inorganic papers

Caesium thorium silicate, Cs$_2$ThSi$_6$O$_{15}$

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A caesium thorium(IV) silicate has been synthesized serendipitously under high-temperature solid-state conditions by the reaction of Th^{IV} with a fused silica/alumina reaction crucible. The compound crystallizes in the orthorhombic space group $Pca2_1$. The crystal structure consists of ThO$_6$ distorted octahedra corner-shared with SiO$_4$ tetrahedra to form an anionic three-dimensional framework possessing extended channels containing Cs$^+$ cations. Cs$_2$ThSi$_6$O$_{15}$ is a phyllosilicate with the same sheet structure as β-K$_3$NdSi$_6$O$_{15}$.

Comment

Thorium silicates have received attention in the past owing to their ability to undergo metamictization, a crystalline-to-amorphous phase change in the presence of fissionable nuclides (Graham & Thornber, 1974; Ewing, 1975). Thorite and huttonite are the two known naturally occurring phases of
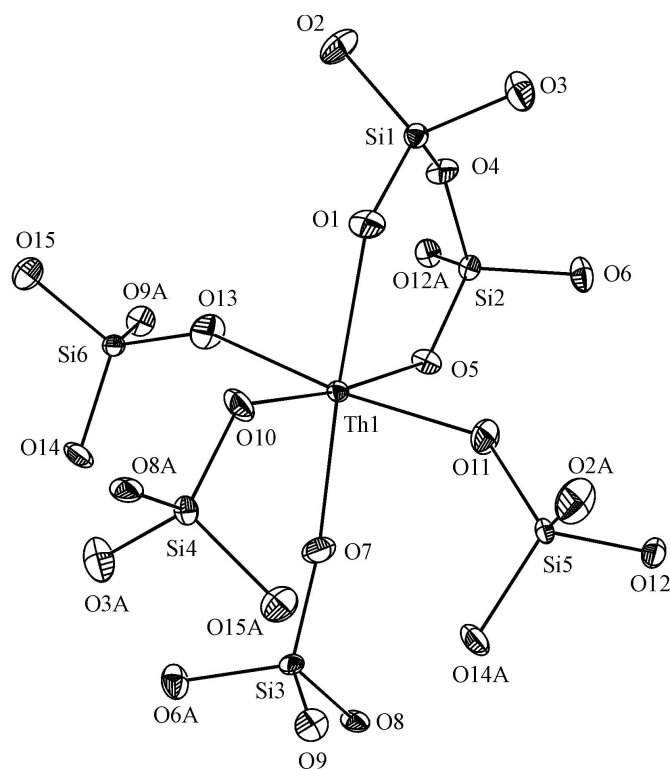

Figure 1
The local coordination environment surrounding a typical Th^{IV} ion in Cs$_2$ThSi$_6$O$_{15}$. 50% probability displacement ellipsoids are depicted. [Symmetry codes for atoms O12A (bound to Si2): $-x, -y, \frac{1}{2} + z$; O6A (Si3): $\frac{1}{2} + x, -y, z$; O3A (Si4): $\frac{1}{2} + x, -y + 1, z$; O8A (Si4): $x, y + 1, z$; O15A (Si4): $\frac{1}{2} - x, y, -\frac{1}{2} + z$; O2A (Si5): $-x, -y + 1, -\frac{1}{2} + z$; O14A (Si5): $\frac{1}{2} - x, y, -\frac{1}{2} + z$; O9A (Si6): $\frac{1}{2} - x, y, \frac{1}{2} + z$].
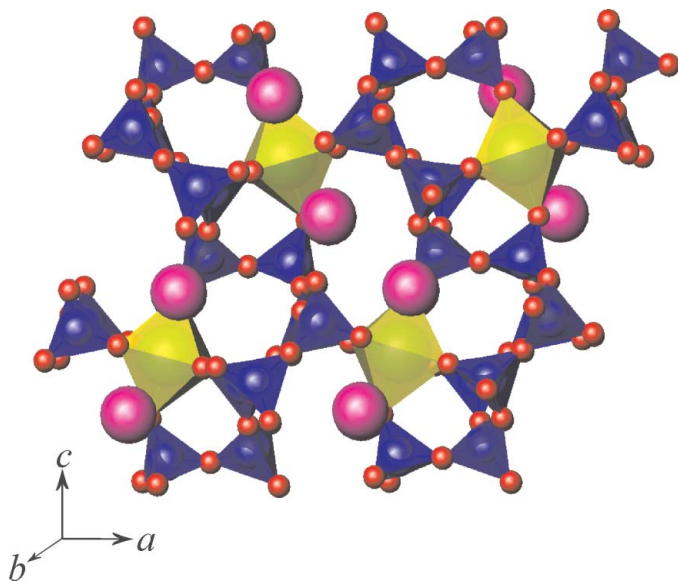
Figure 2
A view down the b axis depicting the $ThSi_6O_{15}^{2-}$ three-dimensional framework. The ThO_6 octahedra corner-share with SiO_4 tetrahedra. The Cs^+ cations are positioned in the channels created by the network structure.

