Supporting Information

The High-Pressure Oxide Tb₃O₅ and its Non-Centrosymmetric Low-Temperature Polymorph–A Comprehensive Study

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Supporting Information for

Experimental Methods

Synthesis

A polycrystalline sample of HT-HP-Tb$_3$O$_5$ was synthesized under high-pressure/high-temperature conditions of 8 GPa and 1050 °C from an equimolar mixture of “Tb$_4$O$_7$” (Smart Elements, Vienna, Austria, 99.99%) and Tb$_2$O$_3$ (Sigma Aldrich, Vienna, Austria, 99.99%). “Tb$_4$O$_7$” alone was found to be applicable as the starting material as well, due to the reducing effect of the α-BN crucible on the reactants. Powder X-ray diffraction analyses of the educts showed no significant crystalline impurities. The educt mixture was finely ground under Ar inert gas atmosphere and filled into boron nitride crucibles (Henze BNP AG, Lauben, Germany), which were sealed with a boron nitride lid. These crucibles were positioned in the center of 18/11 assemblies, which were compressed by eight tungsten carbide cubes (Hawedia, ha-7%Co, Marklkofen, Germany). Details on the construction of the assembly are described in the literature.[1] Quasi-hydrostatic pressure was applied by a Walker-type multianvil module and a 1000 ton press (both Max Voggenreiter GmbH, Mainleus, Germany). Heating was supplied by a resistive graphite tube heating. The sample was compressed up to 8 GPa within 3.5 h, followed by heating it up to 1323 K in 8 min, keeping this temperature for 15 min, and cooling down to 773 K within 20 min. After quenching down to room temperature by switching off the heating, the decompression of the assembly required 10.5 h. The product was isolated by breaking apart the octahedral pressure medium (MgO, Ceramic Substrates & Components Ltd., Newport, Isle of Wight, UK) and careful separation from the surrounding graphite and boron nitride. HT-HP-Tb$_3$O$_5$ was obtained as an air- and water-resistant crystalline product. The color of the product sample changed from dark grey to reddish brown – typical for a mixed-valent compound due to electron charge transfer between Tb$^{3+}$ and Tb$^{4+}$ – when grinding for the purpose of further investigation.
Results and Discussion

Crystal structure of HT-HP-Tb₃O₅

As reported in the main article, the Tb1 ions are coordinated by eight oxygen anions with interatomic distances between 233 and 253 pm in form of a bi-capped trigonal prism. However, another oxygen atom at a distance of 332 pm caps the third face of the trigonal prism, therefore forming a tri-capped trigonal prismatic coordination of Tb1 (see Figure S1). For HT-HP-Tb₃O₅, this oxygen anion cannot be regarded coordinating Tb1 due to its large interatomic distance, though it is included in the coordination description of atoms at the Sb2 position of some intermetallics crystallizing in the β-Yb₅Sb₃ type structure, e.g. Ti₅Sb₃.[2] This is due to the smaller relative interatomic distance deviation of the three capping atoms in Ti₅Sb₃ (335, 334, and 362 pm) in comparison to Tb₂O₅ (240, 233, and 332 pm). Similarly, the second crystallographic independent anions on the Sb1 position are ascribed to be coordinated by eight cations in form of a bi-capped distorted octahedron rather than seven as in HT-HP-Tb₃O₅ (Figure S1). Furthermore, some of the square pyramids are transformed into octahedra by the approach of a sixth atom and the tetrahedra change into trigonal bipyramids in a similar way in for instance Ti₅Sb₃.[2]

The elongated hexagons formed by the oxygen anions as the base planes of the hexagonal prisms in the crystal structure of HT-HP-Tb₃O₅ form a parquet-like patchwork, as is shown in Figure S3. This pattern is also found, more or less distorted, in the structure of Rh₃Ge₃ and all its derivative structure types.[3] We should note that this is the typical symmetry imposed by space group $Pnma$.

