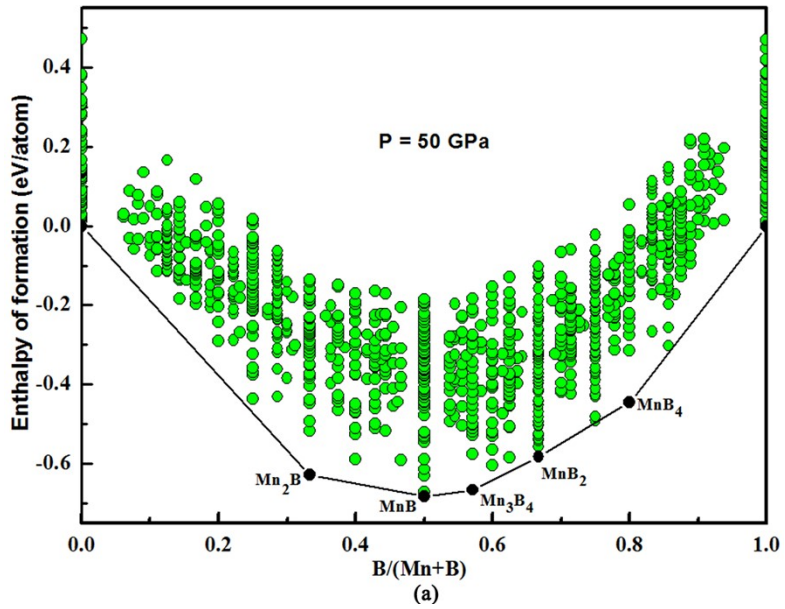
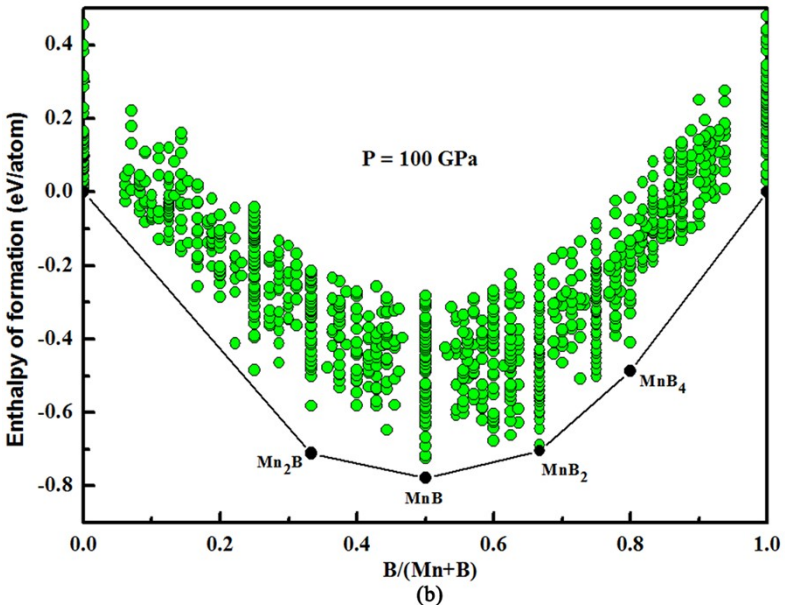
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Figure S1. The enthalpies of formation predicted by variable-composition evolutionary computations for the Mn–B system at (a) 50 GPa, (b) 100 GPa and (c) 200 GPa. Every circle represents an individual structure and the most stable ground-state phases (black circles) are connected to form the convex hull.





