

# Rb<sub>2</sub>CdSiO<sub>4</sub>: Synthesis and Crystal Structure

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IN HONOR OF PROFESSOR PAUL HAGENMULLER ON THE OCCASION OF HIS 80TH BIRTHDAY

The new compound Rb<sub>2</sub>CdSiO<sub>4</sub> has been synthesized from Rb<sub>2</sub>CdO<sub>2</sub> and SiO<sub>2</sub> in the presence of excess Rb<sub>2</sub>O (typical molar ratio 1:1:2) under Ar atmosphere in a sealed Ag container at 330°C (40d). The twinned structure has been refined from X-ray single crystal data. Rb<sub>2</sub>CdSiO<sub>4</sub> was found to crystallize in the space group C222<sub>1</sub> (No. 20) with  $a = 1142.6(2)$  pm,  $b = 1102.3(1)$  pm,  $c = 1672.5(2)$  pm. The lattice constants were refined from X-ray powder data. The crystal structure can be described as a stuffed derivative of the  $\alpha$ -cristobalite modification of SiO<sub>2</sub>. © 2001 Elsevier Science

**Key Words:** crystal structure; silicate; cadmium; rubidium.

## INTRODUCTION

Over the years many efforts have been made to characterize the numerous orthosilicates,  $A_2MSiO_4$  ( $A = \text{Li–Cs}$  and  $M = \text{Be, Mg}$  and transition metals). Still, only limited knowledge of single crystal data is available. At least two modifications of Li<sub>2</sub>BeSiO<sub>4</sub> (1), Na<sub>2</sub>BeSiO<sub>4</sub> (2, 3), Na<sub>2</sub>MSiO<sub>4</sub> ( $M = \text{Zn, Mg}$ ) (4) and one of Li<sub>2</sub>CdSiO<sub>4</sub> (5) have been reported. Furthermore, powder data have been published with cell refinements on the basis of various cations in  $A_2MSiO_4$  type orthosilicates giving isotypic products, e.g. K<sub>2</sub>MSiO<sub>4</sub> ( $M = \text{Co, Zn, Mg, Cd}$ ) (6). This is true in most cases, but there are exceptions. For example, it has been a guideline in the past that [SiO<sub>4</sub>] tetrahedra always connect with other polyhedra via corners. Only recently, numerous compounds have been obtained showing the characteristic feature of shared square-planar and tetrahedral edges, e.g.,  $A_6MSi_2O_8$  and  $A_4MSi_2O_7$  ( $A = \text{K–Cs}$ ,  $M = \text{Ni, Cu}$ ) (7). Cs<sub>5</sub>CoSiO<sub>6</sub> and Cs<sub>2</sub>CoSiO<sub>4</sub> (8) are novel examples for shared tetrahedral edges. However, this interesting feature is not observed in the title compound and is not expected to be observed for divalent 4d elements. Detailed studies of alkali transition metal silicates with the heavier alkali metals (K–Cs) have been reported for K<sub>2</sub>CdSiO<sub>4</sub> (6), A<sub>2</sub>TiSi<sub>6</sub>O<sub>15</sub> ( $A = \text{K, Cs}$ ),

Cs<sub>2</sub>MSi<sub>5</sub>O<sub>12</sub> (Be, Cd, Mn, Co, Cu, Ni), and Rb<sub>2</sub>CdSi<sub>5</sub>O<sub>12</sub> (9) in recent articles. Na<sub>2</sub>Cd<sub>3</sub>Si<sub>3</sub>O<sub>10</sub> and Na<sub>6</sub>Cd<sub>3</sub>Si<sub>6</sub>O<sub>18</sub> (10) are two examples for sodium silicates with cadmium, which have different structures and compositions. Often abnormal interatomic distances,  $d(M–O)$ , for various transition metal cations and sometimes even for silicon result from indexing similar but not isotypic powder data. Therefore, it is of great interest to gain access to good quality structural data and reliable interatomic distances and angles for further detailed studies of physical properties. Here the deviation of the effective ionic radii of the tetrahedrally coordinated cations in Rb<sub>2</sub>CdSiO<sub>4</sub> is discussed as the main cause of a different twinning law compared to Na<sub>2</sub>BeSiO<sub>4</sub> (2).

