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CRYSTALLOGRAPHY

1968

SovietRxiv

Abstract

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UDC 548.736

CRYSTALLOGRAPHY

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CRYSTAL STRUCTURE OF Na,Cd-TRIORTHOSILICATE

$Na_2Cd_3[Si_3O_{10}]$

The objects of the investigation were samples of crystals of synthetic Na,Cd-silicate, obtained in the laboratory of hydrothermal synthesis of the Institute of Crystallography, Academy of Sciences of the USSR, as phase *L* in the system Na_2O—CdO—SiO_2—H_2O (^{1}).

The chemical composition of phase *L*, according to the analysis by V. S. Bykova, Yu. S. Nesterova, and G. A. Arapova (SiO_2 28.23%, CdO 63%, Na_2O 9.5%; $\Sigma = 100.73\%$), is in good agreement with the formula $Na_2Cd_3[Si_3O_{10}]$. With a specific gravity $d = 4.55$ g/cm^3, the monoclinic cell (Laue class $2/m$) with parameters $a = 16.29 \pm 0.02$ Å, $b = 5.083 \pm 0.003$ Å, $c = 10.85 \pm 0.02$ Å; $\beta = 86°$ contains $Z = 4$ formula units of $Na_2Cd_3[Si_3O_{10}]$.

The experimental intensity material consisted of reflections from Weissenberg photographs $h0l$—$h3l$ and $hk0$ (MoK_α radiation, $\max \sin\vartheta/\lambda = 1.1$ Å^{-1}). The intensities of the reflexions were estimated visually according to the standard $\sqrt{2}$-scale of blackening marks, obtained in the X-ray goniometer directly from the crystal under study.

The systematic absences lead to the base-centered X-ray group C—$/c$, i.e., to two Fedorov groups: the acentric $C_s^4 = Cc$ and the holohedral $C_{2h}^6 = C2/c$. In the absence of a piezoelectric effect, a priori both groups are possible.

On the basis of the centrosymmetric arrangement of the Cd and Si atoms in the first projections xz, xy, and also of an analysis of the distribution of interaction peaks (^{2}) over the levels of the three-dimensional Patterson function, the centrosymmetric group $C2/c = C2_{(1)}/c(n)$ was adopted.

In the corresponding unit cell there are 8-fold general positions and only 4-fold special positions, and therefore, among the 12 Cd and 12 Si per cell, at least one quartet of both Cd and Si must occupy special positions, of which there are two types in this group. Four parameterless complexes at inversion centers are divided into two subtypes: in $4a$ and b the inversion centers lie on glide planes c, while in $4c$ and d the inversion centers lie on glide planes n. One (one-parameter) complex ($4e$) consists of positions one on each of the four twofold

Fig. 1. $Na_2Cd_3[Si_3O_{10}]$—phase L. Projection along the short b axis.

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axes. Proceeding from the symmetry of the usual environment of Si and Cd, it is natural to place the first quartet in positions $4e$, and the quartet of Cd at inversion centers (later the quartet of Cd was fixed on the n planes, namely $4c$).

A detailed analysis of the Patterson syntheses $p(uw)$ and $p(uv)$, and the first calculations of electron density, made it possible to localize in the xz and xy projections the Cd and Si atoms, occupying both special and general positions. Further deciphering of the structure was carried out by constructing simple and difference three-dimensional Fourier syntheses. The model structure obtained was refined by the least-squares method. All calculations were performed at the Computing Center of Moscow University on a BESM-4 computer using programs developed by B. L. Tarnopolsky and V. I. Andrianov (^{3}). The final coordinates of the basic atoms of phase L (25 parameters) are given in Table 1. The discrepancy factor corresponding to these

coordinates, for 835 independent and nonzero reflections $R_{hkl} = 13.3\%$. The averaged constant of isotropic vibrations practically went to zero ($B = 0.04$), which should be regarded as a direct consequence of neglecting absorption.

Fig. 1. $Na_2Cd_3[Si_3O_{10}]$—phase L. Projection along the short b axis. The threaded (perpendicular to the projection plane) 2-fold axes of the triorthogroup $[Si_3O_{10}]$ bind into a framework thick trellis walls made of parallel, but shifted, triples of Cd polyhedra. The small circles are Na atoms filling the channels inside the framework. Fractions indicate the heights (y) of the Cd and Si atoms.

