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

Supporting information

Phase relations, thermal conductivity and elastic properties of ZrO_2 and HfO_2 polymorphs at high pressures and temperatures

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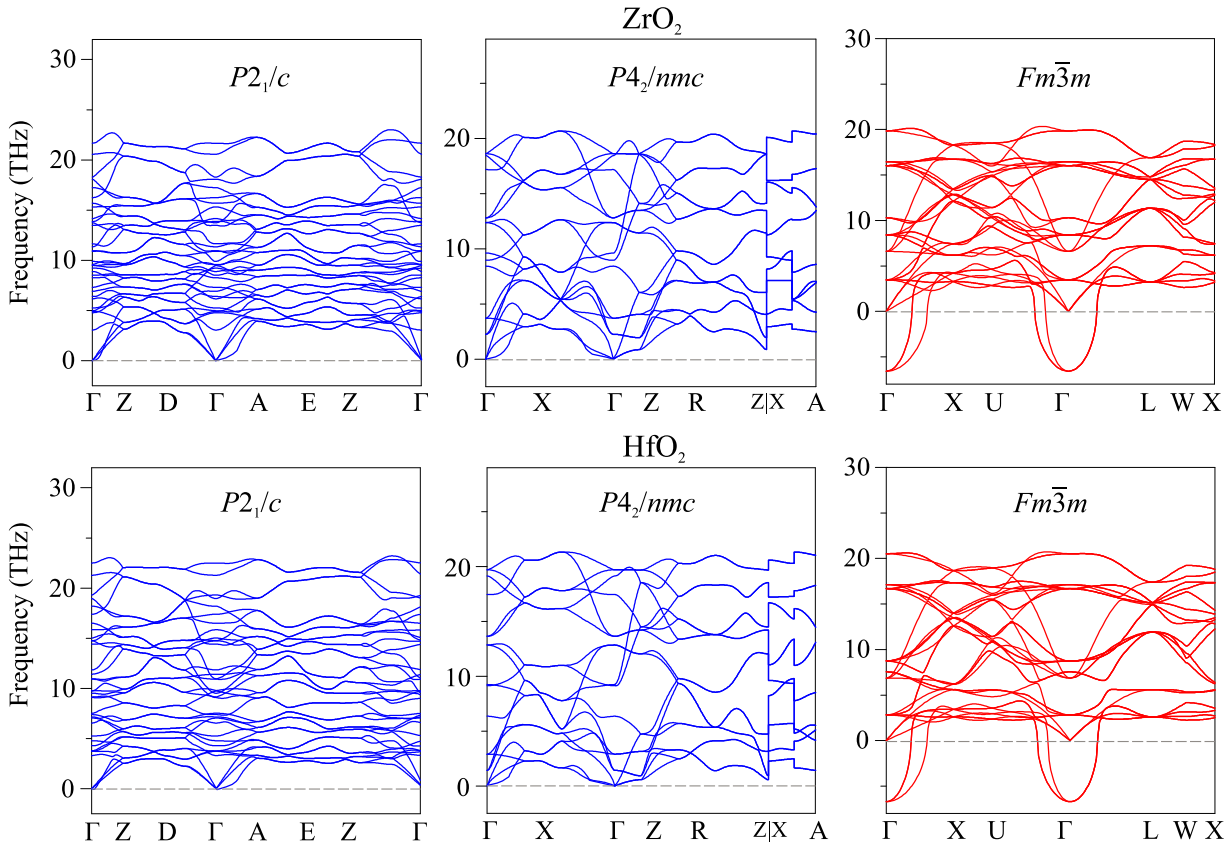

Figure S1: Phonon spectra of low-pressure modifications of ZrO_2 and HfO_2 at 0 GPa.

