Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information

Double-dome superconductivity in germanium phosphides

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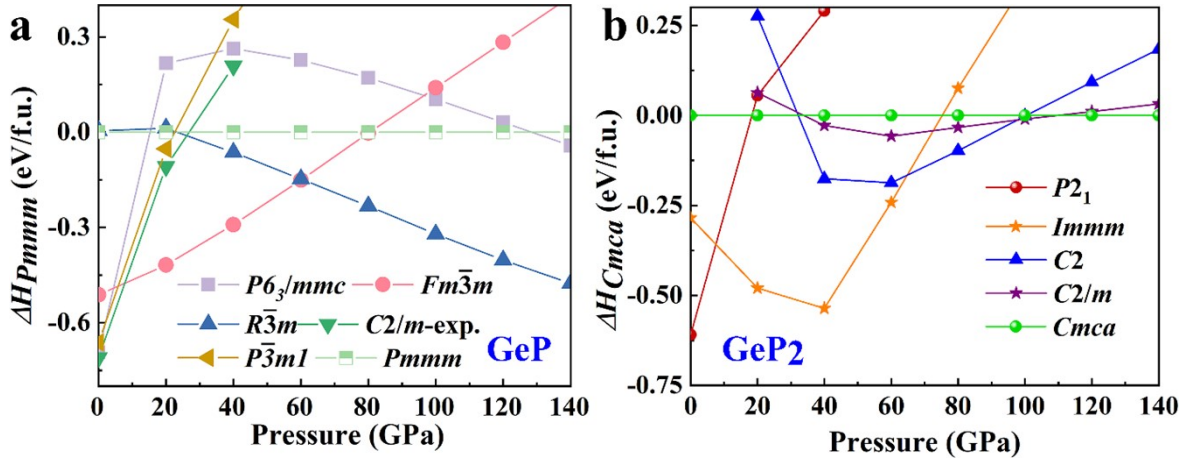

Figure S1: Relative enthalpy per formula unit referenced to the selected phases for GeP (a) and GeP_2 (b).

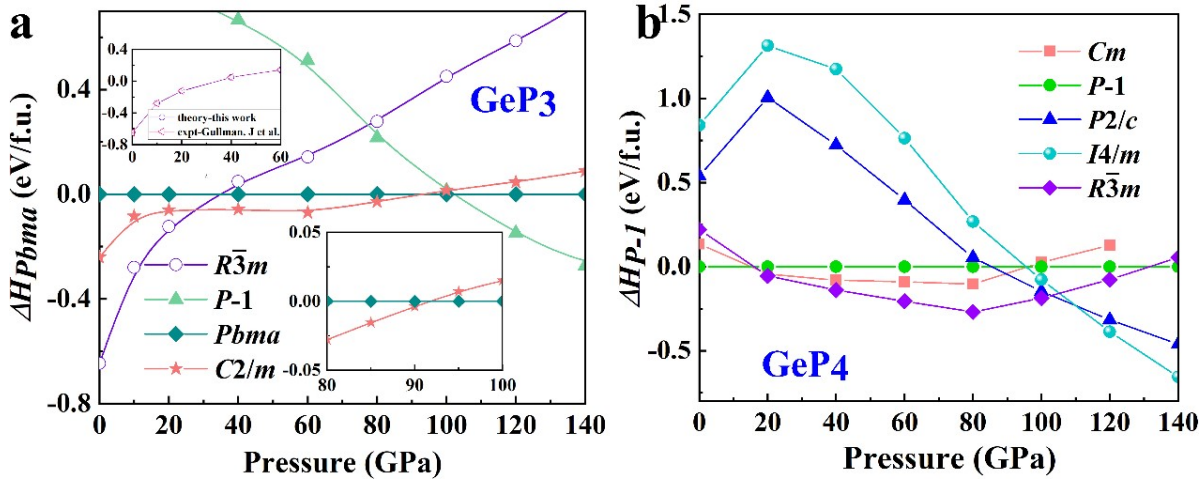

Figure S2: Relative enthalpy per formula unit referenced to the selected phases for GeP_3 (a) and GeP_4 (b).The inset in GeP_3 (a) shows the transition of $C2/m \rightarrow Pbma \rightarrow P\bar{1}$ in more detail.

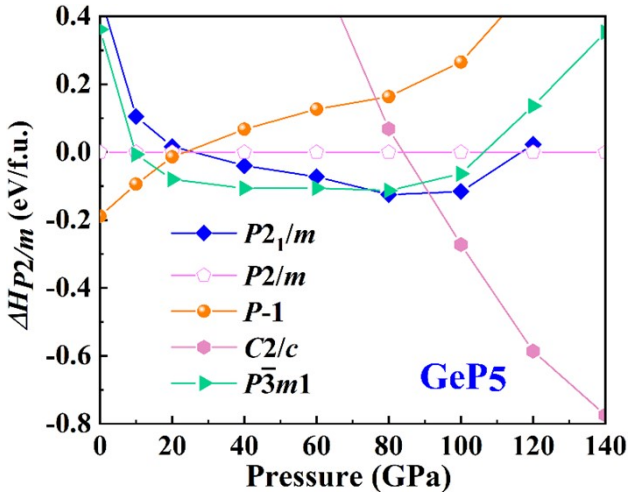

Figure S3: Relative enthalpy per formula unit referenced to the selected phases for GeP_5.

