Supplementary data

Table S1a. Crystal structure details and atomic fractional coordinates for the *Immm* model (average structure) of the high temperature phase of $Mg(BH_4)_2$ (without H atoms): a = 18.537(4) Å, b = 9.325(3) Å, c = 5.456(1) Å. In this refinement, broad peaks (odd order peaks from the parent *Fddd* structure) were simulated as individual pseudo-Voigt lineshapes to minimize their effect to the structure model, omitted in Fig. 2.

Atom	Wyckoff site	Occupancy	*X*	*Y*	*Z*	B_{iso}
Mg1	*8n*	0.5	0.1061	0.3600	0	7.17
Mg2	*8m*	0.5	0.1546	0	0.5707	7.17
B3	*16o*	0.5	0.3888	0.7032	0.1413	11.81
B4	*4f*	1	0.2842	0	0.5	11.81
B5	*2d*	1	0	0.5	0	11.81
B6	*4e*	0.5	0.8781	0	0	11.81

Table S1b. Crystal structure details and atomic fractional coordinates for the *Fddd* model of the high temperature phase of $Mg(BH_4)_2$ except H atoms: a = 37.072(1)Å, b = 18.6476(6)Å, c = 10.9123(3)Å. Note that stated *e.s.d.* is provided by the Rietveld program considering only the statistical error; it is not claimed as standard uncertainty.

Atom	Wyckoff site	Occupancy	*X*	*Y*	*Z*	B_{iso}
Mg1	*32h*	1	0.0775(1)	0.2501(7)	0.5381(6)	6.6(2)
Mg2	*32h*	1	0.0529(1)	0.9298(3)	0.7464(13)	6.6(2)
B3	*32h*	1	0.4460(6)	0.1533(18)	0.4104(22)	10.1(3)
B4	*32h*	1	0.1078(1)	1.0085(3)	0.2636(7)	10.1(3)
B5	*16e*	1	0.3124(4)	0	0	10.1(3)
B6	*32h*	1	0.4441(6)	0.6472(17)	0.5602(24)	10.1(3)
B7	*16g*	1	0	0	0.7730(26)	10.1(3)

Table S2.

The quadratic elongation and bond angle variance as defined by Robinson *et al.* (1971) are

$$\lambda_{tet} = \sum_{i=1}^{4} (l_i / l_o)^2 / 4$$, and

$$\sigma_{\theta^2} = \sum_{i=1}^{6} (\theta_i - \arccos(-1/3))^2 / 5$$,

where l_o is the center to vertex distance of an undistorted tetrahedron of the same volume and the angles θ_i are the B-Mg-B angles.

Central atom	Average bond length (Å)	Polyhedral volume (Å^3)	Quadratic elongation	Bond angle variance (degrees^2)
Low Temperature Phase				
Mg1	2.41	6.70	1.050	187.1
Mg2	2.40	6.42	1.073	254.9
Mg3	2.45	6.68	1.082	294.4
Mg4	2.43	6.90	1.043	150.4
Mg5	2.44	6.69	1.073	258.3
High Temperature Phase				
Mg1	2.39	6.96	1.008	30.4
Mg2	2.39	6.93	1.011	42.4

Polyhedral parameters were obtained using VICS-II developed by Momma & Izumi (2006): http://www.geocities.jp/kmo_mma/crystal/en/vics.html.