Interatomic distances are given in Table 2. In the silico-oxygen tetrahedra they correspond to those usually encountered: $Si_1 - O = 1.57–1.60$ Å, with an average of 1.58 Å; the edges of the Si_1-tetrahedron also do not fall outside the narrow limits 2.54–2.66 Å; $Si_2 - O = 1.57–1.67$ Å (average 1.62) with $O - O = 2.54–2.77$ Å. Common edges of the Si_2-tetrahedron and the Cd and Na polyhedra are shortened, respectively, to 2.55 and 2.54 Å, with the opposite $O - O = 2.68$ Å, and the tetrahedron is elongated (two edges are increased to 2.77 Å). The polyhedra around two sorts of Cd are different: Cd_1 ($4c$) has octahedral coordination; Cd_2 is displaced from the center of the octahedron and has five nearest neighbors at distances of 2.13–2.36 Å; the sixth distance is $Cd_2 - O = 3.03$ Å. Cd in phase R ($Na_4Cd_2[Si_3O_{10}]$) has similar fivefold coordination (^{4}).

Table 1

Coordinates of the basis atoms in the structure $Na_2Cd_3[Si_3O_{10}]$ **(phase** L**)**

Atoms	x/a	y/b	z/c
Cd_1	0.250	0.250	0.000
Cd_2	0.342	0.709	0.206
Si_1	0.000	0.827	0.250
Si_2	0.150	0.688	0.100
Na	0.045	0.232	0.031
O_1	0.352	0.953	0.028
O_2	0.451	0.479	0.156
O_3	0.062	0.635	0.172
O_4	0.224	0.538	0.169
O_5	0.159	0.015	0.101

The decrease of the coordination of Cd_2 to five improves the valence balance according to Pauling, which, with sixfold coordination of Cd_2, would be too strained for O atoms common to two Si atoms (2.53 is replaced by 2.2).

For Na, five neighbors are at distances almost equal to the sum of the ionic radii, 2.29–2.58 Å; the remaining O atoms are more than 3.0 Å distant from Na.

Fig. 2. Cut from the rutile structural motif at an oblique angle (to the 4-fold axis), a trellis wall of Cd octahedra with continuously mutually displaced filaments of thickness one octahedron and width three octahedra. **a**—general view of ideal octahedra; **b**—orthogonal projection of a separate filament of triples on two levels

The structural motif of phase *L* appears quite clearly in the *xz* projection (Fig. 1) with the line of sight along the short axis *b*, i.e., parallel to the 2-fold axis, when compared with Fig. 2a, which highlights the "engineering framework" of the structure. These are walls, parallel to the *yz* plane (faces *bc*), composed of Cd octahedra of a complicated construction, namely of discrete

Table 2

Interatomic distances in the structure of $Na_2Cd_3[Si_3O_{10}]$**. Phase** *L*

Cd_1-octahedron		Cd_2-octahedron		Si_1-tetrahedron		Si_2-tetrahedron		Na-polyhedron	
$Cd_1–O_1$ (2)	2,28	$Cd_2–O_1$	2,29	$Si_1–O_2$(2)	1,57	$Si_2–O'_1$	1,57	$Na–O'_1$	2,38
$Cd_1–O_4$ (2)	2,36	$Cd_2–O_2$	2,13	$Si_1–O_3$(2)	1,60	$Si_2–O_3$	1,61	$Na–O'_2$	2,29
$Cd_1–O_5$ (2)	2,15	$Cd_2–O_4$	2,18	$O_2–O'_2$	2,66	$Si_2–O_4$	1,64	$Na–O''_2$	2,39

Cd_1-octahedron		Cd_2-octahedron		Si_1-tetrahedron		Si_2-tetrahedron		Na-polyhedron	
O_1–O_4 (2)	3,88	Cd_2–O'_4	2,36	O_2–O_3(2)	2,56	Si_2–O_5	1,67	Na–O_3	2,58
O_1–O_5 (2)	3,21	Cd_2–O_5	2,30	O'_2–O'_3(2)	2,55	O'_1–O_3	2,54	Na–O_5	2,33
O'_1–O_4 (2)	2,55	O_1–O_2	3,24	O_3–O'_3	2,54	O'_1–O_4	2,55	O'_1–O'_2	3,44
O'_1–O_5 (2)	3,06	O_1–O_4	3,27			O'_1–O_5	2,77	O'_1–O_3	2,54*
O_4–O_5 (2)	2,97*	O_1–O'_4	3,46			O_3–O_4	2,68	O'_1–O_5	3,06
O'_4–O_5 (2)	3,40	O_2–O_4	3,65			O_3–O_5	2,58	O'_2–O''_2	3,68
		O_2–O'_4	4,34			O_4–O_5	2,76	O'_2–O_3	4,74
		O_2–O_5	3,06					O'_2–O_5	3,39
		O_4–O'_4	3,24					O''_2–O_3	3,83
		O_4–O_5	3,24					O''_2–O_5	3,45
		O'_4–O_5	2,97*					O_3–O_5	3,58
Averages		**Averages**		**Averages**		**Averages**		**Averages**	
Cd_1–O	2,26	Cd_2–O	2,25	Si_1–O	1,58	Si_2–O	1,62	Na–O	2,39
O–O	3,18	O–O	3,38	O–O	2,57	O–O	2,65	O–O	3,52

