

Dicерium orthosilicate selenide and dicерium orthosilicate telluride, $\text{Ce}_2(\text{SiO}_4)Q$ ($Q = \text{Se}$ or Te)

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The crystal structures of two new quaternary compounds, *viz.* dicерium orthosilicate selenide and dicерium orthosilicate telluride, $\text{Ce}_2(\text{SiO}_4)Q$ ($Q = \text{Se}$ or Te), have been determined from single-crystal X-ray diffraction data. Each structure comprises infinite chains of SiO_4 tetrahedra separated by Ce and Q atoms. The site symmetries are Ce m and 2, Si 2 and Q m . The O atoms are in general positions.

Comment

$\text{Ce}_2(\text{SiO}_4)Q$ ($Q = \text{Se}$ or Te) are new members of the $\text{Ln}_2(\text{SiO}_4)Q$ ($Q = \text{S}, \text{Se}$ or Te) series [$Q = \text{S}$ and Ln = Ho (Hartenbach *et al.*, 2002); $Q = \text{Se}$ and Ln = La (Brennan & Ibers, 1991), Nd (Grupe & Umland, 1990), Sm, Dy and Ho (Person *et al.*, 2000), Er (Stöwe, 1994) and Tb (Ijjaali *et al.*, 2002); $Q = \text{Te}$ and Ln = Pr (Weber & Schleid, 1999), Nd (Yang & Ibers, 2000), Sm (Yang & Ibers, 2000; Person *et al.*, 2000)

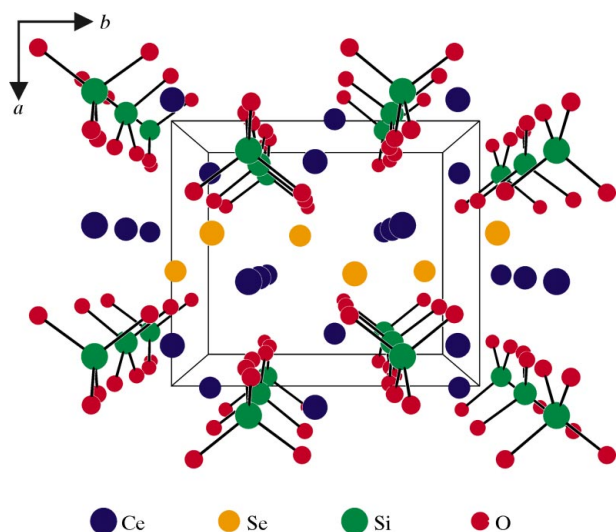


Figure 1
The structure of $\text{Ce}_2(\text{SiO}_4)\text{Se}$, viewed along [001].

and Gd (Ijjaali & Ibers, 2001)], as shown in Table 1. These compounds usually adopt an orthorhombic ($Pbcm$) structure, but some of the $Q = \text{Te}$ compounds are dimorphic and also adopt a monoclinic ($P2_1/c$) structure (Table 1). Each of the two compounds reported here crystallizes in space group $Pbcm$ and has a layered structure.

The structures of the title compounds both comprise infinite chains of SiO_4 tetrahedra along [001], separated by Ln and Q atoms (as shown in Fig. 1 for $Q = \text{Se}$). The SiO_4 tetrahedron in each structure has symmetry m but is somewhat distorted, with O—Si—O angles in the range 104.36 (13)– 119.01 (13) $^\circ$ in $\text{Ce}_2(\text{SiO}_4)\text{Se}$ and 103.0 (2)– 119.79 (13) $^\circ$ in $\text{Ce}_2(\text{SiO}_4)\text{Te}$.

Although the two structures are similar, they are not strictly isostructural, differing in the coordination about the Ce atoms (Figs. 2 and 3).

