Crystal structure of germanium tetrabromide, β-$GeBr_4$, *low temperature modification*

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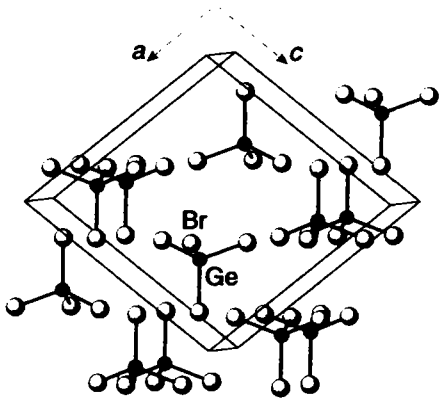

Abstract

Br_4Ge, monoclinic, $P12_1/c1$ (no. 14), a = 10.183(2) Å, b = 6.779(1) Å, c = 10.292(2) Å, β = 102.53(3)°, V = 693.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.061, $wR_{ref}(F^2)$ = 0.138, T = 93 K.

Source of material

Liquid $GeBr_4$ (Chempur, m.p. 26 °C) was sealed in a glass capillary of 0.03 mm diameter under argon. In this capillary colorless transparent single crystals of $GeBr_4$ were grown by repeated careful freezing and melting on a single crystal diffractometer with a temperature control equipment.

Discussion

$GeBr_4$ was obtained for the first time by C. Winkler, the discoverer of the element Ge, through direct reaction of the elements [1]. Large amounts of pure $GeBr_4$ were synthesized by heating Ge powder in a flowing bromine/nitrogen gas stream [2]. However, no detailed structural data of $GeBr_4$ are known so far, in contrast to its homologues GeF_4 [3], $GeCl_4$ [4] and GeI_4 [5]. Temperature dependent X-ray powder diffraction studies show that from room temperature down to approximately –60 °C a cubic α-modification and at lower temperatures a monoclinic β-modification [6] of $GeBr_4$ exist. The cubic α-$GeBr_4$ is isotypic to GeI_4 and adopts the SnI_4 type structure.

The monoclinic β-$GeBr_4$ crystallizes like $GeCl_4$ in the $SnBr_4$ type structure and can be described in terms of a hexagonal close packing of Br atoms in which one eighth of the tetrahedral holes are occupied by Ge atoms. Each Ge atom is surrounded by four crystallographically different Br atoms with Ge—Br distances ranging from 2.264(1) Å to 226.9(1) Å. The Br–Ge–Br angles lie between 109° and 110°, close to the angle in an ideal tetrahedron. Each Br atom is *anti*-cuboctahedrally surrounded by other Br atoms, whereby the three Br—Br distances belonging to a $GeBr_4$ tetrahedron range from 3.69 Å to 3.71 Å, and the remaining nine Br—Br distances are only slightly longer (3.90 Å to 4.14 Å).

Table 1. Data collection and handling.

Crystal:	transparent colorless cube, size 0.3 × 0.3 × 0.3 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	273.27 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS I, ω
$2\theta_{max}$:	63.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7931, 2199
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1817
$N(param)_{refined}$:	47
Program:	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}
Ge	4*e*	0.25184(7)	0.5741(1)	0.63885(8)	0.0160(3)	0.0164(3)	0.0217(4)	0.0001(2)	0.0034(3)	0.0002(2)
Br(1)	4*e*	0.30407(9)	0.4165(1)	0.4628(1)	0.0357(4)	0.0364(4)	0.0267(5)	0.0053(3)	0.0074(3)	–0.0081(3)
Br(2)	4*e*	0.43250(7)	0.5697(1)	0.81234(9)	0.0216(3)	0.0325(4)	0.0284(5)	–0.0005(3)	–0.0032(3)	–0.0013(3)
Br(3)	4*e*	0.07742(8)	0.4173(1)	0.6985(1)	0.0220(3)	0.0381(4)	0.0382(6)	–0.0069(3)	0.0069(3)	0.0094(3)
Br(4)	4*e*	0.19133(8)	0.8899(1)	0.5829(1)	0.0334(4)	0.0190(3)	0.0376(5)	0.0047(3)	0.0052(3)	0.0048(3)

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