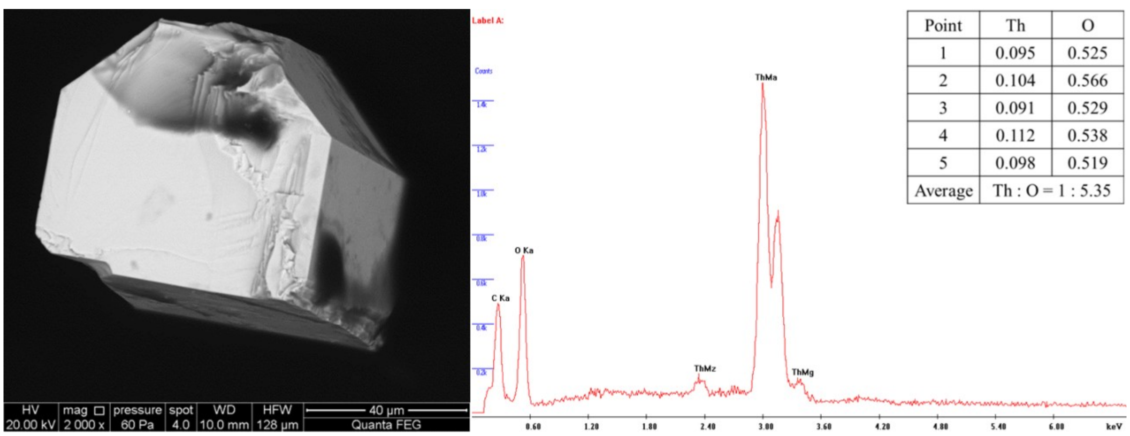
Supporting information

Understanding the Role of Flux, Pressure and Temperature on Polymorphism in ThB_2O_5



Point	Th	O
1	0.095	0.525
2	0.104	0.566
3	0.091	0.529
4	0.112	0.538
5	0.098	0.519
Average	Th : O = 1 : 5.35	

Figure S1. SEM image and EDS measurement for β-ThB_2O_5

Table S1. Selected Important Bond Lengths (angstroms) for β-ThB_2O_5.

Th(1)-O(3)#1	2.302(5)	Th(1)-O(3)#2	2.302(5)
Th(1)-O(2)#3	2.370(6)	Th(1)-O(1)	2.583(6)
Th(1)-O(4)#4	2.520(7)	Th(1)-O(2)	2.514(6)
Th(1)-O(3)#5	2.539(5)	Th(1)-O(3)#6	2.539(5)
Th(1)-O(3)	3.067(6)	Th(1)-O(3)	3.067(6)
B(1)-O(1)	1.472(11)	B(1)-O(3)	1.455(7)
B(1)-O(4)	1.471(11)	B(1)-O(3)#7	1.455(7)
B(2)-O(2)	1.356(11)	B(2) - O(1)	1.380(11)
B(2)-O(4) #3	1.390(11)		

Symmetry transformations used to generate equivalent atoms:
#1 -x, -y, -z+2, #2 -x, y+1/2, -z+2, #3 x-1, y, z, #4 x+1, y, z+1, #5 x, -y+1/2, z+1, #6 x, y, z+1, #7 x, - y+1/2, z.

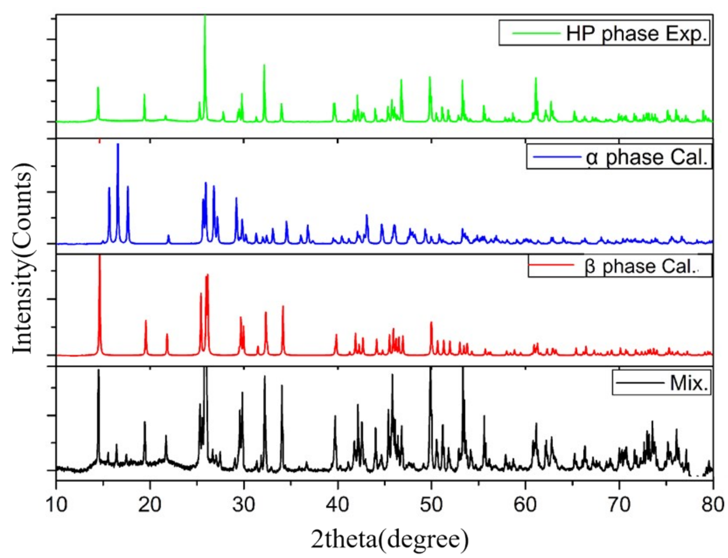


Figure S2. PXRD patterns of High-Pressured (4GPa) phase of ThB_2O_5, calculated α-, β-ThB_2O_5 and the mixture of α- and β-ThB_2O_5.

