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Dicerium disilicate, $Ce_2[Si_2O_7]$

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Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(i–O) = 0.006 Å
R factor = 0.024
wR factor = 0.055
Data-to-parameter ratio = 13.6

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

Dicerium disilicate, $Ce_2[Si_2O_7]$, crystallizes in space group $P4_1$ of the tetragonal system. It has isostructural analogues among the disilicates of the larger rare-earth elements, namely $Ln_2[Si_2O_7]$ (Ln is La, Pr, Nd or Sm). The structure consists of discrete Ce^{3+} cations and $[Si_2O_7]^{6-}$ anions; the asymmetric unit containing four cations and two anions. Each anion is formed from two SiO_4 tetrahedra that share a vertex.

Comment

$Ce_2[Si_2O_7]$ is a member of the $Ln_2[Si_2O_7]$ (Ln is a rare earth) family, which includes at least seven different structure types (Felsche, 1973; Müller-Bunz & Schleid, 2000). It crystallizes in space group $P4_1$ and is a Type A structure in the nomenclature of Felsche (1973). $Ce_2[Si_2O_7]$ is isostructural with $La_2[Si_2O_7]$ (Dago *et al.*, 1980; Müller-Bunz & Schleid, 2000), $Pr_2[Si_2O_7]$ (Felsche, 1970, 1971, 1973), $Nd_2[Si_2O_7]$ (Chi *et al.*, 1997) and $Sm_2[Si_2O_7]$ (Smolin *et al.*, 1970). Its structure differs minimally from those of the others, mainly in increased precision and in slight changes in the distances about the Ln atoms engendered by the lanthanide contraction and by the low temperature of data collection.

The crystal structure of this family of $Ln_2[Si_2O_7]$ compounds was described in detail earlier (Felsche, 1973). Fig. 1 shows the asymmetric unit of $Ce_2[Si_2O_7]$ and Fig. 2 shows the crystal structure, which comprises discrete Ce^{3+} cations and isolated $[Si_2O_7]^{6-}$ anions. These are arranged in four sheets perpendicular to [001]. Within each of the four adjacent sheets, the (Si_2O_7) units and Ce atoms form rows parallel to [110].

Table 1 provides selected geometric parameters. The coordination numbers for Ce1, Ce2, Ce3 and Ce4 are 8, 9, 8 and 7, respectively, for Ce—O distances less than 3.0 Å. The Ce—O distances range from 2.356 (6) to 2.909 (6) Å, compared to La—O distances of 2.395 (7)–2.859 (7) Å in $La_2[Si_2O_7]$

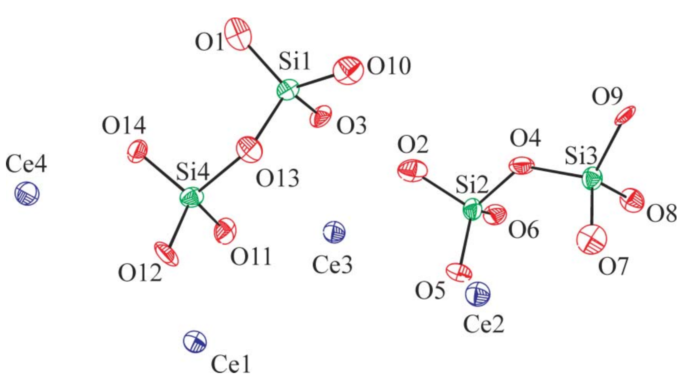

Figure 1
A view of the asymmetric unit of $Ce_2[Si_2O_7]$, with displacement ellipsoids at the 90% probability level.

