SUPPORTING INFORMATION

Structural, Electronic, and Optical Properties of the Bulk Boric Acid 2*A* and 3*T* Polymorphs: Experimental and Density Functional Theory Calculations

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Supplementary Figures

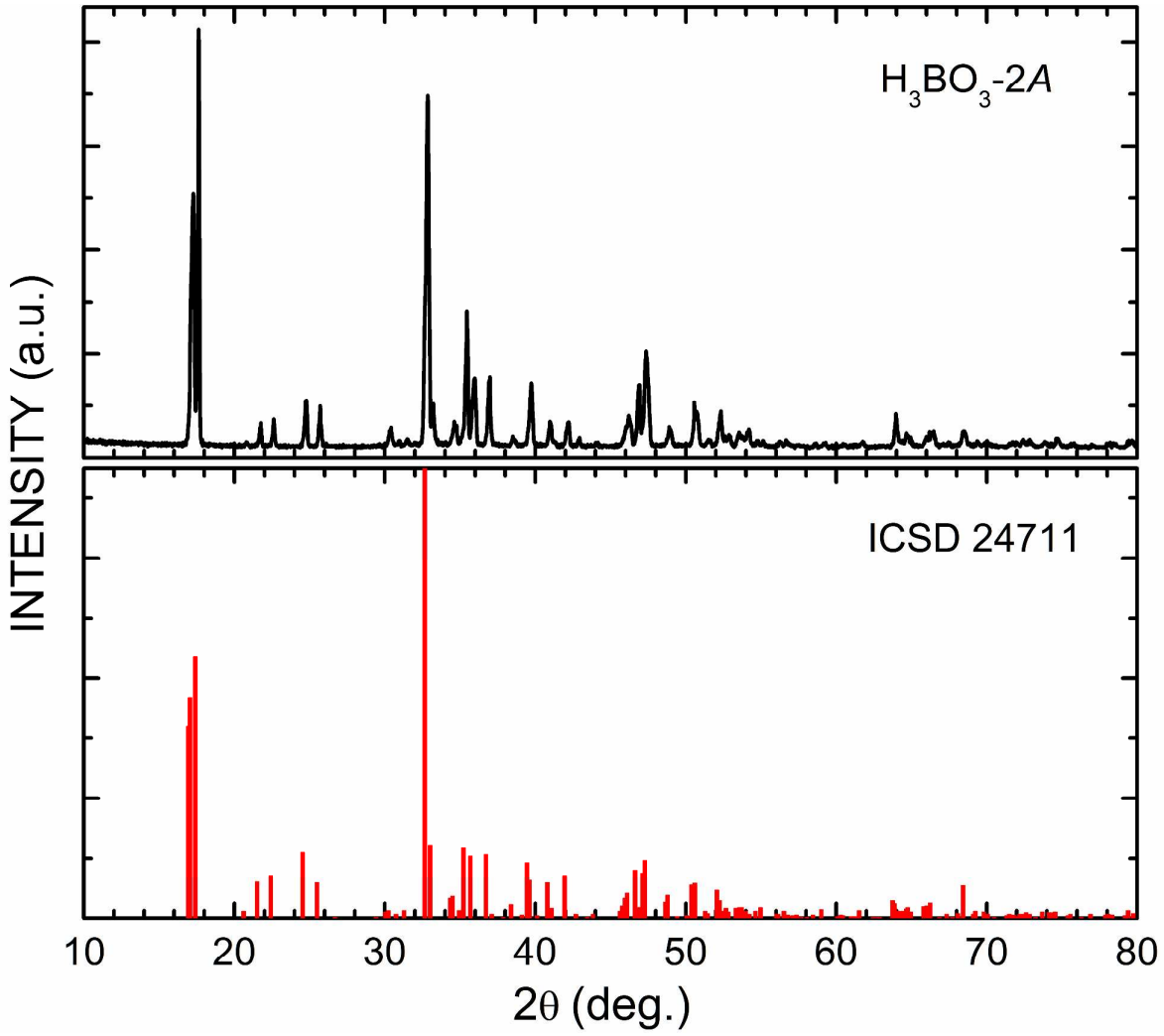

Figure S1. Top: X-ray diffraction pattern obtained from the H_3BO_3-2*A* boric acid polymorph samples used in the optical absorption measurements. Bottom: the X-ray data for the H_3BO_3-*2A* boric acid polymorph, ICDSD 24711, from the Inorganic Crystal Structure Database (ICSD).

