Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Experimental and computational characterization of phase transitions in CsB_3H_8

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Content

S1. Hydration study

Beside the peaks due to $B_3H_8^-$, the IR spectrum of the as received sample (blue curve on the figure S1) displayed other absorptions. In order to isolate absorptions by the water-related impurities, the sample was hydrated and dried. The ATR-FTIR spectra of the samples after drying and hydration are shown on Figure S1.

The peak at 1638 cm^{-1} observed in as received and hydrated samples, was assigned to H-O-H bending, indicating that molecular water can be absorbed by the sample. The corresponding -OH stretching could be observed in 3500-3000 $^{-1}$ regions. In addition, multiple modes that are related to lattice water and hydrolysis products arise in the low-frequency region (<1500 cm^{-1}).

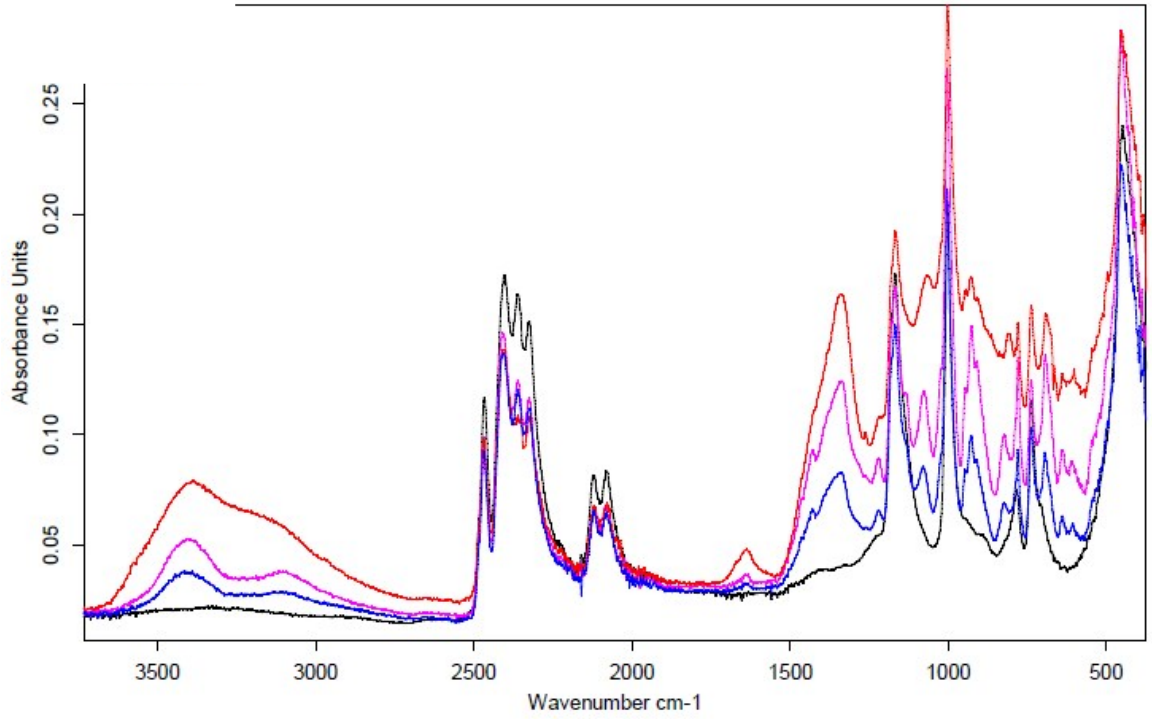

Figure S1. ATR-FTIR spectra of hydrated CsB3H8 upon drying, **blue**: as received sample; **red**: wetted with a drop of H_2O, **pink**: dried in air in a fume hood for 1 h; **black**: dried in vacuum furnace for 18 h at 120 ^oC.