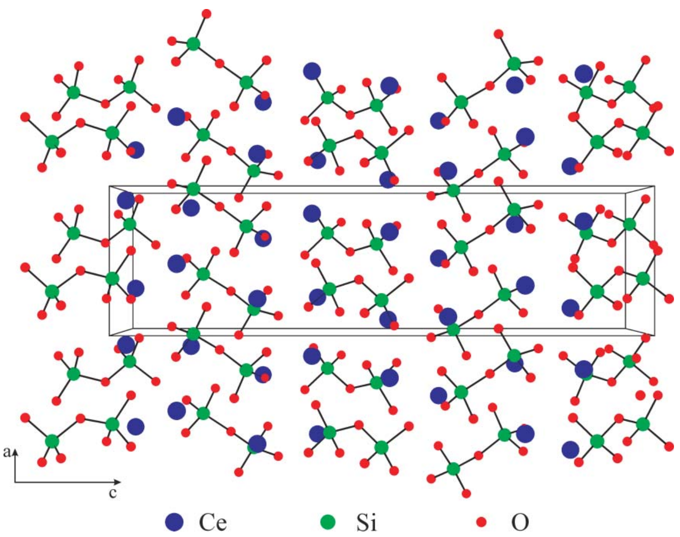

Figure 2
The structure of $Ce_2[Si_2O_7]$, viewed down [010].

(Müller-Bunz & Schleid, 2000). The Si—O bond lengths involving the bridging O atom are generally longer than the other Si—O bonds: for $Ce_2[Si_2O_7]$, 1.644 (6)–1.679 (6) Å *versus* 1.581 (6)–1.658 (6) Å; for $La_2[Si_2O_7]$, 1.645 (7)–1.670 (7) Å *versus* 1.593 (7)–1.636 (7) Å. The O—Si—O angles range from 100.7 (3) to 116.6 (3)° in the Ce compound and from 101.9 (4) to 115.8 (4)° in the La compound. The Si—O—Si angles are 129.1 (3) and 132.3 (3)° in the Ce compound, *versus* 128.0 (4) and 132.1 (4)° in the La compound.

Experimental

$Ce_2[Si_2O_7]$ was obtained accidentally as green blocks from a solid-state reaction of Ce (45 mg, Alfa Aesar, 99.9%), V_2O_5 (25 mg, Aldrich, 99.5%), TeO_2 (40 mg, Aldrich, 99.995%) and CsCl (250 mg, Aldrich, 99.9%). The reactants were loaded into an unprotected fused-silica tube that was then evacuated to 10^{-4} Torr (1 Torr = 133.322 Pa). 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 deionized water and dried with acetone. Qualitative energy dispersive spectroscopy (EDS) analysis verified the presence of Ce and Si.

Crystal data

$Ce_4[Si_2O_7]_2$
M_r = 896.84
Tetragonal, $P4_1$
a = 6.7964 (3) Å
c = 24.7282 (14) Å
V = 1142.22 (10) Å^3
Z = 4
D_x = 5.215 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2729 reflections
θ = 3.0–28.9°
μ = 16.14 mm^{-1}
T = 153 (2) K
Block, green
0.102 × 0.042 × 0.040 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
ω scans
Absorption correction: numerical, face-indexed using *SHELXTL* (Sheldrick, 2003)
T_{min} = 0.482, T_{max} = 0.741
10 648 measured reflections
2729 independent reflections
2637 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 28.9°
h = −9 → 9
k = −8 → 9
l = −31 → 31

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.055
S = 1.15
2729 reflections
200 parameters
$w = 1/[\sigma^2(F_o^2) + (0.028P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 2.40 e Å^{-3}
$\Delta\rho_{min}$ = −1.19 e Å^{-3}
Extinction correction: none
Absolute structure: Flack (1983), with 1284 Friedel pairs
Flack parameter: 0.522 (19)

Table 1
Selected geometric parameters (Å, °).

