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Novel structural phases and electrical properties of Si_3B under high pressure

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Table S1. Predicted lattice constants, atomic coordinates and relative formation enthalpy per atom ΔH of Si_3B at zero pressure.

structure	lattice parameters (Å, deg)	atomic coordinates (fractional)
$P2_1/m$	a = 3.49, b = 3.03, c = 10.63,	Si 2e (–0.618, –0.250, 0.577)
	$\alpha = \gamma = 90$, $\beta = 95.8$	Si 2e (–0.904, –0.250, 1.018)
		Si 2e (–0.809, –0.750, 0.546)
		B 2e (–0.482, –0.750,–0.107)
$C2/m$	a = 9.99, b = 3.18, c = 14.07,	Si 4i (0.760, 0.000, 0.626)
	$\alpha = \gamma = 90$, β= 152.8	Si 4i (–0.801, 0.000, 0.051)
		Si 4i (1.079, 0.000, 0.680)
		B 4i (–0.453, 0.000, 0.169)
$Imm2$	a = 16.09, b = 2.92, c =4.25,	Si 4c (0.123, 0.000, 0.893)
	$\alpha = \beta = \gamma = 90$	Si 4c (0.421, 0.000, 0.860)
		Si 4c (0.273, 0.500, 0.939)
		B 2b (0.000, 0.500, 0.936)
$Cmcm$	a = 3.73, b = 18.36, c = 2.98,	Si 4c (0.000, 0.197, 0.250)
	$\alpha = \beta = \gamma = 90$	Si 4c (0.000, 0.059, 0.250)
		Si 4c (0.500, 0.142, 0.750)
		B 4c (0.000, 0.474, 0.250)
$Immm$	a = 9.27, b = 2.71, c = 4.05,	Si 4e (0.720, 0.500, 0.500)
	$\alpha = \beta = \gamma = 90$	Si 1a (0.220, 0.000, 0.000)
		Si 2b (0.000, 0.500, 0.500)
		B 2a (0.000, 0.000, 0.000)
$Imma$	a = b = c = 7.26,	Si 1a (0.501, 0.151, 0.150)
	α =48.1, β =154.6, γ =139.9	Si 1a (0.501,0.351, 0.350)
		Si 1a (0.500, 0.849, 0.850)
		Si 1a (0.500, 0.649, 0.650)
		Si 1a (0.000, 0.000, 0.500)
		Si 1a (0.000, 0.500, 0.000)
		B 1a (0.998, 0.248, 0.750)
		B 1a (0.002, 0.752, 0.250)
$P4/mmm$	a = b = 2.77, c = 6.39,	Si 2g (0.000, 0.000, 0.694)
	$\alpha = \beta = \gamma = 90$	Si 1a (0.000, 0.000, 0.306)
		Si 1c (0.500, 0.500, 0.000)
		B 1d (0.500, 0.500, 0.500)
$P3_121$	a = b = 4.86, c = 6.44,	Si 6c (0.488, 0.903, 0.033)
	$\alpha = \beta = 90$, $\gamma = 120$	Si 1a (0.903, 0.488, 0.967)
		Si 3a (0.908, 0.000, 0.333)
		B 3a (0.504, 0.504, 0.000)
P-31m	a = b = 5.30, c = 4.15,	Si 6k (0.000, 0.688, 0.763)
	$\alpha = \beta = 90$, $\gamma = 120$	Si 1a (0.312, 0.312, 0.763)
		Si 1a (0.688, 0.000, 0.763)

		B 2d (0.333, 0.667, 0.500)
R-3*m*	*a* = 7.09, b = 7.09, c = 7.09,	Si 1a (0.500, 0.500, 0.500)
	α = β = γ = 25.3	Si 1a (0.384, 0.384, 0.384)
		Si 1a (0.616, 0.616,0.616)
		B 1a (0.000, 0.000, 0.000)
$P6_322$	*a* = b = 5.29, c = 4.21,	Si 6g (0.711, 0.711, 0.500)
	α = β = 90, γ = 120	Si 1a (0.000, 0.289, 0.500)
		Si 1a (0.711, 0.000, 0.000)
		B 2c (0.333, 0.667, 0.250)
Pm-3*m*	*a* = b = c = 3.665,	Si 1a (0.000, 0.500, 0.500)
	α = β= γ = 90	Si 1a (0.500, 0.000, 0.500)
		Si 1a (0.500, 0.500, 0.000)
		B 1a (0.000, 0.000, 0.000)

Table S2 The calculated bond parameters, Mayer bond order (MBO), and hardness of *C*2/*m* and $P2_1/m$ at 0 GPa computed by the Gao's model.

