High-Pressure Synthesis and Characterization of New Actinide Borates, \( \text{AnB}_4\text{O}_8 \) (An = Th, U)

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Abstract: New actinide borates \( \text{ThB}_4\text{O}_8 \) and \( \text{UB}_4\text{O}_8 \) were synthesized under high-pressure, high-temperature conditions (5.5 GPa/1100°C for thorium borate, 10.5 GPa/1100°C for the isotopic uranium borate) in a Walker-type multianvil apparatus from their corresponding actinide oxide and boron oxide. The crystal structure was determined on basis of single-crystal X-ray diffraction data that were collected at room temperature. Both compounds crystallized in the monoclinic space group C2/c (Z = 4). Lattice parameters for \( \text{ThB}_4\text{O}_8 \): \( a = 1611.3(3) \), \( b = 419.86(8) \), \( c = 730.6(2) \) pm; \( \beta = 114.70(3) \); \( V = 449.0(2) \) Å\(^3\); \( R_1 = 0.0255 \), \( wR_2 = 0.0653 \) (all data). Lattice parameters for \( \text{UB}_4\text{O}_8 \): \( a = 1589.7(3) \), \( b = 422.14(8) \), \( c = 723.4(2) \) pm; \( \beta = 114.13(3) \); \( V = 443.1(2) \) Å\(^3\); \( R_1 = 0.0227 \), \( wR_2 = 0.0372 \) (all data).

Keywords: actinides • borates • density functional theory • high-pressure chemistry • Raman spectroscopy

Introduction

Over the last decade, our research into the high-pressure chemistry of borates has led to the synthesis of several new compounds with fascinating structures, owing to the efficient use of the multianvil technique.[1] For example, we discovered the rare-earth borate \( \text{Dy}_4\text{B}_6\text{O}_{15} \),[2] which was the first borate that exhibited edge-sharing \( \text{BO}_4 \) tetrahedra. Later on, HP-NiB\(_4\)O\(_8\) was synthesized,[3] which was the first borate in which all of the \( \text{[BO}_4\text{]}^2- \) tetrahedra showed a linkage through a common edge to a second tetrahedron, as well as HP-KB\(_5\)O\(_{13}\),[4] which simultaneously contained all three possible conjunction modes, that is, corner-sharing \( \text{BO}_4 \) groups, corner-sharing \( \text{BO}_3 \) units, and edge-sharing \( \text{BO}_4 \) tetrahedra.

Following our interest in the high-pressure chemistry of alkali, alkaline-earth, transition-metal, and rare-earth borates, we decided to broaden our research activities into the field of actinide borates. This field of structural chemistry is highly topical, as reflected by the considerable number of new actinide borates with interesting structures and properties that have been synthesized within the last few years.[5–11] A closer look at the existing compounds with \( \text{An-B-O} \) ternary systems only showed a few phases. Just six compounds with the actinide cations thorium, uranium, and americium are known, namely: \( \text{Th} (\text{B}_2\text{O}_5) \),[12] \( \text{ThB}_6\text{O}_{21} \),[13] \( \text{UB}_4\text{O}_8 \),[14] \( \text{U} (\text{BO}_3) \),[14] \( \text{AmB}_6\text{O}_{18} \),[15] and \( \text{AmBO}_3 \).[15] To the best of our knowledge, no ternary actinide borates have been synthesized under high-pressure conditions so far. However, recent studies on the chemistry of high-pressure alkaline uranyl borates demonstrated the feasibility of this approach.[10] Historically, Berzelius has already reported the possible presence of a thorium borate in a mineral that was found in Norway in 1824.[16] Furthermore, there are several existing hydrated actinide borates of the actinides thorium, uranium, neptunium, plutonium, and americium. Research into actinide borates is of urgent importance in the question of the storage of nuclear waste. Owing to the high stability and insolubility of borates, they are of interest for the immobilization of nuclear waste. In this context, borates in which the metal cation is in the oxidation state 4+ have a special position, because the cation (especially cerium) can be regarded as a “dummy” for plutonium, owing to their comparable ionic radii. Herein, we describe the syntheses, single-
crystal structural determinations, and Raman spectroscopic investigations of $\text{Ar}_n\text{B}_4\text{O}_8$ ($\text{Ar} = \text{Th}, \text{U}$), as well as quantum-chemical calculations of the harmonic vibrational frequencies of $\text{ThB}_4\text{O}_8$.