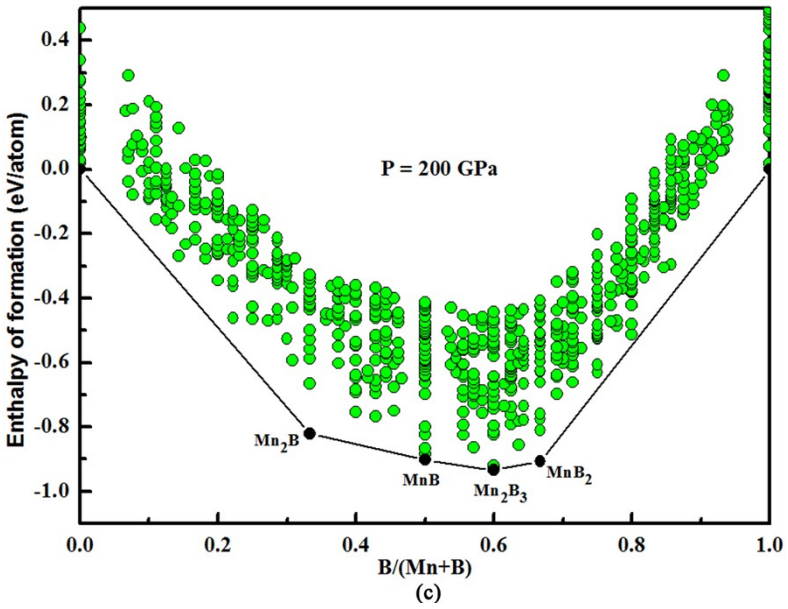


Table S1. Lattices Parameters and atomic coordinates of *Cmcm*-Mn_2B_3 at ambient pressure.

	Lattices Parameters (Å)	Atoms	x	y	z
	a = 2.952	Mn (4c)	0.00000	0.20468	0.75000
Cmcm-Mn_2B_3	b = 17.957	Mn (4c)	0.00000	0.07245	1.25000
	c = 2.965	B (4c)	0.50000	0.97591	1.25000
P = 0 GPa	α = β = γ = 90º	B (4c)	0.50000	0.17365	1.25000
		B (4c)	0.50000	0.88011	1.25000

Table S2. Lattices Parameters and atomic coordinates of *C*2/*m*-Mn_2B_3 at ambient pressure.

	Lattices Parameters (Å)	Atoms	x	y	z
	a = 7.554	Mn (4i)	0.05607	0.50000	0.85428
C2/m-Mn_2B_3	b = 2.953	Mn (4i)	0.20309	0.50000	0.61177
	c = 8.114	B (4i)	0.25716	0.50000	0.18584
P = 0 GPa	α =γ = 90º	B (4i)	0.48782	0.50000	0.60603
	β =121.107º	B (4i)	0.12637	0.00000	0.08799

Table S3. Lattices Parameters and atomic coordinates of *C*2/*c*-Mn_2B_3 at ambient pressure.

	Lattices Parameters (Å)	Atoms	x	y	z
	a = 6.968	Mn (8f)	0.35295	0.36384	0.35411
C2/c-Mn_2B_3	b = 4.025				
	c = 5.507	B (8f)	0.13691	0.36249	0.00206
P = 0 GPa	α =γ = 90º				
	β =150.324º	B (4e)	0.00000	0.65684	0.75000

Table S4. Unit cell parameters of binary borides Ti_2B_3, Mn_2B_3, Nb_2B_3, V_2B_3 and Cr_2B_3.

Phase	a (Å)	b (Å)	c (Å)	V (Å^3)
Mn_2B_3	2.952	17.957	2.965	157.216
Cr_2B_3	2.930	18.170	2.949	156.977
	3.027[a]	19.119[a]	2.954[a]	162.016[a]
V_2B_3	3.034	18.408	2.979	166.325
	3.061[b]	18.400[b]	2.984[b]	168.066[b]
Nb_2B_3	3.324	19.603	3.141	204.711
	3.306[c]	19.481[c]	3.129c[b]	201.528[c]
Ti_2B_3	3.243	19.024	3.038	187.422
	3.243[d]	19.025[d]	3.038[d]	187.431[d]

Ref a: Okada S.; Atoda T.; Higashi I. Structural investigation of Cr_2B_3, Cr_3B_4, and CrB by single-crystal diffractometry. *J. Solid State Chem*. **1987**, *68*, 61-67.

Ref b: Spear, K. E, Gilles, P. W. Phase and structure relationships in the vanadium-boron system. *HIGH TEMP SCI*. **1969**, *1*, 86-97.

Ref c: Yu, Y.; Tergenius, L. E.; Lundström, T.;Okada, S., A structural investigation of V_2B_3 by single-crystal diffractometry. *J. Alloys Compd.* **1995,** *221*, 86-90.

Ref d: Li, P. F.; Zhou, R. L.;Xiao, C. Z., Computational Analysis of Stable Hard Structures in the Ti–B System, *ACS Appl. Mater. Interfaces.* **2015,** *7*, 15607.

