A NEW SILICON-OXYGEN RADICAL $[Si_3O_{10}]$ IN THE STRUCTURE OF $Na_4Cd_2[Si_3O_{10}]$

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A NEW SILICON-OXYGEN RADICAL $[Si_3O_{10}]$ IN THE STRUCTURE OF $Na_4Cd_2[Si_3O_{10}]$

Single crystals of Na,Cd silicate (phase R) were obtained in the hydrothermal-synthesis laboratory of the Institute of Crystallography, Academy of Sciences of the USSR, in the system $Na_2O—CdO—SiO_2—H_2O$ at a temperature of 450°, pressure $\sim$ 2000 atm, and NaOH concentration of 30-40% (^{1}).

The chemical composition of phase R, according to the analysis of V. S. Bykova, G. A. Arapova, and Yu. S. Nesterova (SiO_2 31.5%; CdO 43.5%; Na_2O 25.8%; $\Sigma = 100.8\%$), may be expressed by the approximate formula $Na_4Cd_2Si_3O_{10}$. The monoclinic cell (Laue class $2/m$) with parameters $a = 10.00 \pm 0.03$ Å; $b = 5.83 \pm 0.02$ Å; $c = 16.80 \pm 0.05$ Å; $\beta = 80°$, at a specific gravity $d = 3.71$, contains $Z = 4$ formula units $Na_4Cd_2Si_3O_{10}$. The experimental intensity material (Mo radiation) consisted of reflections from scans (Weissenberg patterns) $h0l—h5l$, $hk0$, and $0kl$ ($\max \sin \vartheta/\lambda = 1.2$). The intensities of the reflections were estimated visually by comparison with a standard $\sqrt{2}$-scale of blackening marks obtained in a diffractometer using reflection 208.

Systematic extinctions lead to the X-ray group $C—/c$, i.e., to two Fedorov groups: the acentric $C_s^4 = Cc$ and the holohedral $C_{2h}^6 = C2/c$. Since the piezoelectric effect is absent, both groups are possible *a priori.*

From the Patterson projections (uw) and (vw) there followed a centrosymmetric arrangement of the cadmium and silicon atoms. In the presence of two kinds of heavier atoms of the phase (signs), the structural amplitudes will be determined by specifying only the “centrosymmetric”coordinates of the heavier atoms, which makes it possible to calculate electron-density syntheses for phase R within the holohedral group $C2/c$. Further analysis of the links between the interaction peaks (^{2}) of the three-dimensional Patterson function also testified in favor of the centrosymmetric group $C2/c$, which was subsequently confirmed.

Table 1

$Na_4Cd_2[Si_3O_{10}]$. Coordinates of the basis atoms

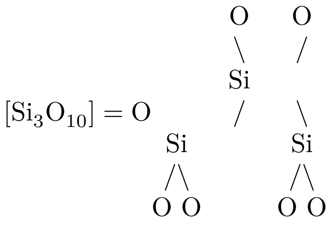
	x/a	y/b	z/c
Cd	0.402	0.599	0.085

	x/a	y/b	z/c
Si_1	0.500	0.381	0.250
Si_2	0.566	0.107	0.101
Na_1	0.329	0.895	0.245
Na_2	0.747	0.565	0.061
O_1	0.394	0.531	0.209
O_2	0.591	0.202	0.187
O_3	0.701	0.953	0.073
O_4	0.562	0.331	0.044
O_5	0.424	0.961	0.118

Analysis of the Patterson projections uw, vw made it possible to localize the Cd and Si atoms. At the following stages of the interpretation, the principal role was played by three-dimensional Fourier syntheses. The resulting structural model was refined by the least-squares method on the basis of 1609 independent nonzero reflections from the layers $h0l$—$h5l$. All calculations were carried out at the Computing Center of Moscow University on a BESM-4 using programs developed by B. L. Tarnopol' skii and V. I. Andrianov (^{3}). The final coordinates of the basis atoms of phase R (28 parameters) are given in Table 1. The discrepancy factor for

for these coordinates, for 1609 reflections differing from zero, $R_{hkl} = 16.4\%$. The averaged constant of isotropic thermal vibrations practically became zero ($B = 0.07$), which must be regarded as a direct consequence of the neglect of absorption.

