of a fixed origin in the single glide plane of the group Pn).

Table 2

Coordinates of the basis atoms in the structure of Na_2ZnSiO_4

Atoms	x/a	y/b	z/c
Zn	0.000	0.168	0.000
Si	0.249	0.686	0.006
O_I	0.223	0.396	0.047

Atoms	x/a	y/b	z/c
O_{II}	0.283	0.800	0.281
O_{III}	0.064	0.812	0.891
O_{IV}	0.444	0.749	0.857
Na_1	0.243	0.314	0.478
Na_2	0.004	0.815	0.480

The interatomic distances are given in Table 3. In the silicon-oxygen tetrahedron they correspond to those usually encountered: Si—O = 1.59-1.66 Å, on average 1.625 Å; the edges of the tetrahedron likewise do not fall outside the narrow limits 2.55-2.69 Å. In the Zn tetrahedron the scatter is somewhat greater: Zn—O = 1.93-2.08 Å.

The polyhedra around the two sorts of Na are somewhat unusual: for Na_1, three neighbors are at distances almost equal to the sum of the ionic radii, 2.23; 2.35; 2.40 Å; three more neighbors may be regarded as already being in the second coordination sphere: 2.87; 2.93; 3.12 Å. These six oxygen atoms form a strongly distorted octahedron. The remaining anions are more than 3.42 Å from Na_1 and were not included by us in its coordination.

Still more unexpected is the coordination of Na_2, with four neighbors at short distances 2.23; 2.24; 2.32; 2.52 Å, whereas the fifth is 3.02 Å away. The remaining O atoms are more than 3.20 Å away from Na_2, and thus Na_2 is in a polyhedron with c.n. 5 (in a first approximation—in a tetrahedron !?)—inside a distorted trigonal bipyramid with displacement (immersion) from the mean plane toward one of its vertices.

Table 3

Interatomic distances in the structure of Na_2ZnSiO_4 (Å)

Si-tetrahedron		
$Si—O_{I} = 1.62$	$O_{I}—O_{II} = 2.57$	$O_{II}—O_{III} = 2.58$
$Si—O_{II} = 1.62$	$O_{I}—O_{III} = 2.68$	$O_{II}—O_{IV} = 2.55$
$Si—O_{III} = 1.59$	$O_{I}—O_{IV} = 2.67$	$O_{III}—O_{IV} = 2.69$
$Si—O_{IV} = 1.66$		

Zn-tetrahedron	Na_1-polyhedron	Na_2-polyhedron
$Zn—O_{I} = 2.01$	$Na_1—O_{I} = 2.35$	$Na_2—O_{I}^{**} = 2.32$
$Zn—O_{II} = 1.93$	$Na_1—O_{II} = 2.87$	$Na_2—O_{II} = 2.24$
$Zn—O_{III} = 2.08$	$Na_1—O_{II}^{*} = 2.93$	$Na_2—O_{III} = 2.23$
$Zn—O_{IV} = 2.00$	$Na_1—O_{I}^{*} = 3.12$	$Na_2—O_{IV}^{**} = 2.52$
	$Na_1—O_{III}^{**} = 2.40$	$Na_2—O_{II}^{**} = 3.02$

Fig. 1

Figure 1: Fig. 1

Zn-tetrahedron	Na_1-polyhedron	Na_2-polyhedron
	Na_1—$O^{**}_{IV} = 2.23$	

* Translationally identical atoms.
** Atoms related to the basis atoms by the glide plane of symmetry.

In the structure, the tetrahedral coordination of Zn is again clearly manifested; the corresponding tetrahedra are discrete and are not directly connected with one another (unlike clinohedrite (^{3}), where Zn forms metazincate chains). In each Zn tetrahedron its four vertices are common with four Si tetrahedra and vice versa. Thus—

Thus, Zn and Si participate equally in the construction of a single three-dimensional framework, and the phase Na_2ZnSiO_4 may be assigned to the zincosilicates, just as bafertisite (^{4}) and lamprophyllite (^{5}) are assigned to the titanosilicates. The three-dimensional linkage of tetrahedra of two kinds is especially clearly expressed in the xy projection (Fig. 1). It is convenient to regard it as the result of collective condensation of pyroxene-type chains extending in the direction of the y axis, with "mixed" diorthogroups $[ZnSiO_7]$;

Fig. 1. Na–Zn silicate Na_2ZnSiO_4. **A** $-xy$ projection. **B** $-yz$ projection

per translation b there is one such unit. Taking any one of the chains as the "initial" one (for example, the upper one in Fig. 1), it is easy to see that it is connected with an identical chain parallel to it, but lowered below the plane of the drawing by $1/2(a' + c)$, the second chain being the mirror reflection of the first in the glide plane n, with a displacement along y by $\sim 1/2b$ (the cell, with respect to the two pyroxene chains passing through it, proves to be pseudocentered along the second diagonal $a'c$).

Upon condensation, each Zn tetrahedron is linked with one Si tetrahedron of the upper chain (through a common vertex) and with another Si tetrahedron of the lower chain. The same applies to the linkages of Si tetrahedra with neighboring Zn tetrahedra. In the xy projection, six-membered windows-rings are clearly distinguished, which in the three-dimensional framework correspond to channels parallel to the z axis. However, the larger Na cations are located not inside the channels but on the walls, namely, quite precisely above (and below) the O atoms that link alternating Si and Zn within a single pyroxene chain. Marking in Fig. 1 with circles the positions of the two kinds of Na atoms, one can state that we have before us yet another illustration of the proposition, often expressed in works on the structure of silicates with large cations (^{6}), that Na (Ca, etc.) "pull" onto themselves (onto their polyhedron) the diorthogroups

$[Si_2O_7]$, and in the present case the equivalent mixed diorthogroup $[ZnSiO_7]$, which here plays the role of the principal architectural brick constructing the three-dimensional framework, just as the bricks $[Si_2O_7]$, through intermediate batisite chains (7), build ribbons in narsarsukite (8) or deformed flat nets in sanbornite (9).

The unusual coordination of Na (Na_2) does not prevent a quite satisfactory valence balance in phase D (Table 4).

If, however, one treats sufficiently rigorously the distinction between Si- and Zn-tetrahedra, then the structure analyzed for phase $D = \mathrm{Na_2ZnSiO_4}$ once again confirms the empirical rule of hydrothermal synthesis, which states—

Table 4

Valence balance in the structure of $\mathrm{Na_2ZnSiO_4}$

Anion	Cation	Cation	Cation	Cation	$\Sigma = \frac{\omega_i}{n_i}$
Anion	Zn	Si	Na_1	Na_2	$\Sigma = \frac{\omega_i}{n_i}$
O_I	1/2	1	$2 \times 1/6$	1/4 (1/5)*	$2^1/12$ ($2^4/30$)
O_{II}	1/2	1	$2 \times 1/6$	1/4 (2/5)	$2^1/12$ ($2^7/30$)
O_{III}	1/2	1	$2 \times 1/6$	1/4 (1/5)	$1^{11}/12$ ($1^{26}/30$)
O_{IV}	1/2	1	$2 \times 1/6$	1/4 (1/5)	$1^{11}/12$ ($1^{26}/30$)

* In parentheses are given the valence strengths per one O atom at the coordination number of Na_2, equal to 5.

that an increase in the alkalinity of the medium lowers the ability of Si-increments ($\mathrm{SiO_4, Si_2O_7}$) to polymerize, and that in strongly alkaline solutions only orthosilicate phases are obtained.

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