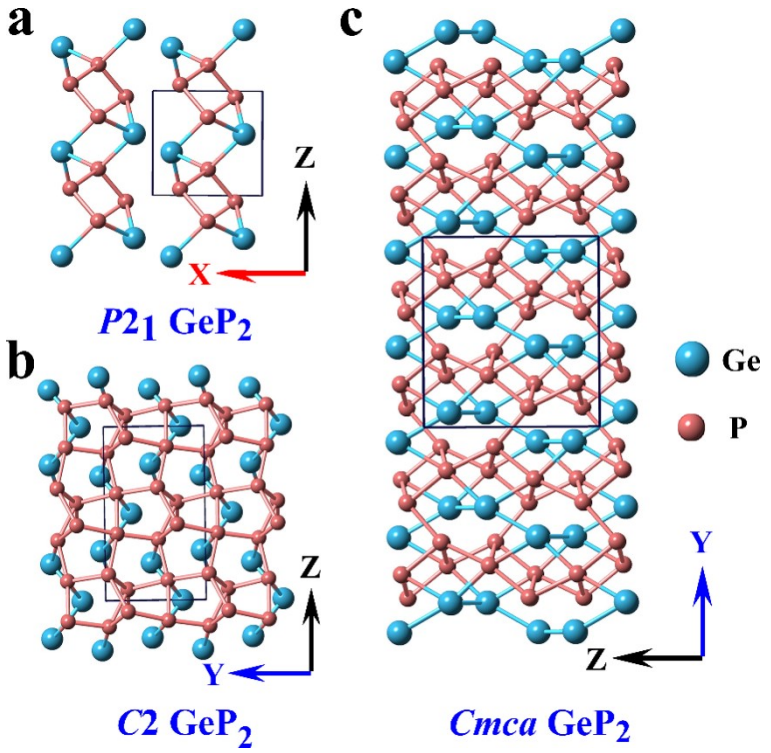

Figure S4: Crystal features of the predicted phosphorous-rich germanium. Energetically favorable structures of GeP_2 $P2_1$ at 0 GPa (a), $C2$ at 80 GPa (b) and *Cmca* at 120 GPa (c). Large sky blue and small pink spheres represent germanium and phosphorus atoms, respectively.

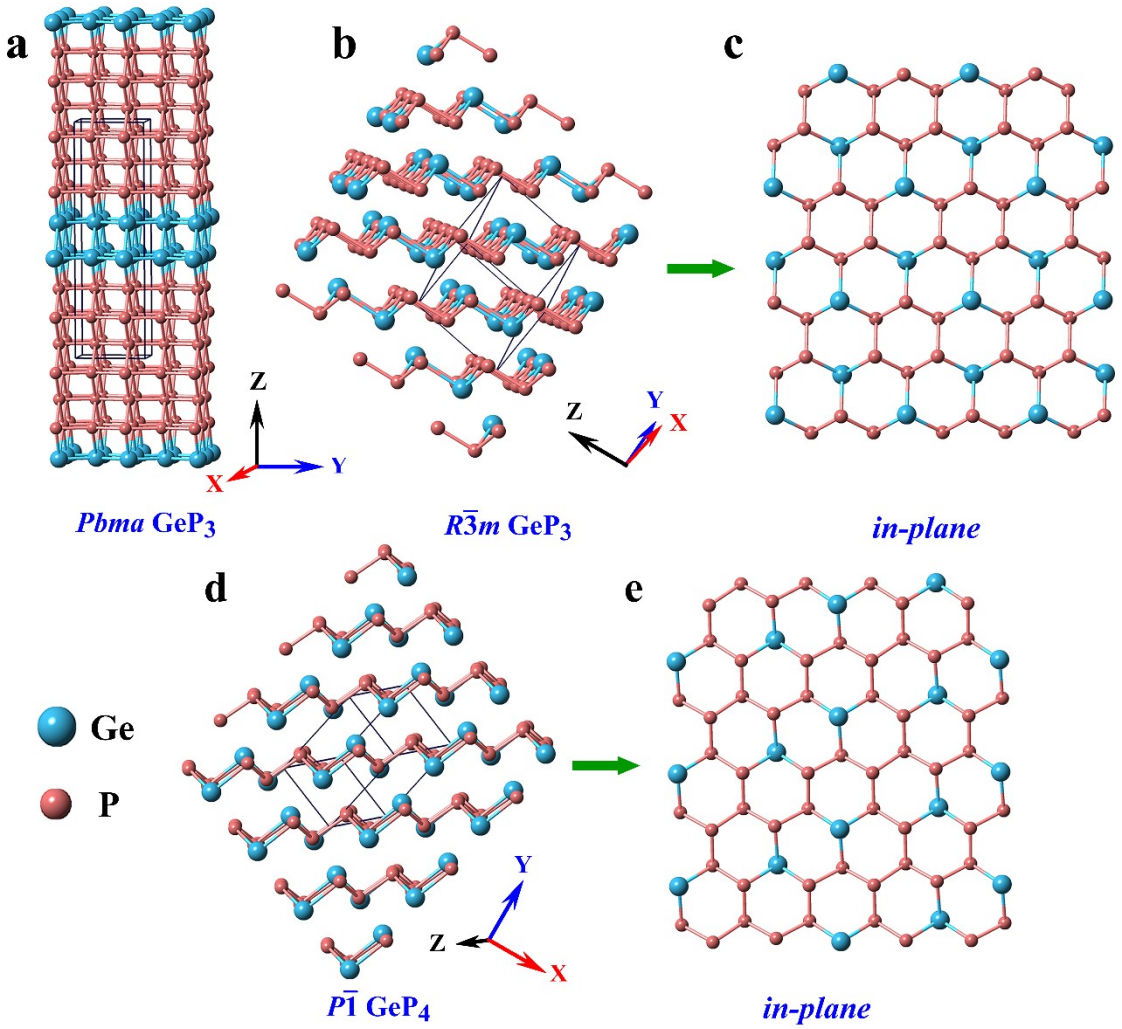

Figure S5: Crystal features of the predicted phosphorous-rich germanium. Energetically favorable structures of GeP_3 *Pbam* at 120 GPa (a), $R\bar{3}m$ at 0 GPa (b-c); GeP_4 $P\bar{1}$ at 0 GPa (d-e). Large sky blue and small pink spheres represent germanium and phosphorus atoms, respectively.