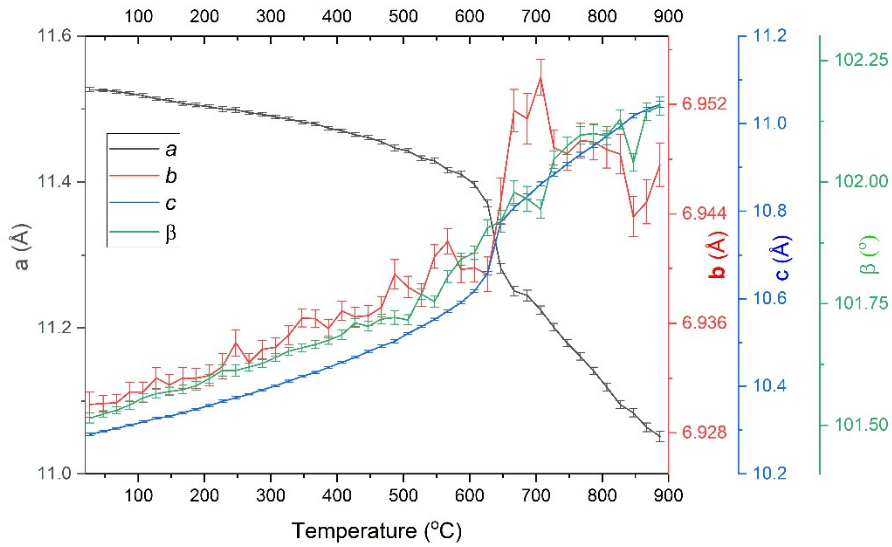


Figure S3. Thermal dependence of the *a, b, c* and β lattice parameters of *a*-ThB_2O_5 determined from refinements against *in situ* PXRD data using the Le Bail method.

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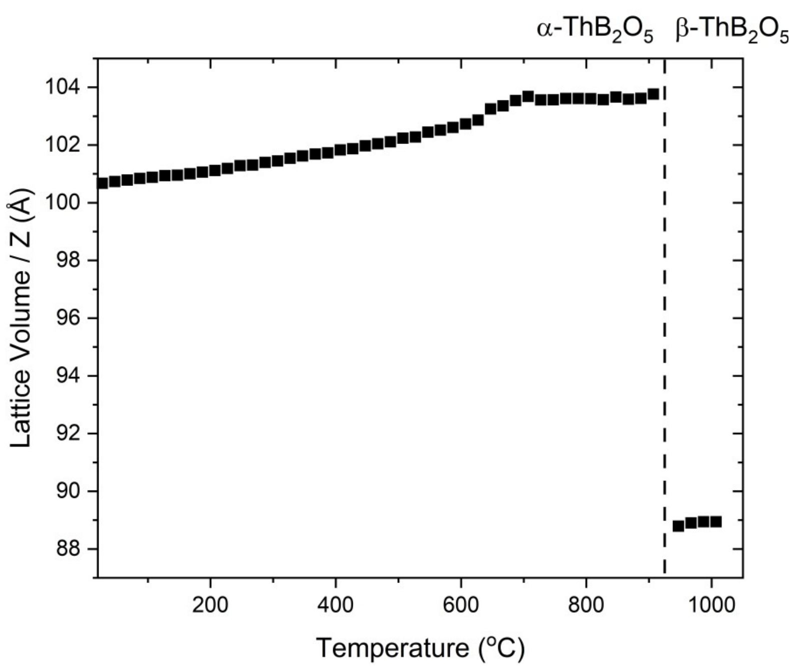


Figure S4. Thermal dependence of the lattice volume normalized per formula unite.