The structural motif of phase R appears most clearly in the basic xz projection (Fig. 1). Its architectural basis is formed by pairs of Cd polyoctahedra (coordination number 5!), having a common edge (a side of the pseudosquare base), at the middle of which is located a center of symmetry (the origin of the cell). In the direction of the c axis, successive pairs of Cd five-vertex polyhedra (neighboring pairs are connected by intermediate twofold axes; only the 1st and 3rd, etc., are translationally identical; Fig. 1) are joined into chains by hitherto unencountered forked ("soro,"according to H. Strunz) silicosilicate radicals, each of three Si tetrahedra at two levels along b ("bracket," Fig. 2) with the formula



$$[\mathrm{Si_3O_{10}}] = \mathrm{O}\ \begin{array}{ccc} & \mathrm{O} & \mathrm{O} \\ & \backslash & / \\ & \mathrm{Si} & \\ & / & \backslash \\ \mathrm{Si} & & \mathrm{Si} \\ /\backslash & & /\backslash \\ \mathrm{O}\ \mathrm{O} & & \mathrm{O}\ \mathrm{O} \end{array}$$

From the standpoint of the systematics of silicate structures this radical (O :

Fig. 1. Basic xz projection of phase R (Na4Cd2[Si3O10]).

Figure 1: Fig. 1. Basic xz projection of phase R (Na4Cd2[Si3O10]).

Si = 3.33) should be considered the most characteristic feature of phase *R*. The middle tetrahedron of the triorthogroup lies on a second-order axis. The two angles Si − O − Si are 130°52′.

Fig. 1. Basic *xz* projection of phase *R* ($Na_4Cd_2[Si_3O_{10}]$). In addition to the silicate tetrahedra, only the flattened polyhedra (polyoctahedra) around Cd are shown. The Na atoms shown by spheres form helical chains inside channels parallel to the *b* axis. The fractions indicate the heights (y) of the centers of the Cd polyoctahedra and Si tetrahedra.

Translationally identical along the short *b* axis (Fig. 3), and also repeated by an oblique translation ($a + b$), the pairs of Cd polyoctahedra (along *a* in Fig. 1) are connected with one another by the terminal silicosilicate tetrahedra in each case from two different $[Si_3O_{10}]$ groups (Figs. 1 and 3). In the *ac* projection (Fig. 1), crystallographically identical pairs of Cd polyoctahedra and central Si tetrahedra are located at two different heights along *b*, and therefore it is convenient to regard as the basis of the structure of phase *R* an openwork net, distinguished in the *bc* projection (Fig. 3), where all crystallographically identical details are at one height (along *a*). There are two such nets per cell, at levels $x = 0$ and $x = 1/2$; they are mutually shifted by a half-translation along *b* (*C*-centering) and, interlocking,

(Fig. 1), form a three-dimensional framework with channels of hexagonal cross section parallel to the axis *b*. In these channels are located large cations (Na_1), forming helical (around the 2_1 axis) chains (Fig. 1). The other half of the cations (Na_2) along the axis *b* alternates with the free (terminal) O in the triorthogroups (the nearest pairs Na_2 are related by centers of symmetry).

The coordination of the cadmium and sodium atoms appears unusual. The Cd atoms are surrounded by five O atoms in the form of a semioctahedron with a distorted pseudosquare base (Fig. 1, 3). The distances from Cd to the five nearest O atoms do not go beyond the limits already known (2.3 Å). If the semioctahedron is completed to the more usual octahedron for Cd, then the sixth Cd—O distance, equal to 3.76 Å, is much greater than the standard values (^{4}) (the Cd atom has "fallen through" into one half of the octahedron). A similar coordination is possessed by Ti in the titanosilicate phase *E* (Na_2TiSiO_5), also obtained under hydrothermal conditions in a highly alkaline medium (^{5}). For the two kinds of Na the coordination polyhedron is a large tetrahedron: for Na_1, four neighbors at distances almost equal to the sum of the ionic radii (2.2–2.39 Å), while two further neighbors may be regarded as already lying in the second coordination sphere (2.91 Å, 3.07 Å); for Na_2 there is more clearly expressed tetrahedral coordination: the four nearest O at distances

Fig. 2. Angular triorthogroup $[Si_3O_{10}]$ in the structure of $Na_4Cd_2[Si_3O_{10}]$