Results and Discussion

Synthesis and crystal-structure analysis: The compounds $\text{ThB}_4\text{O}_8$ and $\text{UB}_4\text{O}_8$ were synthesized from their corresponding actinide oxides and $\text{B}_2\text{O}_3$, under high-pressure, high-temperature conditions ($5.5 \text{ GPa}$ and $1100^\circ \text{C}$ for $\text{ThB}_4\text{O}_8$; $10.5 \text{ GPa}$ and $1100^\circ \text{C}$ for $\text{UB}_4\text{O}_8$) in a 1000 ton multianvil press that was fitted with a Walker-type module. A detailed description of the syntheses is provided in the Experimental Section. Figure 1 shows the diffraction patterns of $\text{ThB}_4\text{O}_8$ (top) and $\text{UB}_4\text{O}_8$ (bottom), as well as reflections of the corresponding actinide oxide (marked with lines) and reflections of another still-unknown side product (marked with circles). The single-crystal intensity data were collected at room temperature on a Nonius Kappa-CCD diffractometer with graphite-monochromated Mo $K_{\alpha}$ radiation ($\lambda = 70.173 \text{ pm}$). Tables 1, Table 2, and Table 3 list the details of the data collection and evaluation, as well as the positional parameters of the refinement. Interatomic distances and interatomic angles are listed in Table 4 and Table 5.

| Table 1. Crystal data and structure refinement of $\text{AnB}_4\text{O}_8$ ($\text{An} = \text{Th, U};$ space group $\text{C2/c}$); standard deviations are given in parentheses. |
|-----------------|-----------------|-----------------|
| Empirical formula | $\text{ThB}_4\text{O}_8$ | $\text{UB}_4\text{O}_8$ |
| molar mass [g mol$^{-1}$] | 403.28 | 409.27 |
| crystal system | monoclinic | monoclinic |
| space group | $\text{C2/c (No. 15)}$ | $\text{C2/c (No. 15)}$ |

| Single-crystal data |
|---------------------|
| single-crystal diffractometer | Enraf-Nonius Kappa CD | Enraf-Nonius Kappa CD |
| radiation | $\text{MoK}_{\alpha}$ ($\lambda = 70.173 \text{ pm}$) | $\text{MoK}_{\alpha}$ ($\lambda = 70.173 \text{ pm}$) |
| $a$ [Å] | 1161.3(5) | 1590.7(3) |
| $b$ [Å] | 419.86(8) | 422.14(8) |
| $c$ [Å] | 730.6(2) | 723.4(2) |
| $\beta$ [°] | 114.70(3) | 114.13(3) |
| $V$ [Å$^3$] | 449.0(2) | 443.1(2) |
| formula units per cell | 4 | 4 |
| $\rho_{\text{calc}}$ [g cm$^{-3}$] | 5.97 | 6.14 |
| crystal size [mm$^3$] | 0.08/C1480.15/C1480.05 | 0.02/C1480.02/C1480.01 |
| $\theta$ range [°] | 2.8–30.0 | 2.8–30.0 |
| range in $hkl$ | $\pm 2$, $\pm 5$, $\pm 10$ | $\pm 2$, $\pm 5$, $\pm 10$ |
| independent reflections | 655 | 640 |
| $R_{\text{int}}$ | 0.0652 | 0.0365 |
| $wR_{\text{int}}$ | 0.0653 | 0.0372 |
| $R_{\text{wp}}$ | 0.0653 | 0.0372 |
| $R_{\text{min}}$ | 5.925/–1.990 | 1.512/–1.191 |