## EXPERIMENTAL DETAILS

Red-brown single crystals of Rb<sub>2</sub>CdSiO<sub>4</sub> were obtained under an inert gas atmosphere (Ar) by annealing intimate mixtures of Rb<sub>2</sub>CdO<sub>2</sub> (from Rb<sub>2</sub>O and CdO) and SiO<sub>2</sub> in the presence of excess Rb<sub>2</sub>O (typical molar ratio 1:1:2) in a sealed Ag container at 330°C (40 d). For protection the containers were encapsulated in glass ampoules. The compound is sensitive to moisture and, therefore, for the selection of single crystals a microscope attached to a glove box (Braun, D) was used. The single crystal data were collected on an IPDS diffractometer (Stoe & Cie, D). The program system X-RED/X-SHAPE was used for the numerical absorption correction (Stoe & Cie, D). Powder samples were obtained from equimolar ratios of the binary oxides. If Rb<sub>2</sub>O was used in excess, Rb<sub>2</sub>CdO<sub>2</sub> and Rb<sub>2</sub>Cd<sub>2</sub>O<sub>3</sub> were also detected by X-ray powder diffraction using CuK $\alpha$  radiation (STADI P, Stoe & Cie, D). Therefore, powder samples with 5% excess of CdO, then used as an internal standard, were prepared and only reflections of CdO and the title compound were observed in the powder diffractogram.

## RESULTS AND DISCUSSION

The crystal structure of Rb<sub>2</sub>CdSiO<sub>4</sub> has been determined from X-ray diffraction data. Only twinned crystals were

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**TABLE 1**  
**Crystallographic Data for Rb<sub>2</sub>CdSiO<sub>4</sub>**

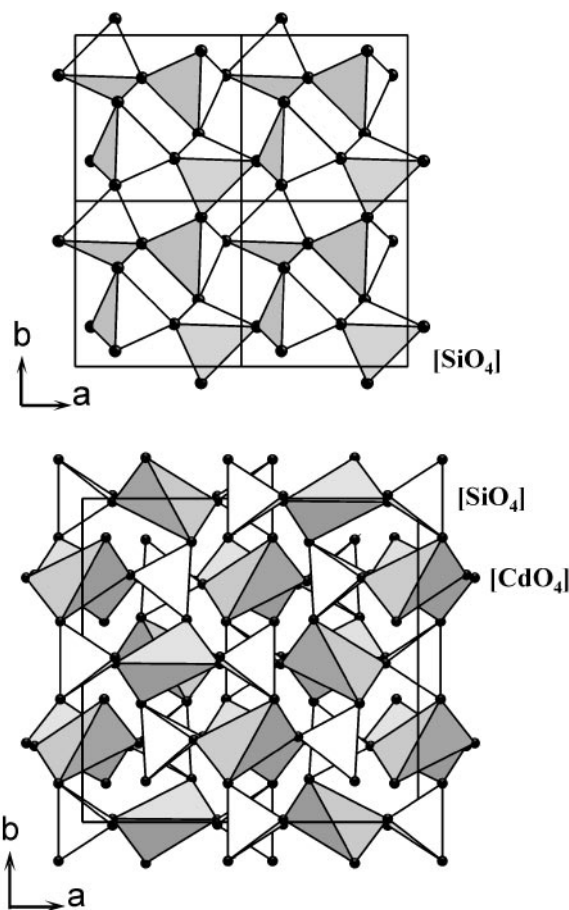
Crystal system	orthorhombic
Space group	$C222_1$ (No. 20)
Temperature [K]	293
Lattice constants [pm]	$a = 1142.6(2)$ , $b = 1102.3(1)$ , $c = 1672.5(2)$
single crystal data	$a = 1141.9(1)$ , $b = 1100.9(1)$ , $c = 1671.6(2)$
powder data (56 indexed reflections)	
Cell volume [pm <sup>3</sup> ]	$2106.4 \times 10^6 / 2101.4(3) \times 10^6$
Formula units per unit cell	$Z = 8$
Crystal size [mm]	$0.05 \times 0.05 \times 0.05$
Diffractometer	Stoe IPDS
Scan	125 images, 2° steps
Radiation (MoK $\alpha$ ) [pm]	71.073 (graphite monochromator)
Range	$2.9^\circ < 2\theta < 48^\circ$ $-13 \leq h \leq 13$ , $-11 \leq k \leq 12$ , $-19 \leq l \leq 19$
$F(000)$	2688
Absorption correction	numerical (18)
Absorption coefficient [mm <sup>-1</sup> ]	$\mu = 22.31$
No. of measured reflections	8428
No. of observed reflections	4518
No. of unique reflections	1622
$R_{int}$	0.063
Structure determination	SHELXS-86; SHELXL-93 (19)
Refined parameters	148
Goodness-of-fit	0.915
$R1 [I_o > 2\sigma(I)]$	0.031
$R1/wR2$ (all data)	0.051/0.054
Twin component	0.36(4)