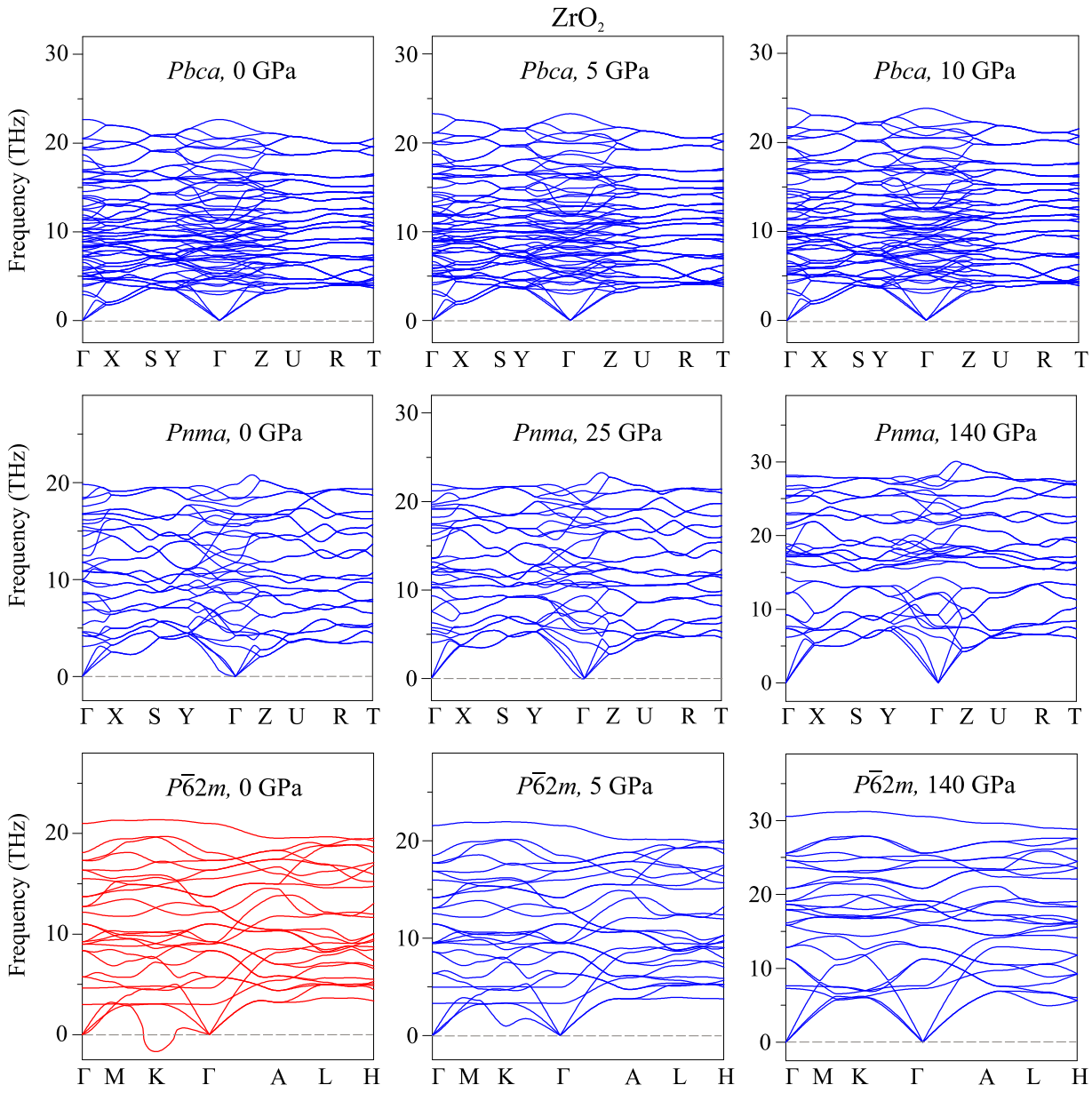

Figure S2: Phonon spectra of high-pressure modifications of ZrO_2.