Figure S2. Phonon dispersion curves and phonon density of states for *Cmcm*-Mn_2B_3, at (a) 0 GPa. *C*2/*m*-Mn_2B_3, at (b) 0 GPa and (c) 80 GPa. *C*2/*c*-Mn_2B_3, at (d) 0 GPa and (e) 200 GPa.

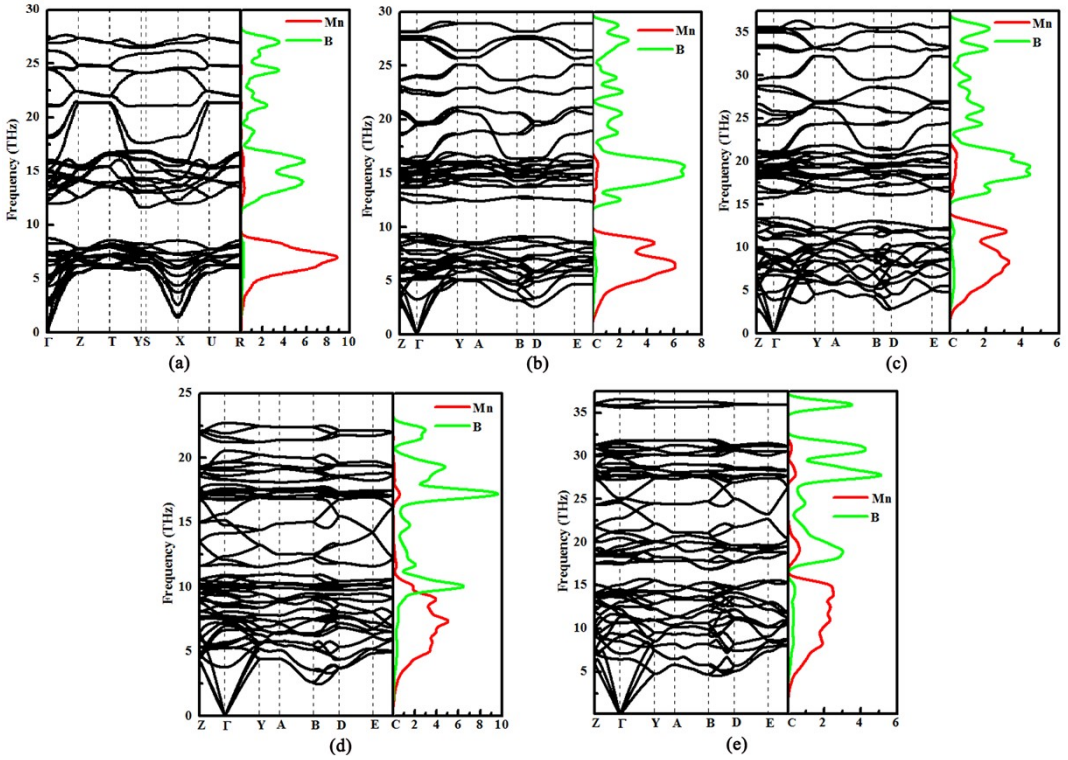


Table S5. Elastic constants of TM_2B_3s (SG: *Cmcm*) including Mn_2B_3, Cr_2B_3, V_2B_3, Nb_2B_3, and Ti_2B_3, as well as *C*2/*m*- and *C*2/*c*-Mn_2B_3 at ambient pressure.

Phase (SG)	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{15}	C_{23}	C_{25}	C_{35}	C_{46}
Mn_2B_3 (*Cmcm*)	321	481	526	205	172	155	101	125		127			
Cr_2B_3 (*Cmcm*)	450	596	593	217	219	182	178	191		169			
V_2B_3 (*Cmcm*)	496	654	640	245	255	224	138	148		112			
Nb_2B_3 (*Cmcm*)	472	537	574	215	236	223	172	159		129			
Ti_2B_3 (*Cmcm*)	438	543	595	237	244	218	119	108		70			
Mn_2B_3 (*C*2/*m*)	430	494	430	188	155	172	127	194	24	179	-10	63	17
Mn_2B_3 (*C*2/*c*)	439	478	448	151	190	93	227	230	-23	199	38	-17	25

Table S6 Calculated bond parameters and Vickers hardness of Mn_2B_3(SG:*Cmcm*).