obtained and investigated. For crystallographic data and details of the structure solution see Tables 1 and 2. The systematically absent  $hkl$  indices indicated the space group  $C222_1$  (acentric). For the structure refinement, the twin matrix (010 100 00-1) was used with the fractional contribution of 0.36 for the second component. A possible racemic twinning of the two components was investigated and could be excluded.

The lattice parameters are close to tetragonal and the twinning law is according to what can be expected for  $a \approx b$  (in this case:  $a^{\text{average}} \approx 1120$  pm,  $c = 1672$  pm). It can be understood from modifying the archetype structure of  $\alpha$ -cristobalite. This modification of SiO<sub>2</sub> crystallizes in the space group  $P4_12_12$  (11). From *translationengleiche* symmetry reduction  $\mathbf{t}2$  ( $2a = a'$ ,  $2c = c'$ ) and cell transformation the direct subgroup  $C222_1$  results (12) and shows the relation between the 4<sub>1</sub> screw axis and the remaining symmetry element 2<sub>1</sub> in the structure of Rb<sub>2</sub>CdSiO<sub>4</sub> (Fig. 1). Therefore, the pseudo tetragonal cell can be transformed and the lattice parameters directly calculated from the cell constants of  $\alpha$ -cristobalite ( $a = 497.1$  pm,  $c = 697.1$  pm) (11) with  $2a = a' = b' = 994$  pm, and  $2c = c' = 1394$  pm). The larger cations (Rb<sup>+</sup>, Cd<sup>2+</sup>) incorporated in the cell enlarge the cell

to the observed lattice constants of  $a = 1142.6(2)$  pm,  $b = 1102.3(1)$  pm, and  $c = 1672.5(2)$  pm (single-crystal data) by  $729 \times 10^6$  pm<sup>3</sup> or  $54$  cm<sup>3</sup>/mol. From Biltz's volume increments (13) with  $V_m(\text{Rb}^+) = 20$  cm<sup>3</sup>/mol ( $\times 2$ ) and  $V_m(\text{Cd}^{2+}) = 6$  cm<sup>3</sup>/mol one calculates  $46$  cm<sup>3</sup>/mol which is approximately what can be expected for the incorporation of larger cations into the three-dimensional tetrahedral network of the  $\alpha$ -cristobalite structure.

It must be noted that for Na<sub>2</sub>BeSiO<sub>4</sub> a different twinning law has been described related to the  $\beta$ -cristobalite type of structure (2). In this case six components have been used to solve the crystal structure ( $Pca2_1$  with  $a = 986.1(2)$  pm,  $b = 491.1(1)$  pm, and  $c = 1387.5(3)$  pm). It is obvious that the derived cell constants do match with the structure of Rb<sub>2</sub>CdSiO<sub>4</sub> reported here when the  $b$  axis is multiplied by two. Another subcell with  $a = 793.8$  pm,  $b = 1672.5$  pm,  $c = 793.8$  pm,  $\beta = 92.05^\circ$  (space group:  $Cm$ ) represents the reduced cell and has been suggested from running the program PLATON-00 (14) as



**FIG. 1.** Projection of the crystal structure of  $\alpha$ -cristobalite with four unit cells (above) and Rb<sub>2</sub>CdSiO<sub>4</sub> (below). The rubidium atoms are not included for clarity reasons.