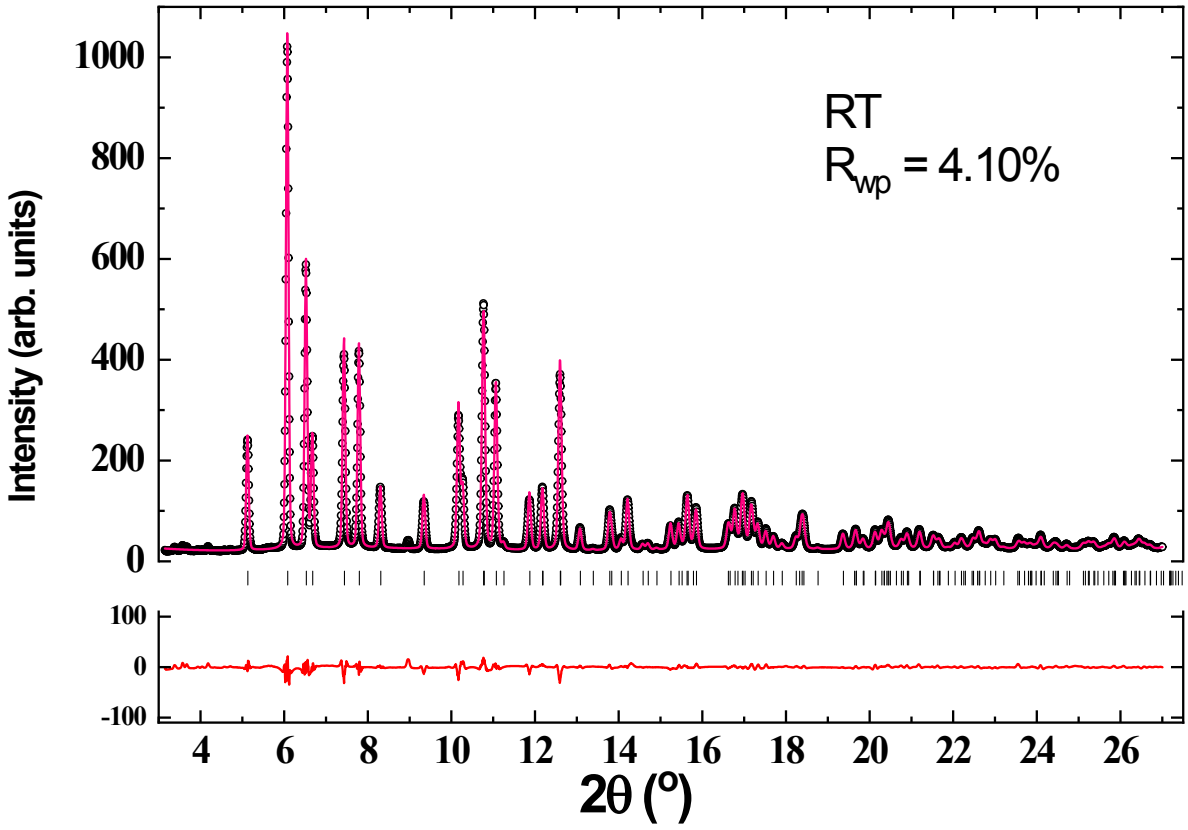

Figure S2. The Rietveld refinement of the R*T* phase of CsB_3H_8 α-CsB_3H_8

S3. Calculated Raman and FTIR spectra for the three phases of CsB_3H_8.