* Common edges are shortened in accordance with Pauling’ s rule.

infinite (along the *c* axis) sheets, each one Cd octahedron thick and three octahedra wide; however, these sheets are oriented obliquely (at an angle of ~ 30°) to the parallel face *bc* of the thicker, massive wall of the trellis type. In each sheet, according to the law of double-layer closest packing, triplets of occupied octahedra alternate parallel to the *b* axis with triplets of empty ones. In neighboring sheets the levels of the occupied triplets and the empty ones interchange (with the geometrical aid of the 2_1 axes, Fig. 2b). The trellis wall appears to be

Fig. 3

Figure 2: Fig. 3

borrowed from the well-known rutile motif with the ends of infinite columns of octahedra alternating in a checkerboard pattern. From this rutile motif a layer (Fig. 2a) three octahedra thick is cut out along each rutile column, but at a very steep angle, $\sim 60^\circ$, to the 4-fold axis of rutile.

In the direction of the *a* axis (Fig. 1), two trellis walls belonging to the corresponding period are connected with one another by an oblique (*C*—) translation, i.e., are mutually displaced by $b/2$, but the right part of the left wall and the left part of the right wall lie at one level, being connected by twofold rotation axes passing between the walls, and on these axes are strung nearly linear silicon-oxygen radicals $[Si_3O_{10}]^{8-}$, each of three Si tetrahedra (Fig. 3). A similar cluster radical (according to Strunz, an island sororadical, a triorthogroup) was recently found by us (4) in the *R*-phase of the same system Na_2O—CdO—SiO_2—H_2O, but there the triorthogroup was as it were an incomplete square (“bracket”); in the *L* phase, however, the triorthogroup is almost linear, although two Si—O—Si angles, equal to 130°17′, are the same as in the *R* phase (130°52′); what differ are the rotations of the outer Si tetrahedra.

Fig. 3. $Na_2Cd_3[Si_3O_{10}]$. An almost linear cluster triorthogroup $[Si_3O_{10}]$, but with an angular arrangement of the Si centers ($\angle$Si—O—Si $\approx 131^\circ$).

The lower symmetry of the cation Cd^{2+} (not of the noble-gas type) permits edges of different length in its polyhedra, and the Cd_1 octahedron has a common (shortened) edge with an Si tetrahedron, whereas a Si_2O_7 group adjoins the elongated polar edge of the Cd_2 half-octahedron (rules of Chapters 1 and 2 of the crystal chemistry of silicates). In both phases obtained from highly alkaline solutions, *R* and *L*, the large Na cation has low coordination: in the *R* phase it is tetrahedral, in the *L* phase fivefold; i.e., in concentrated NaOH solutions and in the silicates crystallizing from them, the coordination features of Na are close to what is characteristic of crystalline Na_2O (4-fold coordination). In accordance with the formulas of the phases *R*-$Na_4Cd_2[Si_3O_{10}]$ and *L*-$Na_2Cd_3[Si_3O_{10}]$, the Cd cations are represented by centrosymmetric pairs in the first and by triplets strung on 2-fold axes in the second. Correspondingly, the bonds between Na cations, which in both structures are arranged in chains inside channels, are also rearranged: in the *R* phase they are strung on a screw axis 2_1, whereas in the *L* phase the Na pyramids are connected by inversion centers ($4a$, in one of them the origin of the cell).

The authors consider it a pleasant duty to express their gratitude to D. P. Shashkin for active assistance in the work, and are especially grateful to V. S. Bykova, Yu. S. Nesterova, and G. A. Arapova (IGEM) for precise chemical analyses of both the *R* phase and the *L* phase.

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Received
29 III 1968

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