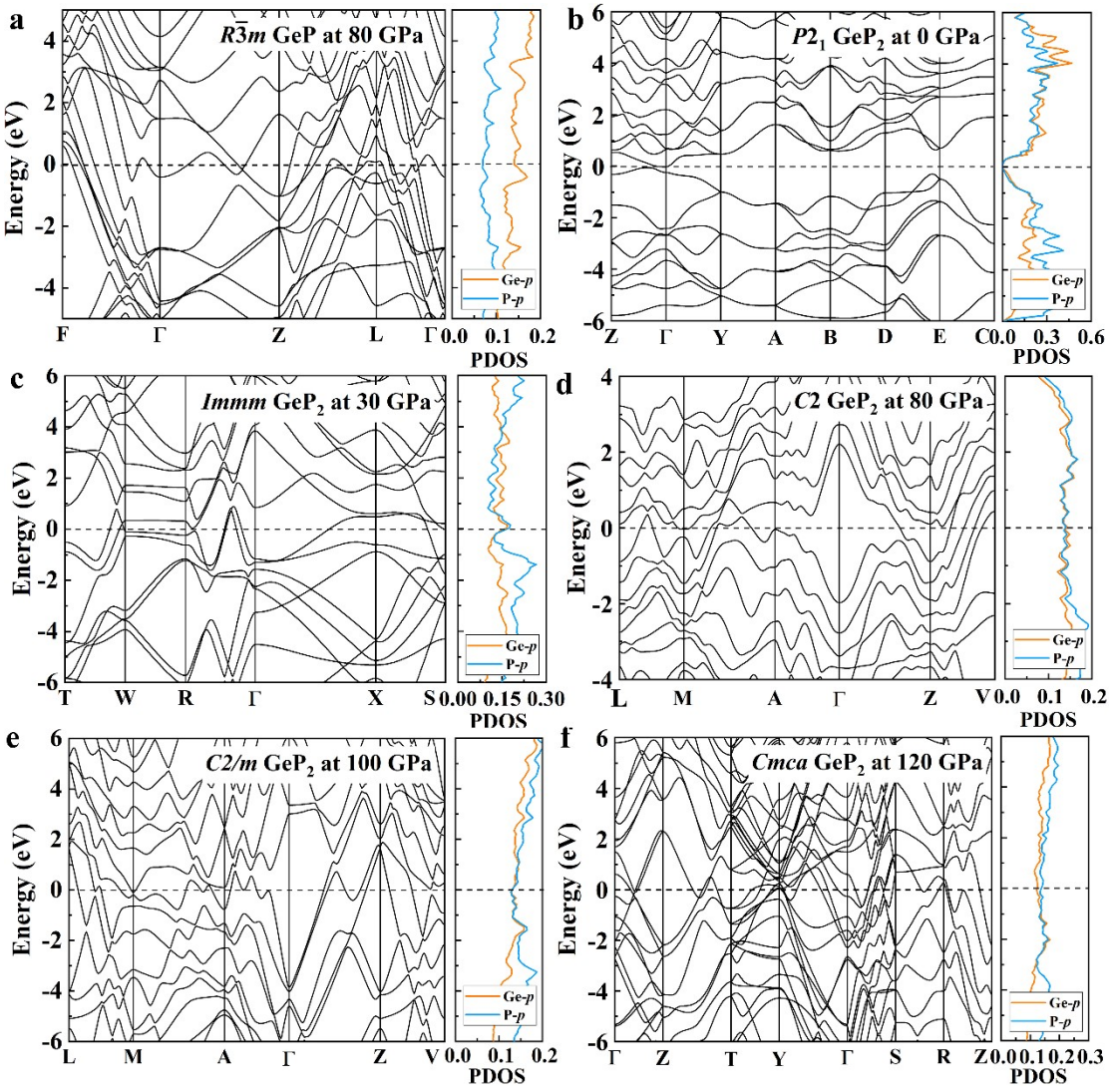

Figure S6: Calculated electronic band structure and projected density of states (PDOS) of GeP $R\bar{3}m$ at 0 GPa (a) and GeP_2 $P2_1$ at 0 GPa (b), *Immm* at 30 GPa (c), *C*2 at 80 GPa (d), *C*2/*m* at 100 GPa (e) and *Cmca* at 120 GPa (f).