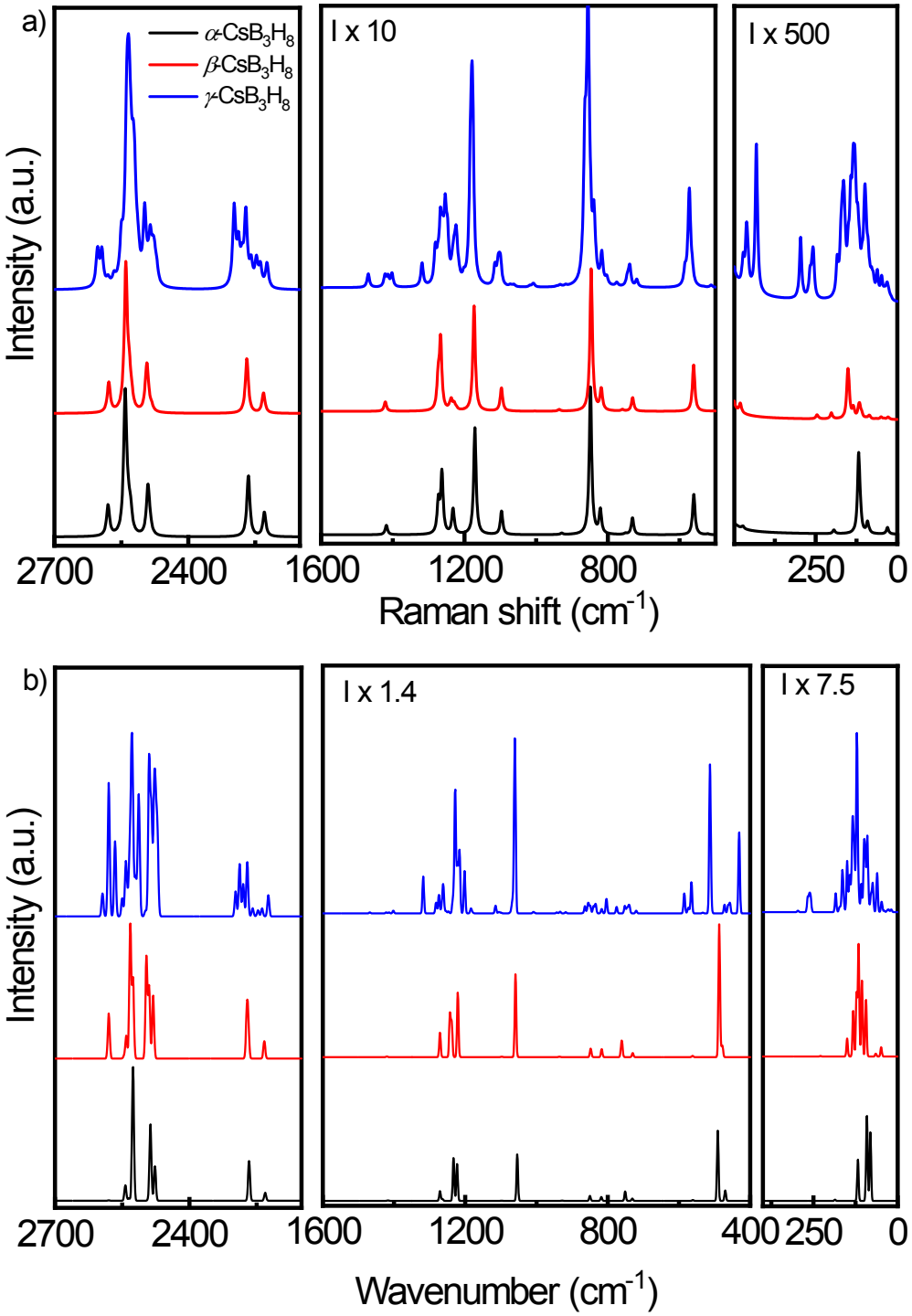

Figure S3. Calculated (a) Raman and (b) infrared spectra as obtained at the B3LYP level on periodic models of the three CsB_3H_8 phases.

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S4. Analysis of the PXRD patterns of the decomposition phases.