In $\text{Ce}_2(\text{SiO}_4)\text{Se}$, the Ce—O distances are in the range 2.475 (3)– 2.578 (2) Å, which may be compared with the range of 2.374 (3)– 2.523 (5) Å observed in $\text{Ce}_{3.67}\text{Ti}_2\text{O}_3\text{Se}_6$ (Tougaït

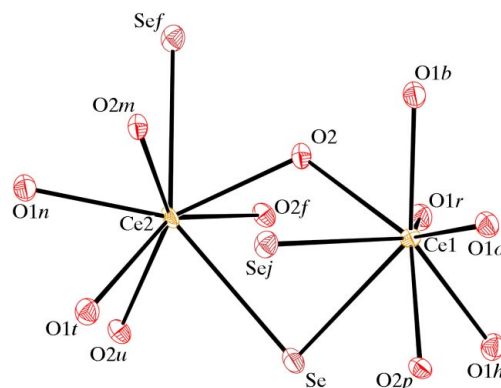


Figure 2
The coordination geometries of atoms Ce1 and Ce2 in $\text{Ce}_2(\text{SiO}_4)\text{Se}$. Displacement ellipsoids are drawn at the 90% probability level. [Symmetry codes: (b) $x, y - 1, z$; (f) $x, \frac{1}{2} - y, -z$; (h) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (j) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (m) $1 - x, -y, -z$; (n) $1 - x, 1 - y, -z$; (o) $x, y - 1, \frac{1}{2} - z$; (p) $x, y, \frac{1}{2} - z$; (r) $-x, \frac{1}{2} - y, z$; (t) $1 - x, y - \frac{1}{2}, z$; (u) $1 - x, \frac{1}{2} + y, z$.]

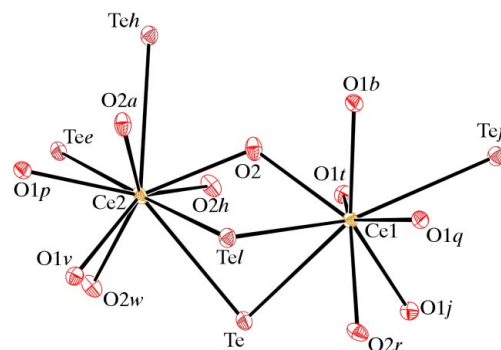


Figure 3
The coordination geometries of atoms Ce1 and Ce2 in $\text{Ce}_2(\text{SiO}_4)\text{Te}$. Displacement ellipsoids are drawn at the 90% probability level. [Symmetry codes: (b) $x, y - 1, z$; (c) $x, y + 1, z$; (h) $x, \frac{1}{2} - y, -z$; (j) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (l) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (o) $1 - x, -y, -z$; (p) $1 - x, 1 - y, -z$; (q) $x, y - 1, \frac{1}{2} - z$; (r) $x, y, \frac{1}{2} - z$; (t) $-x, y - \frac{1}{2}, z$; (v) $1 - x, y - \frac{1}{2}, z$; (w) $1 - x, \frac{1}{2} + y, z$.]

& Ibers, 2000). The Ce—Se distances are in the range 3.0157 (7)–3.1926 (4) Å, compared with a range of 2.8999 (9)–3.2864 (12) Å in Ce_{3.67}Ti₂O₃Se₆. In Ce₂(SiO₄)Te, the Ce—O distances are in the range 2.495 (3)–2.621 (3) Å, which may also be compared with the range in Ce_{3.67}Ti₂O₃Se₆.

The Ce—Te distances are in the range 3.2082 (5)–3.3704 (5) Å, compared with 3.1898 (8)–3.3032 (11) Å in K₂Ag₃CeTe₄ (Patschke *et al.*, 1998).