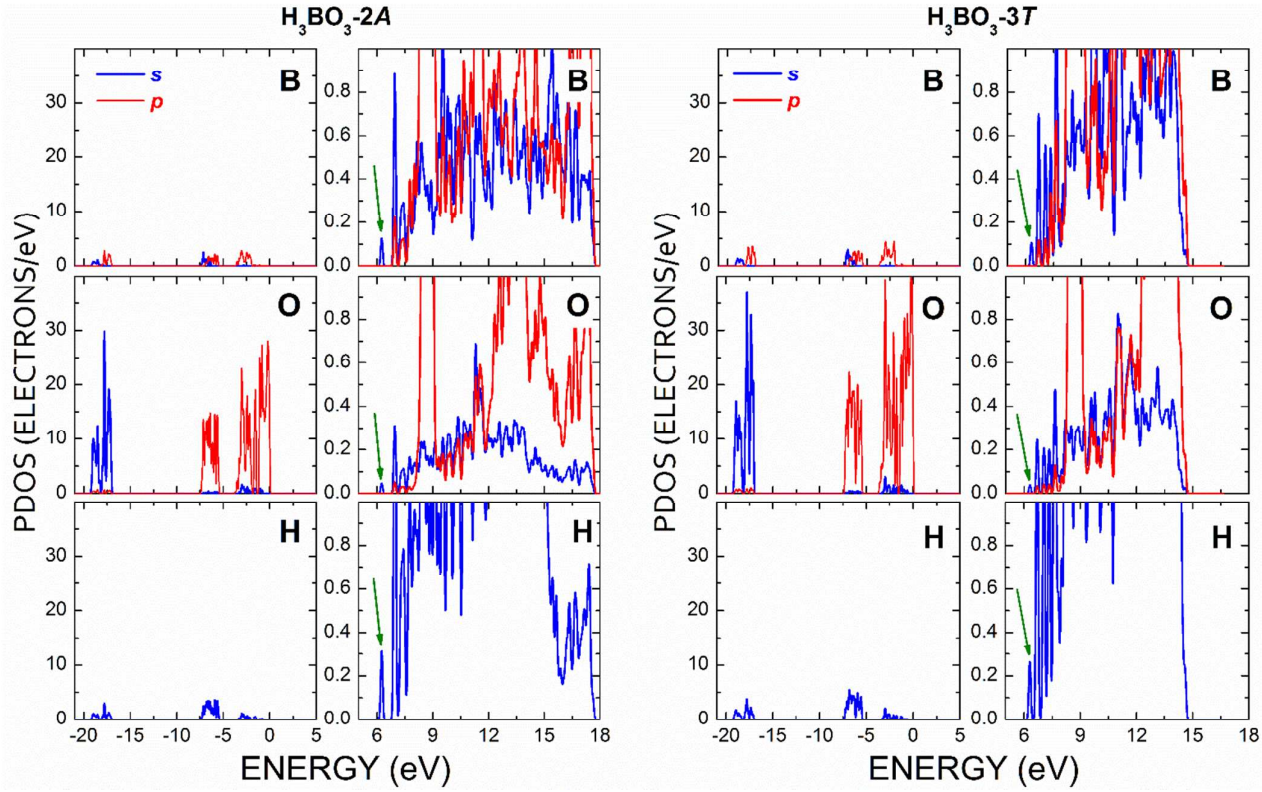

Figure S2. Partial densities of states per atom and per orbital for the H_3BO_3-*2A* (left) and H_3BO_3-3*T* (right) polymorphs calculated at the GGA+TS_{830} level. The arrows indicate the main DOS contribution to the band gap.