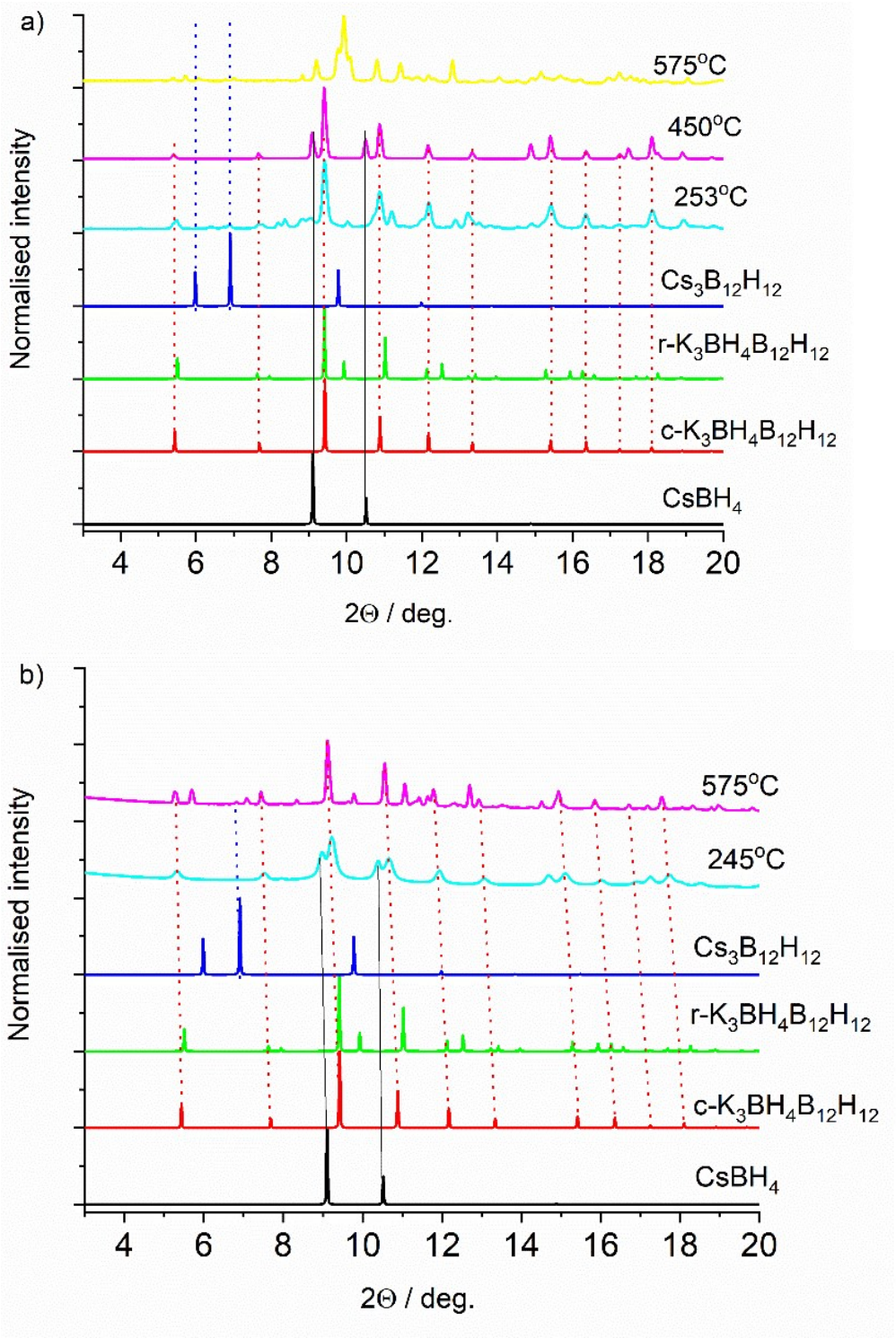


Figure S4 Phase matching of the decomposition phases with the known structures of Cs- and related hydroborates: a) ex-situ PXRD patterns obtained at RT; b) in-situ PXRD patterns obtained at the indicated temperatures with the related shifts in peak positions due to thermal expansion. The .cif files of the reference compounds were obtained from the references [1] [2]

S5. Crystal structures of *α*-, β-, and γ-CsB_3H_8 obtained via Rietveld refinement of SR-PXRD patterns and DFT calculations

α-CsB_3H_8 (R*T*-phase)

Experimental: *Ama*2 (No.62) a = 8.86567(14) Å, b = 8.66340(14) Å, c = 7.42725(13) Å, α=β=γ= 90°; V = 570.463629 Å^3; Z=4

Calculated: *Ama*2 (No.62) a = 8.9881 Å, b = 8.7653 Å, c = 7.4220 Å, α=β=γ= 90°; Z=4; V = 584.73 Å^3

Name	WP#	Sym.	x		y		z		Occ.	Biso (Å^2)*
			exp.	calc.	exp.	calc.	exp.	calc.		
Cs1	4b	m..	0.75	0.7500	0.17731(10)	0.1760	0	0.9900	1	2.79(4)
B1	4b	m..	0.75	0.7500	0.09310(15)	0.1000	0.454(3)	0.4900	1	16.8(17)
B2	8c	1	0.6481(10)	0.6494	0.27000(11)	0.2732	0.454(2)	0.4900	1	16.8(17)
H1	8c	1	0.593(4)	0.5905	0.135(4)	0.1437	0.463(10)	0.4900	1	20(4)
H2	4b	m..	0.75	0.7500	0.001(11)	0.0254	0.327(13)	0.3548	1	20(4)
H3	4b	m..	0.75	0.7500	0.02(14)	0.0254	0.592(14)	0.6251	1	20(4)
H4	8c	1	0.607(6)	0.6048	0.343(8)	0.3310	0.321(6)	0.3534	1	20(4)
H5	8c	1	0.603(7)	0.6048	0.332(9)	0.3310	0.592(9)	0.6267	1	20(4)
# Wyckoff position *exp.										

