Crystal structure of tetracerium(III) trisulfide heptaoxodisilicate(IV), $\text{Ce}_4\text{S}_3[\text{Si}_2\text{O}_7]$

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Abstract

$\text{Ce}_4\text{O}_7\text{S}_3\text{Si}_2$, tetragonal, $I4_1/amd$ (No. 141), $a = 12.0543(8)$ Å, $c = 14.2351(9)$ Å, $V = 2068.4$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.027$, $wR_{\text{ref}}(F^2) = 0.060$, $T = 298$ K.

Source of material

Colourless transparent single crystals of $\text{Ce}_4\text{S}_3[\text{Si}_2\text{O}_7]$ were obtained as almost regular octahedra by the reaction of cerium dioxide and cerium with sulfur and silicon dioxide (molar ratio 3:1:6:4) in an excess of molten cerium trichloride as fluxing agent at 1123 K for seven days in an evacuated silica ampoule. The crystals of the title compound emerged as main product (along with traces of CeOCl and $\text{Ce}_2\text{O}_2\text{S}$ as by-products) and remain stable to air and water.

Discussion

Although compounds of the general formula $\text{M}_4\text{S}_3[\text{Si}_2\text{O}_7]$ ($\text{M} = \text{La} - \text{Nd}, \text{Sm}, \text{Gd} - \text{Yb}$) are already known [1–8], it was not possible to synthesize the single-crystalline isotypic cerium compound up to now [9].

The title compound contains isolated pyroanionic $[\text{Si}_2\text{O}_7]^{6-}$ units surrounded by twelve cerium atoms as terminal and edge-spanning ligands. The $(\text{Ce}1)^{3+}$ cations are even able to connect

the bridging oxygen (O3) although this Ce—O distance is rather long (326 pm). Both crystallographic independent Ce^{3+} cations show tricapped trigonal prisms ($\text{CN} = 9$) as coordination polyhedra built of four oxygen and five sulfur atoms in case of Ce1 but seven O^{2-} and two S^{2-} for Ce2. The $\text{Ce}^{3+} - \text{O}^{2-}$ distances with values of 241 pm – 267 pm (except the very long distance of 326 pm mentioned before) range in the region expected for those separations just like the $\text{Ce}^{3+} - \text{S}^{2-}$ bond lengths ($d(\text{Ce} - \text{S}) = 290$ pm – 344 pm). All oxygen atoms belong to vertex-shared double tetrahedra of disilicate anions $[\text{Si}_2\text{O}_7]^{6-}$ showing Si—O distances of 161 pm – 164 pm and O—Si—O angles of $104^\circ - 120^\circ$ very much like almost every other compound containing single or vertex-connected $[\text{SiO}_4]^{4-}$ tetrahedra. The bridging angle (Si—O—Si) of the disilicate unit lies with 132° close to those of the A- and G-type rare-earth disilicates ($\text{M}_2[\text{Si}_2\text{O}_7]$) [10]. Finally, the crystal structure distinguishes three S^{2-} anions that once exhibit an environment of six Ce^{3+} cations in the shape of a rather distorted octahedron (S1), and twice one of four cerium atoms either forming a seesaw (S2) or a flat square (S3), respectively. The whole structure consists of layers of disilicate anions parallel (001) containing both types of cerium cations as well as the $(\text{S}2)^{2-}$ and the $(\text{S}3)^{2-}$ anions. These are separated by the high-coordinated sulfide atoms in position S1. The stacking order can be considered as A, -B, B, -A where A and B are the same layers but perpendicular rotated against each other around the c -axis, as can be seen in the figure.

Table 1. Data collection and handling.

Crystal:	colourless octahedron, size $0.08 \times 0.08 \times 0.08$ mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ :	181.17 cm^{-1}
Diffractionmeter, scan mode:	Nonius Kappa-CCD, ϕ/ω
$2\theta_{\text{max}}$:	55.3°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	9174, 669
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 616
$N(\text{param})_{\text{refined}}$:	47
Program:	SHELXL-97 [11]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ce(1)	16h	0	0.01366(4)	0.34060(4)	0.0154(3)	0.0176(3)	0.0155(3)	0	0	−0.0014(2)
Ce(2)	16g	0.17510(3)	x+1/4	7/8	0.0100(2)	U ₁₁	0.0112(3)	0.0011(2)	−0.0001(1)	−U ₁₃
S(1)	16f	0.3512(2)	0	0	0.0066(9)	0.027(1)	0.010(1)	0	0	0.0072(9)
S(2)	4b	0	1/4	3/8	0.009(1)	U ₁₁	0.016(2)	0	0	0
S(3)	4a	0	3/4	1/8	0.005(1)	U ₁₁	0.013(2)	0	0	0
Si	16h	0	0.3728(2)	0.0959(2)	0.0030(9)	0.0048(9)	0.008(1)	0	0	−0.0004(8)
O(1)	32i	0.1154(3)	0.1133(3)	0.0402(3)	0.010(2)	0.011(2)	0.012(2)	−0.001(2)	0.003(2)	−0.001(2)
O(2)	16h	0	0.0250(4)	0.1715(4)	0.010(3)	0.005(2)	0.009(3)	0	0	0.004(2)
O(3)	8e	0	1/4	0.6074(5)	0.010(4)	0.019(4)	0.005(4)	0	0	0

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