Acta Crystallographica Section E
**Structure Reports**
**Online**

ISSN 1600-5368

# Parawollastonite-type $Cd_3[Si_3O_9]$

**Matthias Weil**

Institute for Chemical Technologies and Analytics, Division of Structural Chemistry, Vienna University of Technology, Getreidemarkt 9/164-SC, A-1060 Vienna, Austria

Correspondence e-mail:
mweil@mail.zserv.tuwien.ac.at

Received 5 May 2005
Accepted 13 May 2005
Online 21 May 2005

$Cd_3[Si_3O_9]$ (tricadmium trisilicate) crystallizes in the monoclinic space group $P2_1/c$ and is isotypic with the mineral parawollastonite, $Ca_3[Si_3O_9]$-2*M*. The structure contains distorted $CdO_6$ octahedra and $SiO_4$ tetrahedra that are organized in unbranched dreier single chains with three $SiO_4$ tetrahedra in the repeat unit. All atoms occupy general positions 4*e*.

**Key indicators**

Single-crystal X-ray study
$T = 293$ K
Mean $\sigma$(Si–O) = 0.002 Å
*R* factor = 0.023
*wR* factor = 0.064
Data-to-parameter ratio = 17.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

## Comment

Cadmium silicates are of particular interest because of their properties as host materials for luminescent applications when doped with rare earth or transition metal ions. Recently, some $CdSiO_3$:*RE* phosphors (*RE* = rare earth) with a long-lasting phosphorescence upon UV-light excitation were reported (Liu *et al.*, 2005).

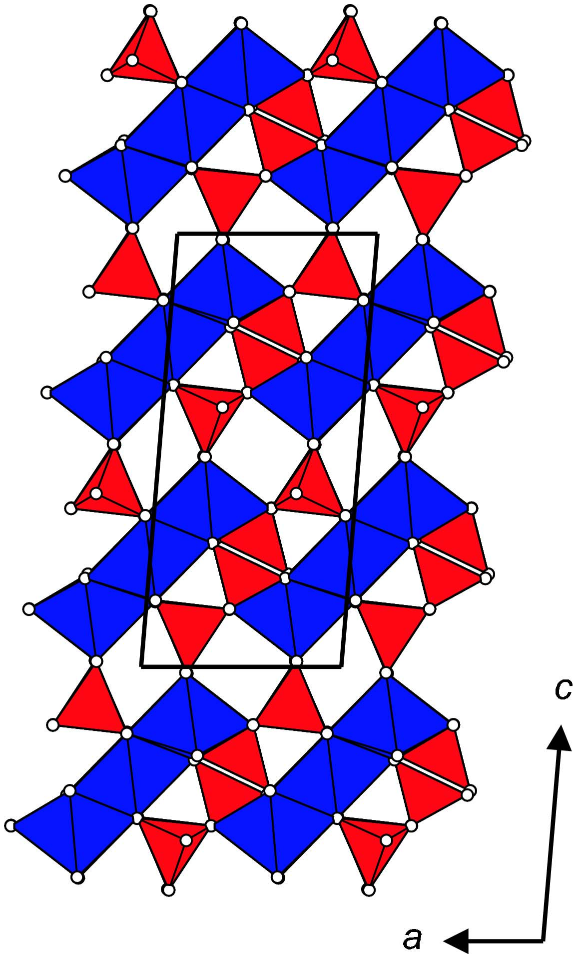

**Figure 1**
The crystal structure in polyhedral representation, projected along [010]. Key: $CdO_6$ octahedra blue and $SiO_4$ tetrahedra red.

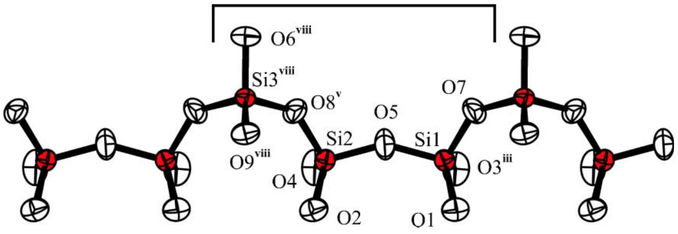

**Figure 2**
Part of a dreier single chain with atom labelling and indicated periodicity which corresponds with the length of the *b* axis. Displacement ellipsoids are drawn at the 97% probability level. Symmetry codes are as given in Table 1.