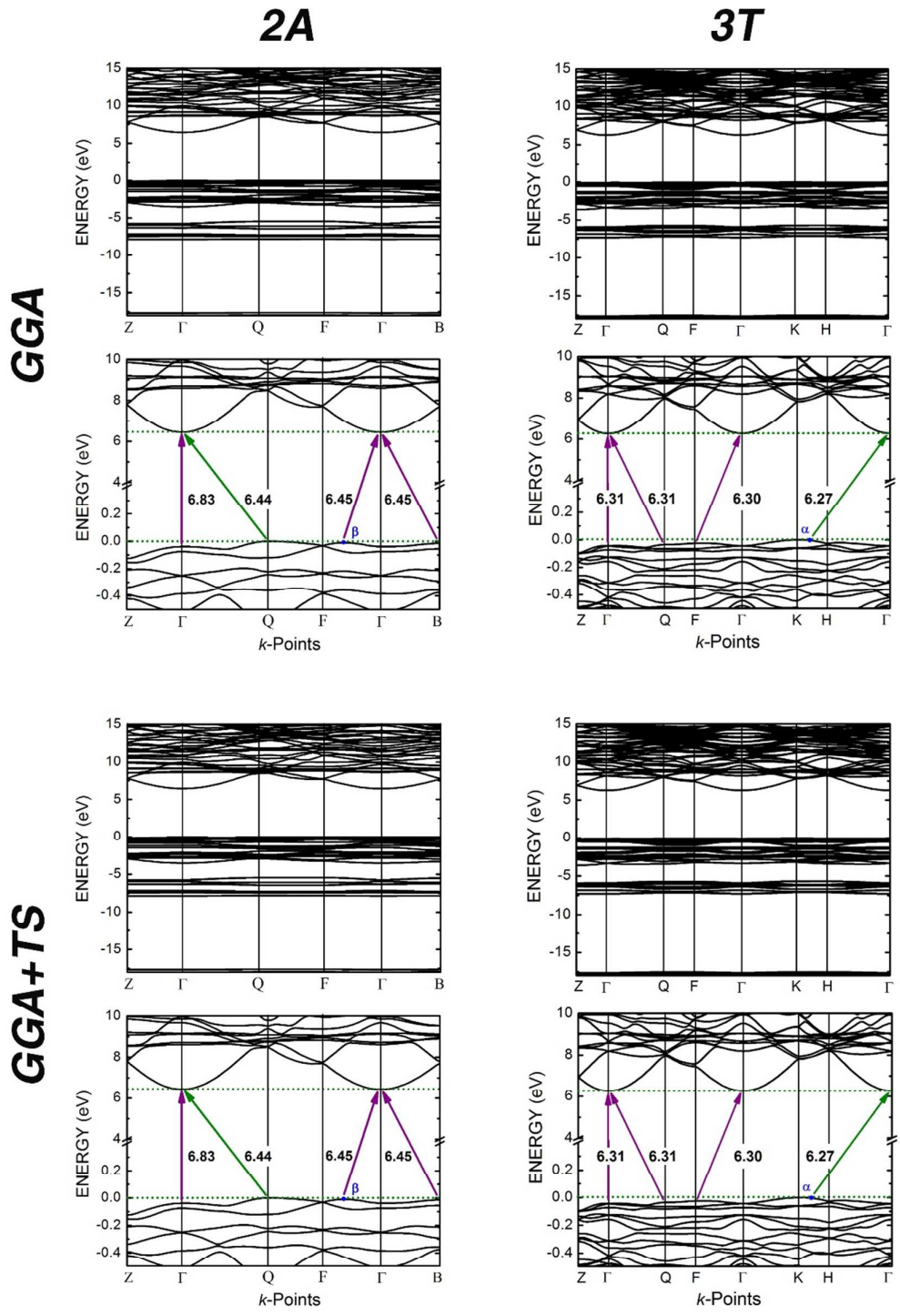

Figure S3. Kohn-Sham band structures for the H_3BO_3-*2A* (left) and H_3BO_3-3*T* (right) polymorphs obtained using the experimental lattice parameters at the GGA (top) and GGA+TS levels (bottom). The arrows show the most relevant energy gap values. The GGA and GGA+TS band curves are practically identical.