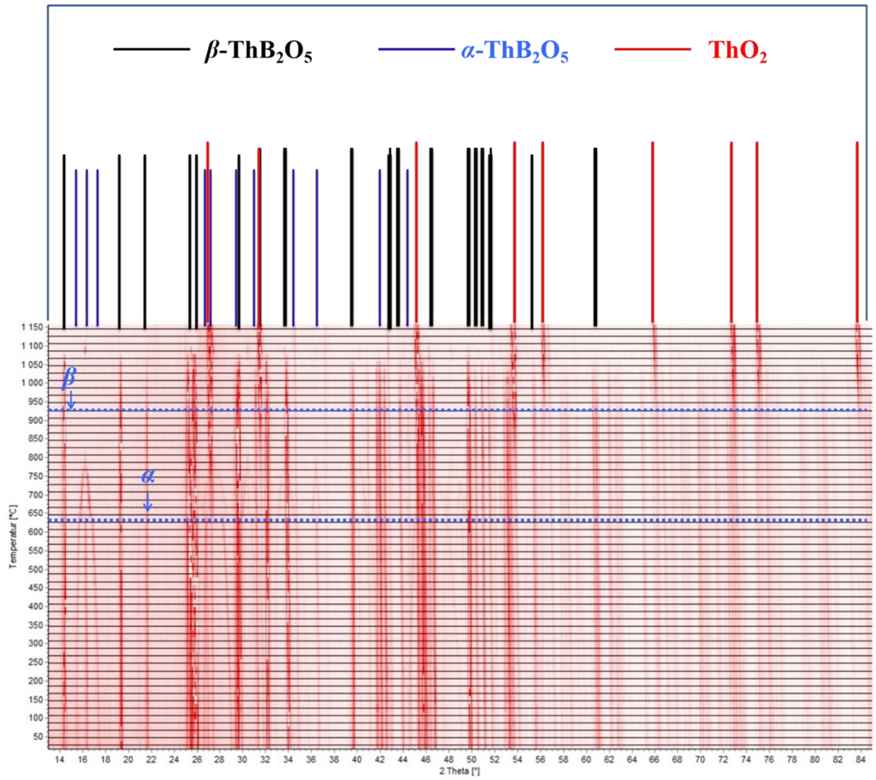


Figure S5. HT-PXRD pattern of a mixture of α-(34 %), β-ThB_2O_5 (66 %) and PXRD pattern of calculated ThO_2.

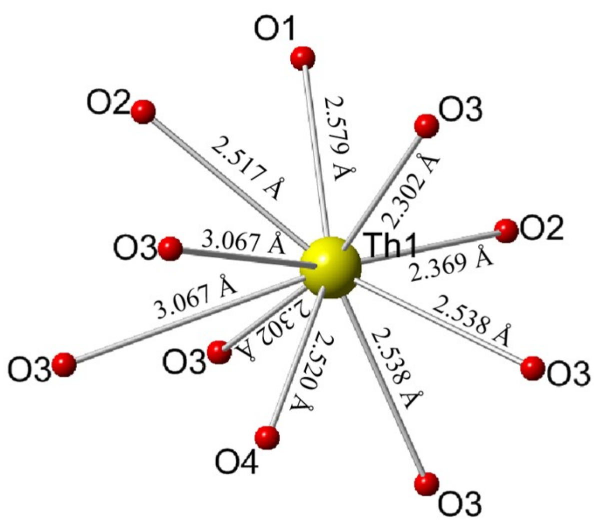


Figure S6. The Th-coordination environment with Th-O bond lengths in the structure of β-ThB_2O_5. Thorium atom, B1 atom are shown in yellow and cyan, oxygen atoms in red.