β-CsB_3H_8 (H*T*-1 phase)

Experimental: *Pnma* (No.62), a = 11.4197(3) Å; b = 8.87676(16) Å; c = 5.80554(11) Å, α=β=γ= 90°; Z=4; V = 588.505(19) Å^3

Theoretical: *Pnma* (No.62), a = 11.34297 Å, c = 9.03894 Å, c = 5.75032 Å, α=β=γ= 90°; Z=4; V = 589.571 Å^3

Name	WP#	Sym.	x		y		z		Occ.	Biso (Å^2)*
			exp.	calc.	exp.	calc.	exp.	calc.		
Cs1	4	.m.	0.64280(13)	0.6594	0.25	0.2500	0.6536(2)	0.6543	1	5.69(4)
B1	4	.m.	0.448(2)	0.4502	0.25	0.2500	0.110(5)	0.1500	1	7.0(5)
B2	8	1	0.3664(18)	0.3624	0.3498(14)	0.3501	0.322(3)	0.3493	1	7.0(5)
H1	8	1	0.423(7)	0.4288	0.406(8)	0.4086	0.158(17)	0.2014	1	7.0(13)
H2	4	.m.	0.416(7)	0.5548	0.25	0.2500	-0.089(18)	0.1769	1	7.0(13)
H3	4	.m.	0.556(7)	0.4205	0.25	0.2500	0.11(2)	0.9500	1	7.0(13)
H4	8	1	0.270(8)	0.3999	0.398(9)	0.3942	0.277(12)	0.5320	1	7.0(13)
H5	8	1	0.412(6)	0.2658	0.393(7)	0.3948	0.500(12)	0.2988	1	7.0(13)
# Wyckoff position *exp.										

γ-CsB_3H_8 (H*T*-2 phase)

Experimental: *Fm*-3*m*, a = 8.44149(19) Å; α=β=γ= 90°; Z=4; V = 601.53(4) Å^3

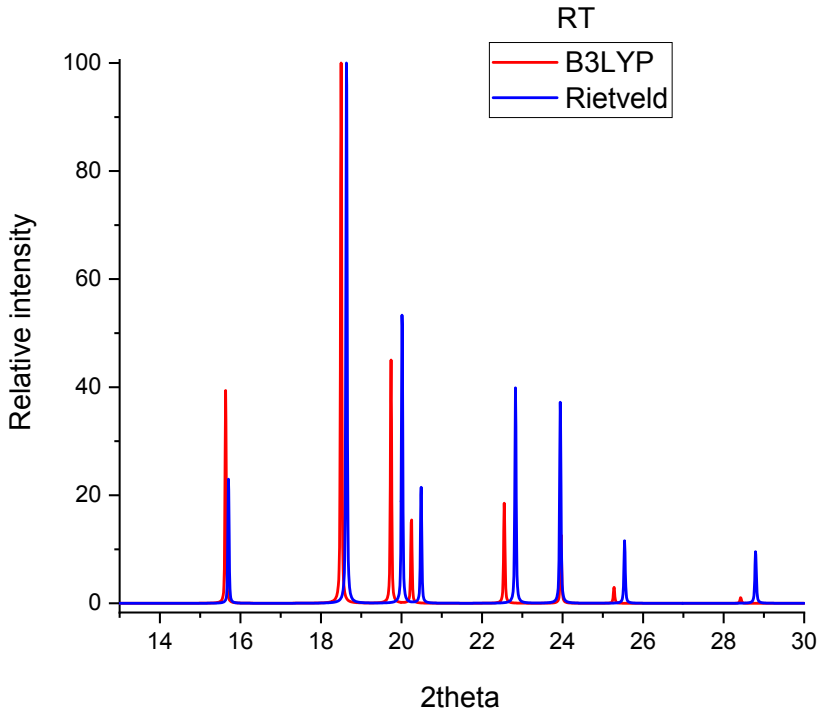
Name	WP#	Sym.	x	y	z	Occ.	Biso (Å^2)*
Cs1	32f	.3m	0.0497(3)	0.0497(3)	0.9503(7)	0.042	5.5(6)
B1	48i	m.m2	0.412(2)	0.412(2)	0.5	¼	10(4)
H1	96k	..m	0.357(17)	0.58(10)	0.58(10)	0.083	15(15)

H2	96k	..m	0.41(3)	0.69(3)	0.25	¼	15(15)
# Wyckoff position *exp.							

