

High-Pressure Synthesis and Crystal Structure of the New Orthorhombic Polymorph β -HgB₄O₇

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The new orthorhombic polymorph β -HgB₄O₇ has been synthesized under high-pressure and high-temperature conditions in a Walker-type multianvil apparatus at 7.5 GPa and 600 °C. β -HgB₄O₇ is isotypic to the known ambient pressure phases MB₄O₇ ($M = \text{Sr, Pb, Eu}$) and the high-pressure phase β -CaB₄O₇ crystallizing with two formula units in the space group $Pmn2_1$ with lattice parameters $a = 1065.6(2)$, $b = 438.10(9)$, and $c = 418.72(8)$ pm. The relation of the crystal structure of the high-pressure phase β -HgB₄O₇ to the normal pressure phase α -HgB₄O₇ as well as the relation to the isotypic phases MB₄O₇ ($M = \text{Sr, Pb, Eu}$) and β -CaB₄O₇ are discussed.

Key words: High-Pressure, Mercury, Borates, Crystal Structure

Introduction

In the system HgO-B₂O₃ three mercury oxoborates have been characterized so far. At normal pressure the orthoborate Hg₃(BO₃)₂ and the tetraborate α -HgB₄O₇ were prepared by solid state reaction of the oxides HgO and B₂O₃ at 380 °C [1], whereas the metaborate Hg₄O(BO₂)₆ was synthesized under high-pressure conditions (2.4 to 4.0 GPa) at 700 to 900 °C [2]. For all three compounds, polycrystalline products were obtained and diffraction patterns were published.

During a systematic investigation of the preparation and crystal chemistry of various mercury oxo-compounds, a method for single-crystal growth of Hg₃(BO₃)₂ and α -HgB₄O₇ was established. In this context, the previously reported crystal structure of Hg₃(BO₃)₂, refined from X-ray powder data using the Rietveld method [3], was redetermined with higher precision on the basis of single-crystal data [4], and the structure of α -HgB₄O₇ was reported for the first time [5].

Hg₃(BO₃)₂ is isotypic with its Ca [6], Sr [7], and Eu [8] analogues. The rhombohedral structure (space group $R\bar{3}c$) is composed of isolated BO₃-triangles which share oxygen atoms with the eight-coordinated metal atoms. α -HgB₄O₇ is a member of the isotypic MB₄O₇ family crystallizing in space group $Pbca$ with $M = \text{Mg}$ [9], Mn [10], Co [11], Zn [12], and Cd [13].

This structure type is made up of a framework of corner-sharing BO₃-triangles and BO₄-tetrahedra with the metal atoms situated in the cavities of this arrangement. Hg₄O(BO₂)₆ has a cubic lattice. From a fully indexed X-ray powder diffraction pattern [2], isotypism with zinc metaborate, Zn₄O(BO₂)₆ [14], has been revealed. The crystal structure of the latter (space group $I\bar{4}3m$) consists of a three-dimensional framework of BO₄-tetrahedra. The zinc atom is surrounded by three oxygen atoms of the metaborate units and one free oxygen atom forming a slightly distorted ZnO₄-tetrahedron.

In this paper we report about the results of phase formation experiments in the system HgO-B₂O₃ under high-pressure and high-temperature conditions, which led to single-crystal growth of a new HgB₄O₇ polymorph. We have named the known polymorph obtained at normal pressure ' α -HgB₄O₇' and the new polymorph obtained under high-pressure conditions presented here ' β -HgB₄O₇'.

Experimental Section

According to eq. (1), the starting materials for the synthesis of orthorhombic β -HgB₄O₇ was a 1:2 molar mixture of HgO [Merck, p. A.] and B₂O₃ [Strem Chemicals, Newburyport, U.S.A., 99.9%].

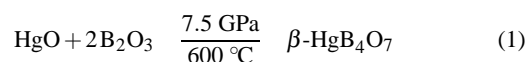


Table 1. Crystal data and structure refinement for β -HgB₄O₇.

