Crystal structure of terbium antimonide oxide, $Tb_9Sb_5O_5$

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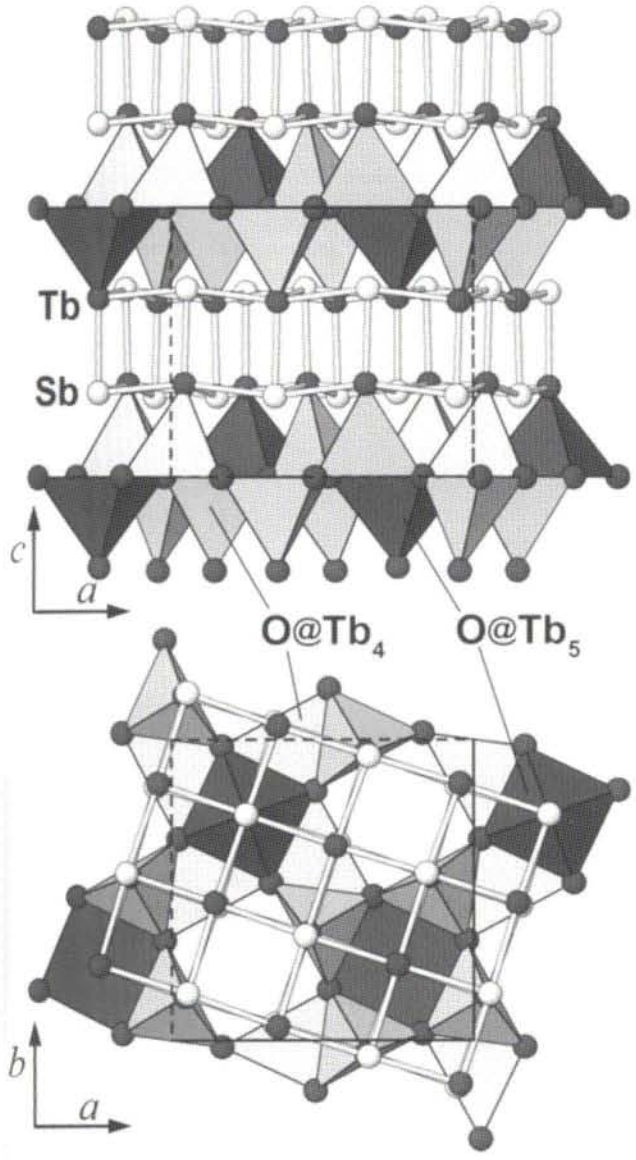

Abstract

$O_5Sb_5Tb_9$, tetragonal, *P4/n* (no. 85), $a = 9.862(1)$ Å, $c = 8.838(2)$ Å, $V = 859.5$ Å^3, $Z = 2$, $R_{gt}(F) = 0.030$, $wR_{ref}(F^2) = 0.049$, $T = 296$ K.

Source of material

$Tb_9Sb_5O_5$ has been synthesized from terbium metal, antimony, and Sb_2O_3. Stoichiometric amounts of the starting materials were mixed and sealed in a tantalum ampoule. The following temperature profile was applied: 298 → 1923 K (50 Kh^{-1}, subsequent annealing for 12 h); 1923 → 1673 K (20 Kh^{-1}, subsequent annealing for 48 h); 1673 → 298 K (20 Kh^{-1}).

Discussion

$Tb_9Sb_5O_5$ crystallize in the $La_9Sb_5O_5$ type of structure [1,2]. The atoms Tb2, Tb3 and Sb1, Sb2 are aranged in a corrugated double layer [TbSb], which can be regarded as a two-dimensional slab analogous to NaCl. Each [TbSb] fragment is sandwiched between two layers built from Tb1 and O1, O2. The NaCl-like double sheet is also a feature common to the structures of Eu_4Sb_2O [3] or Sc_2Sb [4]. In the latter compound the interlayer exclusively consists of Sc atoms. In the case of $Tb_9Sb_5O_5$ this layer is composed of Tb and O atoms with the composition Tb_4O_5, and only 4/5 of the possible metal positions are occupied by terbium. Therefore, the structure can be regarded as a defect variant of Sc_2Sb, stuffed with oxygen: $Tb_9\square Sb_5O_5 = Sc_{10}Sb_5\square_5$. From the originally square Sc_5 pyramids, with their tips alternating up and down along the [001] direction, 4/5 transform into tetrahedra and 1/5 remain unchanged. All tetrahedral and square-pyramidal holes are filled with O atoms. The partial structure (Tb_9Sb_5) also corresponds to the inverted Hf_5Sb_9 type of structure [5]. The buckling of the NaCl-like slabs is one way to fit the dimensions of their meshes to the sandwiched sheets inbetween [6]. Here in $Tb_9Sb_5O_5$, the present of vacancies in the $Tb_4\square O_5$ sublattice, allows an additional adjustment, which is needed because of d(Tb—Sb) = 3.143 Å < $2^{1/2}$ d(Tb—O) = 3.325 Å.

Table 1. Data collection and handling.

Crystal:	dark silver block, size 0.01 × 0.02 × 0.02 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	441.78 cm^{-1}
Diffractometer, scan mode:	SMART APEX II, Bruker AXS, ω
$2\theta_{max}$:	74.4°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	16398, 2211
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1615
$N(param)_{refined}$:	47
Programs:	SHELXS-97 [7], SHELXL-97 [8], ATOMS [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)	8*g*	0.33120(2)	0.02250(2)	0.99800(3)	0.0049(1)	0.0073(1)	0.00766(9)	0.00007(8)	–0.00054(9)	0.00030(9)
Tb(2)	2*c*	¼	¼	0.33136(6)	0.0093(1)	U_{11}	0.0057(2)	0	0	0
Tb(3)	8*g*	0.14585(3)	–0.04496(3)	0.65470(3)	0.0090(1)	0.0090(1)	0.0055(1)	–0.00048(9)	0.00012(9)	–0.00048(9)
Sb(1)	2*c*	¼	¼	0.68537(9)	0.0071(2)	U_{11}	0.0109(3)	0	0	0
Sb(2)	8*g*	0.15426(4)	–0.05428(3)	0.30038(4)	0.0071(2)	0.0079(2)	0.0067(1)	–0.0003(1)	0.0004(1)	0.0001(1)
O(1)	2*c*	¼	¼	0.067(1)	0.012(2)	U_{11}	0.023(5)	0	0	0
O(2)	8*g*	0.1284(4)	–0.0239(4)	0.9117(4)	0.009(2)	0.007(2)	0.008(2)	–0.001(1)	0.000(1)	–0.000(1)

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