Structure	V(Å^3)	bond	d^{μ}(Å)	MBO	P^{μ}	ν_b^{μ}	H_v^{μ}	H_v(GPa)
*C*2/*m*	204.113	B-Si	2.077	1.30	0.39	4.55	22.5	14.5
		B-Si	2.142	1.32	0.27	5.00	13.2	
		B-Si	2.149	1.32	1.15	5.04	56.9	
		B-Si	2.157	1.33	0.94	5.10	45.5	
		Si-Si	2.526	1.35	0.23	8.19	4.9	
		Si-Si	2.584	1.35	0.74	8.77	14.5	
		Si-Si	2.629	1.34	0.68	9.24	12.2	
		Si-Si	2.724	1.33	0.05	10.27	0.6	
$P2_1/m$	112.211	B-B	1.759	0.7	1.33	2.78	178.6	14.2
		B-Si	2.039	0.92	1.13	4.34	72.4	
		B-Si	2.306	0.92	0.01	6.27	0.35	
		Si-Si	2.516	1.31	0.74	8.14	16.6	
		Si-Si	2.528	1.30	1.41	8.26	30.9	
		Si-Si	2.542	1.30	0.54	8.40	11.5	

Table S3 The calculated bond parameters and hardness of *C*2/*m* and $P2_1/m$ at 0 GPa

computed by the Oganov's model.

Structure	V(Å)	$bond_{a-b}$	n_a	n_b	R_a	R_b	H_k(GPa)
$C2/m$	204.113	B-Si	3	4	0.80	1.18	13.2
		B-Si	3	4	0.80	1.18	
		B-Si	3	4	0.80	1.18	
		B-Si	3	4	0.80	1.18	
		Si-Si	4	4	1.18	1.18	
		Si-Si	4	4	1.18	1.18	
		Si-Si	4	4	1.18	1.18	
		Si-Si	4	4	1.18	1.18	
$P2_1/m$	112.211	B-B	3	3	0.80	0.80	19.2
		B-Si	3	4	0.80	1.18	
		B-Si	3	4	0.80	1.18	
		Si-Si	4	4	1.18	1.18	
		Si-Si	4	4	1.18	1.18	
		Si-Si	4	4	1.18	1.18	

Table S4 The calculated bond parameters and hardness of $C2/m$ and $P2_1/m$ at 0 GPa

calculated by the Šimůnek's model.

Structure	V(Å^3)	bond$_{a\text{-}b}$	d^{μ}(Å)	R_a	R_b	e_a	e_b	H(GPa)
$C2/m$	204.113	B-Si	2.077	0.80	1.18	3.75	3.39	13.2
		B-Si	2.142	0.80	1.18	3.75	3.39	
		B-Si	2.149	0.80	1.18	3.75	3.39	
		B-Si	2.157	0.80	1.18	3.75	3.39	
		Si-Si	2.526	1.18	1.18	3.39	3.39	
		Si-Si	2.584	1.18	1.18	3.39	3.39	
		Si-Si	2.629	1.18	1.18	3.39	3.39	
		Si-Si	2.724	1.18	1.18	3.39	3.39	
$P2_1/m$	112.211	B-B	1.759	0.80	0.80	3.75	3.75	17.8
		B-Si	2.039	0.80	1.18	3.75	3.39	
		B-Si	2.306	0.80	1.18	3.75	3.39	
		Si-Si	2.516	1.18	1.18	3.39	3.39	
		Si-Si	2.528	1.18	1.18	3.39	3.39	
		Si-Si	2.542	1.18	3.39	3.39	3.39	

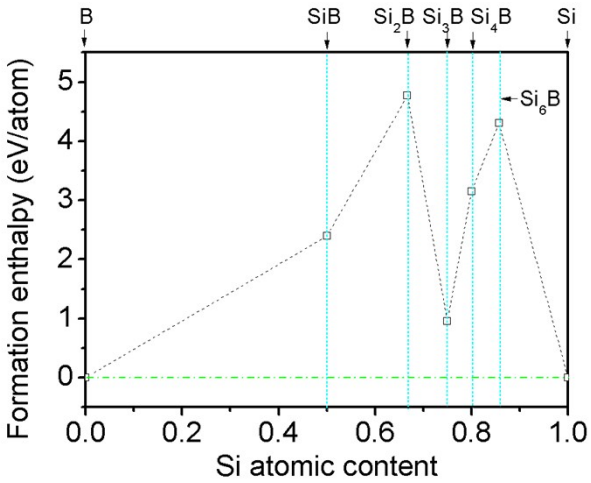

Figure S1 The relative enthalpies of formation per atom with respect to Si and B for

different Si-B phases at ambient pressure. The convex hulls are shown by solid lines. Dotted lines through the neighboring points residing above the convex hull are guiding for the eye. It shows that (i) all of the Si-B compounds on the Si-rich side are unstable and (ii) Si_3B has the lowest formation energy and SiB follows Si_3B tightly in formation energy at ambient pressure.