Table 2. Atomic coordinates, Wyckoff positions, and equivalent isotropic displacement parameters ($U_{\text{eq}}$ [Å$^2$]) of $\text{AnB}_4\text{O}_8$ ($\text{An} = \text{Th, U};$ space group $\text{C2/c}$); standard deviations are given in parentheses.$^a$

| Atom | Wyckoff position | $x$ | $y$ | $z$ | $U_{\text{eq}}$ |
|------|-----------------|-----|-----|-----|-------------|
| Th1  | 4e              | 0   | 0.19137(4) | 0.25 | 0.0035(2) |
| O1   | 8f              | 0.2163(3) | 0.1546(2) | 0.1675(7) | 0.0033(7) |
| O2   | 8f              | 0.3428(3) | 0.152(2) | 0.4908(7) | 0.0042(8) |
| O3   | 8f              | 0.3678(4) | 0.3026(7) | 0.2043(8) | 0.0044(9) |
| O4   | 8f              | 0.4480(3) | 0.261(2) | 0.0129(7) | 0.0057(8) |
| B1   | 8f              | 0.3038(5) | 0.304(2) | 0.298(2) | 0.003(2) |
| B2   | 8f              | 0.3584(6) | 0.189(2) | 0.008(2) | 0.004(2) |
| U1   | 4e              | 0   | 0.16776(6) | 0.25 | 0.0048(2) |
| O1   | 8f              | 0.2163(2) | 0.1544(8) | 0.1679(5) | 0.0041(6) |
| O2   | 8f              | 0.3452(2) | 0.1510(9) | 0.4292(5) | 0.0050(6) |
| O3   | 8f              | 0.3688(2) | 0.3048(8) | 0.2012(5) | 0.0033(6) |
| O4   | 8f              | 0.4484(2) | 0.2652(8) | 0.0038(6) | 0.0066(7) |
| B1   | 8f              | 0.3049(4) | 0.304(2) | 0.296(1) | 0.004(2) |
| B2   | 8f              | 0.3603(4) | 0.187(2) | 0.0062(8) | 0.006(2) |

$^a$ $U_{\text{eq}}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

![Figure 1. Top: Experimental and theoretical powder X-ray diffraction (PXRD) patterns of $\text{ThB}_4\text{O}_8$ (space group $\text{C2/c}$); the reflections of an unknown phase are indicated by circles. The reflections of $\text{UB}_4\text{O}_8$ are marked with lines. Bottom: Experimental and theoretical PXRD patterns of $\text{UB}_4\text{O}_8$ (space group $\text{C2/c}$); reflections of an unknown phase are indicated by circles. The reflections of $\text{UB}_4\text{O}_8$ are marked with lines. The theoretical PXRD patterns are based on the single-crystal diffraction data.](image-url)
Crystal structures: The new isotypic actinide borates ThB₄O₈ and UB₄O₈ crystallize in the monoclinic space group C₂/c, with four formula units per unit cell. Lattice parameters for ThB₄O₈: a = 1611.3(3), b = 419.86(8), c = 723.4(2) pm; β = 114.70(3). Lattice parameters for UB₄O₈: a = 1589.7(3), b = 422.14(8), c = 742.3(4) pm; β = 114.51(3). Figure 2 shows the crystal structure of AnB₄O₈ (An = Th, U) along the b axis, which is comprised of layers of corner-sharing [BO₄]⁻ tetrahedra that are separated by layers of actinide cations. As in most high-pressure boranes, such as RE₂B₆O₁₈ (RE = Dy, Ho[24,25]), α-RE₂B₆O₁₈ (RE = Sm–Tb, Ho[26,27]), and the rare-earth meta-borates β-RE₂B₆O₁₈, (RE = Ce, La[28,29]), this structure is exclusively built up from tetrahedral borate groups. Figure 3 shows the composition of the borate layers. A closer look at the layers exhibits infinite chains along the b axis, which consist of [B₂O₄]⁻ tetrahedra that are connected through one common oxygen atom, O₃ (Figure 3, large spheres). These chains of [B₂O₄]⁻ tetrahedra and antiparallel-oriented chains alternate along the c axis and are linked together through the common oxygen atoms of the [B₁O₄]⁻ and [B₂O₄]⁻ tetrahedra (O₁, O₂, and O₃). Figure 4 shows the layers along the a, b, and c directions. The BO₄ groups form a central “dreier ring”, a “vierer ring”, and different “sechser rings”. [24] The corners of the “dreier rings” are formed from two O₃ atoms and one O₂ atom that are located along the b axis. The “vierer rings” are composed of two [B₁O₄]⁻ groups and two [B₂O₄]⁻ groups that are linked together through the O₂ and O₃ atoms; these “vierer rings” form empty channels along the b axis, as shown in Figure 4. These rings can be represented by a unit that is comprised of five [B₂O₄]⁻ groups and four
[\text{BIO}_4]^5^-\text{ groups, as shown in Figure 5. The crystal structure of } AnB_4O_8 (An = Th, U) contains four crystallographically distinguishable oxygen atoms: Oxygen atoms O1 and O2 are twofold-coordinated by boron atoms. Oxygen atom O4 is a terminal oxygen atom that is orientated towards the cation layer: a view along the c axis shows the terminal O4 oxygen atoms of the borate layers. The O3 oxygen atom is exceptional, in that it is a threefold-coordinated oxygen atom. Figure 6 shows the [BO_4]^5^- unit, which is comprised of two [B_2O_4]^6- tetrahedra and one [BIO_4]^5^- tetrahedron. The B-O3B angles sum up to 360°, as expected from the trigonal-planar geometry. The two crystallographically distinguishable boron atoms in the actinide borates ThB_4O_8 and UB_4O_8 are tetrahedrally coordinated by four oxygen atoms. The mean values of the boron–oxygen distances inside the tetrahedra vary between 144.3(8) (B1–O2) and 152.1(6) pm (B2–O1), with a mean value of 147.2 pm for ThB_4O_8, and between 144.0(6) (B1–O3) and 152.1(7) pm (B2–O1), with a mean value of 147.2 pm for UB_4O_8. These values agree well with the known average value for the B–O distance in [BO_4]^5^- groups (147.6 pm).\textsuperscript{25-27} The oxygen–boron–oxygen angles in the tetrahedral [BO_4]^5^- groups in \textit{AnB_4O_8} (An = Th, U) are listed in Table 5 and correspond well with the expected angles of tetrahedrally coordinated groups. Figure 7 shows the coordination sphere of the actinide cations in AnB_4O_8 (An = Th, U). Ten oxygen atoms coordinate to both the thorium and uranium cations. Owing to the two longest actinide–oxygen distances (Th1–O4'' = 285.9(5) pm (×2), U1–O4'' = 300.2(4) pm (×2)) and the large difference between the third-longest An–O distances (Th1–O3 = 259.7(5) pm, U1–O3 = 252.2(4) pm), the description as an 8+2 coordination mode for the Th1 and U1 atoms is reasonable. These coordination spheres result in thorium–oxygen distances of between 240.3(5) and
were calculated for comparison with the MAPLE values as

