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

Supplementary material to: Structural Variety beyond Appearance: High-pressure Phases of CrB_4 in comparison with FeB_4

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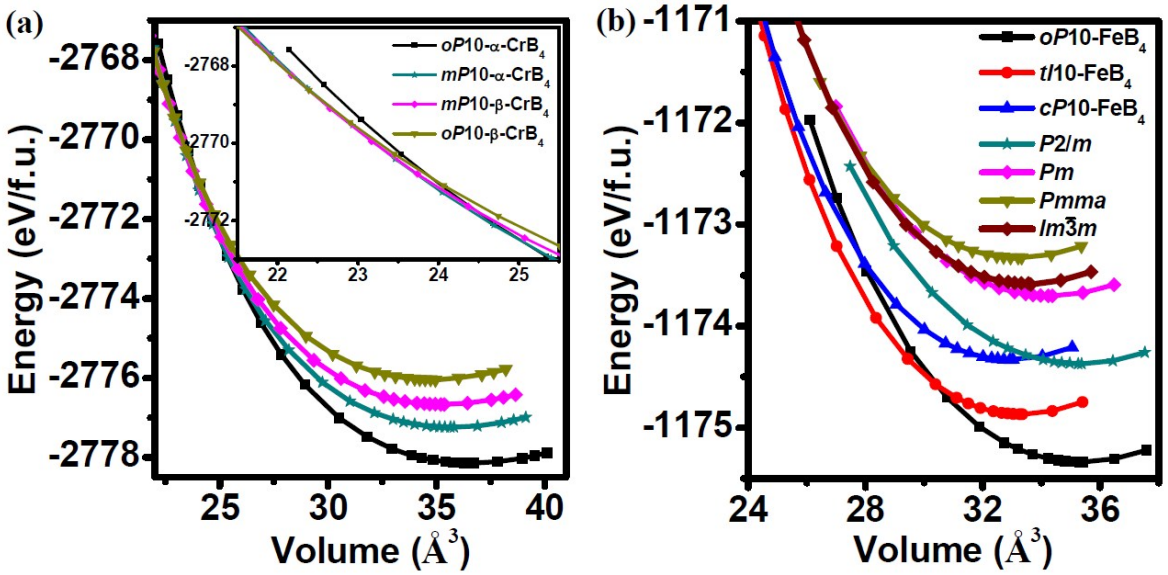

Fig. S1 Total energy as a function of unit volume (per f.u.) curves for (a) CrB_4 and (b) FeB_4.

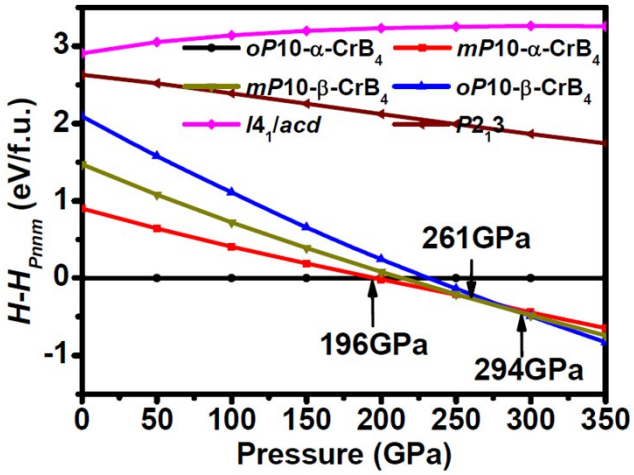

Fig. S2 Enthalpy difference (relative to *Pnnm* structure) as a function of pressure for $I4_1/acd$-type and $P2_13$-type CrB_4 compared with the *mP*10-α-CrB_4, *mP*10-β-CrB_4, and *oP*10-β-CrB_4.