Figure S1. Coordination of the terbium atoms in the crystal structure of HT-HP-Tb₃O₅, including one more non-coordinating oxygen atom each for comparison with isostructural compounds.
Figure S2. Top: Coordination of the terbium atoms in the crystal structure of HT-HP-Tb₃O₅, highlighting the bi-capped trigonal prismatic coordination of Tb1 (a) and the mono-capped distorted octahedral coordination of Tb2 (b). Bottom: Coordination of the oxygen atoms O1 (c) and O2,3,4 (d) in the crystal structure of HT-HP-Tb₃O₅.
Figure S3. Layer of atoms in HT-HP-Tb$_3$O$_5$ at $y = \frac{1}{4}$ as viewed along [010], highlighting the elongated hexagons built by the oxygen atoms and the terbium atoms off center of these hexagons. The nature of the parquet-like pattern of these hexagons is characteristic for compounds exhibiting the $\beta$-Yb$_2$Sb$_3$ type structure (in general for space group $Pnma$).
Figure S4. Hexagonal channels in the crystal structure of HT-HP-Tb₃O₅ viewed along [010], highlighting the hexagonal base plane (green) and the zig-zag chain of rhombs in the centre of the hexagonal channels.
Table S1. Powder and single-crystal X-ray diffraction data and structural parameters from refinement of HT-HP-Tb$_3$O$_5$ (standard deviations in parentheses).

| Empirical formula | Tb$_3$O$_5$ |
|-------------------|-------------|
| Formula weight    | 556.76      |
| Crystal system    | orthorhombic|
| Space group       | Pnma        |
| Crystal color     | red brown   |

**Powder data**

| Powder diffractometer | Stoe Stadi P |
|------------------------|--------------|
| Radiation; $\lambda$, pm | Mo-\(K_\alpha\); 70.93 |
| $a$, pm                | 978.97(8)    |
| $b$, pm                | 670.36(4)    |
| $c$, pm                | 604.35(4)    |
| $V$, nm$^3$            | 0.39661(3)   |

**Single-crystal data**

| Single-crystal diffractometer | Bruker D8 Quest (Photon 100) |
|-------------------------------|-----------------------------|
| Radiation; $\lambda$, pm      | Mo-\(K_\alpha\); 71.073    |
| $a$, pm                       | 979.30(6)                   |
| $b$, pm                       | 670.64(4)                   |
| $c$, pm                       | 604.23(3)                   |
| $V$, nm$^3$                   | 0.39683(4)                  |
| Formula units per cell ($Z$)  | 4                           |
| Calculated density, g cm$^{-3}$ | 9.32                       |
| Crystal size, mm$^3$          | 0.06 $\times$ 0.04 $\times$ 0.04 |
| Temperature, K                | 300(2)                      |
| Absorption coefficient, mm$^{-1}$ | 52.8                      |
| $F(000)$, e                   | 940                          |
| $\theta$ range, deg          | 3.7 $\sim$ 35.0             |
| Range in $hkl$                | $\pm15$, $\pm10$, $\pm9$   |
| Total no. of reflections      | 20919                       |
| Independent reflections / $R_{int}$ | 939 / 0.0378              |
| Reflections with $I > 2\sigma(I)$ / $R_{\sigma}$ | 893 / 0.0149 |
| Data / ref. parameters        | 939 / 44                    |
| Absorption correction         | multi-scan                  |
| (Bruker Difabs 2014/5)        |                             |
| GoF on $F^2$                   | 1.202                       |
| $R_1$ / $wR_2$ [I > 2\sigma(I)] | 0.0150 / 0.0366          |
| $R_1$ / $wR_2$ (all data)     | 0.0160 / 0.0371             |
| Residual density, $\times$ 10$^{-6}$ e pm$^{-3}$ | 2.55 / -1.19 |
Table S2. Synchrotron powder X-ray diffraction data and structure refinements for HT-HP-Tb₃O₅ (300 K) and LT-HP-Tb₃O₅ (2 K).