Bond type	d^{μ} (Å)	v_b^{μ} (Å^3)	P	f_m ($\times 10^{-3}$)	H_v (GPa)
B-B	1.709	0.661	0.98	0	20.0
	1.719	0.673	0.95	0	
	1.798	0.770	0.81	0	
	2.952	3.409	0.06	0	
	2.952	3.409	0.04	0	
Mn-B	2.061	1.160	0.04	5.940	
	2.134	1.288	0.26	5.940	
	2.235	1.479	0.34	5.940	
	2.261	1.532	0.05	5.940	
	2.261	1.532	0.09	5.940	
	2.263	1.536	0.05	5.940	
	2.386	1.800	0.05	5.940	
Mn-Mn	2.952	3.409	0.03	5.940	
	2.965	3.454	0.09	5.940	

Table S7 Calculated bond parameters and Vickers hardness of Cr_2B_3(SG:*Cmcm*).

Bond type	d^{μ} (Å)	v_b^{μ} (Å^3)	P	f_m ($\times 10^{-3}$)	H_v (GPa)
B-B	1.707	0.634	0.88	0	29.9
	1.729	0.659	0.82	0	
	1.766	0.702	0.76	0	
	2.930	3.208	0.05	0	
	2.930	3.208	0.02	0	
	2.930	3.208	0.03	0	
Cr-B	2.119	1.214	0.02	2.314	
	2.152	1.271	0.21	2.314	
	2.247	1.447	0.07	2.314	
	2.255	1.462	0.05	2.314	
	2.264	1.480	0.25	2.314	
	2.270	1.492	0.02	2.314	
	2.342	1.638	0.04	2.314	
Cr-Cr	2.930	3.208	0.07	2.314	
	2.949	3.271	0.02	2.314	

Table S8 Calculated bond parameters and Vickers hardness of V_2B_3(SG:*Cmcm*).

Bond type	d^{μ} (Å)	v_b^{μ} (Å^3)	P	f_m ($\times 10^{-3}$)	H_v (GPa)
B-B	1.724	0.893	0.89	0	22.9
	1.729	0.901	0.85	0	
	1.760	0.950	0.82	0	
V-B	2.230	1.932	0.18	1.542	
	2.293	2.101	0.04	1.542	
	2.296	2.109	0.06	1.542	
	2.300	2.120	0.01	1.542	
	2.330	2.204	0.24	1.542	
	2.358	2.285	0.05	1.542	
V-V	2.979	4.607	0.08	1.542	

Table S9 Calculated bond parameters and Vickers hardness of Nb_2B_3(SG:*Cmcm*).

Bond type	d^{μ} (Å)	v_b^{μ} (Å^3)	P	f_m ($\times 10^{-3}$)	H_v (GPa)
B-B	1.808	1.009	0.81	0	22.7
	1.816	1.023	0.77	0	
	1.845	1.072	0.75	0	
Nb-B	2.403	2.369	0.20	1.113	
	2.460	2.542	0.05	1.113	
	2.462	2.548	0.09	1.113	
	2.508	2.693	0.08	1.113	
	2.601	3.004	0.24	1.113	
Nb-Nb	2.951	4.388	0.04	1.113	

Table S10 Calculated bond parameters and Vickers hardness of Ti_2B_3(SG:*Cmcm*).

Bond type	d^{μ} (Å)	v_b^{μ} (Å^3)	P	f_m ($\times 10^{-3}$)	H_v (GPa)
B-B	1.753	0.842	0.90	0	28.9
	1.758	0.849	0.84	0	
	1.773	0.871	0.87	0	
Ti-B	2.352	2.032	0.20	1.368	
	2.382	2.111	0.04	1.368	
	2.386	2.122	0.06	1.368	
	2.393	2.141	0.09	1.368	
	2.425	2.228	0.06	1.368	
	2.520	2.500	0.24	1.368	
Ti-Ti	2.828	3.533	0.07	1.368	

Table S11 Calculated bond parameters and Vickers hardness of Mn_2B_3(SG:*C*2/*m*).