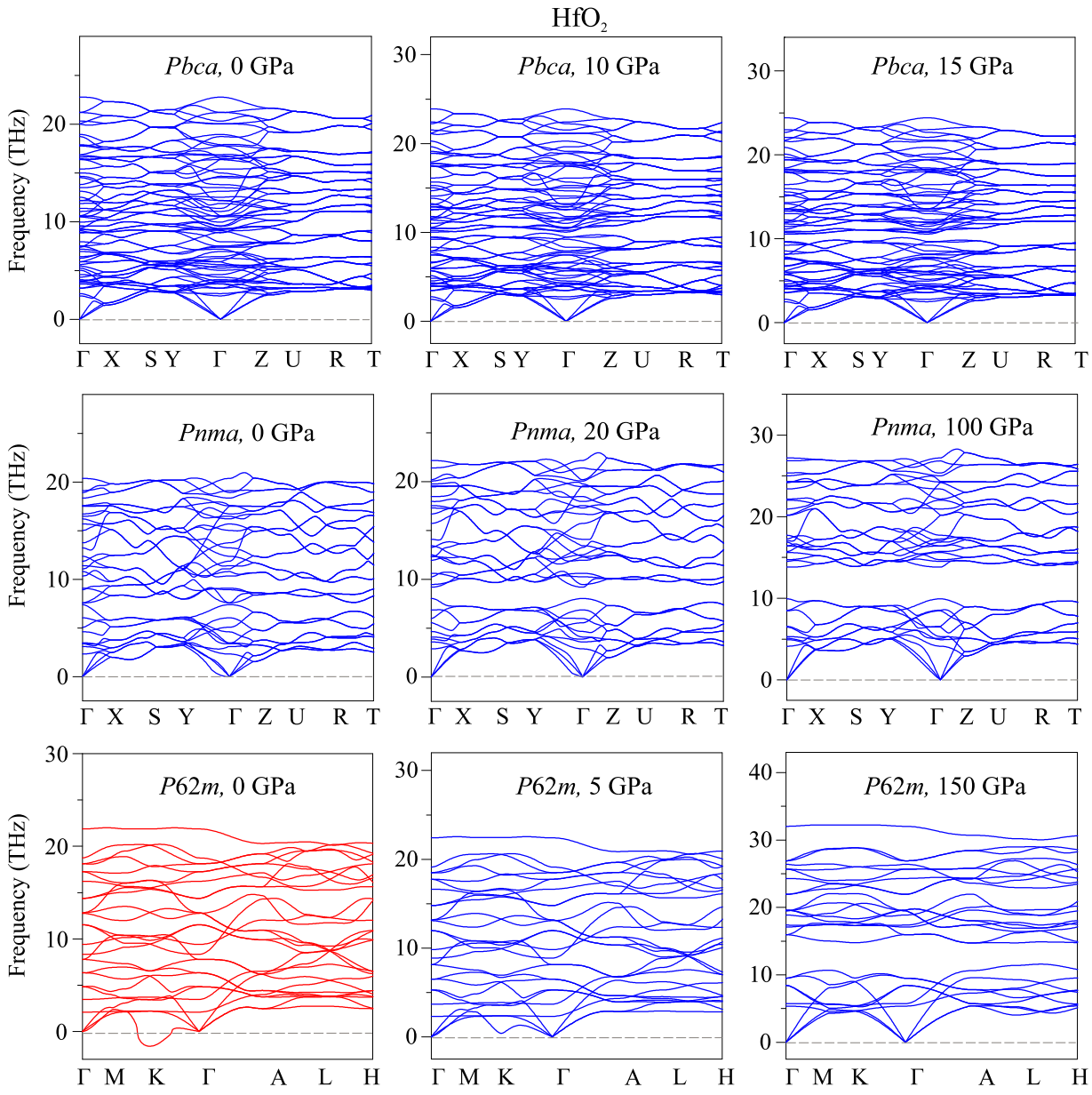

Figure S3: Phonon spectra of high-pressure modifications of HfO_2.

Table S1: Calculated bulk modulus (B), shear modulus (G), Poisson's ratio (ν), Young's modulus (E), the B/G ratio, and hardness (H_V) of ZrO_2 depended on pressure.