Experimental

The reactive flux, Cs₂Se₃, was prepared by the stoichiometric reaction of Cs (Aldrich, 99.5%) and Se (Aldrich, 99.5%) in liquid NH₃. Most of the compounds listed in Table 1 were synthesized accidentally, and the present compounds were no exception. Clear light-red needles of Ce₂(SiO₄)Se were obtained accidentally in the reaction of Ce (71 mg, Alfa Aesar, 99.9%), Se (40 mg, Aldrich, 99.5%), CsCl (150 mg, Aldrich, 99.9%) and Cs₂Se₃ (150 mg). The materials were mixed and sealed in an unprotected fused-silica tube that was then evacuated to 10^{−4} Torr (1 Torr = 133.322 Pa). The tube was heated to 1173 K, kept at 1173 K for 72 h, cooled at 4 K h^{−1} to 473 K, and then the furnace was turned off. The reaction mixture was washed with deionized water and finally dried with acetone. Qualitative energy dispersive spectroscopy (EDS) analysis verified the presence of Ce, Si, and Se. The light-yellow needles of Ce₂(SiO₄)Te were grown accidentally in the reaction of Ce (70 mg, Alfa Aesar, 99.9%), Ti (48 mg, Aldrich, 99.9%), TeO₂ (80 mg, Aldrich, 99.995%), Te (80 mg, Strem, 99.9%) and KCl (150 mg, Aldrich, 99.9%). The mixture was sealed in an unprotected fused-silica tube that was then evacuated to 10^{−4} Torr. The tube was heated to 1073 K, kept at 1073 K for 72 h, cooled at 4 K h^{−1} to 373 K, and then the furnace was turned off. The reaction product was washed with water and dried with acetone. Qualitative EDS analysis verified the presence of Ce, Si, and Te.

Compound (I)

Crystal data

Ce₂(SiO₄)Se
M_r = 451.29
Orthorhombic, *Pbcm*
a = 6.2250 (6) Å
b = 7.2354 (7) Å
c = 11.0739 (10) Å
V = 498.77 (8) Å³
Z = 4
D_x = 6.010 Mg m^{−3}

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
0.3° ω scans
Absorption correction: numerical (*SHELXTL*; Sheldrick, 2003)
T_{min} = 0.067, T_{max} = 0.274
5011 measured reflections

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.021
wR(F²) = 0.059
S = 1.49
662 reflections
42 parameters
w = 1/[σ²(F_o²) + (0.03P)²]
where P = (F_o² + 2F_c²)/3

Mo Kα radiation
Cell parameters from 5011 reflections
θ = 2.8–29.0°
μ = 25.46 mm^{−1}
T = 153 (2) K
Needle, light red
0.125 × 0.032 × 0.030 mm

662 independent reflections
643 reflections with I > 2σ(I)
R_{int} = 0.029
θ_{max} = 29.0°
h = −8 → 8
k = −9 → 9
l = −14 → 14

(Δ/σ)_{max} < 0.001
Δρ_{max} = 2.03 e Å^{−3}
Δρ_{min} = −1.49 e Å^{−3}
Extinction correction: *SHELXTL* (Sheldrick, 2003)
Extinction coefficient: 0.0019 (3)

Table 1

The currently known Ln₂(SiO₄)Q (Q = Te, Se, S) compounds.

Q = Te	Q = Se	Q = S
Ce ₂ (SiO ₄)Te ^a (<i>Pbcm</i>)	La ₂ (SiO ₄)Se ^b (<i>Pbcm</i>)	Ho ₂ SiO ₄ S ^c (<i>Pbcm</i>)
Pr ₂ (SiO ₄)Te ^d (<i>Pbcm</i> and <i>P2₁/c</i>)	Ce ₂ (SiO ₄)Se ^e (<i>Pbcm</i>)	
Nd ₂ (SiO ₄)Te ^f (<i>Pbcm</i> and <i>P2₁/c</i>)	Nd ₂ (SiO ₄)Se ^f (<i>Pbcm</i>)	
Sm ₂ (SiO ₄)Te ^{e,g} (<i>Pbcm</i> and <i>P2₁/c</i>)	Sm ₂ (SiO ₄)Se ^g (<i>Pbcm</i>)	
Gd ₂ (SiO ₄)Te ^h (<i>Pbcm</i>)	Tb ₂ (SiO ₄)Se ⁱ (<i>Pbcm</i>)	
	Dy ₂ (SiO ₄)Se ^g (<i>Pbcm</i>)	
	Ho ₂ (SiO ₄)Se ^g (<i>Pbcm</i>)	
	Er ₂ (SiO ₄)Se ^j (<i>Pbcm</i>)	

Notes: (a) This work; (b) Brennan & Ibers (1991); (c) Hartenbach *et al.* (2002); (d) Weber & Schleid (1999); (e) Yang & Ibers (2000); (f) Grupe & Umland (1990); (g) Person *et al.* (2000); (h) Ijjaali & Ibers (2001); (i) Ijjaali *et al.* (2002); (j) Stöwe (1994).