In the system CdO—$SiO_2$, three compounds are known to exist: the orthosilicate $Cd_2SiO_4$ which crystallizes in the thenardite structure type (Dent Glasser & Glasser, 1964), the oxyorthosilicate $Cd_3OSiO_4$ with a unique structure (Eysel, 1970), and the polysilicate $CdSiO_3$ for which only powder data were published (Dent Glasser & Glasser, 1964). In the original work, it was not possible to determine the space group of $CdSiO_3$ unequivocally because the crystals were polysynthetically twinned. However, powder data revealed a structural relation to the calcium analogue, $CaSiO_3$. The latter occurs in different polymorphs with structurally quite different arrangements. The high-temperature phase is a cyclosilicate called $\alpha$-wollastonite or pseudowollastonite. Its structure contains rings of three corner-shared $SiO_4$ tetrahedra organized in a layered arrangement. Depending on the stacking sequence of the layers, a number of polytypes were reported for pseudowollastonite (Yamanaka & Mori, 1981). The low-temperature phases of calcium polysilicate are made up of unbranched single chains of corner-shared $SiO_4$ tetrahedra. Two polytypes have been reported for the low-temperature phase, often referred to as $\beta$-wollastonites. They are distinguished by the symbols $nT$ and $nM$, where $T$ and $M$ symbolize the triclinic and monoclinic symmetry, and $n$ indicates the number of subcells. The polytype $1T$ is also named wollastonite whereas the polytype $2M$ is a synonym for parawollastonite (Trojer, 1968; Hesse, 1984). For all polymorphs, the chemical formulae $CaSiO_3$, $Ca_3(SiO_3)_3$ or $Ca_3[Si_3O_9]$ are reported in the literature.

Although it was reported that cadmium polysilicate can occur in different polytypes (Dent Glasser & Glasser, 1964), only the form that is isotypic with parawollastonite was obtained during the present investigation. In accordance with the nomenclature of condensed silicates given by Liebau (1985), the formula of the title compound is written as $Cd_3[Si_3O_9]$.

The $Cd_3[Si_3O_9]$ structure differs only slightly from that of the isotypic Ca phase (Hesse, 1984), mainly in changes in the Cd—O distances *versus* the Ca—O distances resulting from the different ionic radii (Shannon, 1976) of 0.95 ($Cd^{2+}$; CN = 6) and 1.00 Å ($Ca^{2+}$; CN = 6), respectively.

The three independent Cd atoms are each surrounded by six O atoms, forming distorted $CdO_6$ octahedra which are arranged in slabs parallel to [010]. Three such slabs constitute ribbons which are separated from each other by unbranched silicate chains that are formed by corner-sharing $SiO_4$ tetrahedra (Fig. 1). The silicate chains have a repeating period of three $SiO_4$ tetrahedra (Fig. 2) which corresponds with the length of the $b$ axis. According to Liebau's (1985) notation, $Cd_3[Si_3O_9]$ is a dreier single chain polysilicate.

The mean Cd—O distances of 2.326 (Cd1), 2.333 (Cd2) and 2.341 Å (Cd3) are slightly shorter than the corresponding mean Ca—O distances of 2.385 (Ca1), 2.378 (Ca2) and 2.385 Å (Ca3), whereas the mean Si—O distances in $Cd_3[Si_3O_9]$ and $Ca_3[Si_3O_9]$ are virtually the same, *viz*. 1.620, 1.627 and 1.635 Å in the Cd compound *versus* 1.620, 1.617 and 1.630 Å in the Ca compound. The O—Si—O angles of the silicate chains are very similar in both isotypic structures and are in the range 102.06 (9)–122.12 (10)° in the Cd compound *versus* 102.5 (1)–122.0 (1)° in the Ca compound.

## Experimental

$CdCO_3$ (Merck, p. A.) and high-surface silica (Degussa–Hüls) were mixed in the stoichiometric ratio 2:1 and slowly heated in a platinum crucible to 1023 K for 24 h. X-ray powder diffraction of the polycrystalline material revealed a mixture of $Cd_2SiO_4$ (Dent Glasser & Glasser, 1964) and $Cd_3[Si_3O_9]$. The mixture was then heated to 1473 K, left at that temperature for 2 h and cooled slowly to 1173 K at a rate of 4 K $h^{-1}$. The furnace was then shut down. After cooling to room temperature, the colourless melt was crushed and a plate-like single-crystal was used for the data collection. X-ray powder diffraction of the final product yielded $Cd_3[Si_3O_9]$, isotypic with $Ca_3[Si_3O_9]$-2$M$, and only minor amounts of $Cd_2SiO_4$.

### *Crystal data*

$Cd_3[Si_3O_9]$
$M_r$ = 565.47
Monoclinic, $P2_1/c$
$a$ = 6.9463 (8) Å
$b$ = 7.2563 (9) Å
$c$ = 15.0697 (18) Å
$\beta$ = 94.791 (2)°
$V$ = 756.93 (16) Å$^3$
$Z$ = 4
$D_x$ = 4.962 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 4479 reflections
$\theta$ = 2.7–31.2°
$\mu$ = 8.86 mm$^{-1}$
$T$ = 293 (2) K
Plate, colourless
0.26 × 0.14 × 0.02 mm

### *Data collection*

Bruker SMART APEX CCD diffractometer
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{\min}$ = 0.203, $T_{\max}$ = 0.816
8622 measured reflections
2412 independent reflections
1980 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.037
$\theta_{\max}$ = 31.2°
$h = -8 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -21 \rightarrow 19$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.064
$S$ = 1.07
2412 reflections
137 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0215P)^2 + 1.0847P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 1.60 e Å$^{-3}$
$\Delta\rho_{\min}$ = −1.38 e Å$^{-3}$
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00358 (19)