γ-CsB_3H_8 (H*T*-2 phase)

Theoretical: *P*3221 (No. 154), a = 8.44100000; b = 8.44100000; c = 8.44100000, α=β=γ= 90°; Z=24; V = 601.425307 Å^3

Name	WP#	Sym.	x	y	z	Occ.
CS1	6c	1	-0.00277	0.09463	0.04467	1
CS2	6c	1	0.09354	-0.3953	-0.498	1
CS3	6c	1	-0.44605	0.11039	-0.46272	1
CS4	6c	1	0.41169	-0.4141	5.8E-4	1
B5	6c	1	0.49439	-0.46044	-0.39015	1
B6	6c	1	0.48932	-0.47032	0.39712	1
H7	6c	1	0.43977	0.42044	-0.33377	1
H8	6c	1	0.43067	-0.34016	-0.34835	1
H9	6c	1	-0.37801	-0.46815	0.33125	1
H10	6c	1	-0.2598	-0.3341	0.49144	1
H11	6c	1	0.42575	-0.35295	0.34821	1
B12	6c	1	-0.32825	-0.45767	0.49873	1
H13	6c	1	-0.37056	-0.45085	-0.33051	1
H14	6c	1	-0.24596	0.42648	-0.49732	1
H15	6c	1	0.43123	0.4068	0.35384	1
B16	6c	1	0.43402	0.04791	-0.05805	1
B17	6c	1	-0.41951	-0.00134	0.08237	1
H18	6c	1	-0.42002	0.06484	-0.0804	1
H19	6c	1	0.38196	0.17839	-0.0812	1
H20	6c	1	0.49019	-0.0623	0.2244	1
H21	6c	1	0.33333	0.10915	0.21606	1
H22	6c	1	-0.34547	0.10218	0.14521	1
B23	6c	1	0.38107	-0.00375	0.1436	1
H24	6c	1	0.39355	-0.05174	-0.15183	1
H25	6c	1	0.28874	-0.11179	0.13407	1
H26	6c	1	-0.34751	-0.12086	0.0571	1
B27	6c	1	-0.0335	0.03117	0.43688	1
B28	6c	1	-0.05124	-7.1E-4	-0.35377	1
H29	6c	1	-0.10883	0.14636	0.40024	1
H30	6c	1	-0.06445	-0.08702	0.36354	1
H31	6c	1	0.07789	-2.8E-4	-0.28109	1
H32	6c	1	0.23067	-0.06196	-0.45255	1