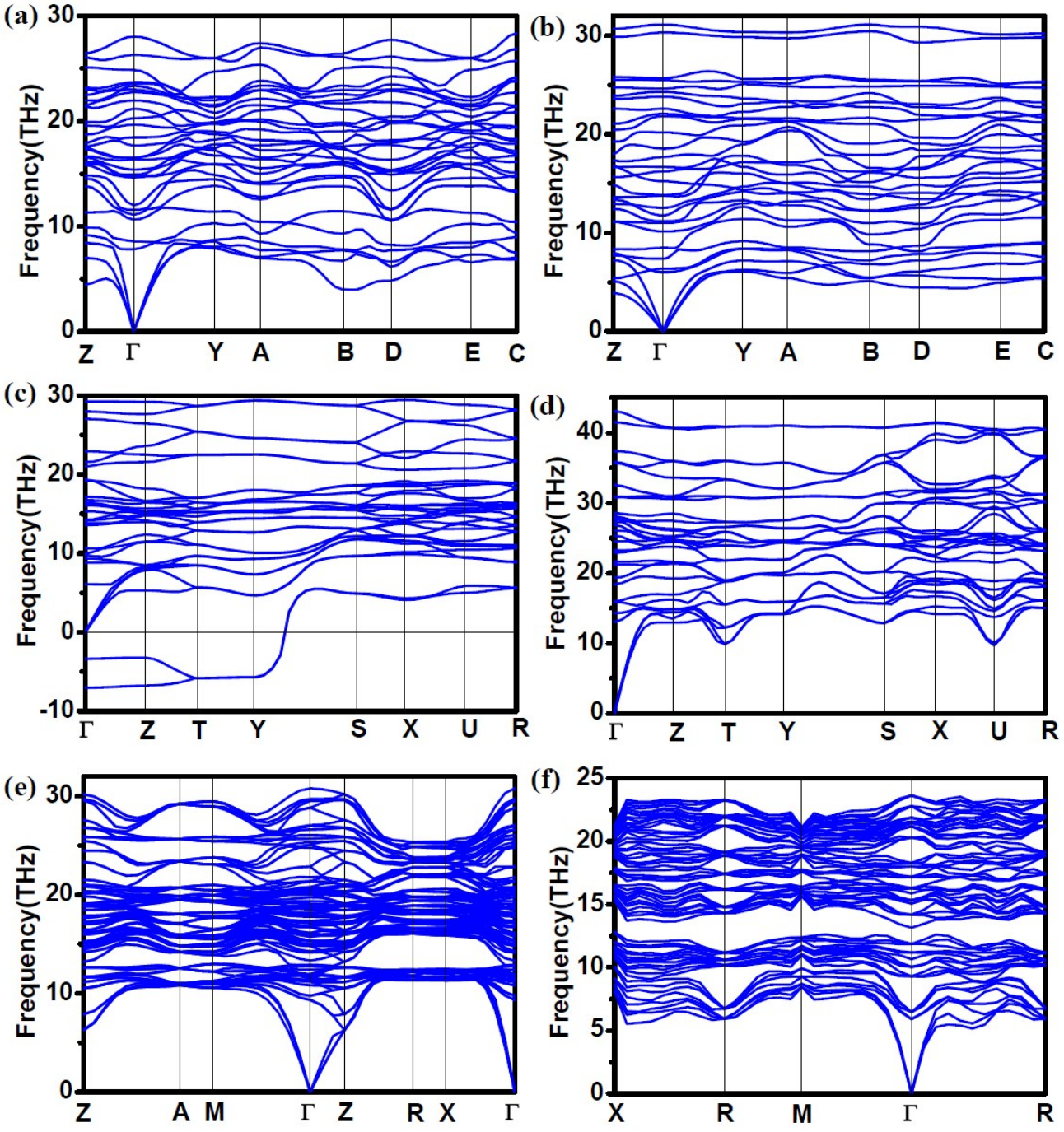

Fig. S3 Phonon dispersion curves of high pressure phases for CrB_4 and FeB_4. (a) *mP*10-α-CrB_4; (b) *mP*10-β-CrB_4; (c) *oP*10-β-CrB_4 at 0 GPa; (d) *oP*10-β-CrB_4 at 294 GPa; (e) *tI*40-FeB_4; (f) *cP*20-FeB_4. The *oP*10-β-CrB_4 is dynamically unstable at zero pressure with imaginary frequency in the Brillouin Zone. At pressure above 294 GPa, however, the *oP*10-β-CrB_4 becomes dynamically stable with all frequencies become positive. The other phases are dynamically stable at zero pressure with the absence of imaginary phonon frequencies throughout the Brillouin Zone. A supercell with 3×5×3 k-points for *mP*10-α-CrB_4, with 3×5×3 k-points for *mP*10-β-CrB_4, with 3×6×3 k-points for *oP*10-β-CrB_4, with 3×3×1 k-points for *tI*40-FeB_4, and with 4×4×4 k-points for *cP*20-FeB_4 were adopted.

Table SI Calculated elastic constants C_{ij} (GPa) of the *mP*10-α-CrB4 and *mP*10-β-CrB4.

	S.G.	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}	C_{15}	C_{25}	C_{35}	C_{46}
*mP*10-α-CrB_4	*P*2/*m*	592	490	477	186	225	224	125	179	173	67	-11	95	35
*mP*10-β-CrB_4	*Pm*	580	486	535	105	184	179	106	136	125	29	2	-18	-3