Table 2

Selected geometric parameters (Å, °) for (I).

Ce1—O1 ⁱ	2.480 (3)	Ce2—O1 ^{iv}	2.504 (3)
Ce1—O1 ⁱⁱ	2.486 (3)	Ce2—O2 ^v	2.518 (3)
Ce1—O2	2.578 (2)	Ce2—Se	3.1926 (4)
Ce1—Se ⁱⁱⁱ	3.0157 (7)	Si—O2	1.630 (3)
Ce1—Se	3.1802 (6)	Si—O1 ⁱ	1.647 (3)
Ce2—O2	2.475 (3)		
O2 ^{vi} —Si—O2	106.2 (2)	O2—Si—O1 ⁱ	104.36 (13)
O2 ^{vi} —Si—O1 ⁱ	119.01 (13)	O1 ^{vii} —Si—O1 ⁱ	104.8 (2)

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

Compound (II)

Crystal data

Ce₂(SiO₄)Te
M_r = 499.93
Orthorhombic, *Pbcm*
a = 6.3647 (6) Å
b = 7.2807 (7) Å
c = 11.2743 (10) Å
V = 522.45 (8) Å³
Z = 4
D_x = 6.356 Mg m^{−3}

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
0.3° ω scans
Absorption correction: numerical (*SHELXTL*; Sheldrick, 2003)
T_{min} = 0.244, T_{max} = 0.423
5770 measured reflections

Mo Kα radiation
Cell parameters from 5770 reflections
θ = 3.2–28.9°
μ = 22.82 mm^{−1}
T = 153 (2) K
Needle, light yellow
0.080 × 0.052 × 0.042 mm

690 independent reflections
666 reflections with I > 2σ(I)
R_{int} = 0.034
θ_{max} = 28.9°
h = −8 → 8
k = −9 → 9
l = −15 → 14

Table 3

Selected geometric parameters (Å, °) for (II).

Ce1—O1 ⁱ	2.495 (3)	Ce2—O1 ^v	2.524 (3)
Ce1—O1 ⁱⁱ	2.522 (3)	Ce2—O2 ^{vi}	2.547 (3)
Ce1—O2	2.621 (3)	Ce2—O2 ^{vii}	2.555 (3)
Ce1—Te ⁱⁱⁱ	3.2082 (5)	Ce2—Te ^{viii}	3.3819 (3)
Ce1—Te ^{iv}	3.3604 (5)	Si—O2	1.633 (3)
Ce1—Te	3.3704 (5)	Si—O1 ⁱ	1.653 (3)
O2—Si—O2 ^{vi}	106.2 (2)	O2 ^{vi} —Si—O1 ⁱ	119.79 (13)
O2—Si—O1 ⁱ	104.55 (13)	O1 ^{ix} —Si—O1 ⁱ	103.0 (2)

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

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.057$

$S = 1.34$

690 reflections

42 parameters

$w = 1/[\sigma^2(F_o^2) + (0.031P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.99 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\min} = -2.03 \text{ e } \text{Å}^{-3}$

Extinction correction: *SHELXTL*

Extinction coefficient: 0.0071 (4)

In $\text{Ce}_2(\text{SiO}_4)\text{Se}$, the highest residual electron density is 0.03 Å from the Ce2 site and the deepest hole is 0.69 Å from this same site. In $\text{Ce}_2(\text{SiO}_4)\text{Te}$, the highest residual electron density is 0.01 Å from the Ce2 site and the deepest hole is 0.61 Å from Te.

For both compounds, data collection: *SMART* (Bruker, 2003); cell refinement: *SAINTE-Plus* (Bruker, 2003); data reduction: *SAINTE-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *XP* in *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1760). Services for accessing these data are described at the back of the journal.

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