**TABLE 2**  
**Atomic Coordinates, Anisotropic<sup>a</sup> and Equivalent<sup>b</sup> Displacement Factors in pm<sup>2</sup> for Rb<sub>2</sub>CdSiO<sub>4</sub>**

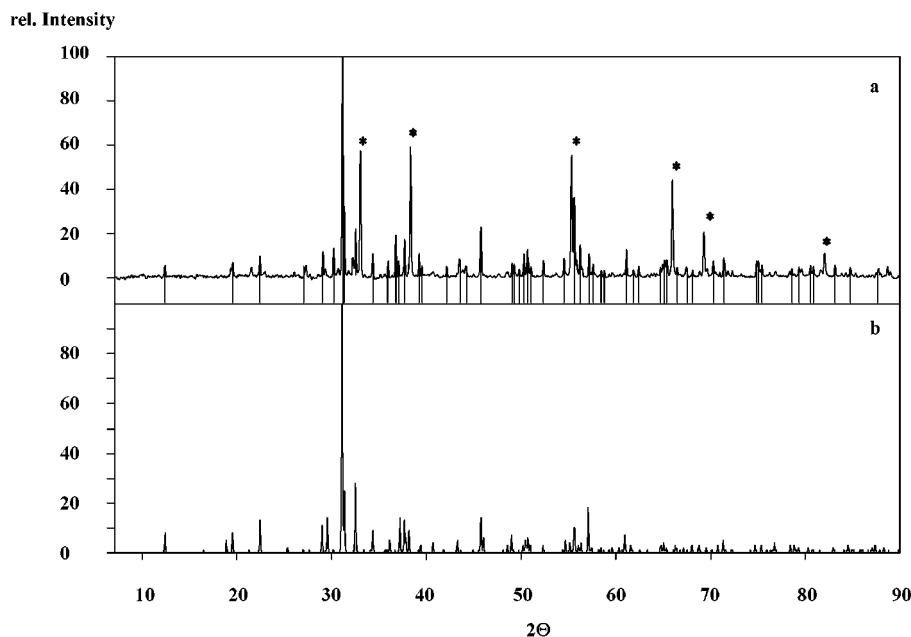
Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>eq</sub>
Cd1	8c	0.2510(1)	0.5177(1)	0.1558(1)	124(8)	259(7)	100(6)	-7(5)	-6(6)	41(8)	161(4)
Cd2	8c	0.49145(9)	0.7402(1)	0.0936(1)	142(8)	325(9)	111(7)	1(5)	-1(5)	32(7)	193(4)
Rb1	8c	0.2497(2)	0.2989(3)	0.01148(9)	171(11)	193(13)	273(7)	-2(7)	35(12)	-13(9)	212(5)
Rb2	8c	0.2492(2)	0.4942(1)	0.3915(1)	198(15)	203(16)	141(11)	11(5)	-7(9)	9(16)	181(7)
Rb3	8c	0.0048(1)	0.7484(1)	0.1414(1)	184(15)	261(17)	157(11)	7(6)	5(6)	21(17)	200(7)
Rb4	4b	0	0.0415(3)	0.25	124(14)	245(16)	244(12)	0	-6(13)	0	204(7)
Rb5	4b	0	0.4480(4)	0.25	187(16)	224(17)	313(13)	0	-6(15)	0	241(7)
Si1	8c	0.263(1)	0.7488(4)	0.2543(2)	132(49)	231(44)	128(23)	29(36)	3(18)	-5(21)	164(19)
Si2	4a	0.488(1)	0.5	0	125(53)	98(46)	32(38)	-17(30)	0	0	85(19)
Si3	4a	0.019(1)	0.5	0	94(52)	90(53)	97(44)	20(31)	0	0	94(21)
O1	8c	0.571(1)	0.620(2)	0.002(1)	238(87)	167(102)	211(81)	-24(53)	-131(59)	-86(70)	205(41)
O2	8c	0.332(1)	0.745(2)	0.1669(7)	161(69)	395(88)	154(60)	55(71)	86(48)	96(76)	236(35)
O3	8c	0.934(1)	0.620(2)	0.990(1)	111(75)	81(83)	292(89)	63(56)	-25(58)	74(57)	161(38)
O4	8c	0.358(1)	0.735(2)	0.3295(7)	227(75)	292(95)	176(63)	-25(61)	-66(51)	-32(63)	232(38)
O5	8c	0.175(1)	0.633(1)	0.256(1)	148(79)	197(78)	90(61)	-9(52)	23(51)	49(54)	145(34)
O6	8c	0.189(1)	0.873(1)	0.260(1)	178(87)	164(85)	369(94)	-24(70)	-11(67)	-103(60)	237(41)
O7	8c	0.098(1)	0.508(2)	0.080(1)	196(77)	487(119)	178(94)	-74(71)	-190(60)	145(72)	287(45)
O8	8c	0.409(2)	0.489(2)	0.9203(9)	444(97)	395(116)	129(89)	34(71)	-56(65)	-178(87)	322(47)

<sup>a</sup>The anisotropic temperature factor is defined as:  $\exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{13}hla^*c^*)]$ .