Bond type	d^{μ} (Å)	v_b^{μ} (Å^3)	P	f_m ($\times 10^{-3}$)	H_v (GPa)
B-B	1.714	1.444	0.82	0	20.9
	1.727	1.478	1.78	0	
	1.780	1.618	0.73	0	
	1.834	1.770	0.71	0	
	2.782	6.176	0.06	0	
Mn-B	2.073	2.555	0.22	3.458	
	2.162	2.899	0.12	3.458	
	2.168	2.923	0.23	3.458	
	2.190	3.013	0.48	3.458	
	2.192	3.021	0.12	3.458	
	2.195	3.034	0.29	3.458	
	2.203	3.067	0.12	3.458	
	2.246	3.25	0.02	3.458	
	2.428	4.106	0.24	3.458	

Table S12 Calculated bond parameters and Vickers hardness of Mn_2B_3(SG:*C*2/*c*).

Bond type	d^{μ} (Å)	v_b^{μ} (Å^3)	P	f_m ($\times 10^{-3}$)	H_v (GPa)
B-B	1.791	0.990	0.79	0	15.6
	1.854	1.099	0.69	0	
	1.938	1.255	0.57	0	
	2.232	1.917	0.04	0	
Mn-B	2.147	1.706	0.14	5.507	
	2.158	1.732	0.04	5.507	
	2.159	1.735	0.15	5.507	
	2.163	1.744	0.28	5.507	
	2.294	2.081	0.13	5.507	
	2.328	2.175	0.11	5.507	
	2.391	2.356	0.01	5.507	
Mn-Mn	2.565	2.909	0.01	5.507	

Table S13. The Bader charge analysis of five TM_2B_3s (TM = Mn, Cr, V, Nb and Ti), *C*2/*m*- and *C*2/*c*-Mn_2B_3 in 2×2×1 cells. The positive (negative) sign denotes the loss (gain) of electrons. There is the number of atoms in brackets.

	TM (e)	**B (e)**
Mn_2B_3	+0.55 (16), +0.78 (16)	-0.38 (8), -0.41 (8), -0.46 (16), -0.47 (16)
Cr_2B_3	+0.69 (16), +0.89 (16)	-0.45 (8), -0.49 (8), -0.51 (16), -0.59 (16)
V_2B_3	+1.12 (16), +0.87 (16)	-0.59 (8), -0.61 (16), -0.63 (8), -0.78 (16)
Nb_2B_3	+0.95 (16), +1.28 (16)	-0.61 (8), -0.63 (8), -0.74 (16), -0.88 (16)
Ti_2B_3	+1.04 (16), +1.29 (16)	-0.64 (4), -0.68 (20), -0. 66 (8), -0.99 (2), -1.00 (14),
***C*2/*m*-Mn_2B_3**	+0.53 (16), +0.78 (16)	-0.36 (8), -0.38 (8), -0.44 (8), -0.45 (24),
***C*2/*c*-Mn_2B_3**	+0.56 (32)	-0.16 (16), -0.48 (32)

Table S14. The averaged –ICOHP values (in eV/per bond) and bond lengths (Å) computed for some stronger TM-B and B-B bonds in five TM_2B_3s (TM = Mn, Cr, V, Nb and Ti), *C*2/*m*- and *C*2/*c*-Mn_2B_3.

	TM-B, B-B	bond length	-ICOHP
Mn_2B_3	Mn-B	2.185	1.282
		2.165	0.843
		2.121	0.782
	B-B	1.720	3.615
		1.717	3.525
		1.769	3.151
Cr_2B_3	Cr-B	2.262	2.185
		2.151	1.933
		2.117	1.769
	B-B	1.706	6.869
		1.732	6.735
		1.766	6.601
V_2B_3	V-B	2.318	2.198
		2.229	1.801
		2.212	1.518
	B-B	1.732	6.914
		1.725	6.867
		1.761	6.404
Nb_2B_3	Nb-B	2.403	2.193
		2.602	1.984
		2.379	1.925
	B-B	1.817	6.051
		1.809	5.901
		1.843	5.549

Ti_2B_3	Ti-B	2.510 2.353 2.341	1.862 1.590 1.256
	B-B	1.773 1.761 1.755	6.453 6.624 6.620
	Ti-Ti	2.819 2.991	0.772 0.295
*C*2/*m*-Mn_2B_3	Mn-B	2.175 2.179 2.111	1.234 0.919 0.830
	B-B	1.723 1.789 1.822	3.299 3.021 2.891
*C*2/*c*-Mn_2B_3	Mn-B	2.153 2.317 2.161	1.527 0.903 0.792
	B-B	1.822 1.838	2.983 2.702