\[
\text{An} \text{ThB}_4\text{O}_8, \quad \text{and between 231.4(4) and 300.2(4) pm, with 285.9(5) pm, with a mean value of 255.9 pm for Th1 in Figure 7. Coordination spheres of the actinide ions in ThB}_4\text{O}_8 \text{.}
\]

This divergence emerges from the higher ionic radius of Th\(^{4+}\). As expected, the \(\text{An} \text{O} - \text{An} \text{U} \) (An = U, Th) distances in ThB\(_4\)O\(_8\) are larger, because of the larger ionic radius of Th\(^{4+}\). A comparison of the tetrahedral borate groups shows no greater deviations in the bond lengths and angles. In addition, the bond-valence sums for all atoms of ThB\(_4\)O\(_8\) and UB\(_4\)O\(_8\) were calculated by using the bond-length/bond-strength (\(\Sigma V\))[28,29] and CHARDI concepts (charge distribution in solids, \(\Sigma Q\))[30]. The results of these calculations are listed in Table 6. All of the calculated values correspond well with the expected values of the formal ionic charges.

Owing to the fact that the structure type of AnB\(_4\)O\(_8\) (An = Th, U) is exclusively built up from BO\(_4\) tetrahedra, one could imagine a structural relationship with the structures of well-known uranium and thorium silicates. However, both of the ThB\(_4\)O\(_8\) and UB\(_4\)O\(_8\) structures exhibit three-fold-coordinated oxygen atoms, a structural motif that is unknown in the chemistry of silicates. Therefore, there is no visible direct structural relationship.