<sup>b</sup>The equivalent temperature factor is defined as  $U_{eq} = 1/3[U_{11} + U_{22} + U_{33}]$  (20).

a possibility to deal with the pseudosymmetry. X-ray diffraction of powder samples of Rb<sub>2</sub>CdSiO<sub>4</sub> was used to check which is the correct unit cell and space group in this case. It became immediately clear that observed reflec-

tions  $2\Theta \leq 16^\circ$  and all reflections with intensities larger than 5% could only be indexed in the space group  $C222_1$  with the refined cell constants:  $a = 1141.9(1)$  pm,  $b = 1100.9(1)$  pm, and  $c = 1671.6(2)$  pm (Fig. 2). Therefore,



**FIG. 2.** X-ray powder diffraction profile of Rb<sub>2</sub>CdSiO<sub>4</sub>: (a) observed profile with indexed (|) and CdO (\*) reflections indicated. (b) Illustration of the theoretical profile obtained from single crystal data.

it seems safe to proceed with the crystal structure description in *C222*<sub>1</sub>.

Rb<sub>2</sub>CdSiO<sub>4</sub> can be described as a three-dimensional network of corner-shared tetrahedra similar to the  $\alpha$ -cristobalite type of structure. Layers of isolated [CdO<sub>4</sub>] and [SiO<sub>4</sub>] units, respectively, alternate in different orientations along [110], so that only [CdO<sub>4</sub>] tetrahedra connect with [SiO<sub>4</sub>] units and vice versa (see Fig. 1). Two crystallographically independent sites are occupied by Cd. These two differ somewhat in their degree of distortion,  $d(\text{Cd1-O}) = 216\text{--}228$  pm and  $d(\text{Cd2-O}) = 214\text{--}222$  pm with  $\angle(\text{O-Cd1-O}) = 93^\circ\text{--}139^\circ$  and  $\angle(\text{O-Cd2-O}) = 94^\circ\text{--}138^\circ$  (see Tables 3 and 4). The interatomic distances are in the expected range for  $d(\text{Cd-O})$ , although the deviation of the angles, almost flattening the [CdO<sub>4</sub>]-polyhedra are somewhat larger than observed in Rb<sub>2</sub>CdO<sub>2</sub> with  $90^\circ\text{--}126^\circ$  (15). There are three crystallographically independent Si sites and all [SiO<sub>4</sub>] units do show the expected small deviation from the ideal tetrahedral symmetry. The extent of the distortion of the network can be understood as a result of connecting tetrahedra centered with cations, e.g., Si<sup>4+</sup> and Cd<sup>2+</sup>, with such a large difference in the mean effective ionic radii (16). From MAPLE calculations (17) these radii can be obtained as  $r(\text{Cd1}) = 85$  pm,  $r(\text{Cd2}) = 87$  pm,  $r(\text{Si1}) = 39$  pm,  $r(\text{Si2}) = 38$  pm, and  $r(\text{Si3}) = 38$  pm. Therefore, it is obvious that these cations cannot accommodate equivalent tetrahedral sites as present in Na<sub>2</sub>BeSiO<sub>4</sub> (*Pca2*<sub>1</sub>) for approximate the same ionic radii of Be<sup>2+</sup> and Si<sup>4+</sup> (2). The structure of K<sub>2</sub>CdSiO<sub>4</sub> has also been refined from X-ray powder data in *Pca2*<sub>1</sub> (6) with the result of averaged Si-O and Cd-O distances of 179–189 pm, which represents no sophisticated description of the compound.