$ThSiO_4$ (Taylor & Ewing, 1978). Thorite is isostructural with zircon ($ZrSiO_4$), while huttonite rarely occurs in nature and is isostructural with monazite ($CePO_4$) (Pabst & Hutton, 1951; Fuchs & Gebert, 1958; Sinha & Prasad, 1973). These phases exhibit markedly different metamictization processes (Mumpton & Roy, 1961). In contrast, naturally occurring and synthetic alkali and alkaline earth metal thorium silicates are scarce and include thornasite $[Na_{12}Th_3(Si_8O_{19})_4(H_2O)_{18}]$, ekanite ($ThCa_2Si_8O_{20}$) and turkestanite $[Th(Ca_{0.70-}Na_{0.25})_2K_{0.53}(Si_8O_{20})]$ (Szymanski et al., 1982; Kabalov et al., 1998; Li et al., 2000). This paper reports the crystal structure of a caesium thorium silicate, $Cs_2ThSi_6O_{15}$.

The structure of $Cs_2ThSi_6O_{15}$ consists of an anionic, three-dimensional thorium silicate network with Cs^+ cations occupying channels. The local coordination environment surrounding the Th^{IV} ion is depicted in Fig. 1. The ThO_6 units adopt a slightly distorted octahedral geometry, being coordinated by six O atoms from the silicate moieties. The Th—O bond lengths are similar and range from 2.269 (7) to 2.319 (7) Å: note the bent O5—Th—O10 [173.8 (2)°] and O11—Th—O13 [173.5 (3)°] axes, while the O1—Th—O7 angle is relatively linear [177.0 (2)°]. The cis-O—Th—O bond angles deviate appreciably from 90°, ranging from 84.7 (2) to 96.7 (3)°. The Th—O and Si—O bond lengths are similar to those found in other thorium silicates (Taylor & Ewing, 1978). Two of the silicate ligands share a single oxygen bridge. Bond valence sum calculations provide a value of 4.26 for Th, supporting a compound that contains Th^{IV} atoms (Brese & O'Keeffe, 1991).

A polyhedral representation of the anionic three-dimensional framework, viewed along the b axis, is shown in Fig. 2. The framework consists of ThO_6 distorted octahedra that

corner-share with SiO_4 tetrahedra. The Si—O bonds corner-shared with the ThO_6 octahedra [1.577 (7)–1.587 (7) Å] are slightly shorter than those corner-shared with adjacent silicate tetrahedra [1.600 (8)–1.635 (7) Å]. The silicate moieties share corners with adjacent tetrahedra as well. The interconnected SiO_4 and ThO_6 polyhedra form cyclic arrays of various sizes to generate channels that extend throughout the structure. The caesium cations are positioned within the channels. The cations interact with O atoms, forming ten contacts with Cs^+—O distances ranging from 3.096 (6) to 3.806 (7) Å.

$Cs_2ThSi_6O_{15}$ is a phyllosilicate with the same sheet structure as β-$K_3NdSi_6O_{15}$ (Haile & Wuensch, 1997). The silicate sheets consist of four-, six- and eight-membered SiO_4 rings.