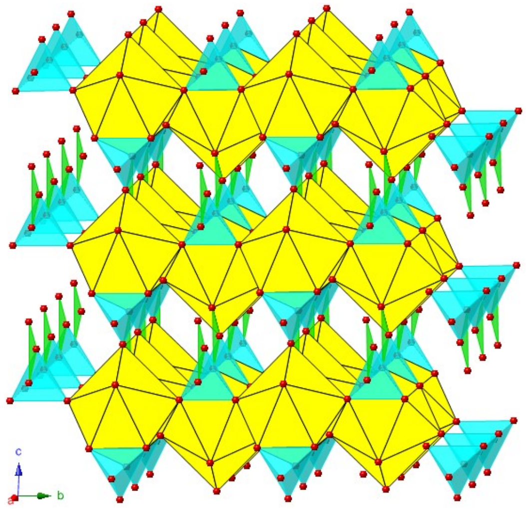


Figure S7. The 3D Th borate framework formed by B-O chains link the 2D Th-based sheets in *β*-ThB_2O_5, through corner (BO_4), edge (BO_3), and face (BO_4) sharing. Thorium polyhedra, BO_3 triangles and BO_4 tetrahedra are shown in yellow, green and cyan.

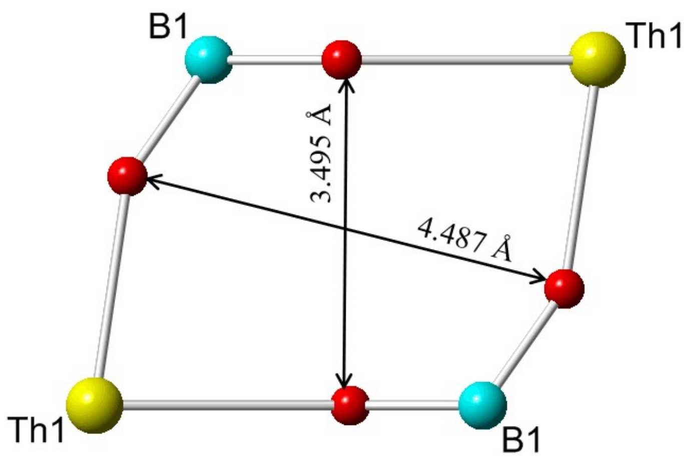


Figure S8. Four membered rings along the *a*-axis in the structure of *β*-ThB_2O_5.

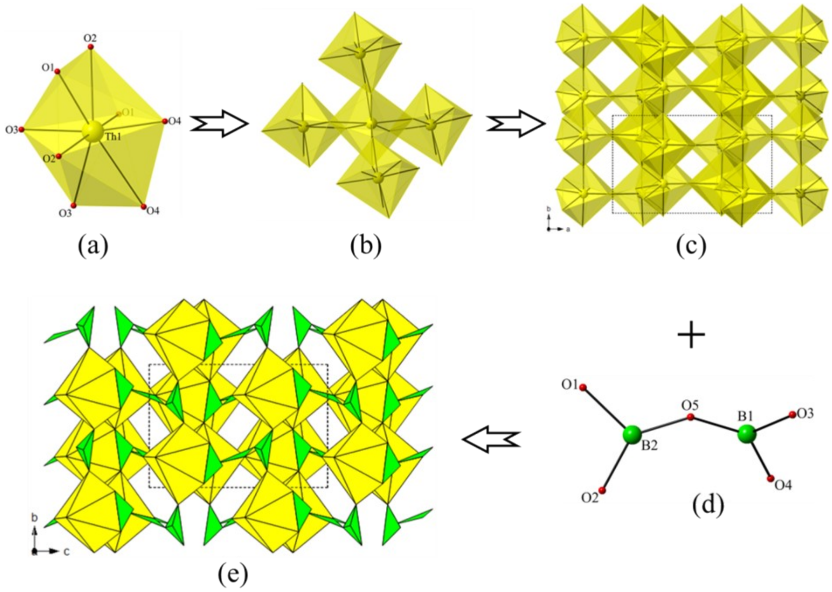
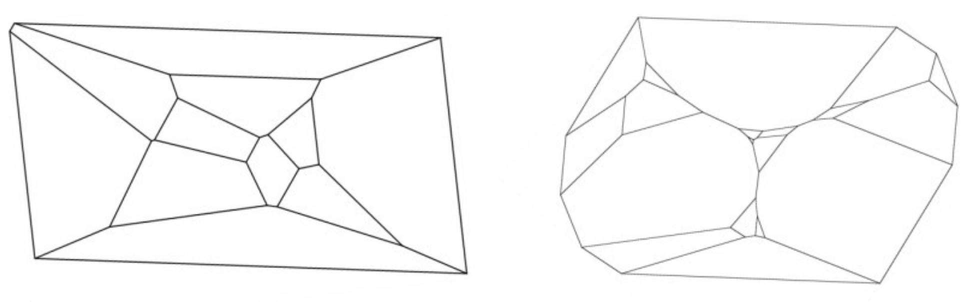