The cavities of the network are occupied by the alkali counter ions. Each rubidium is coordinated by eight oxygen atoms ( $d(\text{Rb-O}) = 284\text{--}326$  pm) (see Table 4 and Fig. 3 (21)). This is different from the description of the tetragonal phase of Na<sub>2</sub>MgSiO<sub>4</sub> reported by Withers *et al.* (4), but not unusual considering the difference in the ionic radii of sodium and rubidium cations. The [Rb1O<sub>8</sub>], [Rb4O<sub>8</sub>], and [Rb5O<sub>8</sub>] polyhedra can be described in a rough approximation as distorted bi-capped trigonal prisms. The nearest description of the coordination sphere of Rb2 and Rb3, respectively, consists of two linked distorted flattened tetrahedra. All [RbO<sub>8</sub>] polyhedra share faces to form dimers with crystallographic equivalent ones except those centered with Rb4, and Rb5, which do interconnect in the analogous way. The dimers are located in two different types of cavities with the shared distorted square face perpendicular to [010] for Rb1, Rb4, and Rb5 and [001] for Rb2 and Rb3. All dimers connect via corners and edges with other rubidium atoms on crystallographically independent sites. The following pairs share trigonal faces built of oxygen atoms: Rb1–Rb2, Rb3–(Rb4, Rb5).

**TABLE 3**  
Interatomic Distances in pm for Rb<sub>2</sub>CdSiO<sub>4</sub>

Rb1–O1	284(2)	Rb2–O5	286(2)	Rb3–O1	290(2)
–O3	291(2)	–O6	294(2)	–O5	296(2)
–O4	301(1)	–O3	295(2)	–O3	301(2)
–O7	311(2)	–O1	303(2)	–O5	301(2)
–O7	314(2)	–O1	305(2)	–O7	303(2)
–O2	317(1)	–O2	306(2)	–O6	309(2)
–O8	317(2) (2×)	–O4	311(2)	–O6	320(2)
		–O3	319(2)	–O8	325(2)
Rb4–O6	285(2) (2×)	Cd1–O7	216(1)	Si1–O6	162(2)
–O4	299(2) (2×)	–O8	221(2)	–O5	163(2)
–O8	305(2) (2×)	–O6	224(2)	–O2	166(1)
–O2	326(2) (2×)	–O5	228(2)	–O4	167(1)
Rb5–O5	286(2) (2×)	Cd2–O4	214(1)	Si2–O8	161(2) (2×)
–O7	312(2) (2×)	–O3	218(2)	–O1	163(2) (2×)
–O4	314(2) (2×)	–O2	219(1)		
–O2	325(2) (2×)	–O1	222(2)	Si3–O7	162(2) (2×)
				–O3	165(2) (2×)

All oxygen atoms are coordinated by six cations, e.g., four rubidium, one cadmium, and one silicon atom. Two different arrangements exist for the cadmium and silicon positions in these highly distorted [OSiCdRb<sub>4</sub>] polyhedra. They can be described as a trans arrangement with  $\angle(\text{Si-O-Cd})$  angles of  $152^\circ\text{--}166^\circ$  and a cis angle of  $\angle(\text{Si-O-Cd}) = 101^\circ\text{--}118^\circ$ . In  $\alpha$ -cristobalite an angle of  $148^\circ$  is observed for  $\angle(\text{Si-O-Si})$  (11).

Calculations of the Madelung Part of the Lattice Energy, MAPLE (17), have been carried out for Rb<sub>2</sub>CdSiO<sub>4</sub>. The value of 10490.2 kcal/mol agrees very well with that derived from the binary oxides with a deviation of 55.6 kcal/mol for  $\Delta\text{MAPLE}(\text{quaternary-binary})$  or 0.5%. A deviation of less than one percent can be regarded as a good agreement and an independent evaluation of the structure determination.

**TABLE 4**  
Selected Angles in Degrees for Rb<sub>2</sub>CdSiO<sub>4</sub>

O7–Cd1–O8	108.9(7)	O4–Cd2–O3	130.0(6)	O6–Si1–O5	110(1)
O7–Cd1–O6	125.8(8)	O4–Cd2–O2	109.2(6)	O6–Si1–O2	109(1)
O7–Cd1–O5	98.6(7)	O4–Cd2–O1	94.1(6)	O6–Si1–O4	112(1)
O7–Cd1–O6	95.0(7)	O3–Cd2–O2	95.3(6)	O5–Si1–O2	107(1)
O8–Cd1–O5	139.0(7)	O3–Cd2–O1	95.8(9)	O5–Si1–O4	109(1)
O6–Cd1–O5	92.7(8)	O2–Cd2–O1	137.8(7)	O2–Si1–O4	111(1)
O8–Si2–O8	112(1)	O7–Si3–O7	112(1)		
O8–Si2–O1	114(1) (2×)	O7–Si3–O3	107(1) (2×)		
O8–Si2–O1	105(1) (2×)	O7–Si3–O3	111(1) (2×)		
O1–Si2–O1	109(1)	O3–Si3–O3	108(1)		