Empirical formula	HgB ₄ O ₇
Molar mass [g·mol ⁻¹]	355.83
Crystal system	orthorhombic
Space group	<i>Pmmn</i> ₂₁ (Nr. 31)
Single crystal diffractometer	Enraf-Nonius Kappa CCD
Radiation	Mo-K α (λ = 71.073 pm)
Single crystal data	
<i>a</i> [pm]	1065.6(2)
<i>b</i> [pm]	438.10(9)
<i>c</i> [pm]	418.72(8)
Volume [nm ³]	0.19548(7)
Formula units per cell	<i>Z</i> = 2
Temperature [K]	293(2)
Calculated density [g·cm ³]	6.045
Crystal size [mm ³]	0.06 × 0.03 × 0.02
Detector distance [mm]	40.0
Exposure time per degree [sec]	110
Absorption coefficient [mm ⁻¹]	39.34
<i>F</i> (000)	312
θ Range [°]	4.0° to 37.0°
Range in <i>hkl</i>	±17, ±7, ±7
Scan type	ϕ/ω
Total no. reflections	3773
Independent reflections	1016 (<i>R</i> _{int} = 0.0346)
Reflections with <i>I</i> > 2 σ (<i>I</i>)	1010 (<i>R</i> _{σ} = 0.0402)
Data / parameters	1016 / 60
Absorption correction	ψ -scans
Goodness-of-fit (<i>F</i> ²)	0.917
Twin-fraction	0.201(12)
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0152 <i>wR</i> 2 = 0.0329
<i>R</i> Indices (all data)	<i>R</i> 1 = 0.0154 <i>wR</i> 2 = 0.0329
Extinction coefficient	0.0181(9)
Largest difference peak, deepest hole [e·Å ⁻³]	1.68 / -1.43

The starting materials were compressed and heated *via* a multianvil assembly. Details of the construction of the assembly can be found in references [15–18]. For the synthesis of β -HgB₄O₇, the 18/11 assembly was compressed within 3 h to 7.5 GPa and heated to 600 °C in the following 10 min. After holding this temperature for 15 min, the sample was cooled down within another 20 min. After decompression, the recovered experimental octahedron was broken apart, and the sample carefully separated from the surrounding boron nitride. β -HgB₄O₇ was obtained as a crystalline product in a mixture with metallic mercury droplets, (yield: about 40 mg per run). The substance is air- and humidity-resistant and crystallizes as thin, pale-yellow plates.

Crystal structure analysis

Small single-crystals of β -HgB₄O₇ were isolated by mechanical fragmentation and examined by Buerger precession photographs. Single-crystal intensity data were collected at room temperature from a regularly shaped pale-yellow crys-

Table 2. Atomic coordinates and isotropic equivalent displacement parameters *U*_{eq} [Å²] for β -HgB₄O₇ (space group *Pmmn*₂₁). *U*_{eq} is defined as one third of the trace of the orthogonalized *U*_{*ij*} tensor.

Atom	Wyckoff Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Hg1	2 <i>a</i>	0	0.18015(2)	0.10333(8)	0.00756(5)
B1	4 <i>b</i>	0.8796(3)	0.6738(5)	0.590(3)	0.0043(8)
B2	4 <i>b</i>	0.7513(3)	0.8258(5)	0.070(2)	0.005(2)
O1	4 <i>b</i>	0.7762(2)	0.8637(5)	0.4272(6)	0.0044(3)
O2	4 <i>b</i>	0.8615(2)	0.3518(4)	0.5155(6)	0.0059(4)
O3	4 <i>b</i>	0.8667(2)	0.7275(6)	0.9322(6)	0.0060(3)
O4	2 <i>a</i>	0	0.7770(7)	0.4809(8)	0.0057(5)

tal (plate) by use of an Enraf-Nonius Kappa CCD, equipped with a rotating anode [Mo-K α radiation (71.073 pm)]. A psi-scan based absorption correction (XPREP [19]) was applied to the intensity data. All relevant information concerning the data collection is listed in Table 1. According to the systematic extinctions *h*0*l* with *h* + *l* ≠ 2*n*, *h*00 with *h* ≠ 2*n*, and 0*k*0 with *k* ≠ 2*n*, the space groups *Pmmn*₂₁ (No. 31) and *Pmmn* (No. 59) were derived. The non-centrosymmetric group was found to be correct during the structure refinement. This was confirmed using the ADDSYM-routine of the program PLATON [20]. The starting positional parameters were deduced from an automatic interpretation of direct methods with SHELXS-97 [21]. The structure was refined using the TWIN-Command due to twinning by inversion. The resulting twin fraction is listed in Table 1. The structure of β -HgB₄O₇ was refined with anisotropic displacement parameters for all atoms with SHELXL-97 [22] (full-matrix least-squares on *F*²). Final difference Fourier synthesis revealed no significant residual peaks in the refinement (see Table 1). Details of the single-crystal structure measurement are shown in Table 1. Additionally, the positional parameters (Table 2), anisotropic displacement parameters (Table 3), interatomic distances (Table 4), and angles (Table 5) are listed. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-415347.