Figure S9. Representation of the α-ThB_2O_5 structure. A one-capped distorted thorium pentagonal bipyramid (a), a four-fold Th-coordinated thorium polyhedron (b), the 3D thorium network structure along the *b*-axis (c), a B_2O_5 dimer (d), the 3D thorium borate framework structure along the *b*-axis (e). ThO_8 polyhedra and BO_3 triangles are shown in yellow and green, O atoms are shown in red.



$4^5 \cdot 5^2 \cdot 6^5$ β-ThB_2O_5

$3^4 \cdot 4^4 \cdot 5^8 \cdot 10^4$ α-ThB_2O_5

Figure S10. Schlegel projections of the Voronoi–Dirichlet polyhedral (VDP) with $4^5 \cdot 5^2 \cdot 6^5$ (β-ThB_2O_5) and $3^4 \cdot 4^4 \cdot 5^8 \cdot 10^4$ (α-ThB_2O_5) combinatorial–topological types (CTTs).

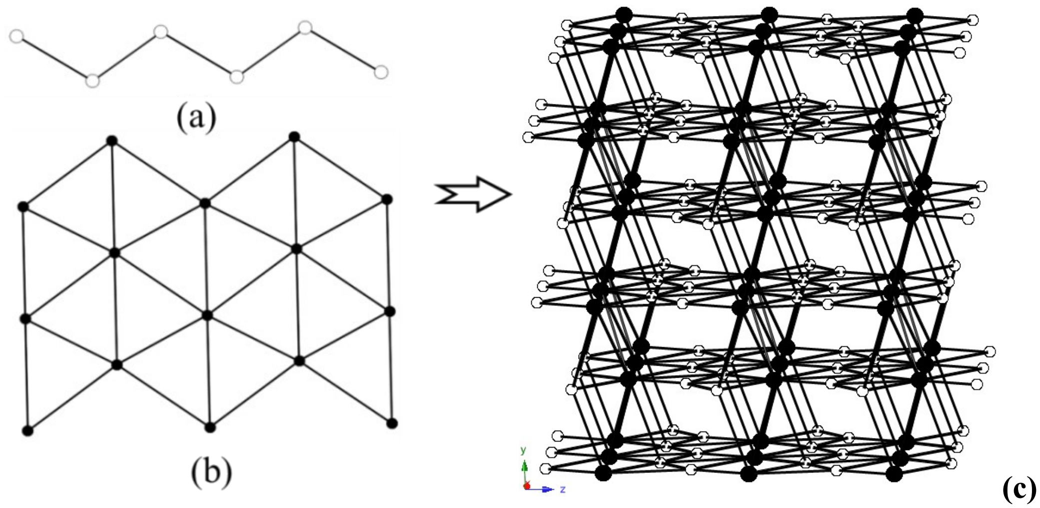


Figure S11. Cationic topology representation of β-ThB_2O_5. (a) A zigzag boron chain ···B1B2B1B2B1···along the *a*-axis, (b) a 2D {3^6} Th-sheet parallel to the *ab*-plain, (c) Topological view of the 3D new 3-nodal cation network along *a*-axis with a point symbol of {3^4, 4^{10}, 5^{10}, 6^4}{3^4, 4^{10}, 5^6, 6}{3^4, 4^4, 5^2}. The Th cations are shown as 8-connected nodes with blackballs, B1 and B2 are 7 and 5-connected nodes as hollow balls.

