inorganic papers

Samarium orthosilicate oxyapatite, $Sm_5(SiO_4)_3O$

Mark G. Morgan, Meitian Wang and Arthur Mar*

Department of Chemistry, University of Alberta, Edmonton, AB, Canada T6G 2G2

Correspondence e-mail: arthur.mar@ualberta.ca

Key indicators

Single-crystal X-ray study
$T = 295$ K
Mean σ(Si–O) = 0.008 Å
R factor = 0.031
wR factor = 0.074
Data-to-parameter ratio = 17.9

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

Samarium orthosilicate oxyapatite, $Sm_5(SiO_4)_3O$, contains SiO_4^{4-} tetrahedra [Si—O 1.611 (7)–1.629 (5) Å] and O^{2-} anions, separated by samarium cations in CN7 [Sm—O 2.2428 (4)–2.641 (7) Å] and CN9 sites [Sm—O 2.428 (5)–2.846 (5) Å]. The full occupancy of the samarium sites implies a mixed valency of four Sm^{3+} and one Sm^{2+} per formula unit.

Comment

Rare-earth (RE) silicate oxyapatites can be derived from the parent apatite structure, $Ca_5(PO_4)_3F$, by substituting Ca^{2+} with RE^{3+}, PO_4^{3-} with SiO_4^{4-}, and F^- with O^{2-}. There are several possibilities for maintaining charge balance. If trivalent RE is assumed, the RE sites must be partially occupied to result in a defect structure, as in $RE_{4.67}(SiO_4)_3O$ (RE = La, Sm; Kuz'min & Belov, 1965). Alternatively, if these sites are to remain fully occupied, they must contain a proportion of divalent cations A^{2+} such as alkaline earths, as in $(RE)_4(A)(SiO_4)_3O$ (Ito, 1968; Grisafe & Hummel, 1970). Yet another possibility is to replace F^-, not with O^{2-}, but with N^{3-}, to form the nitridoapatite $Sm_5(SiO_4)_3N$ (Gaudé et al., 1975). The compound $Sm_5(SiO_4)_3O$ reported here has a non-defect structure, in contrast to that of $Sm_{4.67}(SiO_4)_3O$, previously determined only by photographic methods (Kuz'min & Belov, 1965).

The structure contains discrete SiO_4 tetrahedra (Fig. 1). The Sm1 atoms are coordinated by O atoms in a pentagonal bipyramidal (CN7) geometry and the Sm2 atoms in a tricapped trigonal prismatic (CN9) geometry. Atom O4 resides in a characteristic trigonal-planar site, surrounded by
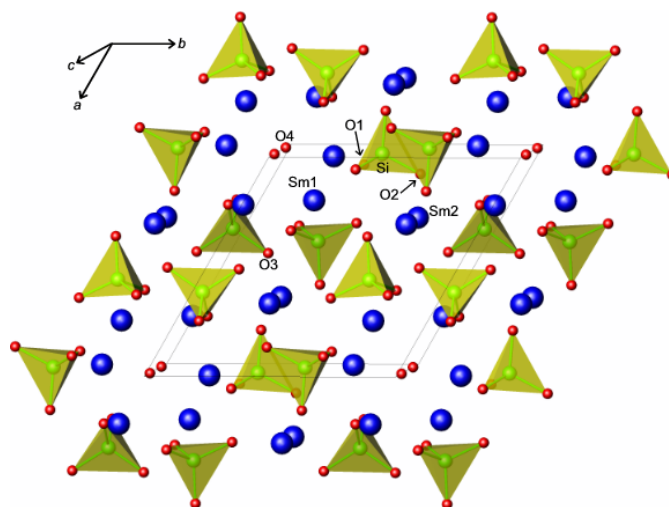

Figure 1
$Sm_5(SiO_4)_3O$, viewed approximately down the c axis. Colour key: Sm blue, SiO_4-tetrahedra yellow, O red.

Sm1 atoms. The Si—O distances within the tetrahedra (Table 1) are normal [1.611 (7)–1.629 (5) Å] and agree well with those found in $Sm_{4.67}(SiO_4)_3O$ (1.62–1.63 Å). The fully stoichiometric formula $Sm_5(SiO_4)_3O$ implies that some divalent Sm must be present, i.e. $(Sm^{3+})_4(Sm^{2+})(SiO_4^{4-})_3(O^{2-})$. This proposal is supported by several observations. First, consistent with the larger ionic radius of Sm^{2+} relative to Sm^{3+}, the cell parameters in $Sm_5(SiO_4)_3O$ [a = 9.4959 (10) Å and c = 7.0361 (7) Å] are larger than in $Sm_{4.67}(SiO_4)_3O$ (a = 9.33 Å and c = 6.85 Å). The Sm1—O distances [2.2428 (4)– 2.641 (7) Å] are similar to those in $Sm_{4.67}(SiO_4)_3O$ (2.21– 2.67 Å) but the Sm2—O distances [2.428 (5)–2.846 (5) Å] are distinctly longer than in $Sm_{4.67}(SiO_4)_3O$ (2.32–2.74 Å). Given the multiplicities of the Sm1 ($6h$) and Sm2 ($4f$) sites, an ordered distribution consistent with a 4:1 ratio of Sm^{3+}:Sm^{2+} is not possible. A reasonable interpretation is that the Sm1 site contains exclusively Sm^{3+}, and the Sm2 site contains a mixture of Sm^{3+} and Sm^{2+}. The bond-valence sums of 2.86 for Sm1 and 2.54 for Sm2 are in good agreement with this model (Brese & O'Keeffe, 1991). Second, an Sr-substituted compound, $Sm_4Sr(SiO_4)_3O$, is known (Ito, 1968). Consistent with the similar ionic radii of Sr^{2+} and Sm^{2+} (Shannon, 1976), its cell parameters (a = 9.51 Å and c = 7.02 Å) are very close to those of the title compound. Third, the crystals of $Sm_5(SiO_4)_3O$ are red, which is characteristic of Sm^{2+}-containing compounds, in contrast to the yellow colour of Sm^{3+}. These crystals were obtained as adventitious byproducts of a reaction in evacuated fused-silica tubes. In contrast to typical preparations of other rare-earth apatites, the low oxygen content under these reaction conditions would be consistent with Sm not being fully oxidized to the trivalent state. A compound having both rare-earth and oxygen defects, $Sm_4(SiO_4)_3$, has been reported; it is red and has cell parameters [a = 9.497 (3) Å and c = 6.949 (3) Å] that suggest the presence of a small amount of Sm^{2+} (McCarthy et al., 1967).