MAPLE values (madelung part of lattice energy)[31–33] were calculated for comparison with the MAPLE values as obtained from the summation of the binary actinide oxides, ThO\(_2\)[34] and UO\(_2\)[35] and with that of the high-pressure modification B\(_2\)O\(_3\)-II.[36] Values of 55317 and 55569 kJ mol\(^{-1}\) were obtained for ThB\(_4\)O\(_8\) and UB\(_4\)O\(_8\), respectively, in comparison with 55421 kJ mol\(^{-1}\) (deviation = 0.2%) and 55721 kJ mol\(^{-1}\) (deviation = 0.3%) for the corresponding binary oxides (ThO\(_2\) (11544 kJ mol\(^{-1}\))+2 B\(_2\)O\(_3\)-II (2 \(\times\) 21938 kJ mol\(^{-1}\)); UO\(_2\) (11544 kJ mol\(^{-1}\))+2 \(\times\) B\(_2\)O\(_3\)-II (2 \(\times\) 21938 kJ mol\(^{-1}\))).

Vibrational spectroscopy: Figure 8 shows the Raman spectra of single crystals of the actinide borates ThB\(_4\)O\(_8\) and UB\(_4\)O\(_8\) within the range 100–1500 cm\(^{-1}\). No OH or water bands could be detected within the range 3000–3600 cm\(^{-1}\). Bands at about 900 cm\(^{-1}\) in borate compounds are usually assigned to the stretching modes of the \([\text{BO}_4]^{5-}\) groups. However, trigonal \([\text{BO}_3]^{3-}\) groups are expected at wavenumbers above 1150 cm\(^{-1}\).[37–40] No bands are observed above 1200 cm\(^{-1}\), as expected from the crystal structure due to the absence of trigonal \([\text{BO}_3]^{3-}\) groups. Bands at smaller wavenumbers than 500 cm\(^{-1}\) can be assigned to \(\text{An} - \text{O} \) (An = Th, U) bonds, to lower-wavenumber-shifted bending and stretching modes of tetrahedral \([\text{BO}_4]^{5-}\) groups, and to lattice vibrations. The large variation in \(\text{B} - \text{O} \) distances and in the linkage of the tetrahedral \([\text{BO}_4]^{5-}\) groups led to various experimentally observed modes.

FTIR-ATR measurements of the products (mixture of the actinide borate, unreacted actinide oxide, and a still-unknown phase) were performed to exclude water or hydrated borates. The spectra showed no bands within the region 3000–4000 cm\(^{-1}\).

Quantum-mechanical calculations of the harmonic vibrational frequencies: To validate the quality of the basis sets and the functional, a geometry optimization of ThB\(_4\)O\(_8\) was performed. Starting from the single-crystal structure, the geometry optimization yielded deviations in the lattice parameters and the atomic positions of less than 1 %. The calculations of the harmonic vibrational frequencies were per-
formed on the optimized geometry. The calculated Raman bands fit quite well with the experimental spectrum of single crystals of ThB$_4$O$_8$. The low deviations were obtained from the approximations in the DFT method and the calculations on just one unit cell. Calculations of larger systems (super cells of ThB$_4$O$_8$) were not possible. Moreover, the calculation did not consider the temperature (297 K for the experiment) and the addition of two Gaussian peaks in the experimental spectrum led to a shift of the maxima. Table 7 lists the modes above 600 cm$^{-1}$. These bands can be assigned to boron–oxygen bending or stretching modes. However, in the assignment, the highly condensed boron–oxygen layers must be considered. An exclusive stretching or bending motion inside a tetrahedral [BO$_4$]$^{3-}$ group was not possible. Each stretching or bending motion induced motions of neighboring atoms. As expected, the calculation yielded no vibrational modes above 1200 cm$^{-1}$. The calculation of the theoretical modes exclusively showed the impossibility of the assignment of one bond to a particular stretching or bending mode inside the [BO$_4$]$^{3-}$ group. For example, the two modes at 1179 and 1182 cm$^{-1}$ derive their origin from a various number of vibrational modes in the boron–oxygen layer.

**Table 7.** Comparison and assignment of selected theoretical and experimental boron–oxygen bands in the Raman spectra of ThB$_4$O$_8$.[a]

