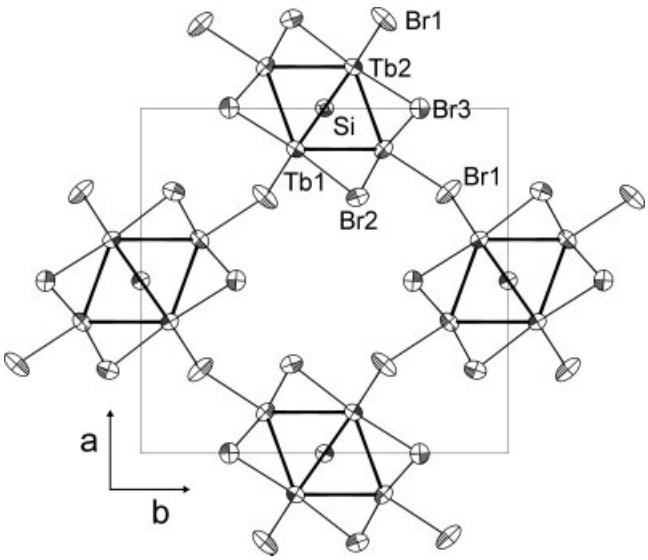
Crystal structure of tetraterbium hexabromide monosilicide, Tb_4Br_6Si

Hj. Mattausch*, O. Oeckler and A. Simon

Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, D-70569 Stuttgart, Germany

Received May 19, 2003, accepted and available on-line July 23, 2003; CSD-No. 409703



Abstract

Br_6SiTb_4, orthorhombic, *Pbam* (No. 55), $a = 13.061(1)$ Å, $b = 13.859(2)$ Å, $c = 4.0407(4)$ Å, $V = 731.4$ Å^3, $Z = 2$, $R_{gt}(F) = 0.029$, $wR_{ref}(F^2) = 0.071$, $T = 293$ K.

Source of material

Tb_4Br_6Si is prepared by heating stoichiometric amounts of $TbBr_3$, Tb and Si under Ar atmosphere in sealed Ta-capsules at 1200 K for 5 days.

Discussion

Tb_4Br_6Si is isotypic with Tb_4Br_6C and Sc_4Cl_6C [1,2]. In the crystal structure, the Tb atoms form octahedra centered by Si atoms. The Tb_6Si octahedra are connected via opposite edges to form octahedral chains. The Br atoms coordinate all free edges. In terms of condensed clusters [3,4] the crystal structure is to be described as $Tb_2Tb_{4/2}SiBr(i)_4Br(a\text{-}a)_{4/2}$. In the related structure of $NaMo_4O_6$ [5] the intercluster spaces are filled with Na-cations, in Tb_4Br_6Si they are not occupied. The distances Tb—Tb range from 3.8826(6) Å to 4.0407(4) Å, the Tb—Br from 2.888(1) Å to 2.945(1) Å, the Tb—Si from 2.7155(6) Å to 2.7757(4) Å.

Table 1. Data collection and handling.

Crystal:	black needle, size 0.08 × 0.04 × 0.18 mm
Wavelength:	Ag K_α radiation (0.56086 Å)
μ:	189.60 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 375 exposures, $\Delta\omega = 0.8°$
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13106, 1458
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 872
$N(param)_{refined}$:	36
Programs:	SHELXL-97 [6], ATOMS [7]

References

1. Simon, A.; Mattausch, Hj.; Miller, G. J.; Bauhofer, W.; Kremer, R. K.: Metal-Rich Halides, Structure, Bonding and Properties. In: *Handbook on the Physics and Chemistry of Rare Earths* (Eds. K. A. Jr. Gschneidner, LeRoy Eyring), Vol. **15,** p. 191-285. Elsevier Science Publishers 1991.
2. Hwu, S.-J.; Corbett, J. D.: Metal-Metal-Bonded Scandium Cluster ($Sc_7Cl_{12}Z$) and Infinite Chain ($Sc_4Cl_6C_4$) Phase Stabilized by Interstitial Boron or Nitrogen (Z). J. Solid State Chem. **64** (1986) 331-346.
3. Simon, A.: Condensed Clusters. Angew. Chem. Int. Ed. Engl. **20** (1981) 1-22.
4. Simon, A.: Clusters of Valence Electron Poor Metals - Structure, Bonding, Properties. Angew. Chem. Int. Ed. Engl. **27** (1988) 159-183.
5. Torardi, C. C.; McCarley, R. E.: Sodium tetramolybdenum hexoxide ($NaMo_4O_6$). A metallic infinite-chain polymer derived by condensation of octahedral clusters. J. Am. Chem. Soc. **101** (1979) 3963-3964.
6. Sheldrick, G. M.: SHELXL-97. Program for refining crystal structures. University of Göttingen, Germany 1997.
7. Dowty, E.: Atoms 5.0, A Complete Program for Displaying Atomic Structures. By Shape Software, Kingsport, TN 37663, USA 1999.

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*h*	0.11930(5)	0.33952(3)	1/2	0.0165(3)	0.0162(2)	0.0142(3)	0.0042(2)	0	0
Tb(2)	4*g*	0.11932(5)	0.57884(3)	0	0.0134(2)	0.0157(2)	0.0119(3)	–0.0019(2)	0	0
Br(1)	4*h*	0.2425(1)	0.16219(9)	1/2	0.0274(7)	0.0298(6)	0.0163(7)	0.0169(5)	0	0
Br(2)	4*g*	0.25818(9)	0.41044(8)	0	0.0166(5)	0.0240(5)	0.0174(7)	0.0031(4)	0	0
Br(3)	4*g*	0.0009(1)	0.24080(7)	0	0.0210(5)	0.0177(4)	0.0189(6)	–0.0002(4)	0	0
Si(1)	2*d*	0	1/2	1/2	0.015(2)	0.016(2)	0.009(2)	–0.001(2)	0	0

* Correspondence author (e-mail: Hj.Mattausch@fkf.mpg.de)