| Compound      | HT-HP-Tb₃O₅ | LT-HP-Tb₃O₅ |
|---------------|-------------|-------------|
| Temperature   | 300 K       | 2 K         |
| Space group   | Pnma        | Pna₂₁       |
| Unit cell dimensions (in pm) | | |
| a = 979.00(1) | 978.53(1)  |
| b = 670.48(1) | 603.23(1)  |
| c = 604.34(1) | 668.45(1)  |
| Volume, nm³ | 0.3967      | 0.3946      |
| Wavelength, nm | 0.6979     | 0.6979     |
| θ range, °  | 0.10-51.19  | 0.07-34.63  |
| Data points / increment | 3352 / 0.015 | 3352 / 0.010 |
| Number of reflections | 455        | 152         |
| Number of parameters | 26         | 28          |
| R-factor / wR-factor | 2.03 / 2.91 | 2.54 / 4.21 |

* last run.

Table S3. Atomic coordinates and isotropic equivalent displacement parameters (Uₑq in Å²) for HT-HP-Tb₃O₅ (space group Pnma) based on single-crystal X-ray diffraction data. Uₑq is defined as one third of the trace of the orthogonalized Uᵢⱼ tensor.

| Atom | Wyckoff position | x         | y          | z          | Uₑq  |
|------|------------------|-----------|------------|------------|-------|
| Tb1  | 8d               | 0.17400(2)| 0.00182(2) | 0.51791(2) | 0.00475(5) |
| Tb2  | 4c               | 0.00538(2)| ¼          | 0.05668(3) | 0.00381(5) |
| O1   | 8d               | 0.0970(2) | 0.5283(3)  | 0.1545(3)  | 0.0059(3)  |
| O2   | 4c               | 0.0034(2) | ¼          | 0.4452(5)  | 0.0066(5)  |
| O3   | 4c               | 0.1863(3) | ¼          | 0.8315(5)  | 0.0065(5)  |
| O4   | 4c               | 0.2899(3) | ¼          | 0.3098(5)  | 0.0059(5)  |
Table S4. Atomic coordinates and isotropic equivalent displacement parameters ($U_{eq}$ in pm$^2$) for HT-HP-Tb$_3$O$_5$ ($Pnma$, 300 K) and LT-HP-Tb$_3$O$_5$ ($Pna2_1$, 2 K) synchrotron powder X-ray diffraction data. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| Atom   | Wyckoff position | x   | y   | z       | $U_{eq}$ |
|--------|------------------|-----|-----|---------|----------|
| Tb1    | 8d               | 0.17308(5) | 0.0006(3) | 0.51774(10) | 35(1)   |
| Tb2    | 4c               | 0.00306(19) | 1/4  | 0.05746(11) | 15(2)   |
| O1     | 8d               | 0.1036(9) | 0.5391(16) | 0.1354(15) | 168(1)  |
| O2     | 4c               | 0.013(2)  | 1/4  | 0.4093(16)  | 168(1)$^a$ |
| O3     | 4c               | 0.1940(16)| 1/4  | 0.8559(19)  | 168(1)$^a$ |
| O4     | 4c               | 0.2857(15)| 1/4  | 0.306(2)    | 168(1)$^a$ |

| Atom   | Wyckoff position | U$_{11}$ | U$_{22}$ | U$_{33}$ | U$_{23}$ | U$_{13}$ | U$_{12}$ |
|--------|------------------|----------|----------|----------|----------|----------|----------|
| Tb1    | 4a               | 0.00396(7) | 0.00517(7) | 0.00511(8) | -0.00085(4) | 0.00028(3) | -0.00013(3) |
| Tb2    | 4a               | 0.00317(8) | 0.00358(8) | 0.00467(9) | 0        | 0.00032(5) | 0        |
| O1     | 4a               | 0.0063(8) | 0.0063(7) | 0.0052(8) | 0.0004(6) | -0.0003(6) | -0.0004(6) |
| O2     | 4a               | 0.003(2)  | 0.009(2)  | 0.007(2)  | 0        | 0.000(1)  | 0        |
| O3     | 4a               | 0.006(1)  | 0.007(1)  | 0.007(2)  | 0        | 0.0022(9) | 0        |
| O4     | 4a               | 0.005(1)  | 0.006(1)  | 0.007(2)  | 0        | 0.000(1)  | 0        |

$^a$ $U_{eq}$ of O1 refined, $U_{eq}$’s of O2, O3 and O4 fixed equal to O1; $^b$ parameter fixed due to floating origin in space group $Pna2_1$; $^c$ $U_{eq}$’s for all atoms fixed in last run.