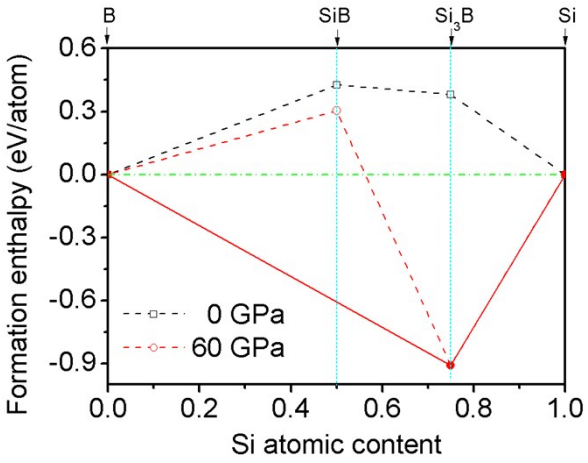

Figure S2 The relative enthalpies of formation per atom with respect to Si and B for different Si-B phases at ambient pressure and high pressure. Extensive structure

searchers on Si_3B and SiB at ambient and high pressures have been performed by using the CALYPSO code. Our results present that SiB with high enthalpy is unstable respect to Si_3B and B at 60 GPa. Combined the results obtained by Figs S1 and S2, we can deduce that other Si-rich Si-B compounds should also be more unstable due to their higher formation enthalpies at pressure < 60 GPa. Therefore, we just focus Si_3B in our study.

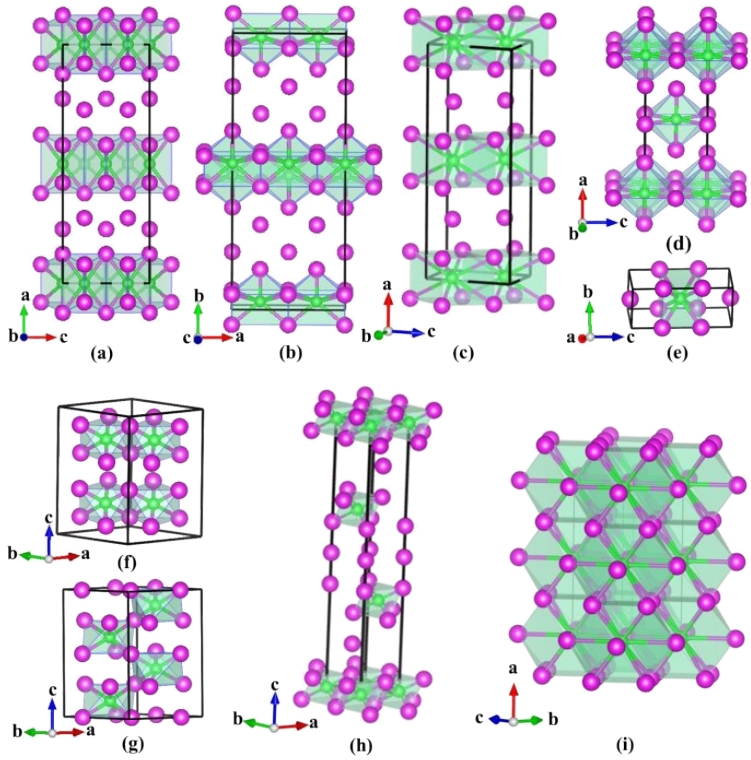

Figure S3 Predicted crystal structures for Si_3B. (a) *Imm*2 structure. (b) *Cmcm* structure. (c) *Imma* structure. (d) *P*-31*m* structure. (e) *Immm* structure. (f) *P*4/*mmm* structure. (g) $P6_322$ structure. (h) *R*-3*m* structure. (i) *Pm*-3*m* structure.