P (GPa)	B (GPa)	G (GPa)	ν	E (GPa)	B/G	H^V_{Chen} (GPa)	H^V_{Tian} (GPa)
0	185	86	0.30	223	2.16	8.0	9.0
3	182	88	0.29	227	2.08	8.6	9.5
7	168	92	0.27	235	1.82	11.0	11.5
7	229	108	0.30	280	2.12	9.8	10.8
10	237	110	0.30	286	2.16	9.7	10.7
14	246	112	0.30	292	2.20	9.6	10.6
14	295	117	0.33	309	2.53	7.9	9.3
20	324	128	0.33	339	2.53	8.5	10.0
40	409	160	0.33	424	2.56	10.0	11.5
60	486	186	0.33	494	2.62	10.8	12.5
80	559	208	0.33	555	2.69	11.3	13.1
100	630	228	0.34	609	2.77	11.5	13.5
120	698	245	0.34	658	2.85	11.6	13.7
140	765	260	0.35	701	2.94	11.6	13.8
140	778	288	0.34	770	2.70	14.2	16.4
150	812	297	0.34	793	2.74	14.2	16.5
160	845	304	0.34	815	2.78	14.2	16.5

Table S2: Calculated bulk modulus (B), shear modulus (G), Poisson's ratio (ν), Young's modulus (E), the B/G ratio, and hardness (H_V) of HfO_2 depended on pressure.

P (GPa)	B (GPa)	G (GPa)	ν	E (GPa)	B/G	H^V_{Chen} (GPa)	H^V_{Tian} (GPa)
0	202	98	0.29	253	2.05	9.6	10.4
5	197	102	0.28	261	1.93	10.9	11.5
10	193	107	0.27	271	1.80	12.4	12.9
8	252	122	0.29	315	2.07	11.2	12.1
12	264	125	0.30	323	2.12	11.0	11.9
16	275	127	0.30	330	2.17	10.8	11.8
20	284	128	0.30	335	2.21	10.5	11.6
15	315	127	0.32	335	2.49	8.7	10.1
30	385	154	0.32	408	2.50	10.1	11.5
45	447	177	0.32	470	2.52	11.0	12.6
60	506	198	0.33	525	2.56	11.7	13.3
75	563	216	0.33	574	2.61	12.1	13.9
90	618	232	0.33	619	2.66	12.4	14.3
105	672	247	0.34	660	2.72	12.6	14.6
120	726	261	0.34	698	2.78	12.6	14.8
135	778	273	0.34	734	2.85	12.7	14.9
125	754	295	0.33	783	2.56	15.6	17.7
140	807	309	0.33	821	2.62	15.6	17.8
155	859	321	0.33	857	2.67	15.5	17.9

Table S3: Comparison of calculated lattice constants of ZrO_2-$P2_1/c$ and HfO_2-$P2_1/c$ with experimental data.

ZrO_2-$P2_1/c$, 0 GPa						
Parameter	Theory			Experiment [1]		
a (Å)	5.191			5.147		
b (Å)	5.244			5.209		
c (Å)	5.379			5.317		
Atoms	x	y	z	x	y	z
Zr	0.275	0.543	0.710	0.275	0.040	0.209
O1	0.065	0.827	0.849	0.069	0.332	0.344
O2	0.451	0.256	-0.024	0.450	0.756	0.478
HfO^2-$P2_1/c$, 0 GPa						
Parameter	Theory			Experiment [2]		
a (Å)	5.191			5.150		
b (Å)	5.244			5.185		
c (Å)	5.379			5.342		
Atoms	x	y	z	x	y	z
Hf1	0.275	0.543	0.710	0.280	0.049	0.217
O1	0.065	0.827	0.849	0.069	0.326	0.343
O2	0.451	0.256	-0.024	0.460	0.749	0.489

Table S4: Comparison of calculated lattice constants of ZrO_2-$P4_2/nmc$ and HfO_2-$P4_2/nmc$ with experimental data.