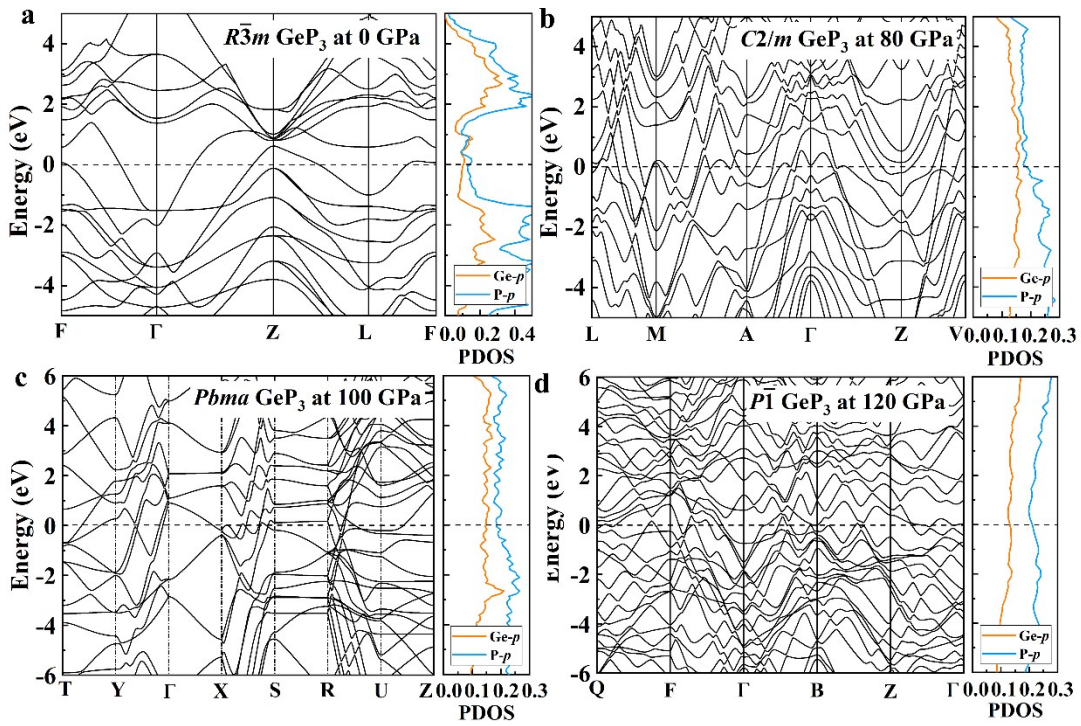

Figure S7: Calculated electronic band structure and projected density of states (PDOS) of GeP_3 $R\bar{3}m$ at 0 GPa (a), $C2/m$ at 80 GPa (b), $Pbma$ at 100 GPa (c) and $P\bar{1}$ at 120 GPa (d).

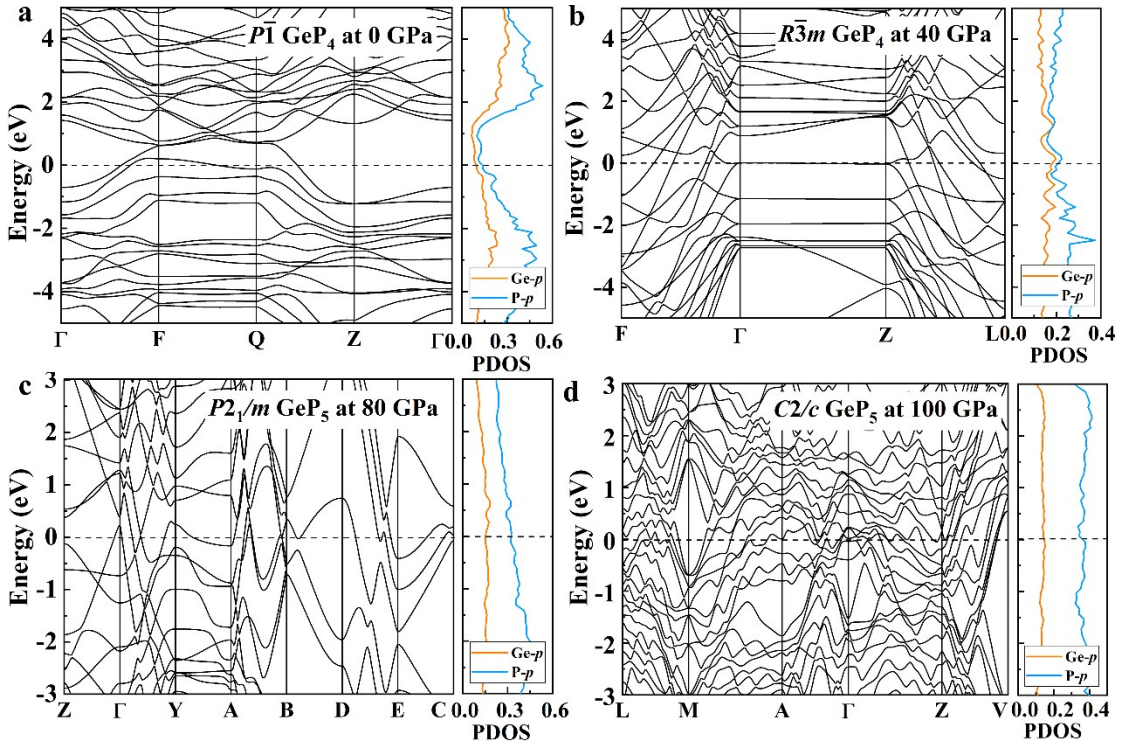

Figure S8: Calculated electronic band structure and projected density of states (PDOS) of GeP_4 $P\bar{1}$ at 0 GPa (a) and $R\bar{3}m$ at 40 GPa (b), GeP_5 $P2_1/m$ at 80 GPa (c) and $C2/c$ at 100 GPa (d).

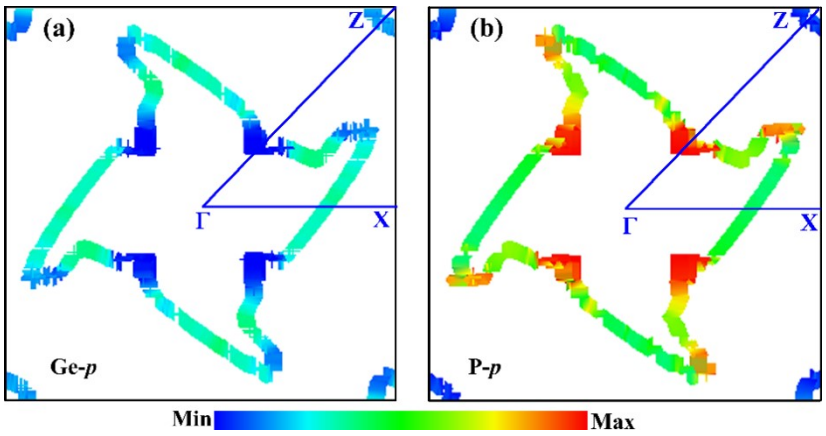

Figure S9: The Ge-*p* and P-*p* orbital projected Fermi surface with a certain band for *I*4/*m* GeP_4 at 120 GPa. The selected band is denoted with red color in Figure 3 of the main text.