Results and Discussion

The high-pressure/high-temperature investigations in the system HgO-B₂O₃ (1:1 molar mixture) performed by Chang & Margrave at 2.4 to 3.2 GPa and at temperatures ranging from 700 to 800 °C for 40 hours [2] led to a yellow product, which was then heated in a H₂ stream at 250 °C for five hours to give a black mercury metaborate Hg₄O(BO₂)₆. Alternatively, the latter compound was obtained after a reaction of a 2:1 molar mixture of purified BN powder and HgO

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg1	0.00726(7)	0.00838(6)	0.00705(7)	0.0001(2)	0	0
B1	0.004(2)	0.0053(9)	0.004(2)	−0.001(2)	−0.001(2)	−0.0003(6)
B2	0.004(2)	0.004(2)	0.006(4)	−0.0005(8)	0.000(2)	0.0006(6)
O1	0.0054(8)	0.0041(7)	0.0037(9)	−0.0009(6)	−0.0006(7)	0.0010(6)
O2	0.0055(9)	0.0043(7)	0.0078(9)	−0.0005(6)	0.0008(7)	−0.0015(6)
O3	0.0042(9)	0.0090(8)	0.0048(9)	−0.0008(7)	−0.0001(7)	0.0008(7)
O4	0.003(2)	0.007(2)	0.007(2)	0.002(2)	0	0

Table 3. Anisotropic displacement parameters [\AA^2] for β -HgB₄O₇ (space group $Pmn2_1$).Table 4. Interatomic distances [pm] calculated with the single crystal lattice parameters in β -HgB₄O₇ (standard deviations in parentheses).

Hg1-O4a	237.1(3)	B1-O4	143.6(6)	O1-B2a	151.5(4)
Hg1-O2a	239.2(3) 2×	B1-O2	145.8(4)	O1-B2b	152.7(8)
Hg1-O3a	254.3(2) 2×	B1-O3	146(2)	O1-B1	154.0(7)
Hg1-O3b	287.8(2) 2×	B1-O1	154.0(7)		Ø152.7
Hg1-O2b	296.7(3) 2×		Ø147.4		
Hg1-O1a	304.0(2) 2×	B2-O3	142.6(5)		
Hg1-O4b	305.5(3)	B2-O2	145.0(4)		
Hg1-O1b	307.4(2) 2×	B2-O1a	151.5(4)		
Hg1-O4c	314.8(4)	B2-O1b	152.7(8)		
	Ø282.4		Ø148.0		

Table 5. Interatomic angles [°] calculated with the single crystal lattice parameters in β -HgB₄O₇ (standard deviations in parentheses).

O3-B1-O1	106.3(4)	O2-B2-O1a	105.0(3)	B2a-O1-B1	116.6(5)
O4-B1-O1	109.1(7)	O3-B2-O1a	106.1(4)	B2a-O1-B2b	116.8(3)
O2-B1-O1	109.5(6)	O3-B2-O1b	106.2(3)	B2b-O1-B1	120.0(5)
O4-B1-O3	110.3(6)	O1a-B2-O1b	108.9(3)		Ø117.8
O4-B1-O2	110.7(5)	O2-B2-O1b	111.0(4)		
O3-B1-O2	110.8(7)	O3-B2-O2	119.2(4)		
	Ø109.5		Ø109.4		

at 4 GPa and 940 °C in a BN-container followed by quenching. For the present investigations, using 1:2 molar mixtures of HgO and B₂O₃, the pressure was increased to 7.5 GPa and the temperature maintained at 600 °C. During these experiments we were not able to observe the black mercury metaborate Hg₄O(BO₂)₆.

The crystal structure of the orthorhombic ambient-pressure modification α -HgB₄O₇ is characterized by an anionic framework structure built up by two crystallographically independent BO₃-triangles and two BO₄-tetrahedra, which form [B₄O₇]^{2−} units by sharing common vertices. The metal atoms are situated in the cavities of this arrangement (Fig. 1).

According to the Pressure-Coordination rule [23], the high-pressure / high-temperature phase β -HgB₄O₇ consists exclusively of corner-sharing BO₄-tetrahedra and is isotypic to the known ambient pressure phases SrB₄O₇ [24–26], PbB₄O₇ [25, 27], EuB₄O₇ [28], and the high-pressure phase β -CaB₄O₇ [29]. Table 6 shows the lattice parameters of the isotypic compounds.

