Crystal structure of diterbium orthosilicate selenide, $Tb_2(SiO_4)Se$

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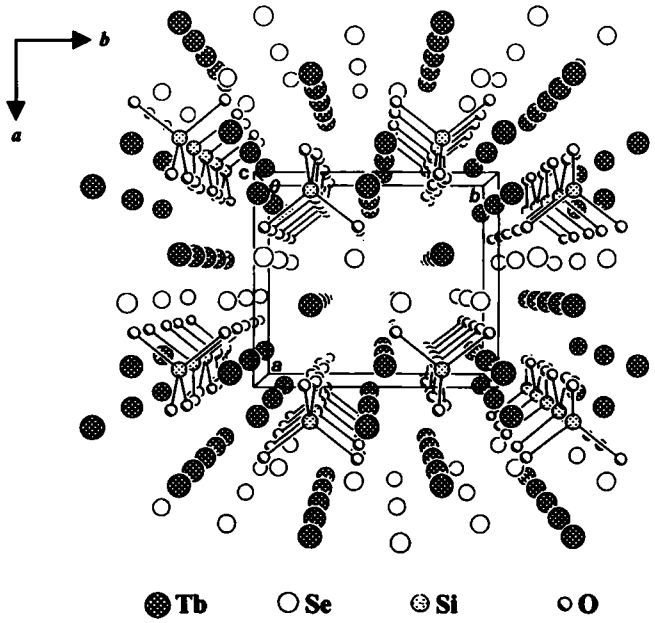

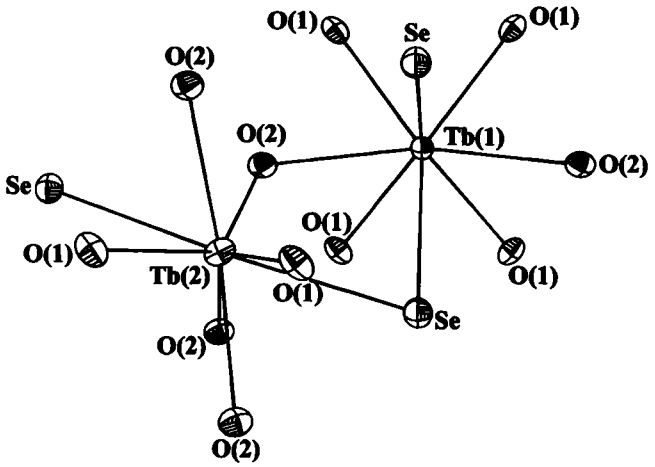

Abstract

$O_4SeSiTb_2$, orthorhombic, *Pbcm* (No. 57), $a = 6.0387(4)$ Å, $b = 6.9855(5)$ Å, $c = 10.8131(7)$ Å, $V = 456.1$ Å^3, $Z = 4$, $R_{gt}(F) = 0.030$, $wR_{ref}(F^2) = 0.073$, $T = 153$ K.

Source of material

The reactive flux Cs_2Se_3 was prepared by the stoichiometric reaction of Cs (Aldrich, 99.5%) and Se (Aldrich, 99.5%) in liquid NH_3. Clear needles of $Tb_2(SiO_4)Se$ were obtained accidentally in the reaction of Tb (0.547 mmol, Alfa Aesar, 99.9%), Cd (0.543 mmol, Alfa Aesar, 99.9%), Se (1.09 mmol, Aldrich, 99.5%), CsCl (0.947 mmol, Aldrich, 99.9%), and Cs_2Se_3 (150 mg). The materials were mixed and sealed in an unprotected fused-silica tube that was then evacuated to 10^{-4} Torr. The tube was heated to 1273 K, kept at 1273 K for 50 h, cooled at 4 K/h to 473 K, and then the furnace was turned off. The reaction mixture was washed with water, then *N,N*-dimethylformamide, and finally dried with acetone. Semi-quantitative energy dispersive spectroscopy (EDS) analysis confirmed the presence of Tb, Si, and Se in ratio 2:1:1. EDS also indicated the presence of O but provided no evidence for the presence of Cd, Cl, or Cs. The compound resulted from the reaction of the starting components with the fused-silica tube.

Discussion

$Tb_2(SiO_4)Se$ is a new member of the $Ln_2(SiO_4)Se$ series (Ln = La [1], Nd [2], Sm [3], Dy [3], Ho [3], and Er [4]). These isostrutural compounds crystallize in space group *Pbcm* of the orthorhombic system. In this layered structure, infinite chains of SiO_4^{4-} tetrahedra extend along the *c* axis, separated by Ln and Se atoms (upper figure). There are two crystallographically distinct Tb atoms, both coordinated by six O atoms and two Se atoms. Atom Tb(1), located within the layer, is in a bicapped trigonal prism; atom Tb(2), located between the layers, is in a dodecahedron (lower figure). The Tb—O distances range from 2.377(5) Å to 2.535(5) Å, which may be compared with the range of 2.177 Å to 2.551 Å in Tb_2O_3 [5]. The Tb—Se distances are 2.8958(11) Å, 2.9990(11) Å, and 3.0570(5) Å, compared with 2.876(1) Å to 2.984(1) Å in Tb_2Se_3 [6]. Also isostructural with the present compound are the related tellurides $Ln_2(SiO_4)Te$ (Ln = Nd [7], Sm [3,7] and Pr [8]). Most of these selenides and tellurides were prepared accidentally.

Table 1. Data collection and handling.

Crystal:	colorless needle, size 0.016 × 0.018 × 0.176 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	388.92 cm^{-1}
Diffractometer, scan mode:	Bruker SMART-CCD, $\Delta\omega = 0.3°$
$2\theta_{max}$:	57.74°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3715, 605
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 556
$N(param)_{refined}$:	42
Program:	SHELXTL [9]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tb(1)	4*d*	0.13113(7)	0.03044(7)	1/4	0.0062(3)	0.0049(3)	0.0046(3)	0.0006(2)	0	0
Tb(2)	4*c*	0.60749(8)	1/4	0	0.0041(3)	0.0057(3)	0.0076(3)	0	0	–0.0013(2)
Se	4*d*	0.4230(2)	0.3778(1)	1/4	0.0062(5)	0.0073(5)	0.0064(5)	–0.0015(3)	0	0
Si	4*c*	0.1127(4)	1/4	0	0.005(1)	0.004(1)	0.004(1)	0	0	0.0009(8)
O(1)	8*e*	0.0542(8)	0.7611(6)	0.1207(5)	0.004(2)	0.007(2)	0.007(2)	0.002(2)	0.001(2)	0.002(2)
O(2)	8*e*	0.2735(8)	0.0707(7)	0.0310(4)	0.006(2)	0.005(2)	0.008(2)	–0.001(2)	0.001(2)	–0.000(2)

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