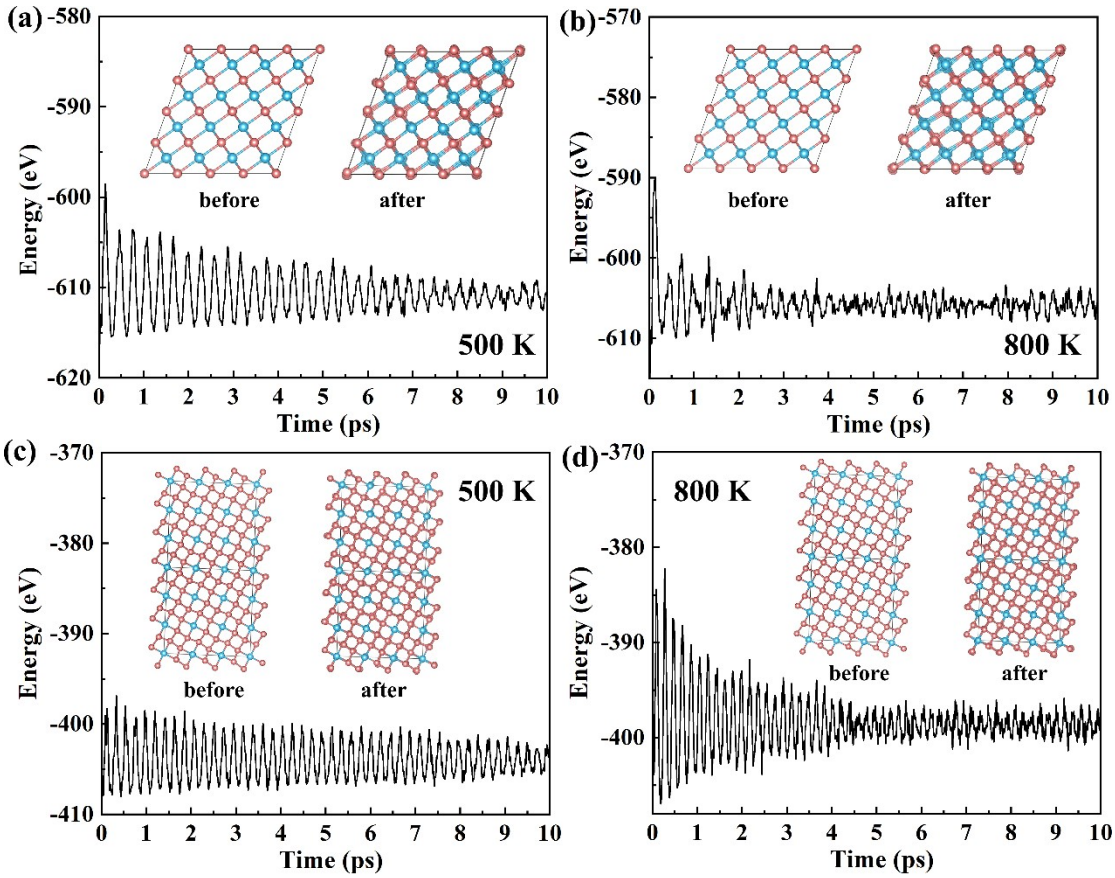

Figure S10: Evolution of the relative energy during an *ab initio* molecular dynamics (AIMD) simulation at 500 and 800 K of $Fm\bar{3}m$ GeP at 8 GPa (a)-(b) and *I*4/m GeP_4 at 120 GPa (c)-(d). The snapshots denote the crystal structures before and after the AIMD simulation, which confirms the thermal stability of the newly predicted structures as no structural reconstruction is present.

