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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 $\text{Na}_2\text{Zn}_2[\text{Si}_2\text{O}_7]$

In studying the system $\text{Na}_2\text{O}-\text{ZnO}-\text{SiO}_2$ under conditions of relatively moderate alkalinity (5–15 wt.% NaOH), by hydrothermal syntheses from a charge with $\text{ZnO} : \text{SiO}_2 = 1 : 1$ and $\text{Na}_2\text{O} : (\text{ZnO} + \text{SiO}_2) = 1 : 1$ (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 $\text{Na}_2\text{Zn}_2\text{Si}_2\text{O}_7$. Biaxial crystals ($N_g = 1.633$, $N_m = 1.615$, $N_p = 1.614$), activated by Mn, luminesce in the green

Fig. 1. Na,Zn-diorthosilicate. Metachains $[\text{Zn}_2\text{O}_6]_\infty$ winding around the screw axis 2_1 , with SiO_4 tetrahedra encrusting them; the latter are paired by a mirror plane into diorthogroups $[\text{Si}_2\text{O}_7]$.

a –frontal projection *ac*; *b* –plan projection *bc*

region of the spectrum; in addition, they exhibit green triboluminescence and X-ray luminescence.

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 $\text{Na}_2\text{Zn}_2\text{Si}_2\text{O}_7$ (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 $F'_e = F_e - F_{T(Zn+Si+Na)}$. 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 berylite $Ba_2Be_2Si_2O_7$ (allowing for the scale factor—the parameter 5.17 in berylite ⁽⁹⁾ corresponds to 4.63 Å). As in berylite, 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 berylite, 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 $\text{Na}_2\text{ZnSiO}_4$ (⁷), is that here at most oxygen atoms not two but three tetrahedra meet: $2\text{Zn}(\text{Be}) + 1\text{Si}$ (as in willemite Zn_2SiO_4).

Table 2

**Interatomic distances in the structure
of $\text{Na}_2\text{Zn}_2\text{Si}_2\text{O}_7$ (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										
<table><tr><td>Na₁ polyhedron</td><td>Na₂ polyhedron</td></tr><tr><td>Na₁-O₂[*] = 2.37 Å (2)</td><td>Na₂-O₁ = 2.58 Å (1)</td></tr><tr><td>Na₁-O₃ = 2.81 (2)</td><td>Na₂-O₁[*] = 3.22 (1)</td></tr><tr><td>Na₁-O₃[*] = 2.88 (2)</td><td>Na₂-O₂ = 2.33 (2)</td></tr><tr><td>Na₁-O₄ = 2.43 (2)</td><td>Na₂-O₄ = 2.62 (2)</td></tr></table>			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)
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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, $\text{BaBe}_2\text{Si}_2\text{O}_7$, the cavities of the three-dimensional framework are occupied by divalent Ba cations; correspondingly, in the larger-scale structure of phase B = $\text{Na}_2\text{Zn}_2\text{Si}_2\text{O}_7$, 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 $2.43 \text{ \AA}$). The

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 ($\times 2$),

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 ($\times 2$), 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, $\text{Na}_2\text{Zn}(\text{Cd})\text{Si}_2\text{O}_6$ ⁽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 $[\text{Si}_2\text{O}_7]$ 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
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...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 $\text{Na}_1\text{—O}_3$ considerably greater than the distances $\text{Na}_1\text{—O}_2$ and $\text{Na}_1\text{—O}_4$, 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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