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cd1—O6 | 2.272 (2) | Cd3—O8 | 2.3743 (16) |
| Cd1—O1$^{i}$ | 2.3045 (18) | Cd3—O6 | 2.4293 (18) |
| Cd1—O9$^{ii}$ | 2.317 (2) | Cd3—O9$^{vii}$ | 2.4573 (18) |
| Cd1—O2$^{iii}$ | 2.3214 (19) | Si1—O3$^{viii}$ | 1.592 (2) |
| Cd1—O1 | 2.3519 (19) | Si1—O1 | 1.620 (2) |
| Cd1—O2 | 2.3869 (19) | Si1—O5 | 1.6219 (15) |
| Cd2—O4$^{iv}$ | 2.1681 (17) | Si1—O7 | 1.6447 (17) |
| Cd2—O3 | 2.2113 (17) | Si2—O4 | 1.602 (2) |
| Cd2—O1$^{i}$ | 2.260 (2) | Si2—O2 | 1.612 (2) |
| Cd2—O7$^{v}$ | 2.3939 (17) | Si2—O5 | 1.6158 (15) |
| Cd2—O6 | 2.4538 (18) | Si2—O8$^{v}$ | 1.6399 (17) |
| Cd2—O9$^{v}$ | 2.5102 (18) | Si3—O6 | 1.599 (2) |
| Cd3—O4$^{vi}$ | 2.2262 (17) | Si3—O9 | 1.605 (2) |
| Cd3—O2$^{iii}$ | 2.249 (2) | Si3—O7$^{v}$ | 1.6529 (16) |
| Cd3—O3 | 2.3073 (17) | Si3—O8 | 1.6611 (16) |
| | | | |
| O3$^{viii}$—Si1—O1 | 115.83 (11) | O5—Si2—O8$^{v}$ | 102.69 (9) |
| O3$^{viii}$—Si1—O5 | 107.63 (9) | O6—Si3—O9 | 122.12 (10) |
| O1—Si1—O5 | 108.44 (9) | O6—Si3—O7$^{v}$ | 104.20 (9) |
| O3$^{viii}$—Si1—O7 | 114.32 (10) | O9—Si3—O7$^{v}$ | 111.27 (9) |
| O1—Si1—O7 | 107.54 (10) | O6—Si3—O8 | 103.48 (9) |
| O5—Si1—O7 | 102.06 (9) | O9—Si3—O8 | 111.02 (9) |
| O4—Si2—O2 | 115.78 (11) | O7$^{v}$—Si3—O8 | 102.80 (9) |
| O4—Si2—O5 | 106.92 (9) | Si2—O5—Si1 | 148.03 (13) |
| O2—Si2—O5 | 109.09 (9) | Si1—O7—Si3$^{vii}$ | 139.89 (11) |
| O4—Si2—O8$^{v}$ | 113.60 (10) | Si2$^{vii}$—O8—Si3 | 140.61 (11) |
| O2—Si2—O8$^{v}$ | 107.89 (10) | | |

Symmetry codes: (i) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $x-1, y, z$; (iii) $-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (v) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (vi) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (vii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (viii) $x, \frac{1}{2}-y, \frac{1}{2}+z$.

The structure was initially refined in space group $P2_1/a$ with the atomic coordinates of the isotypic compound $Ca_3[Si_3O_9]$-2*M* (parawollastonite; Hesse, 1984) as starting parameters. For the present refinement, the standard setting in $P2_1/c$ was used and the structural data were standardized using the program *STRUCTURE-TIDY* (Gelato & Parthé, 1987). The highest peak in the final Fourier map is 0.81 Å from atom Cd1 and the deepest hole is 1.64 Å from O8.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; method used to solve structure: coordinates taken from the isotypic Ca compound; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2004); software used to prepare material for publication: *SHELXL97*.

## References

Bruker (2002). *SADABS*, *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Dent Glasser, L. S. & Glasser, F. P. (1964). *Inorg. Chem.* **3**, 1228–1230.

Dowty, E. (2004). *ATOMS for Windows*. Version 6.1. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.

Eysel, W. (1970). *Neues Jahrb. Mineral. Monatsh.* pp. 534–547.

Gelato, L. M. & Parthé, E. (1987). *J. Appl Cryst.* **20**, 139–143.

Hesse, K. F. (1984). *Z. Kristallogr.* **168**, 93–98.

Liebau, F. (1985). *Structural Chemistry of Silicates: Structure, Bonding and Classification*. Berlin: Springer-Verlag.

Liu, Y., Lei, B. & Shi, C. (2005). *Chem. Mater.* **17**, 2108–2113.

Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Trojer, F. (1968). *Z. Kristallogr.* **127**, 291–308.

Yamanaka, T. & Mori, H. (1981). *Acta Cryst.* B**37**, 1010–1027.