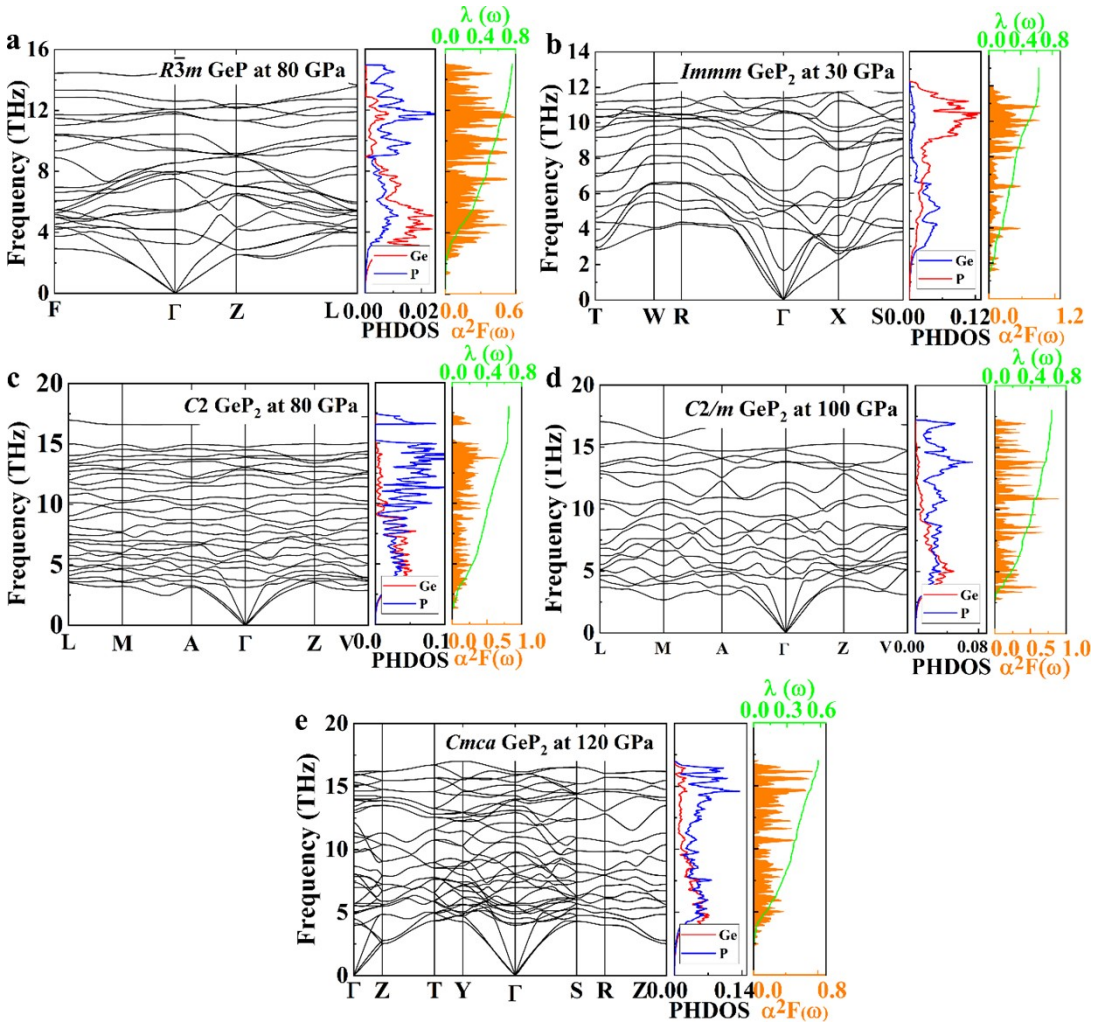

Figure S11: Phonon dispersions, partial phonon density of states (PHDOS) and the partial electron-phonon integral λ(ω) of GeP $R\bar{3}m$ at 80 GPa (a), GeP_2 *Immm* at 30 GPa (b), *C*2 at 80 GPa (c), *C*2/*m* at 100 GPa (d) and *Cmca* at 120 GPa (e).

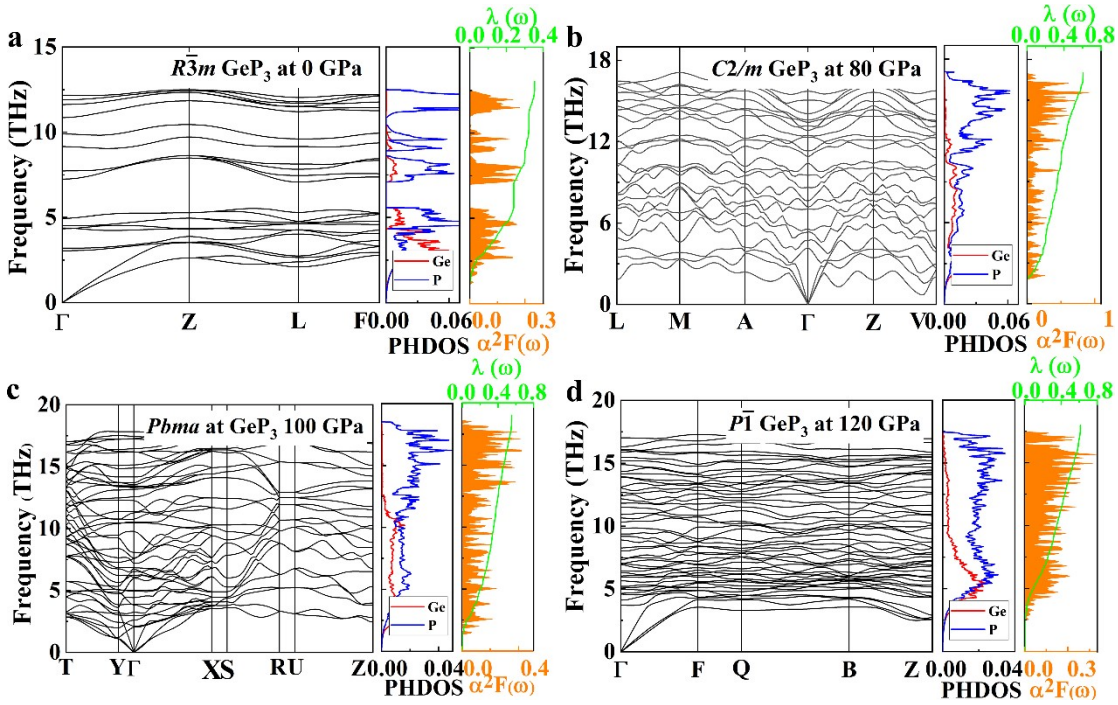

Figure S12: Phonon dispersions, partial phonon density of states (PHDOS) and the partial electron-phonon integral λ(ω) of GeP_3 $R\bar{3}m$ at 0 GPa (a), *C2/m* at 80 GPa (b), *Pbma* at 100 GPa (c), and $P\bar{1}$ at 120 GPa (d).