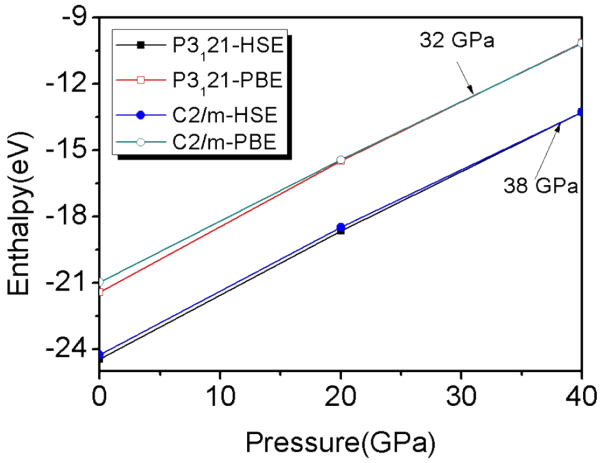

Figure S4 Enthalpy curves of $P3_121$ and $C2/m$ phases for Si_3B in two different ways at high pressures.

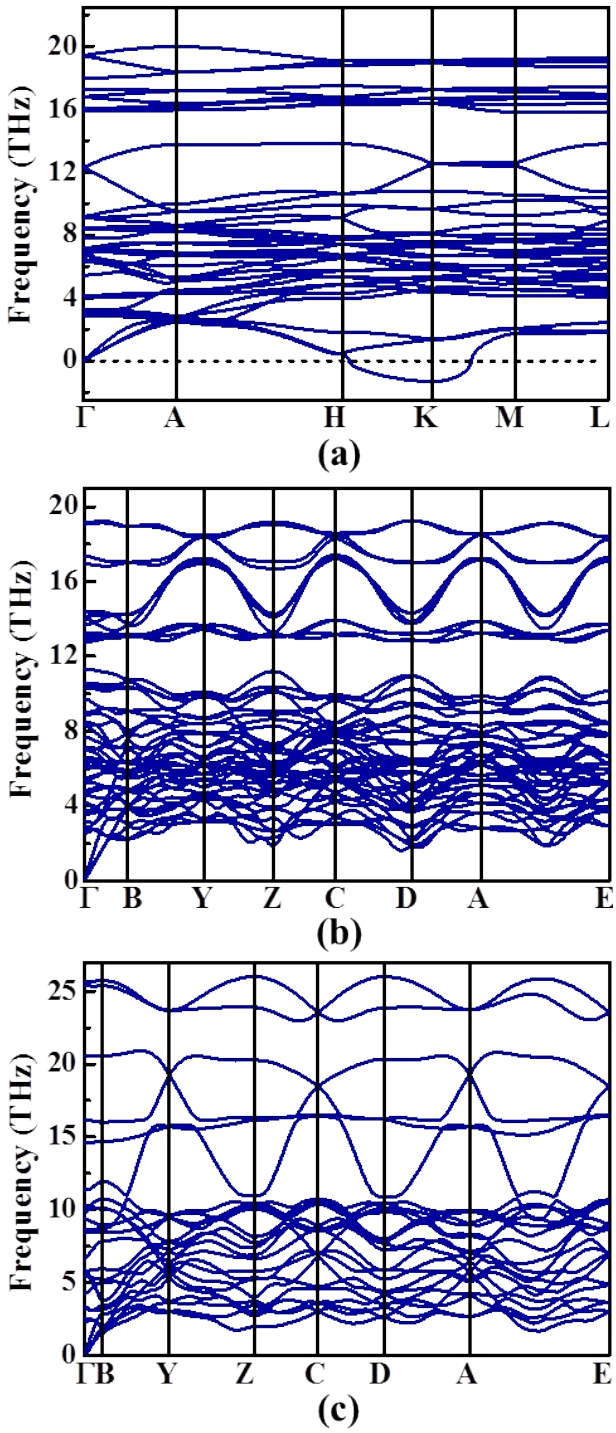

Figure S5 Phonon spectrum for (a) $P3_121$ structure at 0 GPa. (b) $C2/m$ structure at 0 GPa. (e) $P2/m$ structure at 0 GPa.