Table S5. Anisotropic equivalent displacement parameters $U_{ij}$ (Å$^2$) for HT-HP-Tb$_3$O$_5$ (space group $Pnma$) based on single-crystal X-ray diffraction data.

| Atom   | U$_{11}$ | U$_{22}$ | U$_{33}$ | U$_{23}$ | U$_{13}$ | U$_{12}$ |
|--------|----------|----------|----------|----------|----------|----------|
| Tb1    | 0.00396(7) | 0.00517(7) | 0.00511(8) | -0.00085(4) | 0.00028(3) | -0.00013(3) |
| Tb2    | 0.00317(8) | 0.00358(8) | 0.00467(9) | 0        | 0.00032(5) | 0        |
| O1     | 0.0063(8) | 0.0063(7) | 0.0052(8) | 0.0004(6) | -0.0003(6) | -0.0004(6) |
| O2     | 0.003(2)  | 0.009(2)  | 0.007(2)  | 0        | 0.000(1)  | 0        |
| O3     | 0.006(1)  | 0.007(1)  | 0.007(2)  | 0        | 0.0022(9) | 0        |
| O4     | 0.005(1)  | 0.006(1)  | 0.007(2)  | 0        | 0.000(1)  | 0        |
Table S6. Interatomic distances (given in pm) for HT-HP-Tb$_3$O$_5$ (*Pnma*, single-crystal data) and LT-HP-Tb$_3$O$_5$ (*Pna$_2_1_1_0$*, powder data). Standard deviations for the single-crystal data are ±0.2 pm, for the powder diffraction data ±1 pm.

|       | HT-HP-Tb$_3$O$_5$ | LT-HP-Tb$_3$O$_5$ |
|-------|------------------|------------------|
| Tb1   | O1 233.0         | Tb1 O2 225       | Tb3 O2 218 |
|       | O4 237.5         | O1 226           | O4 222    |
|       | O1 239.6         | O3 237           | O3 229    |
|       | O2 239.9         | O4 240           | O1 230    |
|       | O2 243.3         | O4 243           | O5 252    |
|       | O3 244.8         | O5 247           | O4 263    |
|       | O4 246.7         | O3 261           | O2 265    |
|       | O2 252.5         | O2 264           | O3 272    |
| Ø     | **242.2**       | Ø **243**        | Ø **244** |
| **Tb2** | 2× O1 215.4 | **Tb2** | O5 192 |
|       | 2× O1 220.1 | O1 207           |          |
|       | O3 223.4 | O3 219           |          |
|       | O4 225.9 | O4 226           |          |
|       | O2 234.7 | O1 231           |          |
| Ø     | **222.1** | O2 233           |          |
|       |             | O5 241           |          |
| Ø     | **221** |          |          |
| O1    | Tb2 215.4 | O1 207 | Tb5 192 |
|       | Tb2 220.1 | Tb1 226 | Tb2 241 |
|       | Tb1 233.0 | Tb3 230 | Tb1 247 |
|       | Tb1 239.6 | Tb2 231 | Tb3 252 |
| Ø     | **227.0** | Ø **224** | Ø **233** |
| O2    | Tb2 234.7 | O2 218 |          |
|       | 2× Tb1 239.9 | Tb1 225 |          |
|       | 2× Tb1 243.3 | Tb2 233 |          |
| Ø     | **240.2** | Tb1 264 | Tb3 265 |
|       |             | Tb3 265 |          |
| Ø     | **241** |          |          |
| O3    | Tb2 223.4 | O3 219 |          |
|       | 2× Tb1 244.8 | Tb3 229 |          |
|       | 2× Tb1 252.5 | Tb1 237 |          |
| Ø     | **243.6** | Tb1 261 | Tb3 272 |
|       |             | Tb3 272 |          |
| Ø     | **244** |          |          |
| O4    | Tb2 225.9 | O4 222 |          |
|       | 2× Tb1 237.5 | Tb2 226 |          |
|       | 2× Tb1 246.7 | Tb1 240 |          |
| Ø     | **238.9** | Tb1 243 | Tb3 263 |
|       |             | Tb3 263 |          |
| Ø     | **239** |          |          |
Calculations of the Madelung part of lattice energy (MAPLE)