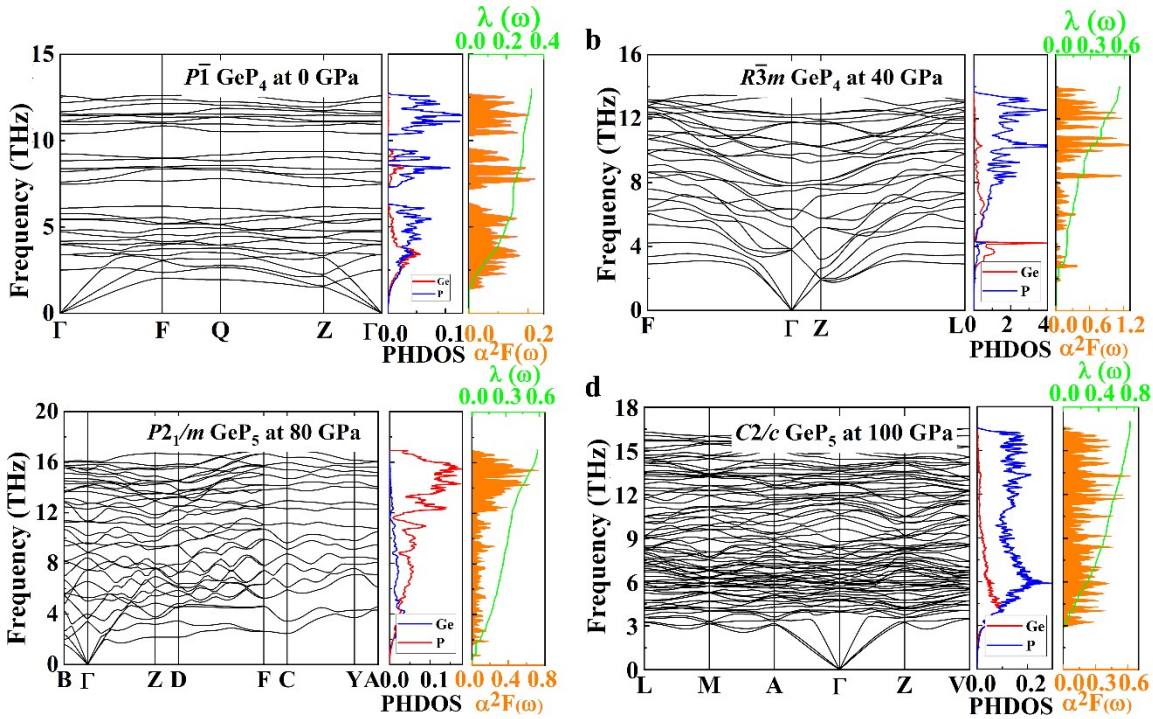

Figure S13: The phonon dispersions, partial phonon density of states (PHDOS) and the partial electron-phonon integral λ(ω) of GeP_4 $P\bar{1}$ at 0 GPa (a) and $R\bar{3}m$ at 40 GPa (b), GeP_5 $P2_1/m$ at 80 GPa (c) and $C2/c$ at 100 GPa (d).

Table S1. Structural information of the predicted stable Ge-P phases.

Phase	Pressure (GPa)	Lattice Parameters (Å)	Atoms	Wyckoff Positions (fractional)		
				x	*y*	*z*
***Fm*$\bar{3}$*m* GeP	8	a = b = c = 3.58	Ge(4b)	0.500	0.500	0.500
			Ge(4a)	0.000	0.000	0.000
***R*$\bar{3}$*m* GeP	80	a =b= 4.02 c = 19.18	Ge(6c)	0.000	0.000	0.566
			Ge(6c)	0.000	0.000	0.700
			P(6c)	0.000	0.000	0.058
			P(6c)	0.000	0.000	0.828
***P*2$_1$ GeP$_2$	0	a = 5.18 b = 4.86 c = 4.94	Ge(2a)	0.171	0.368	0.588
			P(2a)	0.498	0.203	0.249
			P(2a)	0.247	0.016	0.940
***Immm* GeP$_2$	30	a = 10.20 b = 4.77 c = 3.36	Ge(4f)	0.330	0.000	0.500
			P(4e)	0.155	0.000	0.000
			P(2b)	0.500	0.000	0.000
			P(2c)	0.000	0.000	0.500
***C*2 GeP$_2$	80	a = 8.55 b = 4.87 c = 4.80	Ge(4c)	0.284	0.039	0.606
			Ge(2b)	0.500	-0.268	0.500
			P(4c)	0.437	0.277	0.271
			P(4c)	0.384	-0.122	0.053
			P(4c)	0.850	-0.032	0.863

***C*2/*m* GeP_2**	100	a = b = 4.52 c = 6.59	Ge(4i)	-0.895	0.000	-0.585
			P(4i)	-0.277	0.000	-0.242
			P(4i)	-0.603	0.000	-0.961
***Cmca* GeP_2**	120	a = 3.83 b = 8.13 c = 7.50	Ge (8f)	0.500	-0.423	0.854
			P (8f)	0.500	-0.274	1.130
			P (8f)	0.500	-0.604	0.596
***C*2/*m* GeP_3**	30	a = 5.70 b = 3.30 c = 11.37	Ge (4i)	0.307	0.500	0.577
			P (4i)	0.931	0.500	0.500
			P (4i)	0.813	0.500	0.060
			P (4i)	0.558	0.500	0.826
***Pbma* GeP_3**	100	a = 2.80 b = 4.17 c = 14.08	Ge (4d)	0.572	0.565	0.750
			P (4d)	0.177	0.151	0.750
			P (4d)	0.942	0.342	1.250
			P (4d)	0.292	0.862	1.250
***P*$\bar{1}$ GeP_3**	120	a = 4.43 b = 4.43 c = 7.89	Ge (2i)	0.634	0.253	0.050
			Ge (2i)	0.877	0.089	0.353
			P (2i)	0.576	0.769	0.538
			P (2i)	0.333	0.967	0.233
			P (2i)	0.108	0.190	0.913
			P (2i)	0.628	0.581	0.278
			P (2i)	0.112	0.610	0.400
			P (2i)	0.159	0.406	0.156
***P*$\bar{1}$ GeP_4**	0	a = 4.07 b = 5.26 c = 9.26	Ge (2i)	0.411	0.642	0.800
			P (2i)	0.939	0.789	0.004
			P (2i)	0.151	0.986	0.405
			P (2i)	0.731	0.583	0.600

			P (2i)	0.694	0.845	0.204
$R\bar{3}m$ **GeP$_4$**	40	a = b = 3.23 c = 41.09	Ge (6c)	0.000	0.000	0.146
			P (6c)	0.000	0.000	0.048
			P (6c)	0.000	0.000	0.349
			P (6c)	0.000	0.000	0.746
			P (6c)	0.000	0.000	0.556
***I4/m* GeP$_4$**	120	a = 5.96 b = 5.96 c = 2.65	Ge (9d)	0.500	0.500	0.500
			P (36i)	0.320	0.120	0.500
***P*2$_1$*m* GeP$_5$**	80	a = 11.08 b = 3.05 c = 3.87	Ge (2e)	0.952	0.750	0.194
			P (2e)	0.222	0.250	0.141
			P (2e)	0.300	0.750	0.813
			P (2e)	0.858	0.250	0.537
			P (2e)	0.381	0.250	0.490
			P (2e)	0.540	0.250	0.838
***C*2/*c* GeP$_5$**	100	a = 13.00 b = 7.40 c = 7.98	Ge (8f)	-0.383	0.111	-0.342
			P (8f)	0.370	0.863	-0.370
			P (8f)	-0.359	0.144	-0.000
			P (8f)	-0.144	0.893	-0.031
			P (8f)	-0.386	0.610	0.315
			P (8f)	-0.393	0.643	-0.346

Table S2. Calculated the superconducting transition temperature T_c, electron–phonon coupling (EPC) parameter λ(ω), the density of states at the Fermi level per formula unit $N(E_f)$, and the logarithmic average honon frequency ω_{log} for the predicted structures of GeP from 0 to 140 GPa. μ* of 0.1 was selected for the T_c calculation.