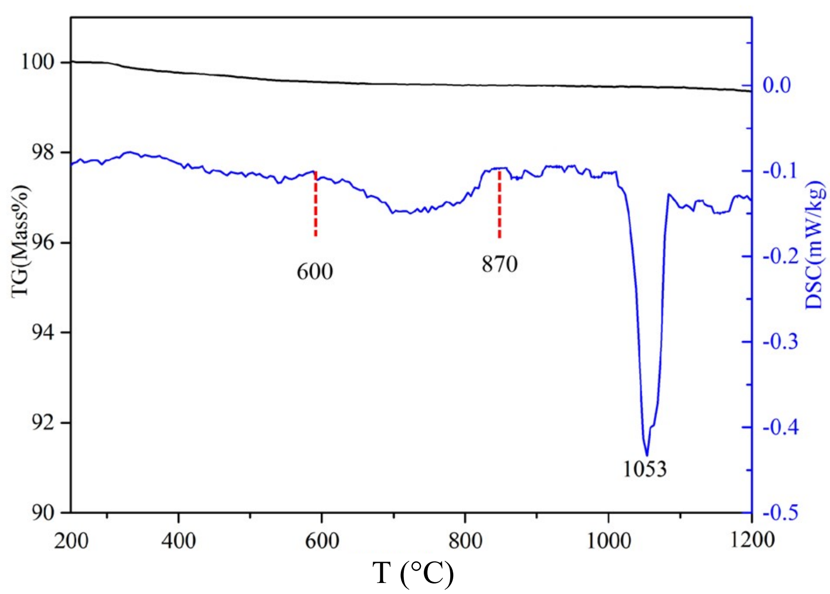


Figure S12. TG and DSC curves of α-ThB_2O_5 from 200 to 1200 ^{o}C.

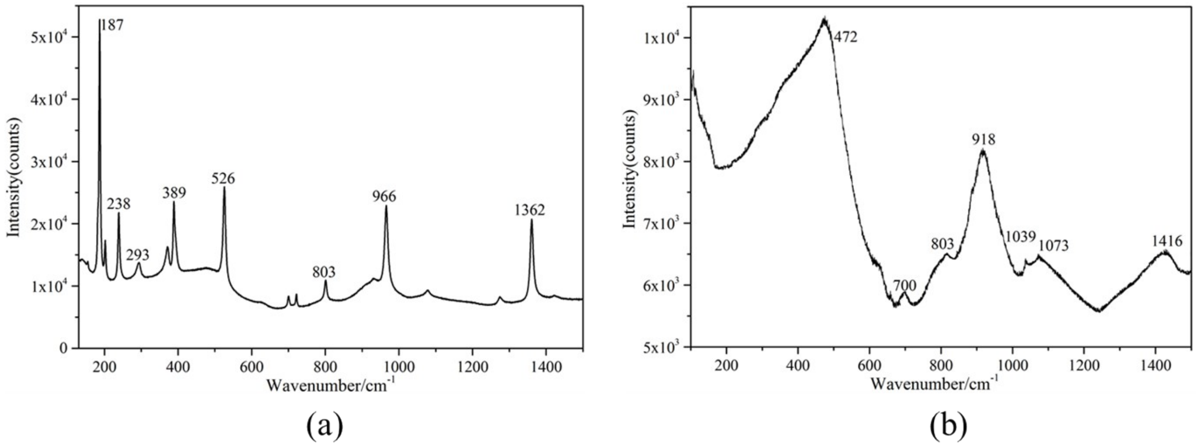


Figure S13. Raman spectra of compound β-ThB_2O_5 (a) and α-ThB_2O_5 (b) presented in the range 100 to 1500 μm.

Table S2. The lattice parameters of α-ThB_2O_5 and β-ThB_2O_5 obtained by DFT studies. In parentheses we report the offset from the measured values.

	β-ThB_2O_5	α-ThB_2O_5
A	4.239 (-0.014)	11.643 (+0.098)
B	6.934 (+0.061)	7.037 (+0.100)
C	6.339 (+0.015)	10.258 (-0.005)
Alpaha	90	90
Betha	106.69 (+0.374)	100.68 (-0.82)
Gamma	90	90
Vol	178.47 (+1.03)	825.96 (+20.52)

Table S3.Computed and measured IR bands positions. The frequencies are reported in cm^{-1}.

β-ThB_2O_5		α -ThB_2O_5	
computed	experimental	computed	experimental
1411	1438,1385	1400	1414
1294	1268	1250, 1252	1257
1078	1072	1028	1027
990,945,914	928	634,630,618	652
790	807	513,508,505	529
715	735		
628	652		
562, 543	580,557		