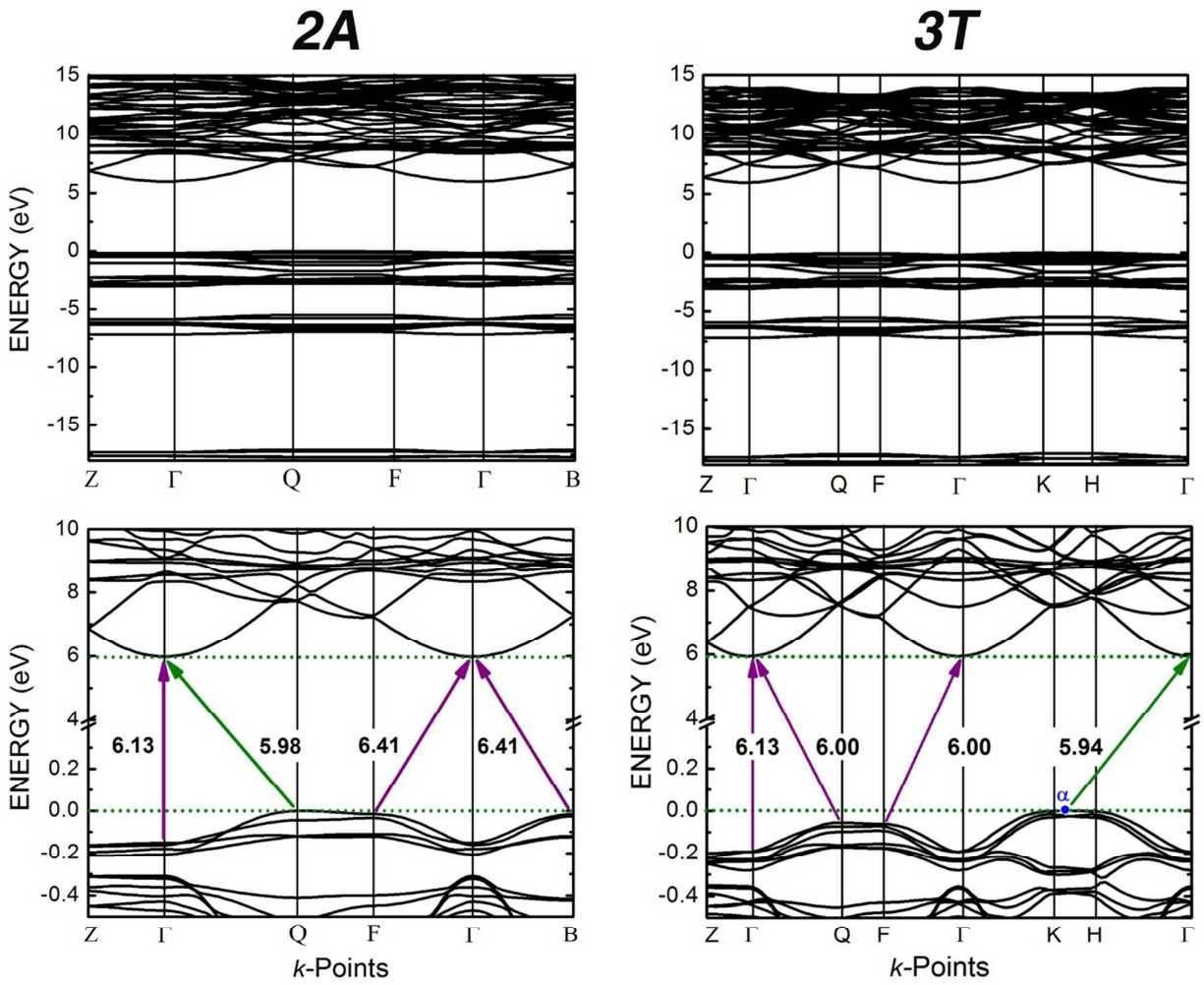

Figure S4. Kohn-Sham band structures for the H_3BO_3-*2A* (left) and H_3BO_3-3*T* (right) polymorphs obtained using the GGA optimized unit cell geometry. The arrows show the most relevant energy gap values.

Supplementary Tables

Table S1. Fractional atomic coordinates and bond lengths for both triclinic H_3BO_3-2*A* and trigonal H_3BO_3- 3*T* boric acid polymorphs at the GGA+TS_{830} level.

H_3BO_3-2*A*	x_{EXP}	y_{EXP}	z_{EXP}	x_{GGA+TS}	y_{GGA+TS}	z_{GGA+TS}
B1	0.6460	0.4270	0.2580	0.6479	0.4281	0.2598
B2	0.3070	0.7600	0.2420	0.3085	0.7593	0.2402
O1	0.4240	0.3020	0.2610	0.4205	0.3004	0.2606
O2	0.7680	0.3280	0.2500	0.7750	0.3271	0.2560
O3	0.7440	0.6500	0.2610	0.7477	0.6557	0.2612
O4	0.5320	0.8850	0.2500	0.5391	0.8887	0.2512
O5	0.2140	0.5400	0.2440	0.2097	0.5317	0.2403
O6	0.1800	0.8560	0.2330	0.1777	0.8573	0.2302
H1	0.3470	0.3610	0.2550	0.3384	0.3857	0.2541
H2	0.6710	0.1720	0.2500	0.6874	0.1599	0.2529
H3	0.8900	0.7090	0.2520	0.9109	0.7336	0.2499
H4	0.6000	0.8170	0.2540	0.6213	0.8032	0.2592
H5	0.0830	0.4690	0.2460	0.0437	0.4514	0.2428
H6	0.2970	0.0060	0.2430	0.2674	1.0254	0.2411
H_3BO_3–3T	x_{EXP}	y_{EXP}	z_{EXP}	x_{GGA+TS}	y_{GGA+TS}	z_{GGA+TS}
B1	0.1837	0.6403	0.2849	0.1862	0.6418	0.2959
B2	0.5180	0.3069	0.2964	0.5181	0.3080	0.3077
O1	0.0621	0.7393	0.2805	0.0581	0.7412	0.2944
O2	0.0864	0.4195	0.2808	0.0872	0.4142	0.2947
O3	0.4090	0.7650	0.2869	0.4142	0.7700	0.3002
O4	0.6437	0.2103	0.2929	0.6468	0.2088	0.3070
O5	0.2950	0.1832	0.2998	0.2906	0.1800	0.3122
O6	0.6136	0.5294	0.2904	0.6181	0.5357	0.3027
H1	0.1330	0.8770	0.3160	0.1446	0.9076	0.3015
H2	0.0570	0.3610	0.3110	0.0792	0.3341	0.2982
H3	0.4830	0.6950	0.3110	0.4943	0.6831	0.3023
H4	0.5650	0.0770	0.3330	0.5606	0.0420	0.3058
H5	0.2430	0.2740	0.3240	0.2106	0.2666	0.3061
H6	0.7550	0.6020	0.3180	0.7845	0.6157	0.2971

