CRYSTAL STRUCTURE OF Na, Cd SILICATE

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CRYSTAL STRUCTURE OF Na, Cd SILICATE

$Na_2CdSi_2O_6 = Na_6Cd_3[Si_6O_{18}]$

The objects of investigation were samples of crystals of a synthetic Na, Cd silicate (“phase *K*”) in the system Na_2O—CdO—SiO_2, obtained* in the laboratory of hydrothermal synthesis of the Institute of Crystallography, Academy of Sciences of the USSR (^{1}). The chemical composition of phase *K*, according to the analysis of V. S. Bykova, G. A. Arapova, and Yu. S. Nesterova (SiO_2 –37.47%; CdO–42.88%; Na_2O–19.3%; $\Sigma = 99.65\%$), may be expressed by the approximate formula $Na_2Cd[Si_2O_6]$, with the metasilicate ratio Si : O = 1 : 3.

The parameters of the pseudotetragonal cell (Laue class *mmm*) of phase *K*:

$$a = 10.40 \pm 0.05\ \text{Å}, \quad b = 10.40 \pm 0.05\ \text{Å}, \quad c = 7.45 \pm 0.03\ \text{Å} \quad (c = {}^1/_2c)$$

were established from rotation x-ray photographs (Mo radiation). Along the short *c* axis there is a distinctly expressed pseudoperiod $c' = {}^1/_2c$.

The experimental intensity material consisted of reflections with the nets $hk0$, $hk2$, $hk3$, $hk4$, $hk6$, $h0l$, $h1l$, and $0kl$** ($\max \sin\vartheta/\lambda = 0.8$). The intensities of the reflections were estimated visually by comparison with a standard blackening scale with a step $\sqrt{2}$; the standards were obtained in a Weissenberg x-ray goniometer using the 440 reflection.

The syngony *mmm* fixed from the Laue photographs was once again confirmed by the symmetry of the obtained nets.

Absence of integral extinctions excludes nonprimitivity of the lattice, but the disappearance of a considerable part of the hkl reflections with $h + k = 2n + 1$ and the weakness of those retained indicate pseudocentering of the face (001), just as the pseudoperiod $c' = {}^1/_2c$ weakened all hkl reflections with $l = 2n + 1$.

Fig. 1. Na, Cd metasilicate (phase *K*). Pseudotetragonal projection of the structure on the plane *xy*. In addition to tetrahedra, polyhedra around Cd are singled out. Spheres are Na cations.

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The only systematic extinctions remaining were in the $hk0$ zone ($h+k = 2n+1$), which leads to the x-ray group $P--n$, i.e., to two space groups $D_{2h}^{13} = Pmmn$ and $C_{2v}^{7} = Pm2_1n$ ($P2_1mn$). In view of the absence of a center of symmetry (presence of a piezoelectric effect), only the hemimorphic space group $C_{2v}^{7} = Pm2_1n$ ($P2_1mn$) is possible. Analysis of the paterson projections and the first calculations for localizing the Cd atoms in the xy projection confirmed that, with a pseudotetragonal setting—choice of axes—the space group of phase K is $C_{2v}^{7} = Pm2_1n$.

At a specific gravity $d = 3.82$, a cell of the indicated dimensions contains $Z = 6$ formula units of $Na_2CdSi_2O_6$. The atoms are distributed over two types of crystallographic positions: fourfold general positions and single twofold special positions on mirror planes m.

The presence in the cell of 6 Cd atoms, with multiplicity 4 for the general positions, made it possible, already from the Patterson projections uv, uw, to determine the coordinates of the Cd atoms; from these, in the xy projection, through a series of electron-density syntheses, it was possible to localize the Si and Na atoms and part of the oxygen atoms.

However, the pseudoperiod along the c axis with the pseudo-centered xy face, as well as the large number of overlaps in all projections, made their interpretation difficult. In the subsequent structural analysis, the main role was played by three-dimensional complete and difference Fourier syntheses. The structural model obtained was refined by the method of successive approximations, since the presence of a pseudoperiod, with a relatively small number of independent nonzero reflections, substantially impeded effective refinement of the atomic coordinates by the least-squares method. All calculations were performed at the Computing Center of Moscow University on a BESM-4 machine, using programs developed by B. L. Tarnopol' skii and V. I. Andrianov (2). The final coordinates of the basis atoms (53 parameters) of phase K are given in Table 1. The discrepancy factor for these coordinates is $R_{hkl} = 11.5\%$. The averaged constant of isotropic thermal

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* Within very narrow concentration limits the dimensions of the crystallites, somewhat elongated along [001], are ~ 0.1 mm.