Ce1—O1	2.414 (5)	Ce3—O5	2.909 (6)
Ce1—O2^{i}	2.450 (6)	Ce4—O6^{vii}	2.420 (5)
Ce1—O11	2.483 (6)	Ce4—O3^{viii}	2.453 (5)
Ce1—O5^{ii}	2.517 (5)	Ce4—O14	2.459 (6)
Ce1—O14^{iii}	2.546 (5)	Ce4—O7^{ix}	2.461 (5)
Ce1—O3	2.553 (5)	Ce4—O10	2.476 (5)
Ce1—O10	2.723 (5)	Ce4—O8^{x}	2.540 (6)
Ce1—O4	2.774 (5)	Ce4—O13^{v}	2.667 (5)
Ce2—O12^{iv}	2.384 (6)	Si1—O1^{ii}	1.611 (6)
Ce2—O6^{v}	2.426 (5)	Si1—O3	1.630 (5)
Ce2—O5	2.521 (6)	Si1—O10	1.638 (6)
Ce2—O11^{vi}	2.541 (5)	Si1—O13^{v}	1.667 (6)
Ce2—O9	2.601 (5)	Si2—O6^{ii}	1.581 (6)
Ce2—O8^{v}	2.637 (5)	Si2—O2^{ii}	1.619 (6)
Ce2—O10^{vi}	2.673 (5)	Si2—O5	1.622 (6)
Ce2—O7	2.711 (6)	Si2—O4^{iv}	1.678 (6)
Ce2—O14^{vi}	2.857 (5)	Si3—O9^{iv}	1.599 (6)
Ce3—O2^{ii}	2.356 (6)	Si3—O7	1.636 (6)
Ce3—O1	2.373 (6)	Si3—O4^{iv}	1.644 (6)
Ce3—O9	2.379 (5)	Si3—O8	1.645 (6)
Ce3—O11	2.453 (5)	Si4—O12	1.602 (6)
Ce3—O7^{ii}	2.503 (5)	Si4—O14	1.632 (6)
Ce3—O3^{iv}	2.603 (5)	Si4—O11	1.658 (6)
Ce3—O8^{ii}	2.666 (5)	Si4—O13	1.679 (6)
O1^{ii}—Si1—O3	112.4 (3)	O9^{iv}—Si3—O7	114.4 (3)
O1^{ii}—Si1—O10	116.3 (3)	O9^{iv}—Si3—O4^{iv}	111.7 (3)
O3—Si1—O10	105.6 (3)	O7—Si3—O4^{iv}	109.3 (3)
O1^{ii}—Si1—O13^{v}	108.9 (3)	O9^{iv}—Si3—O8	108.1 (3)
O3—Si1—O13^{v}	110.2 (3)	O7—Si3—O8	105.8 (3)
O10—Si1—O13^{v}	102.9 (3)	O4^{iv}—Si3—O8	107.1 (3)
O6^{ii}—Si2—O2^{ii}	113.5 (3)	O12—Si4—O14	116.6 (3)
O6^{ii}—Si2—O5	115.5 (3)	O12—Si4—O11	108.0 (3)
O2^{ii}—Si2—O5	106.1 (3)	O14—Si4—O11	105.7 (3)
O6^{ii}—Si2—O4^{iv}	107.8 (3)	O12—Si4—O13	111.9 (3)
O2^{ii}—Si2—O4^{iv}	100.7 (3)	O14—Si4—O13	107.7 (3)
O5—Si2—O4^{iv}	112.4 (3)	O11—Si4—O13	106.3 (3)

Symmetry codes: (i) $-x, -y+1, z-\frac{1}{2}$; (ii) $y, -x, z-\frac{1}{4}$; (iii) $x-1, y, z$; (iv) $-y+1, x, z+\frac{1}{4}$; (v) $y, -x+1, z-\frac{1}{4}$; (vi) $-y, x, z+\frac{1}{4}$; (vii) $-y+1, x, z-\frac{3}{4}$; (viii) $x+1, y, z$; (ix) $-x+1, -y+1, z-\frac{1}{2}$; (x) $-x+1, -y, z-\frac{1}{2}$.

The structure was standardized by means of the program *STRUCTURE TIDY* (Gelato & Parthé, 1987). The chosen crystal was an enantiomeric twin; the Flack parameter (Flack, 1983) refined to 0.522 (19). The highest peak is 0.04 Å from atom Ce2 and the deepest hole is 1.34 Å from the same atom.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2003); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2003); molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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