Phase	**Pressure (GPa)**	**T_c (K)**	**lambda**	**$N(E_f)$ (States/Ry)**	**ω_{log} (K)**
$Fm\bar{3}m$	8	17.49	1.03	5.03	238.92
$Fm\bar{3}m$	10	16.53	0.92	4.95	269.51
$Fm\bar{3}m$	20	9.99	0.67	4.57	327.47
$Fm\bar{3}m$	40	3.75	0.47	4.08	383.41
$Fm\bar{3}m$	60	1.38	0.39	3.82	405.20
$R\bar{3}m$	80	13.14	0.76	19.50	310.74
$R\bar{3}m$	120	3.79	0.48	14.75	356.32
$R\bar{3}m$	140	2.49	0.44	14.16	376.76

Table S3. Calculated the superconducting transition temperature T_c, electron–phonon coupling (EPC) parameter λ(ω), the density of states at the Fermi level per formula unit $N(E_f)$, and the logarithmic average honon frequency ω_{log} for the predicted structures of GeP_2 from 0 to 140 GPa. μ* of 0.1 was selected for the T_c calculation.

Phase	**Pressure (GPa)**	**T_c (K)**	**lambda**	**$N(E_f)$ (States/Ry)**	**ω_{log} (K)**
$P2_1$	0	0	-	-	-
Immm	30	7.51	0.63	12.08	287.91
Immm	40	5.74	0.55	12.17	326.44
Immm	60	3.13	0.46	12.24	369.27
*C*2	80	9.06	0.65	19.86	311.24
*C*2/*m*	100	9.55	0.64	11.20	349.27
Cmca	120	13.14	0.58	24.95	389.67
Cmca	140	3.79	0.53	24.24	413.92

Table S4. Calculated the superconducting transition temperature T_c, electron–phonon coupling (EPC) parameter λ(ω), the density of states at the Fermi level per formula unit N(E_f), and the logarithmic average honon frequency ω_{log} for the predicted structures of GeP_3 from 0 to 140 GPa. μ* of 0.1 was selected for the T_c calculation.

Phase	Pressure (GPa)	T_c (K)	lambda	$N(E_f)$ (States/Ry)	ω_{log} (K)
$R\bar{3}m$	0	0.42	0.35	11.35	222.27
$R\bar{3}m$	10	1.32	0.40	12.44	310.12
$R\bar{3}m$	16	2.91	0.46	13.12	328.60
*C*2/*m*	30	3.46	0.47	14.54	370.93
*C*2/*m*	40	2.91	0.45	14.45	378.76
*C*2/*m*	60	2.91	0.45	14.50	365.44
*C*2/*m*	80	7.77	0.61	17.93	329.59
Pbma	100	5.63	0.55	30.81	317.30
$P\bar{1}$	120	9.88	0.61	34.41	407.86
$P\bar{1}$	140	7.35	0.55	33.12	429.58

Table S5. Calculated the superconducting transition temperature T_c, electron–phonon coupling (EPC) parameter λ(ω), the density of states at the Fermi level per formula unit N(E_f), and the logarithmic average honon frequency ω_{log} for the predicted structures of GeP_4 from 0 to 140 GPa. μ* of 0.1 was selected for the T_c calculation.

Phase	Pressure (GPa)	T_c (K)	λ	N(E_f) (States/Ry)	ω_{log} (K)
$P\bar{1}$	0	0.27	0.33	14.26	216.72
$P\bar{1}$	10	2.71	0.47	17.91	301.89
$R\bar{3}m$	30	6.31	0.54	19.80	363.24
$R\bar{3}m$	40	6.82	0.56	20.55	375.81
$R\bar{3}m$	60	5.11	0.49	20.39	358.42
$R\bar{3}m$	80	1.80	0.41	18.51	355.11
$R\bar{3}m$	100	0.77	0.37	16.49	308.25
I4/m	120	19.02	0.81	12.00	395.24
I4/m	140	14.24	0.69	11.20	424.53

Table S6. Calculated the superconducting transition temperature T_c, electron–phonon coupling (EPC) parameter λ(ω), the density of states at the Fermi level per formula unit $N(E_f)$, and the logarithmic average honon frequency ω_{log} for the predicted structures of GeP_5 from 0 to 140 GPa. μ* of 0.1 was selected for the T_c calculation.

Phase	Pressure (GPa)	T_c (K)	lambda	$N(E_f)$ (States/Ry)	ω_{log} (K)
$P\bar{1}$	0	0.95	0.40	17.85	226.37
$P\bar{1}$	6	2.21	0.45	19.79	281.97
$P\bar{1}$	10	5.83	0.57	20.88	301.58
$P\bar{1}$	14	9.06	0.66	21.58	298.79
$P\bar{3}m1$	20	8.61	0.61	37.83	351.12
$P\bar{3}m1$	30	6.14	0.54	37.18	388.08
$P\bar{3}m1$	40	5.48	0.52	37.16	400.74
$P\bar{3}m1$	60	4.36	0.49	36.93	401.36
$P2_1/m$	80	6.61	0.58	25.94	316.67
$P\bar{1}$	100	14.69	0.75	50.95	357.27
$P\bar{1}$	120	10.66	0.63	48.11	398.28

Table S7. Calculated superconducting transition temperature T_c of $I4/m$ GeP_4 with various μ^*.

μ^*	0.08	0.09	0.10	0.11	0.12
T_c (K)	21.54	20.27	19.02	17.80	16.61