| Theoretical band [cm$^{-1}$] | Experimental band [cm$^{-1}$] | Assignment |
|-----------------------------|------------------------------|------------|
| 1179, 1182                  | 1183                         | b(B$_1$-O$_3$-B$_2$), b(O$_1$-B$_1$-O$_2$), b(O$_2$-B$_2$-O$_1$), b(B$_2$-O$_2$-O$_3$), s(B$_2$-O$_4$) |
| 1056                        | 1077                         | s(B$_2$-O$_2$) |
| 1029                        | 1028                         | s(B$_1$-O$_2$) |
| 1010, 1013                  | 1008                         | s(B$_3$-O$_1$-O$_2$), s(B$_2$-O$_2$-O$_3$), s(B$_2$-O$_4$), s(B$_3$-O$_3$-O$_4$) |
| 992                         | 981                          | s(B$_2$-O$_2$-O$_4$) |
| 959, 969                    | 964                          | s(O$_3$-B$_1$-O$_2$), s(O$_4$-B$_2$-O$_3$), s(B$_2$-O$_3$) |
| 868, 892                    | 880                          | s(B$_1$-O$_1$), s(B$_1$-O$_2$-B$_2$), ss(B$_2$-O$_3$), ss(B$_2$-O$_3$-O$_4$) |
| 643, 669                    | 657                          | ss(B$_2$-O$_3$-O$_4$) |

[a] s = Stretching mode, b = bending mode; pairs of bonded atoms with a large relative motion between them are given in parentheses.

The new actinide borates ThB$_4$O$_8$ and UB$_4$O$_8$. The crystal structures are constructed from layers of linked BO$_4$ tetrahedra. These layers contain threefold-coordinated oxygen atoms. The actinide cations are located between the boron–oxygen layers. In the future, we will attempt the synthesis of isotopic compounds with other cations in the oxidation state +4 that have similar ionic radii, such as Ce$^{3+}$, by using the multianvil high-pressure technique. Furthermore, this research into actinide borates will be a good starting point for synthesizing the first actinide fluoride borate, in analogy to our work in the field of rare-earth fluoride borates.

**Experimental Section**

Caution: Working with UO$_2$ and ThO$_2$ requires appropriate precautions for the handling of radioactive and toxic substances.

**Synthesis:** The syntheses of AnB$_4$O$_8$ (An = Th, U) took place under high-pressure, high-temperature conditions. The synthesis of ThB$_4$O$_8$ was carried out at 5.5 GPa and 1100°C, whilst the isotopic compound UB$_4$O$_8$ was synthesized at 10.5 GPa and 1100°C. Depending on the actinide borate, stoichiometric mixtures of Th$_2$O$_3$ (synthesized by the decomposition of Th(NO$_3$)$_4$·4H$_2$O at 750°C) or UO$_2$ (synthesized by the pyrolysis of UO$_2$(NO$_3$)$_2$·6H$_2$O at 300°C) and B$_2$O$_3$ (Strem Chemicals, 99.99 %) in a 1.2 molar ratio were finely ground together, added into a platinum capsule, and placed in a boron-nitride crucible (Henze BNP GmbH, HeBo-Sint S100, Kempten, Germany). Then, the crucibles were placed into the center of an 18/11 assembly (for the thorium borate) or into the center of a 14/8 assembly (for the uranium borate). All of the synthetic steps were performed inside a glove box. The assemblies were compressed by using tungsten-carbide cubes (TSM-10 Ceratizit, Reutte, Austria). To apply the pressure, a 1000 ton multianvil press with a Walker-type module (both devices were purchased from Vogelegreiter, Mamlens, Germany) was used. The assembly and its preparation are described in refs. [41–45]. For the synthesis of ThB$_4$O$_8$, the 18/11 assembly was compressed up to 5.5 GPa over 160 min, then heated at 1100°C (in a cylindrical graphite furnace) over 10 min, kept at that temperature for 10 min, and cooled to 450°C over 25 min at constant pressure. UB$_4$O$_8$ was synthesized by compressing the 14/8 assembly up to 10.5 GPa over 280 min, then heated at 1100°C (in a cylindrical graphite furnace) for 1 h. Then, the heated sample was cooled to 450°C over 25 min at constant pressure. After natural cooling to RT by switching off the heating, decompression periods of 8 and 14 h were required. The recovered octahedral pressure medium (MgO, Ceramic Substrates & Components Ltd., Newport, Isle of Wight, UK) was broken apart and the samples were carefully separated from the surrounding graphite and boron nitride. Whilst ThB$_4$O$_8$ was obtained as colorless crystals, UB$_4$O$_8$ was obtained as green, air- and water-resistant crystals in a black matrix.