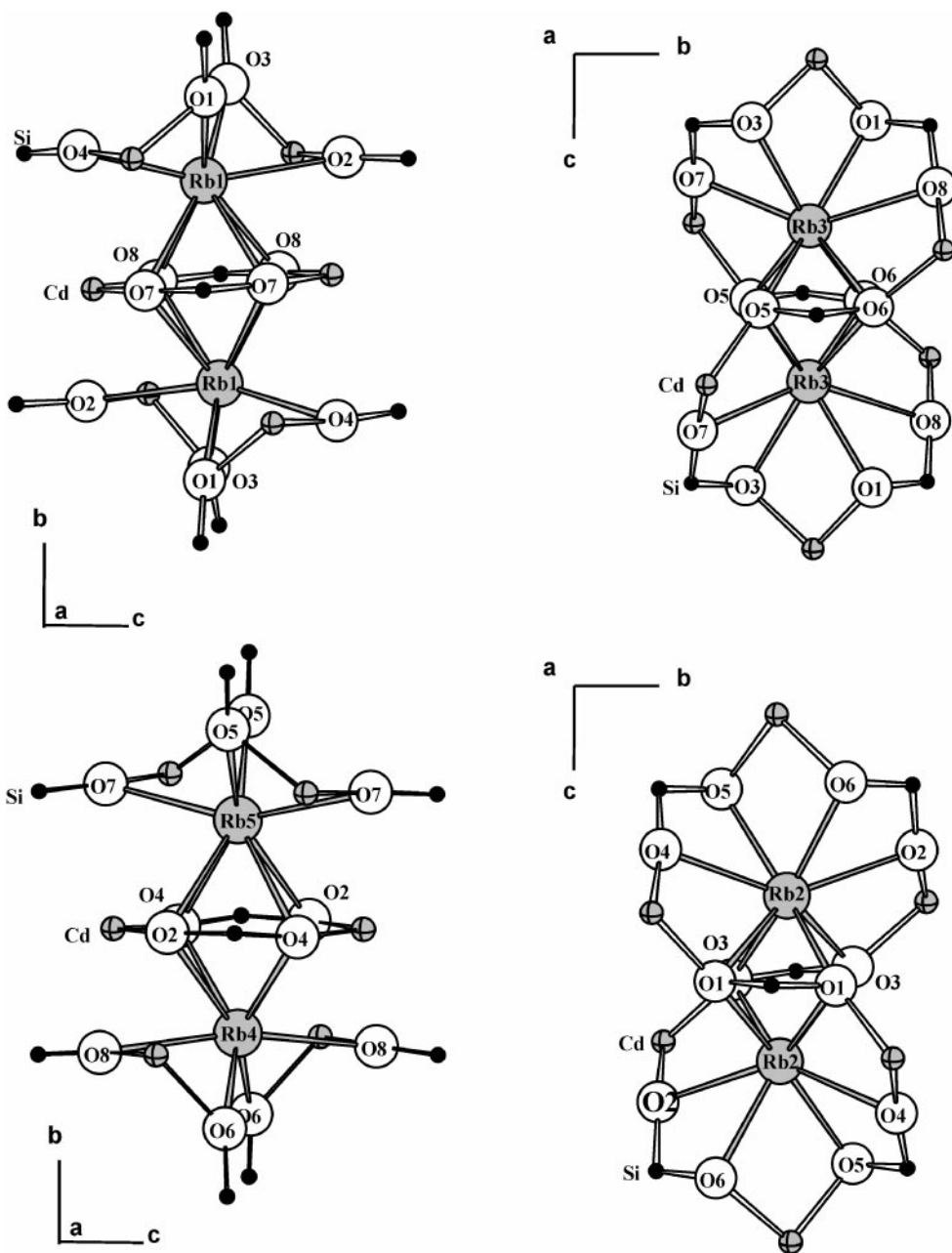


FIG. 3.  $[\text{RbO}_8]$ -polyhedra and the connection via distorted square faces to dimers in  $\text{Rb}_2\text{CdSiO}_4$ .

#### ACKNOWLEDGMENT

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