Experimental

ThOCO₃·H_2O (99.99%, Strem), TeO_3 (99.9%, CERAC) and CsCl (99.9%, Aldrich) were used as received. Reactions were performed in fused silica/alumina crucibles. Caution: Standard procedures for handling radioactive materials should be followed. The reactants ThOCO₃·H_2O (95.6 mg, 0.293 mmol), TeO_3 (154.4 mg, 0.879 mmol) and CsCl (500.0 mg, 2.97 mmol) were loaded into a fused silica/alumina crucible. The crucible was heated within a muffle furnace at 1073 K for 7 d with no specific rate of heating or cooling. The resulting mixture in the crucible consisted of white powder with small quantities of small colorless blocks of $Cs_2ThSi_6O_{15}$. The reaction was originally intended to produce a caesium thorium tellurate. Instead, silica was abstracted from the walls of the reaction vessel to yield a silicate.

Crystal data

$Cs_2ThSi_6O_{15}$	Mo $K\alpha$ radiation
$M_r = 906.40$	Cell parameters from 4001
Orthorhombic, $Pca2_1$	reflections
$a = 16.292$ (1) Å	$\theta = 2.5–28.3°$
$b = 7.2154$ (6) Å	$\mu = 14.25$ mm^{-1}
$c = 13.680$ (1) Å	$T = 193$ (2) K
$V = 1608.1$ (2) Å^3	Block, colorless
$Z = 4$	$0.04 \times 0.03 \times 0.01$ mm
$D_x = 3.744$ Mg m^{-3}	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	4001 independent reflections
	3649 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.058$
Absorption correction: analytical	$\theta_{max} = 28.3°$
(XPREP in SHELXTL;	$h = -21 \rightarrow 21$
Sheldrick, 1997b)	$k = -9 \rightarrow 9$
$T_{min} = 0.452$, $T_{max} = 0.757$	$l = -18 \rightarrow 18$
15290 measured reflections	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.003$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$\Delta\rho_{max} = 1.94$ e Å^{-3}
$wR(F^2) = 0.076$	$\Delta\rho_{min} = -1.69$ e Å^{-3}
$S = 1.07$	Absolute structure: Flack (1983),
4001 reflections	1916 Friedel pairs
218 parameters	Flack parameter: 0.548 (8)
$w = 1/[\sigma^2(F_o^2) + (0.0232P)^2$	
$+ 6.6296P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected geometric parameters (Å, °).

Th—O7	2.269 (7)	Si3—O8	1.623 (7)
Th—O11	2.272 (7)	Si3—O6^{ii}	1.630 (9)
Th—O13	2.273 (8)	Si3—O9	1.635 (7)
Th—O1	2.315 (7)	Si4—O10	1.596 (7)
Th—O5	2.318 (6)	Si4—O3^{iii}	1.614 (9)
Th—O10	2.319 (7)	Si4—O8^{iv}	1.622 (7)
Si1—O1	1.577 (7)	Si4—O15^{v}	1.627 (8)
Si1—O2	1.600 (8)	Si5—O11	1.588 (8)
Si1—O3	1.617 (9)	Si5—O2^{vi}	1.597 (8)
Si1—O4	1.622 (7)	Si5—O12	1.611 (7)
Si2—O5	1.587 (7)	Si5—O14^{v}	1.621 (7)
Si2—O6	1.606 (10)	Si6—O13	1.600 (8)
Si2—O4	1.624 (7)	Si6—O14	1.620 (7)
Si2—O12^{i}	1.633 (7)	Si6—O9^{vii}	1.626 (7)
Si3—O7	1.585 (7)	Si6—O15	1.630 (8)
O7—Th—O11	89.7 (3)	O11—Th—O5	89.9 (2)
O7—Th—O13	96.1 (3)	O13—Th—O5	87.3 (3)
O11—Th—O13	173.5 (3)	O1—Th—O5	89.1 (2)
O7—Th—O1	177.0 (2)	O7—Th—O10	96.7 (3)
O11—Th—O1	87.7 (3)	O11—Th—O10	90.9 (2)
O13—Th—O1	86.4 (3)	O1—Th—O10	84.7 (3)
O7—Th—O5	89.5 (2)	O5—Th—O10	173.8 (2)

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

The highest peak and the deepest hole are located 0.79 and 0.60 Å from Th1 and Cs2, respectively. Note that $Cs_2ThSi_6O_{15}$ crystallizes in the polar space group $Pca2_1$. The crystal of $Cs_2ThSi_6O_{15}$ that was examined proved to be an enantiomorphic twin.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *XP* (Sheldrick, 1997b) and *ATOMS* (Dowty, 1999); software used to prepare material for publication: *SHELXL97*.

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