**Crystal-structure analysis:** The powder X-ray diffraction pattern of AnB$_4$O$_8$ (An = Th, U) were obtained in transmission geometry from flat samples of the reaction product on a STOE STADI P powder diffractometer with graphite-monochromated MoK$_α_1$ radiation ($λ$=70.93 pm). Figure 1 shows the experimental powder X-ray diffraction patterns of ThB$_4$O$_8$ and UB$_4$O$_8$, which matched well with the theoretical patterns that were simulated from the single-crystal data. The respective diffraction patterns showed reflections of ThB$_4$O$_8$ or UB$_4$O$_8$, unreacted ThO$_2$ or UO$_2$.12 (de-noted with lines in Figure 1), and, in both cases, a still-unknown phase (denoted with circles in Figure 1). Small single crystals of ThB$_4$O$_8$ and UB$_4$O$_8$ were isolated by mechanical fragmentation. The single-crystal intensity data were collected at RT on a Nonius Kappa-CCD diffractometer with graphite-monochromated MoK$_α_1$ radiation ($λ$=71.073 pm). The semiautomatic absorption correction based on equivalent and redundant intensities (Scalepack[46]) was applied to the intensity data. All of the relevant details of the data collection and evaluation are listed in Table 1 for both compounds. The structure solution and parameter refinement
(full-matrix least-squares against $F^2$) were performed by using the SHIELX-97 software suite.\[^{37-41}\] According to the systematic extinctions, the monoclinic space group $C2/c$ was derived in both cases. All of the atoms were refined with anisotropic displacement parameters and the final difference Fourier syntheses did not reveal any significant peaks in both refinements. Tables 2–6 list the positional parameters, anisotropic displacement parameters, interatomic distances, and angles in these structures.

CSD-426310 (ThB$_4$O$_8$) and CSD-426311 (UB$_4$O$_8$) contain the supplementary crystallographic data for this paper. These data can be obtained from the Fachinformationszentrum Karlsruhe via http://www.fiz-informationsdienste.de/en/dbs/csd/depot_anforderung.html.

Vibrational spectra: Confoocal Raman spectra of single crystals of An$_2$B$_6$O$_{16}$ (An = Th, U) within the range 50–4000 cm$^{-1}$ were recorded on a Horiba Jobin Yvon Labram-HR 800 Raman microspectrometer. The samples were excited by using the 532 nm emission line of a frequency-doubled 100 mW Nd:YAG laser and by using the 633 nm emission line of a 17 mW HeNe laser with an Olympus ×50 objective lens. The diameter of the laser spot on the surface was approximately 1 μm. The scattered light was dispersed by using an optical grating with 1800 lines/mm $^{-1}$ and collected by using a 1024×256 open-electrode CCD detector. The spectroscopic resolution, as determined by measuring the Rayleigh line, was less than 2 cm$^{-1}$. The spectra were recorded unpolarized. The accuracy of the Raman line shifts, as calibrated by regularly measuring the Rayleigh line, was on the order of 0.5 cm$^{-1}$. Background and Raman bands were fitted by using the built-in spectrometer software LabSpec to a second-order polynomial and convoluted Gaussian-Lorentzian functions, respectively.

The FTIR-ATR (Attenuated Total Reflection) spectra of powdered sam-

DFT calculations: In addition to the experimentally recorded IR and Raman spectra of ThB$_4$O$_8$, quantum-chemical computations of harmonic vibrational frequencies were performed by using the Crystal 09 program.\[^{50-61}\] An important step in any quantum-mechanical calculation is the choice of an adequate basis set and a compromise must often be found between balancing computational effort and the accuracy of the results. To decrease the computational effort, a basis set with an effective core potential (ECP) for thorium was chosen. A suitable basis set for the actinide atom was identified based on geometry optimizations of ThB$_4$O$_8$. All-electron basis sets were employed for boron\[^{52}\] and oxygen atoms.\[^{53}\] Out of the results on the geometry optimization of ThB$_4$O$_8$, the well-tested ECP88MBWB GUESS\[^{54}\] basis set was chosen for the thorium atom. All of the computations were performed by using the PBEOLP functional,\[^{55}\] for the correlation and exchange functionals and the SCF convergence for the energy was set at $10^{-12}$ $E_h$. The overall computation time for the calculations of the harmonic vibrational frequencies of ThB$_4$O$_8$ took 168 h on a cluster with 12 Intel Xeon CPU X5670 2.93 GHz processors.

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