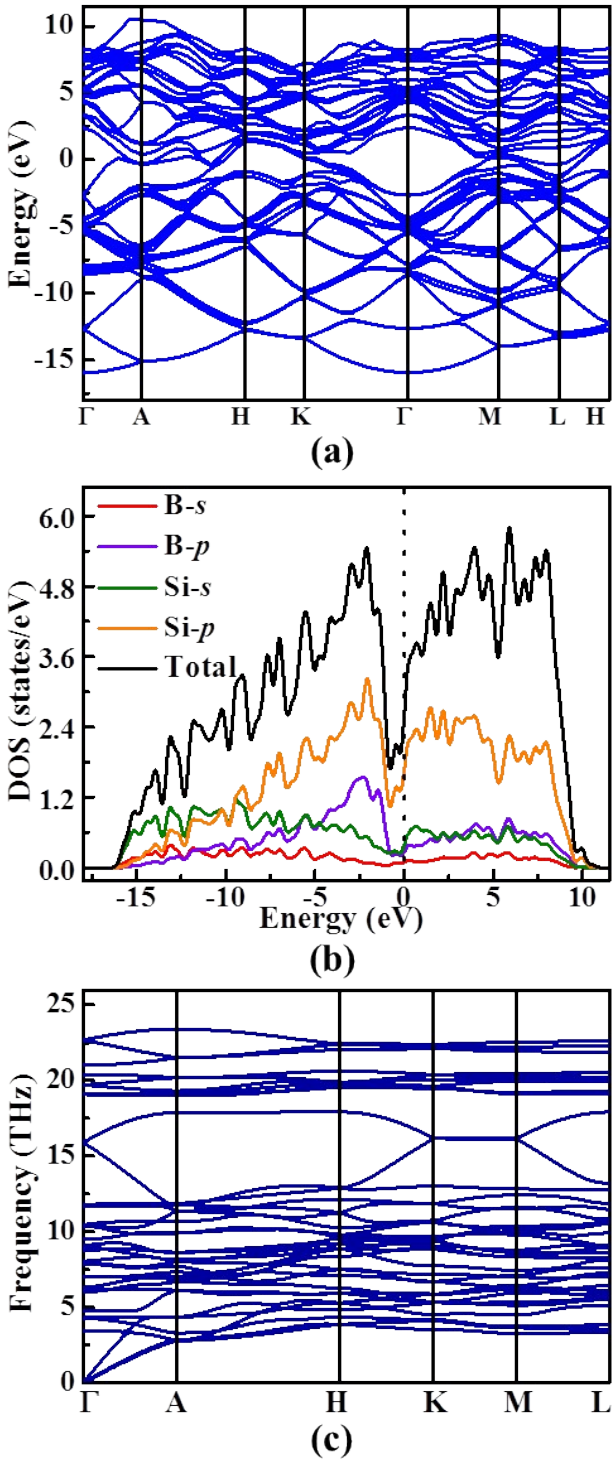

Figure S6 Band structure, DOS and phonon spectrum of $P3_121$ structure for Si_3B at 25 GPa. (a) Band structure. (b)DOS. (c)Phonon spectrum.

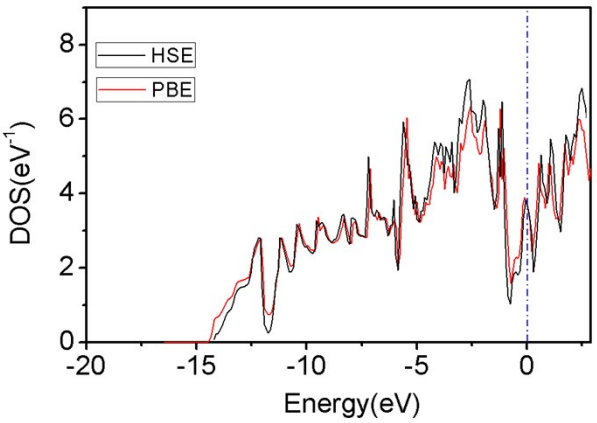

Figure S7 Plots of density of states for Si_3B with $P3_121$ symmetry using two different exchange-correlation functional at ambient pressure.

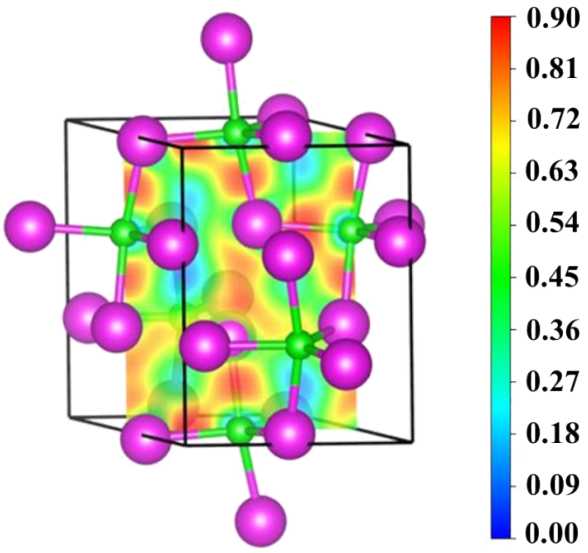

Figure S8 ELF for $P3_121$ structure at 25 GPa.