Refinement of the crystal structure of β-silicon tetrabromide, β-$SiBr_4$, *at 271 K*

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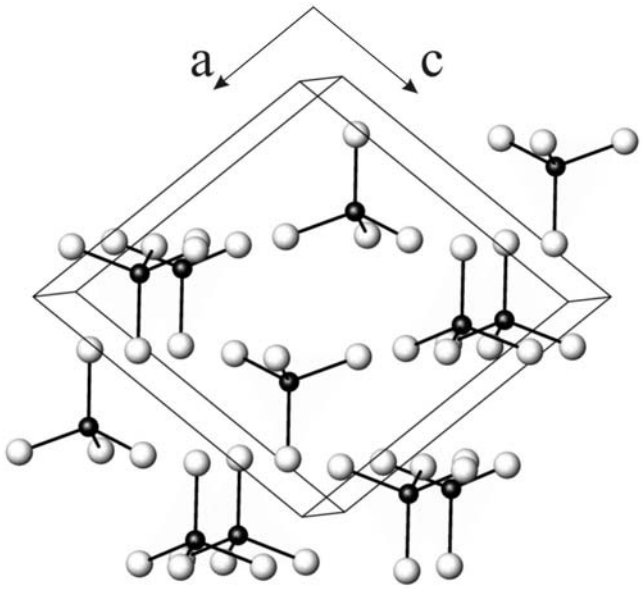

Abstract

Br_4Si, monoclinic, $P12_1/c1$ (no. 14), a = 10.285(2) Å, b = 6.763(1) Å, c = 10.377(2) Å, β = 103.15(3)°, V = 702.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.037, $wR_{ref}(F^2)$ = 0.084, T = 271 K.

Source of material

Liquid $SiBr_4$ (Aldrich, 99.995 %) was filled in capillaries with 0.2 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 271 K on a STOE IPDS II diffractometer with a temperature control equipment.

Discussion

$SiBr_4$ (m.p. 278 K) is known since more than 100 years [1,2]. In 1931 Pohland described that it exists in two modifications by polarization microscopy analysis [2]. That there might exist some more modifications of $SiBr_4$ could recently be shown by global minimization of the lattice energy using the program CRYSCA were found [3]. Our studies show that the cubic high-temperature α-phase of $SiBr_4$ transforms into a monoclinic low-temperature β-phase at 168 K. In capillaries of small diameters crystals of β-$SiBr_4$ can form at even higher temperatures when cooling liquid $SiBr_4$, which is possibly due to the preferred nucleation of β-$SiBr_4$ versus α-$SiBr_4$ under such conditions.

The cubic α-$SiBr_4$ [4] is isotypic to α-$GeBr_4$ [5] and adopts the SnI_4 type structure. Monoclinic β-$SiBr_4$ crystallizes like β-$GeBr_4$ [6] in the $SnBr_4$ type structure [3]. Monoclinic β-$SiBr_4$ can be described in terms of a distorted hexagonal close packing of Br atoms, in which 1/8 of the tetrahedral holes are occupied by Si atoms. Each Si atom is surrounded by four crystallographically different Br atoms with Si—Br distances ranging from 2.165(2) to 2.169(2) Å and the Br–Si–Br angles lie between 109.18(9)° and 109.80(9)°. Each Br atom is surrounded by other 12 Br atoms as *hcp*. The three Br-Br distances at the edges of a $SiBr_4$ tetrahedron range from 3.53 to 3.55 Å, and the remaining nine Br-Br distances are slightly longer (3.93 to 4.55 Å).

Table 1. Data collection and handling.

Crystal:	colorless cube, size 0.2 × 0.2 × 0.2 mm
Wavelength:	Ag K_α radiation (0.56086 Å)
μ:	122.70 cm^{-1}
Diffractometer, scan mode:	STOE IPDS II image plate, ω
$2\theta_{max}$:	39.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5931, 128
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 825
$N(param)_{refined}$:	47
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)	4*e*	0.6938(1)	0.1265(1)	0.0924(1)	0.0806(7)	0.0447(4)	0.0841(7)	–0.0106(4)	0.0148(5)	–0.0103(4)
Br(2)	4*e*	0.58636(9)	0.5803(1)	0.2009(1)	0.0545(6)	0.0812(7)	0.0866(7)	0.0134(4)	0.0159(5)	–0.0190(5)
Br(3)	4*e*	0.7995(1)	0.5781(2)	–0.0234(1)	0.0868(7)	0.0813(7)	0.0588(6)	–0.0148(5)	0.0164(5)	0.0156(5)
Br(4)	4*e*	0.92379(8)	0.4347(1)	0.3092(1)	0.0539(5)	0.0776(6)	0.0640(6)	0.0004(4)	–0.0084(4)	0.0031(5)
Si(1)	4*e*	0.7509(2)	0.4294(3)	0.1443(2)	0.043(1)	0.040(1)	0.046(1)	–0.0007(8)	0.0072(9)	–0.0002(9)

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