H33	6c	1	-0.10168	-0.13137	-0.32968	1
B34	6c	1	0.13505	0.04256	-0.44048	1
H35	6c	1	0.10335	0.06635	0.39172	1
H36	6c	1	0.18929	0.17034	-0.41128	1
H37	6c	1	-0.12595	0.1048	-0.29348	1
B38	6c	1	0.02424	-0.4892	-0.09955	1
B39	6c	1	0.01409	-0.46866	0.11246	1
H40	6c	1	0.09343	0.39151	-0.13572	1
H41	6c	1	0.07979	-0.36932	-0.15216	1
H42	6c	1	-0.12224	-0.46901	0.16963	1
H43	6c	1	-0.23788	-0.36956	-0.01574	1
H44	6c	1	0.06583	-0.34094	0.14838	1
B45	6c	1	-0.16059	-0.48714	-0.00162	1
H46	6c	1	-0.10669	0.49907	-0.16771	1
H47	6c	1	-0.23381	0.39132	0.00683	1
H48	6c	1	0.07846	0.4208	0.17596	1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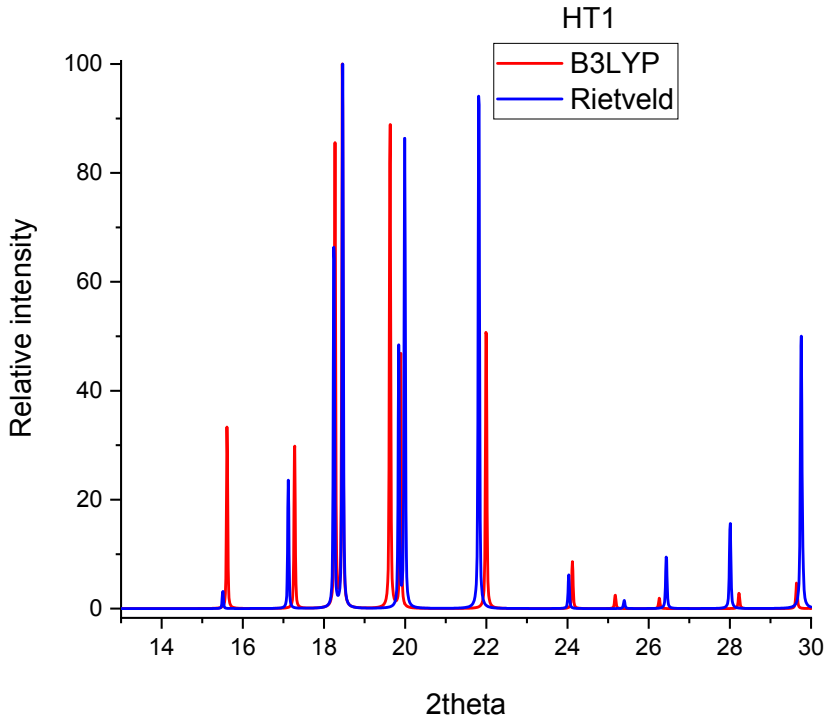
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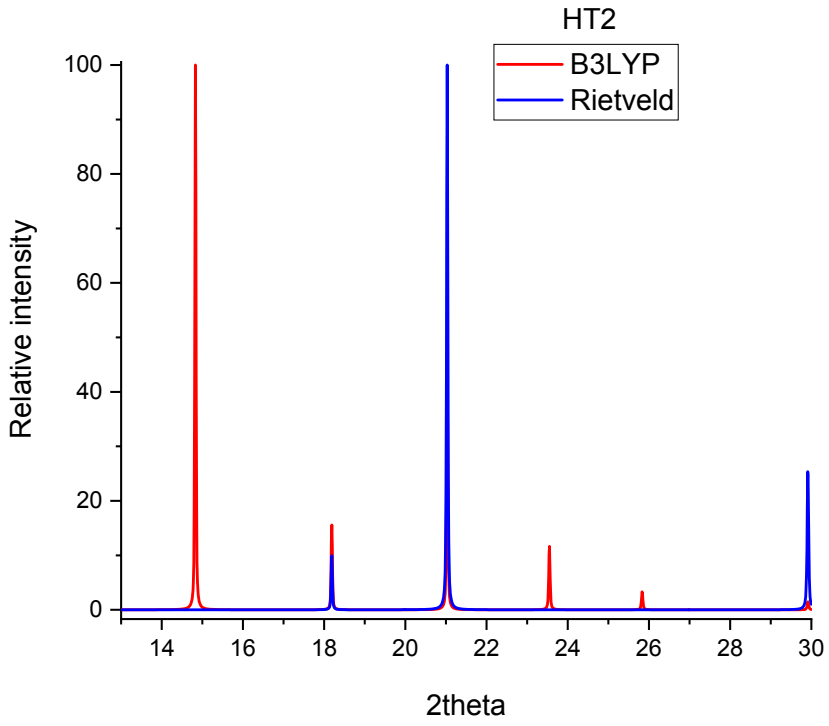

Figure S5. Comparison of the simulated XRD patterns of the three structures of CsB_3H_8 obtained with Rietveld refinement and DFT calculations. The patterns are simulated with the λ = 1.54 Å.

References

1. Y. Sadikin, R. V. Skoryunov, O. A. Babanova, A. V. Soloninin, Z. Lodziana, M. Brighi, A. V. Skripov and R. Černý, *The Journal of Physical Chemistry C*, 2017, **121**, 5503-5514.
2. I. Tiritiris, T. Schleid, K. Müller and W. Preetz, *Zeitschrift für anorganische und allgemeine Chemie*, 2000, **626**, 323-325.