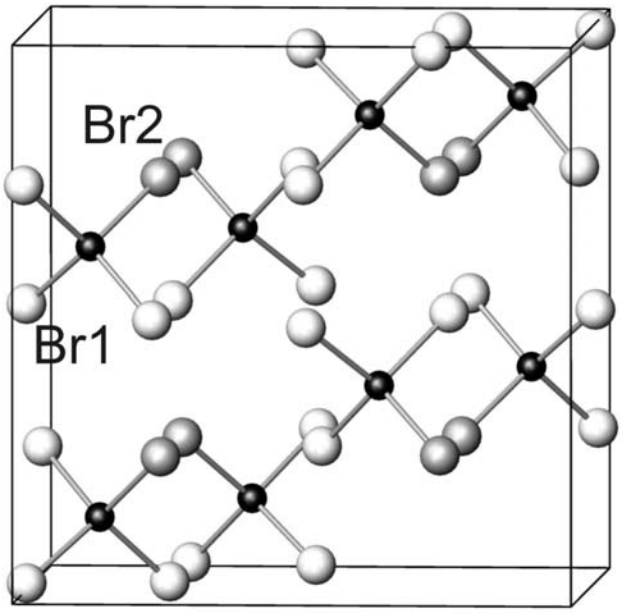
Refinement of the crystal structure of α-silicon tetrabromide, α-$SiBr_4$, *a room temperature modification*

Jianwei Tong, Constantin Hoch, Arndt Simon and Jürgen Köhler*

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

Received November 19, 2010, accepted and available on-line January 24, 2010; CSD no. 710060



Abstract

Br_4Si, $Pa\bar{3}$ (no. 205), a = 11.152(1) Å, V = 1386.9 Å^3, Z = 8, $R_{gt}(F)$ = 0.046, $wR_{ref}(F^2)$ = 0.087, T = 223 K.

Source of material

Liquid $SiBr_4$ (Aldrich, 99.995 %) was filled in capillaries with 0.3 mm diameter under argon. In the capillary colorless transparent single crystals of $SiBr_4$ were grown by rapidly freezing one end of the liquid and solidifying the remaining part slowly at 223 *K* on a STOE IPDS I diffractometer with a temperature control equipment.

Discussion

$SiBr_4$ (m.p. 278 K) is known since more than 100 years [1,2]. Recently, the crystal structures of two out of ten possible structure types for $SiBr_4$ predicted by global minimization of the lattice energy using the program CRYSCA were found [3]. Temperature dependent X-ray powder diffraction studies show that at a transition temperature of 168 K the monoclinic low-temperature β-phase transforms into the high-temperature cubic α-phase.

The cubic α-$SiBr_4$ is isotypic to α-$GeBr_4$ [4] and adopts the SnI_4 type structure [3]. Monoclinic β-$SiBr_4$ [5] crystallizes like β-$GeBr_4$ [6] in the $SnBr_4$ type structure. The structure of the high temperature modification, α-$SiBr_4$, has been refined using single crystal X-ray diffraction data taken at 223 K. It can be described in terms of a cubic close packing of Br atoms in which one eighth of the tetrahedral holes are occupied by Si atoms. In α-$SiBr_4$ each Si atom is surrounded by one Br1 and three Br2 atoms to form a tetrahedron with Si—Br1 distances of 2.193(5) Å and Si—Br2 distances of 2.189(4) Å (3×), respectively. The Br–Si–Br angles are 109.6(1)° and 109.3(1)°, close to the angle in an ideal tetrahedron. Each Br atom is cuboctahedrally surrounded by other Br atoms. The three Br-Br distances belonging to a $SiBr_4$ tetrahedron lie between 3.57 and 3.58 Å, whereas the remaining nine Br-Br distances are longer (3.94 to 4.23 Å).

Table 1. Data collection and handling.

Crystal:	colorless cube, size 0.3 × 0.3 × 0.3 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	232.52 cm^{-1}
Diffractometer, scan mode:	STOE IPDS II, ω
$2\theta_{max}$:	39.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4180, 215
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 188
$N(param)_{refined}$:	17
Programs:	SHELXS-97, SHELXL-97 [7]

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}
Br(1)	8*c*	0.2448(1)	x	x	0.027(1)	U_{11}	U_{11}	–0.0089(5)	U_{12}	U_{12}
Br(2)	24*d*	0.0244(3)	0.0123(2)	0.2450(1)	0.024(1)	0.021(1)	0.022(1)	–0.0040(9)	0.0071(6)	0.0103(5)
Si(1)	8*c*	0.1313(2)	x	x	0.010(2)	U_{11}	U_{11}	0.001(1)	U_{12}	U_{12}

* Correspondence author (e-mail: J.Koehler@fkf.mpg.de)

References

1. Serullas: Pogg. Ann. **24** (1832) 341.
2. Pohland, E.: Zur Kenntnis des Siliziumtetrabromids. Z. Anorg. Allg. Chem. **201** (1931) 265-281.
3. Wolf, A. K.; Glinnemann, J.; Schmidt, M. U.; Tong, J.; Dinnebier, R. E.; Simon, A.; Köhler, J.: $SiBr_4$ - prediction and determination of crystal structures. Acta Crystallogr. **B65** (2009) 342.
4. Köhler, J.; Okudera, H.; Reuter, D.; Simon, A.: Crystal structure of germanium tetrabromide, α-$GeBr_4$, room temperature modification. Z. Kristallogr. **220** (2005) 523.
5. Tong, J.; Hoch, C.; Simon, A.; Köhler, J.: Crystal structure of β-silicon tetrabromide, β-$SiBr_4$, *at 271 K*. Z. Kristallogr. NCS **226** (2011) 5-6.
6. Köhler, J.; Okudera, H.; Simon, A.: Crystal structure of germanium tetrabromide, β-$GeBr_4$, low temperature modification. Z. Kristallogr. **220** (2005) 524.
7. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.