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Figure 2: Fig. 2. Angular triorthogroup [Si_3O_{10}] in the structure of $Na_4Cd_2[Si_3O_{10}]$

Table 2

Interatomic distances in the structure of $Na_3Cd_2[Si_3O_{10}]$ **(in angstroms)**

Cd polyhedron		Si_1-tetrahedron		Si_2-tetrahedron		Na_1-polyhedron		Na_2-polyhedron	
$Cd-O_1$	2.13	$Si_1-O_{1(2)}$	1.60	Si_2-O_2	1.62	Na_1-O_1	2.25	$Na_2-O_{3'}$	2.31
$Cd-O_{3'}$	2.23	$Si_1-O_{2(2)}$	1.68	Si_2-O_3	1.61	$Na_1-O_{1'}$	2.39	Na_2-O_5	2.22
$Cd-O_4$	2.27	$O_1-O_{2(2)}$	2.76	Si_2-O_4	1.66	Na_1-O_5	2.25	$Na_2-O_{3''}$	2.23
$Cd-O_{4'}$	2.22	$O_1-O_{2'(2)}$	2.60	Si_2-O_5	1.61	$Na_1-O_{2'}$	2.34	$Na_2-O_{4''}$	2.36
$Cd-O_5$	2.21	$O_1-O_{1'}$	2.70	O_2-O_3	2.54	$O_1-O_{1'}$	4.16	$O_{3''}-O_5$	3.62
$O_1-O_{3'}$	3.17	$O_2-O_{2'}$	2.60	O_2-O_4	2.58	O_1-O_5	2.96*	$O_{3''}-O_{3'}$	3.44
O_1-O_4	3.27	**Averages**		O_2-O_5	2.57	$O_1-O_{2'}$	4.30	$O_{3''}-O_{4''}$	3.12
O_1-O_5	2.96*	Si_1-O	1.64	O_3-O_4	2.68	$O_5-O_{2'}$	3.54	$O_5-O_{4''}$	4.08
$O_{3'}-O_4$	3.55	$O-O$	2.67	O_3-O_5	2.76	$O_5-O_{1'}$	4.00	$O_5-O_{3'}$	3.78
$O_{3'}-O_{4'}$	3.08			O_4-O_5	2.74	$O_{2'}-O_{1'}$	3.24	$O_{3'}-O_{4''}$	3.94
$O_{3'}-O_5$	3.82			**Averages**					

Fig. 3. Na4Cd2[Si3O10]. Openwork net of paired Cd semioctahedra and triortho groups [Si3O10]

Figure 3: Fig. 3. Na4Cd2[Si3O10]. Openwork net of paired Cd semioctahedra and triortho groups [Si3O10]

Cd polyhedron		Si_1-tetrahedron	Si_2-tetrahedron		Na_1-polyhedron	Na_2-polyhedron
O_4 –O_5	4.06		Si_2 –O	1.625		
$O_{4'}$ –O_4	2.85*		O – O	2.645		
$O_{4'}$ –O_5	3.24					

* Common edges with the Na polyhedron and the Cd polyhedron are shortened in accordance with Pauling’ s rule.

2.2-2.36 Å, while the remaining O atoms are more than 3.2 Å away from Na_2. The primary coordination of Na is the same in phase *D* (Na_2ZnSiO_4) (^{6}). A complete summary of the interatomic distances in the structure of $Na_4Cd_2[Si_3O_{10}]$ is given in Table 2.

The valence balance lies within permissible limits.

It may be noted that the average Si–O distance is increased in the central tetrahedron of the silicooxygen triad in comparison with Si–O in the two terminal ones. More specifically, all distances from silicon to the shared O significantly exceed the distances to the other O atoms.

Until recently, the tetrahedral coordination of Na in elementary Na_2O (antifluorite structural type, also repeated in K_2O, Rb_2O, Cs_2O) was surprising; now fourfold coordination proves to be characteristic of Na also in a whole series of Na silicates obtained from highly alkaline solutions.

Fig. 3. $Na_4Cd_2[Si_3O_{10}]$. Openwork net of paired Cd semioctahedra and triortho groups $[Si_3O_{10}]$

The physical significance of the chain radicals $[Si_3O_{10}]$ with a common direction along the *c* axis is emphasized by the elongation of crystals of phase *R* precisely along this direction.

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