The MAPLE\(^5\) values for HT-HP-Tb\(_5\)O\(_5\) and LT-HP-Tb\(_5\)O\(_5\) were calculated based on the crystal structures and compared with the values received from the oxides used as starting material. A value of 26,781 kJ mol\(^{-1}\) was obtained for HT-HP-Tb\(_5\)O\(_5\), to be compared with 27,132 kJ mol\(^{-1}\) (deviation: 1.29\%) resulting from the starting materials \([1/3 \cdot \text{Tb}_2\text{O}_3]^6\) (15,054 kJ mol\(^{-1}\)) + \([1/3 \cdot \text{Tb}_7\text{O}_{12}]^7\) (66,341 kJ mol\(^{-1}\)). For LT-HP-Tb\(_5\)O\(_5\), a value of 26,928 kJ mol\(^{-1}\) was obtained, to be compared with 27,132 kJ mol\(^{-1}\) (deviation: 0.75\%). This validates the accuracy of the crystal structure solution of HT-HP-Tb\(_5\)O\(_5\) and LT-HP-Tb\(_5\)O\(_5\).

Further details on the charge distribution calculations

Comprehensive calculations and discussions regarding the valence state of the rare earth cations in various cerium oxides – namely the A- and C-type sesquioxides, the dioxide and some intermediate higher oxides – based on calculations applying the bond valence model (BLBS) are reported by Shoko et al.\(^8\) They concluded that Ce\(_5\)O\(_5\) is a homogeneous mixed-valence compound with comparable valences of 3.33 at the Ce1 and 3.37 at the Ce2 sites. This can be argued by the comparable polyhedron sizes with almost equal average Ce–O distances of 244 pm. However, the average Tb–O distances in HT-HP-Tb\(_5\)O\(_5\) are 242 pm for Tb1 and 222 pm for Tb2 (see Table S6). This huge difference in mean interatomic distances accounts for the clearly unequal valence of the two terbium sites in HT-HP-Tb\(_5\)O\(_5\), which could therefore be ascribed Class 1 according to Robin and Day\(^9\) with the two distinct crystallographic sites having integral but unequal valence. Nevertheless, the results obtained by the CHARDI calculations, the lower coordination number of Tb2 of seven, and the fact that the HT-HP-Tb\(_5\)O\(_5\) samples obviously show a strong optical absorption in the visible spectrum rather speak for a Class 2 inhomogeneous mixed valence of the terbium cations.

Powder X-ray diffraction

The experimental powder X-ray diffraction pattern of the reaction product (Figure S5) is consistent with the theoretical powder pattern simulated from single-crystal X-ray diffraction data. Thus, the experimental powder pattern shows some additional reflections (marked with asterisks) assignable to Tb\(_6\)O\(_{11}\) arising as a side product. By indexing the reflections of HT-HP-Tb\(_5\)O\(_5\), we obtained the parameters \(a = 978.97(8)\), \(b = 670.36(4)\), \(c = 604.35(4)\) pm, and a volume of 0.39661(3) nm\(^3\).
Figure S5: Experimental powder X-ray diffraction pattern of HT-HP-Tb₃O₅ (top) in comparison to the theoretical powder pattern simulated from single-crystal X-ray diffraction data (bottom). Reflections marked with asterisks originate from Tb₆O₁₁.
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