** The missing $hk1$ and $hk5$ were not recorded because of the pseudoperiod.

Fig. 2. Na, Cd metasilicate. Principal architectural rods of the structure—ribbons of Cd, Na octahedra in the yz projection

Figure 2: Fig. 2. Na, Cd metasilicate. Principal architectural rods of the structure—ribbons of Cd, Na octahedra in the yz projection

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Table 1

$Na_2CdSi_2O_6$ (phase K). Coordinates of the basis atoms

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Cd_1	0	0	0	O_1	0.280	0.263	0.750
Cd_2	0	0.250	0.250	O_2	0.373	0.363	0.445
Cd_3	0	0.250	0.750	O_3	0.370	0.126	0.997
Si_1	0.267	0.263	0.530	O_4	0.133	0.199	1.010
Si_2	0.279	0.260	0.958	O_5	0.138	0.301	0.437
Si_3	0.500	0.032	0.990	O_6	0.314	0.362	1.095
Si_4	0.500	0.460	0.455	O_7	0.322	0.118	0.482
Na_1	0.208	0.499	0.262	O_8	0.000	0.429	1.153
Na_2	0.246	0.475	0.771	O_9	0.500	0.531	0.642
Na_3	0.000	0.494	0.526	O_{10}	0.500	0.550	0.295
Na_4	0.500	0.240	0.277	O_{11}	0.000	0.458	0.815

oscillations practically became zero ($B = 0.03$ Å), which should be considered a direct consequence of neglecting absorption.

The structural motif of the pseudotetragonal phase K is most clearly seen in the basal projection xy (Fig. 1), with the oxygen tetrahedra around Si and part of the Cd octahedra singled out; the Na atoms are shown as spheres. The basis of the structure consists of ribbons of Cd, Na octahedra, infinite along c (Fig. 2), located at the levels $x = 0$ and $x = \frac{1}{2}$. The ribbons, repeated translationally along b, are connected with one another by a silicic-oxygen radical—the group $[Si_6O_{18}]$, which also cements the ribbons located at different levels.

Fig. 3. Na, Cd metasilicate. Six-membered (pseudotetragonal) rings in axonometry. The upper and two lower ones are connected by a glide plane

The island radical with formula $[Si_6O_{18}]$ is a six-membered ring, similar to lovozerite rings (^{3}, ^{4}): the ring may be described as two parallel diorthogroups Si_2O_7, elongated along the c axis and linked on one side above, and on the other side below, by single SiO_4 tetrahedra situated in the symmetry planes (Figs. 1 and 3)*.

In Fig. 4, in the xz projection, four types of Na polyhedra are shown. Two Na cations (Na_2, Na_3) have six neighbors at distances of 2.24-2.87 Å. The nearest neighbors of Na_1 are seven O atoms at distances of 2.20-2.75 Å. Na_4 is in eightfold coordination (2.2-2.75 Å).

In the arrangement of Cd, Na, Si polyhedra, two levels are clearly distinguished (+ and − zigzags of the ribbon of Cd octahedra) along the c axis, which creates the noted pseudoperiod $c' = \frac{1}{2}c$. The Cd atoms are, moreover, arranged according to the C-law, producing pseudocentering of the face (001).

Fig. 4. Na, Cd metasilicate. Four types of Na polyhedra in the xz projection

With a satisfactory balance of valence forces, the interatomic distances lie within the limits:

$$\begin{aligned} \mathrm{Si-O} &= 1.52\text{–}1.69\ \text{Å} \quad \text{for O} - \text{O} = 2.51\text{–}2.79\ \text{Å}, \\ \mathrm{Na-O} &= 2.2\text{–}2.87\ \text{Å} \quad \text{for O} - \text{O} = 2.62\text{–}4.97\ \text{Å}, \\ \mathrm{Cd-O} &= 2.0\text{–}2.79\ \text{Å} \quad \text{for O} - \text{O} = 2.77\text{–}4.4\ \text{Å}. \end{aligned}$$

* In projection along the pseudotetragonal axis, the ring appears four-membered, resembling a single-story four-membered ring of baotite ([5]) and a two-story four-membered ring in ecanite ([6]), and therefore our ring may be characterized as a compromise one, with two two-story links and two single-story links.

The distances from the bridging atoms in the radical $[Si_6O_{18}]$ to the central Si atoms are somewhat increased (1.64-1.67 Å) compared with the average (1.62 Å). The shared edges of the Cd octahedra are shortened to 2.77 Å. The shared edge of the Na_4 eight-vertex polyhedron with the Si_4 tetrahedron is also shortened, to 2.64 Å.

On the basis of the structure obtained for phase K, its expanded formula should be written as $Na_6Cd_3[Si_6O_{18}]$. The unit cell contains two such units ($Z' = 2$).

Comparison of the solved structure, which has the gross formula $Na_2CdSi_2O_6$, with the structure of $Na_2ZnSi_2O_6$ (phase C', M) demonstrates that complete replacement of Zn atoms, which usually prefer tetrahedral coordination ([7]), by Cd atoms leads to a complete rearrangement of the structure, in particular to the replacement of infinite metachains by a ring-type metaradical ([8]).

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