Table 6. Cell dimensions of the isotypic tetraborates MB₄O₇ (M = Hg, Ca, Sr, Eu, Pb) in the orthorhombic space group $Pmn2_1$.

	a [pm]	b [pm]	c [pm]	V [nm ³]
β -HgB ₄ O ₇ [this work]	1065.6(2)	438.10(9)	418.72(8)	0.195(1)
β -CaB ₄ O ₇ [29]	1059.00(4)	437.20(2)	419.49(2)	0.194(1)
SrB ₄ O ₇ [25]	1070.6(10)	443.1(4)	423.7(4)	0.201(1)
SrB ₄ O ₇ [26]	1072.4(2)	444.7(3)	423.91(11)	0.202(1)
EuB ₄ O ₇ [28]	1073.1(1)	443.5(1)	424.0(1)	0.202(1)
PbB ₄ O ₇ [25]	1084.0(10)	445.7(4)	424.4(4)	0.206(1)
PbB ₄ O ₇ [27]	1086.0(3)	446.3(3)	425.1(2)	0.205(1)

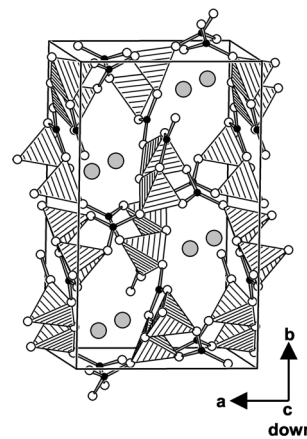
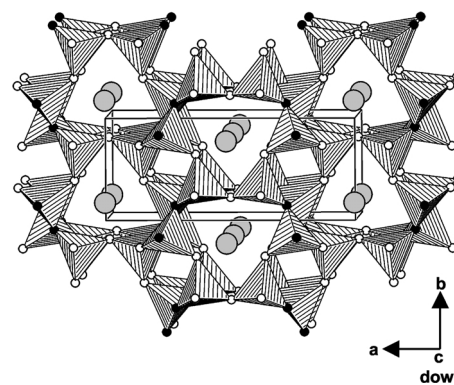
Fig. 1. Crystal structure of α -HgB₄O₇, view approximately along [001]. The mercury cations are shown as large grey spheres, oxygen atoms as white spheres, and boron as black spheres. BO₄-tetrahedra are given in the polyhedral representation.Fig. 2. Crystal structure of β -HgB₄O₇, view along [001]. The mercury cations are shown as large grey spheres, O^[2] coordinated oxygen atoms as white spheres, and O^[3] coordinated oxygen atoms as black spheres.

Table 7. Cycle-class sequence of β -HgB₄O₇ [38–41].

Ring size n	3	4	5	6	7	8	9	10
β -HgB ₄ O ₇	4	4	8	20	44	124	336	928

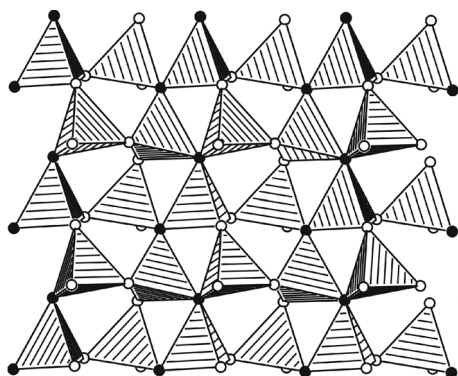
Fig. 3. View of the bc -plane in β -HgB₄O₇ only built up by BO₄-tetrahedra with a large fraction of three-coordinate oxygen atoms O^[3] (black spheres).

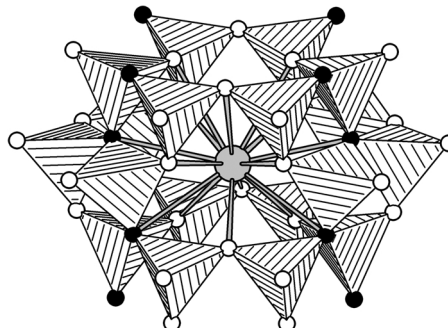
Fig. 2 gives a view of the crystal structure of β -HgB₄O₇ which exhibits a network of corner-sharing BO₄-tetrahedra forming channels along $[00\bar{1}]$ built up from four- and six-membered rings. The mercury cations lie in the six-membered ring channels, while the four-membered ring channels remain empty. Fig. 3 gives a view of the highly condensed layers along $[100]$ partially built up by three coordinate oxygen atoms O^[3] (black spheres), which are also found in a few other oxoborates, *e.g.* β -ZnB₄O₇ [30], β -RE(BO₂)₃ [31,32], γ -RE(BO₂)₃ [33], and minerals like *tunnelite* (SrB₆O₉(OH)₂ · 3 H₂O) [34], *strontioginorite* ((Sr, Ca)₂B₁₄O₂₀(OH)₆ · 5 H₂O) [35], *aristaraitite* (Na₂Mg[B₆O₈(OH)₄]₂ · 4 H₂O) [36], and the high-pressure modification of B₂O₃ [37] itself.