Table S2. Bond angles for both the H_3BO_3-2*A* triclinic and H_3BO_3- 3*T* hexagonal boric acid polymorphs obtained at GGA+TS_{830} level.

H_3BO_3-2*A*: B-A-C	A-B_{EXP}	A-C_{EXP}	B-A-C_{EXP}	A-B_{DFT}	A-C_{DFT}	B-A-C_{DFT}
O1-B1-O2	1.36	1.36	119.61	1.37	1.37	119.82
O1-B1-O3	1.36	1.36	120.18	1.37	1.37	120.11
O2-B1-O3	1.36	1.36	120.21	1.37	1.37	120.07
O4-B2-O5	1.36	1.35	118.77	1.37	1.37	119.76
O4-B2-O6	1.36	1.36	120.29	1.37	1.37	120.10
O5-B2-O6	1.35	1.36	120.94	1.37	1.37	120.15
B1-O1-H1	1.36	0.83	119.30	1.37	1.00	114.53
B1-O2-H2	1.36	0.96	108.06	1.37	1.00	114.62
B1-O3-H3	1.36	0.91	109.86	1.37	1.00	114.64
B2-O4-H4	1.36	0.83	115.81	1.37	1.00	114.60
B2-O5-H5	1.35	0.80	118.01	1.37	1.00	114.83
B2-O6-H6	1.36	0.95	98.480	1.37	1.00	114.18
H_3BO_3–3T : B-A-C	**A-B_{EXP}**	**A-C_{EXP}**	**B-A-C_{EXP}**	**A-B_{DFT}**	**A-C_{DFT}**	**B-A-C_{DFT}**
O1-B1-O2	1.35	1.35	120.44	1.37	1.37	120.11
O1-B1-O3	1.35	1.38	119.86	1.37	1.37	120.08
O2-B1-O3	1.35	1.38	119.62	1.37	1.37	119.81
O4-B2-O5	1.36	1.36	120.73	1.37	1.37	120.15
O4-B2-O6	1.36	1.36	120.21	1.37	1.37	119.72
O5-B2-O6	1.36	1.36	119.00	1.37	1.37	120.12
B1-O1-H1	1.35	0.91	112.90	1.37	1.00	114.40
B1-O2-H2	1.35	0.93	108.42	1.37	1.00	114.47
B1-O3-H3	1.38	0.91	116.64	1.37	1.00	114.58
B2-O4-H4	1.36	0.90	107.16	1.37	1.00	114.61
B2-O5-H5	1.36	0.91	107.24	1.37	1.00	114.41
B2-O6-H6	1.36	0.90	114.22	1.37	1.00	114.75

Table S3. Mulliken and Hirshfeld atomic charges for both the triclinic H_3BO_3-2*A* and hexagonal H_3BO_3- 3*T* polymorphs calculated at the LDA_{830} and $GGA+TS_{830}$ levels.

ATOM	Mulliken		Hirshfeld	
	LDA_{830}	**$GGA+TS_{830}$**	**LDA_{830}**	**$GGA+TS_{830}$**
B1	1.13	1.17	0.25	0.27
O1	-0.83	-0.86	-0.19	-0.21
O2	-0.83	-0.86	-0.19	-0.21
O3	-0.83	-0.86	-0.19	-0.21
H1	0.45	0.47	0.11	0.12
H2	0.45	0.47	0.11	0.12
H3	0.45	0.47	0.11	0.12