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CRYSTALLOGRAPHY

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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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CRYSTALLOGRAPHY

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CRYSTAL STRUCTURE OF SYNTHETIC Na,Zn-DIORTHOSILICATE $Na_2Zn_2[Si_2O_7]$

In studying the system Na_2O–ZnO–SiO_2 under conditions of relatively moderate alkalinity (5-15 wt.% NaOH), by hydrothermal syntheses from a charge with ZnO : SiO_2 = 1 : 1 and Na_2O : (ZnO + SiO_2) = 1 : 1 (^{1}), a crystalline phase B was obtained of composition: Na_2O 18.65%, ZnO 45.65%, SiO_2 34.17%, H_2O 0.50% ($\Sigma = 98.97\%$, analysis by V. S. Bykova), which corresponds well to the formula $Na_2Zn_2Si_2O_7$. Biaxial crystals ($N_g = 1.633$, $N_m = 1.615$, $N_p = 1.614$), activated by Mn, luminesce in the green region of the spectrum; in addition, they exhibit green triboluminescence and X-ray luminescence.

Fig. 1. Na,Zn-diorthosilicate. Metachains $[Zn_2O_6]_\infty$ winding around the screw axis 2_1, with SiO_4 tetrahedra encrusting them; the latter are paired by a mirror plane into diorthogroups $[Si_2O_7]$.
a –frontal projection *ac*; *b* –plan projection *bc*

The parameters of the rhombic cell found by us, $a = 5.17$, $b = 9.41$, $c = 13.73$ Å, are close to those reported earlier (^{2}); $Z = 4$ formula units of $Na_2Zn_2Si_2O_7$ (specific gravity 3.82).

The X-ray group $mmmC--c$, established from systematic extinctions, corresponds, in addition to the holohedral group $Cmcm$, also to two acentric Fedorov groups: $Cmc2_1$ and $C2cm$. The choice in favor of the latter (C_{2v}^4) was made in the initial analysis of the three-dimensional Patterson function, constructed from 360 nonzero intensities recorded from Weissenberg photographs $0kl$—$3kl$ and $hk0$ (Mo radiation, $\max \sin\theta/\lambda = 0.86$ Å; $\sqrt[4]{2}$ scale of blackening marks). The absence of linkage peaks (^{3}) in the Harker sections $u00$ and $uv\frac{1}{2}$ made impossible a plane m in the first position of the C symbol and an axis 2_1 in the third.

The coordinates of the heavy Zn atom and of the average Si atom were determined directly from the three-dimensional Patterson function. In the subsequent refinement by successive approximations, a methodological difficulty arose in localizing three O atoms. The concentration of Zn and Si near the levels $0yz$ and $\frac{1}{2}yz$ made the latter, at the first stage, pseudosymmetry planes, whose negative —interfering—role was further inten-

was eliminated by placing the Na atoms (two 4-fold positions) and one O atom (one 4-fold position) on the same levels. As a consequence, parasitic peaks associated with the true glide plane of symmetry were present in the intermediate electron-density syntheses. These peaks, however, disappeared in zero difference syntheses $\rho_0(xyz)$ by $F'_e = F_e - F_{\mathrm{T(Zn+Si+Na)}}$. The discrepancy factor, which after cycle IV was 17%, after introduction of the thermal correction and least-squares refinement was 9.5%; individualization of the temperature factors reduced R over all nonzero reflections to 8%. The final coordinates of the 8 independent—basic—atoms ($20 - 1$ parameters) are given in Table 1, and the interatomic distances calculated from them are given in Table 2.

Table 1

Coordinates of the basis atoms in the structure of $Na_2Zn_2Si_2O_7$ **(phase B)**

Atoms	x/a	y/b	z/c	B
Zn	0.560	0.215	0.078	0.3
Si	0.038	0.380	0.140	0.2
Na_1	0.000	0.000	0.000	0.9
Na_2	0.070	0.037	0.250	0.9
O_1	0.103	0.310	0.250	0.4
O_2	0.734	0.389	0.128	0.7
O_3	0.187	0.265	0.064	0.8
O_4	0.679	0.033	0.128	0.4

The Zn atoms, as in a number of other (zinc) silicates—clinohedrite (4), hodgkinsonite (5), willemite (6), phase D (7)—are located in large oxygen tetrahedra. The distances are Zn—O 1.94-2.06 Å (mean 1.99 Å). In slightly distorted Si tetrahedra: Si—O 1.58-1.69 Å (mean 1.64 Å), O—O edges 2.62-2.76 Å (mean 2.67 Å). The Si—O—Si angle for the two tetrahedra related by the mirror plane is equal to 132°. Zn tetrahedra form the principal architectural details of phase B, namely infinite polar chainlets extending along the short axis $a = 5.17$ Å with a link consisting of two tetrahedra $[Zn_2O_6]_\infty$. The chainlets are similar to those in clinohedrite and hardystonite (8), but in their "morphology" they are closest to the $[Be_2O_6]_\infty$ chainlets in barylite $Ba_2Be_2Si_2O_7$ (allowing for the scale factor —the parameter 5.17 in barylite (9) corresponds to 4.63 Å). As in barylite, so in phase B the chainlets are not only encrusted (9) by orthotetrahedra $[SiO_4]$, but also (Fig. 1) these SiO_4 (from neighboring Zn chains) pair through the plane of symmetry into diortho groups $[Si_2O_7]$. In barylite, however, chainlets with opposite polarity alternate (being linked by a pseudocenter of symmetry), whereas in phase B all chainlets have one polarity (a significant piezoelectric effect). Although in both barylite and phase B the Zn chainlets are discrete, nevertheless by orthogroups of tetrahedra they are linked into a three-dimensional framework; the essential difference of this from ordinary (alumo)silicate frameworks, or even from the zincosilicate framework in phase D Na_2ZnSiO_4 (^{7}), is that here at most oxygen atoms not two but three tetrahedra meet: 2Zn(Be) + 1Si (as in willemite Zn_2SiO_4).