To examine the ring sizes in the structure topologically, we calculated the cycle class sequence for β -HgB₄O₇, specifying the relative abundance of B_{*n*}O_{*n*} ring sizes (for $n = 3 - 10$) per unit cell [38–41]. The results, which are identical with the results of the isotopic MB₄O₇ ($M = \text{Ca, Sr, Eu, Pb}$) phases, are given in Table 7.

An examination of the B-O distances in β -HgB₄O₇ (Table 4) shows variations between 143 and 154 pm. The average value is 147.7 pm which corresponds well to the known average value of 147.6 pm for oxoborates [42,43]. As expected, the bonds to three-coordinated oxygen atoms O^[3] are significantly longer (152–154 pm, with a mean value of 152.7 pm) than the average. The corresponding average B-O^[3] dis-

Table 8. Charge distribution in β -HgB₄O₇ calculated with the bond-length/bond-strength concept (ΣV) [44, 45] and the CHARDI concept (ΣQ) [46].

	Hg	B1	B2	O1	O2	O3	O4
ΣV	+1.77	+3.06	+3.01	-2.06	-1.95	-1.92	-2.07
ΣQ	+1.95	+2.95	+3.07	-1.83	-2.05	-2.05	-2.14

Fig. 4. Coordination of Hg²⁺ (grey sphere) in the crystal structure of β -HgB₄O₇.

tances in the isotopic compounds are 155.0 (SrB₄O₇), 155.4 (PbB₄O₇), 154.4 (EuB₄O₇), and 153.7 pm (β -CaB₄O₇). The O-B-O angles in the two crystallographically independent BO₄-tetrahedra range from 105° to 119° (Table 5) with an average value of 109.4°. The O-B-O angles in the OB₃-group are 116.6(5)°, 116.8(3)°, and 120.0(5)° with a mean value of 117.8° (Table 5).

Inside α -HgB₄O₇ the Hg²⁺ cations are surrounded by seven oxygen atoms in a [4+3] coordination polyhedron ($d(\text{Hg-O}) = 222 - 299$ pm), whereas in the high-pressure polymorph β -HgB₄O₇ the coordination number is increased to 15 (Fig. 4). The Hg-O distances vary between 237 and 315 pm with an average value of 282 pm (Table 3). Noteworthy, the isotopic high-pressure phase β -CaB₄O₇ exhibits the same high coordination number for the Ca²⁺ cations within a range of 242–316 pm, but with a much lower average value of 265 pm.

For further clarification, we calculated bond-valence sums for β -HgB₄O₇ with the bond-length/bond-strength [44,45] and CHARDI (**Charge Distribution in Solids**) concept (Table 8) [46]. The formal ionic charges of the atoms, acquired by the X-ray structure analysis, are in agreement within the limits of the concepts. Additionally, we calculated the MAPLE value (**Madelung Part of Lattice Energy**) [47–49] for β -HgB₄O₇ to compare it with the MAPLE value from the binary component HgO and the high-pressure modification

B₂O₃-II [1·HgO (4,050 kJ mol⁻¹) [50] +2·B₂O₃-II (21,938 kJ mol⁻¹) [37]. The deviation of the calculated value 47,937 kJ mol⁻¹ comes to 0.02% in comparison to the MAPLE value obtained from the binary oxides (47,926 kJ mol⁻¹).

As the isotypic SrB₄O₇ (SBO) is a potential NLO material with excellent mechanical and optical properties including a high powder SHG coefficient, high optical damage threshold, and high hardness [51], similar investigations on the physical properties of β -HgB₄O₇ are planned.

Conclusions

In this paper, we have described the synthesis of the new mercury(II) oxoborate β -HgB₄O₇ via multi-anvil high-pressure techniques from HgO and B₂O₃. The structure was solved from single-crystal data. Following the Pressure-Coordination rule [23], the coordination

numbers of boron, mercury, and part of the oxygen atoms are increased in comparison to the α -modification. Specifically all boron atoms are coordinated tetrahedrally and the mercury atoms have the coordination number 15 (in contrast to seven in α -HgB₄O₇). A comparison of the calculated densities of both modifications shows that the high-pressure modification β -HgB₄O₇ is about 34% more dense (6.045 g/cm³) than the normal-pressure modification α -HgB₄O₇ (4.520 g/cm³).

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