Experimental

A 0.25 g mixture of elemental samarium, gallium, and bismuth in a 1:2:1 ratio (Sm, 99.9%, Cerac; Ga, 99.9999%, Alfa–Aesar; Bi, 99.999%, Cerac) was reacted in phase studies of ternary rare-earth bismuth systems. The reactants were heated in an evacuated fused-silica tube at 1223 K for 4 d, cooled to 773 K over 4 d, and then cooled to room temperature over 1.5 d. Partial attack was observed on the walls of the silica tube, on which were deposited dark-red needle-shaped crystals. Windowless semiquantitative EDX (energy-dispersive X-ray) analysis on a Hitachi S-2700 scanning electron microscope revealed the presence of Sm, Si, and O in these crystals.

Crystal data

$Sm_5(SiO_4)_3O$	Mo $K\alpha$ radiation
M_r = 1044.02	Cell parameters from 4159
Hexagonal, $P6_3/m$	reflections
a = 9.4959 (10) Å	θ = 4.3–32.5°
c = 7.0361 (7) Å	μ = 26.70 mm^{-1}
V = 549.46 (10) Å^3	T = 295 (2) K
Z = 2	Needle, red
D_x = 6.310 Mg m^{-3}	0.32 × 0.02 × 0.02 mm

Data collection

Bruker Platform/SMART	716 independent reflections
1000 CCD diffractometer	650 reflections with $I > 2\sigma(I)$
ω scans (0.2° frames)	R_{int} = 0.055
Absorption correction: numerical	θ_{max} = 32.6°
(SHELXTL; Sheldrick, 1997)	h = −13 → 14
T_{min} = 0.179, T_{max} = 0.643	k = −14 → 14
6710 measured reflections	l = −10 → 10

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0365P)^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.031	$+ 5.6399P]$
$wR(F^2)$ = 0.074	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.18	$(\Delta/\sigma)_{max} < 0.001$
716 reflections	$\Delta\rho_{max}$ = 2.75 e Å^{-3}
40 parameters	$\Delta\rho_{min}$ = −2.73 e Å^{-3}
	Extinction correction: SHELXL97
	Extinction coefficient: 0.0015 (3)

Table 1
Selected interatomic distances (Å).

Sm1—O4	2.2428 (4)	Sm2—O2	2.508 (5)
Sm1—O1^i	2.383 (5)	Sm2—O1	2.846 (5)
Sm1—O2^{ii}	2.421 (6)	Si—O3^{iv}	1.611 (7)
Sm1—O1	2.497 (5)	Si—O2	1.623 (7)
Sm1—O3	2.641 (7)	Si—O1	1.629 (5)
Sm2—O3^{iii}	2.428 (5)		

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

Refinements on the absorption-corrected data were performed, in which the occupancies of successive sites were allowed to vary. These converged to values of 1.00 (4) for Sm1, 0.97 (4) for Sm2, 1.00 (4) for Si, 1.00 (5) for O1, 1.12 (5) for O2, 1.07 (5) for O3, and 1.10 (7) for O4, with reasonable displacement parameters for each site. These results support a fully stoichiometric model, and the occupancies were fixed at 1.00 for all atoms in the final refinement. The atomic positions were standardized with the program STRUCTURE TIDY (Gelato & Parthé, 1987).

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

References

Brese, N. E. & O'Keeffe, M. (1991). Acta Cryst. B47, 192–197.
Bruker (1997). SMART. Version 5.051. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2000). SAINT. Version 6.02. Bruker AXS Inc., Madison, Wisconsin, USA.
Dowty, E. (1999). ATOMS. Version 5.1. Shape Software, Kingsport, Tennesee, USA.
Gaudé, J., L'Haridon, P., Hamon, C., Marchand, R. & Laurent, Y. (1975). Bull. Soc. Fr. Mineral. Cristallogr. 98, 214–217.
Gelato, L. M. & Parthé, E. (1987). J. Appl. Cryst. 20, 139–143.
Grisafe, D. A. & Hummel, F. A. (1970). Am. Mineral. 55, 1131–1145.
Ito, J. (1968). Am. Mineral. 53, 890–907.
Kuz'min, E. A. & Belov, N. V. (1965). Dokl. Akad. Nauk SSSR, 165, 88–90.
McCarthy, G. J., White, W. B. & Roy, R. (1967). J. Inorg. Nucl. Chem. 29, 253–254.
Shannon, R. D. (1976). Acta Cryst. A32, 751–767.
Sheldrick, G. M. (1997). SHELXTL. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.