Table 2

Interatomic distances in the structure of $Na_2Zn_2Si_2O_7$ (phase B)

Zn tetrahedron		
$Zn{-}O_2 = 1.99$ Å	$O_2{-}O_3 = 3.18$ Å	$O_3{-}O_3^* = 3.13$ Å
$Zn{-}O_3 = 1.99$	$O_2{-}O_3^* = 3.01$	$O_3{-}O_4 = 3.46$
$Zn{-}O_3^* = 2.06$	$O_2{-}O_4 = 3.36$	$O_3^*{-}O_3 = 3.24$
$Zn{-}O_4 = 1.94$		
Mean 1.995 Å		Mean 3.203 Å

Si tetrahedron		
$Si{-}O_1 = 1.68$ Å	$O_1{-}O_2 = 2.64$ Å	$O_2{-}O_3 = 2.76$ Å
$Si{-}O_2 = 1.58$	$O_1{-}O_3 = 2.62$	$O_2{-}O_4^* = 2.67$
$Si{-}O_3 = 1.69$	$O_1{-}O_4^* = 2.71$	$O_1{-}O_4^* = 2.67$
$Si{-}O_4^* = 1.62$		
Mean 1.642 Å		Mean 2.678 Å

Na_1 polyhedron	Na_2 polyhedron
$Na_1{-}O_2^* = 2.37$ Å (2)	$Na_2{-}O_1 = 2.58$ Å (1)
$Na_1{-}O_3 = 2.81$ (2)	$Na_2{-}O_1^* = 3.22$ (1)
$Na_1{-}O_3^* = 2.88$ (2)	$Na_2{-}O_2 = 2.33$ (2)
$Na_1{-}O_4 = 2.43$ (2)	$Na_2{-}O_4 = 2.62$ (2)

* The asterisk indicates atoms related to the basis atoms by symmetry operations. The number of bonds is given in parentheses.

In the structure of barylite, $BaBe_2Si_2O_7$, the cavities of the three-dimensional framework are occupied by divalent Ba cations; correspondingly, in the larger-scale structure of phase B = $Na_2Zn_2Si_2O_7$, the cavities here contain twice the number of monovalent Na cations of two crystallographic types with different coordination. The four atoms Na_1, lying on twofold axes, have four neighboring O atoms at distances close to the sum of the ionic radii (2.37 and 2.43 Å). The

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Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

large tetrahedron formed by them may be regarded as the first "coordination sphere." Four more O atoms are farther from Na_1, but not so far as to exclude them from the coordination environment (2.81 and 2.88 Å), which, "in total," is described as a twisted Thomson cube.

The coordination of the Na_2 cation lying in the mirror plane is somewhat unexpected: five close neighbors at distances 2.33 (×2),

Fig. 2. A trellis net of Na_1-octavertices. Frontal projection

Fig. 3. Combination of the trellis net of Na_1-polyhedra with discrete Na_2-pentavertices

2.62 (×2), and 2.58 Å form a pseudorhombic pyramid—half of an irregular octahedron, whose sixth vertex is removed to 3.22 Å and therefore can be assigned to Na_2 only with considerable strain. A similar "hemimorphy" —the collapse of Na into one half of its "ideal" polyhedron—was encountered in the structure of Zn-chkalovite, $Na_2Zn(Cd)Si_2O_6$ (^{10}). As is usual for voluminous polyhedra around cations, they occupy a large part of the area in the drawing.

Thomson cubes, through common vertices (but not edges), are linked into a very open "trellis" wall (Fig. 2), parallel to the centered face $C = ab$. It appears very interesting to see here features similar to garnet; namely, along the c axis each twisted cube has two edges (related by a twofold axis) in common with two Si tetrahedra; however, between two successive Thomson cubes (along c) there is not a single Si tetrahedron, but a diortho group, the two halves of which are related by a plane of symmetry. The two shorter edges of the trigonal prism in which the $[Si_2O_7]$ group is inscribed are the basal edges of two Na_2 pyramids; the third long edge is divided in half by the "fifth" vertex of the neighboring Na_2 pyramid (Fig. 3). The reality of chains of Thomson cubes and Si tetrahedra (of quasi-garnet type) is emphasized by the parallelism of their axes to the elongation of the crystals.

Table 3

Anions	Zn	Si	Na_1	Na_2	
O_1	–	2×1	–	$^1/_5$–	$2^1/_5$ (–)
O_2	$^1/_2$	1	$^1/_8$+	$^1/_5$+	$1^{33}/_{40}$ (++)
O_3	$2 \times {}^1/_2$	1	$2 \times {}^1/_8$–	–	$2^1/_4$ (—)
O_4	$^1/_2$	1	$^1/_8$+	$^1/_5$+	$1^{33}/_{40}$ (++)

In Table 3 the valence balance according to Pauling is given. It is quite satisfac –

···satisfactory from the standpoint of the usual tolerances, but becomes still better if one takes into account the remark made above concerning the two “coordination spheres” around Na_1, with four distances Na_1—O_3 considerably greater than the distances Na_1—O_2 and Na_1—O_4, and if the corresponding contributions of Na_1 to the valence balances of the oxygen atoms are estimated as 1/8− and 1/8+. The same also applies to the atom Na_2, with four nearer neighbors (1/5+) and one more distant one (1/5−).

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