ZrO_2-$P4_2/nmc$, 0 GPa						
Parameter	Theory			Experiment [3]		
a (Å)	3.622			3.578		
b (Å)	3.622			3.578		
c (Å)	5.279			5.162		
Atoms	x	y	z	x	y	z
Zr1	0.750	0.250	0.250	0.000	0.000	0.000
O1	0.250	0.250	-0.056	0.000	0.500	0.048
HfO_2-$P4_2/nmc$, 0 GPa						
Parameter	Theory			Experiment [4]		
a (Å)	3.594			3.593		
b (Å)	3.594			3.593		
c (Å)	5.229			5.225		
Atoms	x	y	z	x	y	z
Hf1	0.750	0.250	0.250	0.000	0.000	0.000
O1	0.250	0.250	-0.054	0.000	0.500	0.195

Table S5: Comparison of calculated lattice constants of ZrO_2-$Fm\bar{3}m$ and HfO_2-$Fm\bar{3}m$ with experimental data.

ZrO_2-$Fm\bar{3}m$, 0 GPa						
Parameter	Theory			Experiment [5]		
a (Å)	5.118			5.090		
Atoms	x	y	z	x	y	z
Zr1	0.000	0.000	0.000	0.000	0.000	0.000
O1	0.250	0.250	0.250	0.250	0.250	0.250
HfO_2-$Fm\bar{3}m$, 0 GPa						
Parameter	Theory			Experiment [6]		
a (Å)	5.080			5.115		
Atoms	x	y	z	x	y	z
Hf1	0.000	0.000	0.000	0.000	0.000	0.000
O1	0.250	0.250	0.250	0.250	0.250	0.250

Table S6: Comparison of calculated lattice constants of ZrO_2-*Pbca* and HfO_2-*Pbca* with experimental data.

ZrO_2-*Pbca*, 0 GPa						
Parameter	Theory			Experiment [7]		
a (Å)	10.054			10.086		
b (Å)	5.261			5.261		
c (Å)	5.078			5.091		
Atoms	x	y	z	x	y	z
Zr1	0.884	0.034	0.253	0.884	0.032	0.256
O1	0.791	0.377	0.131	0.791	0.371	0.131
O2	-0.023	0.738	0.497	0.978	0.748	0.495
HfO_2-*Pbca*, 0 GPa						
Parameter	Theory			Experiment [8]		
a (Å)	10.068			10.017		
b (Å)	5.252			5.228		
c (Å)	5.089			5.060		
Atoms	x	y	z	x	y	z
Hf1	0.884	0.036	0.254	0.884	0.034	0.253
O1	0.789	0.372	0.124	0.796	0.380	0.138
O2	-0.022	0.739	0.498	0.977	0.750	0.490

Table S7: Comparison of calculated lattice constants of ZrO_2-*Pnma* and HfO_2-*Pnma* with experimental data.

ZrO_2-*Pnma*, 0 GPa						
Parameter	Theory			Experiment [9]		
a (Å)	5.601			5.587		
b (Å)	3.375			6.485		
c (Å)	6.550			3.330		
Atoms	*x*	*y*	*z*	*x*	*y*	*z*
Zr1	0.249	0.250	0.107	0.246	0.111	0.250
O1	0.361	0.250	0.423	0.360	0.425	0.250
O2	-0.021	0.250	0.658	0.025	0.339	0.750
HfO_2-*Pnma*, 0 GPa						
Parameter	Theory			Experiment [9]		
a (Å)	5.560			5.554		
b (Å)	3.335			6.457		
c (Å)	6.514			3.307		
Atoms	*x*	*y*	*z*	*x*	*y*	*z*
Hf1	0.751	0.250	0.892	0.246	0.110	0.250
O1	0.020	0.250	0.341	0.359	0.426	0.250
O2	0.139	0.250	-0.077	0.024	0.339	0.750

Table S8: Comparison of calculated lattice constants of ZrO_2-$P\bar{6}2m$ and HfO_2-$P\bar{6}2m$ with experimental data.

ZrO_2-$P\bar{6}2m$, 150 GPa		
Parameter	Theory	Experiment [10]
a (Å)	5.139	5.134
b (Å)	5.139	5.134
c (Å)	2.951	2.950
HfO_2-$P\bar{6}2m$		
Parameter	Theory (150 GPa)	Experiment (177 GPa) [11]
a (Å)	5.131	5.074
b (Å)	5.131	5.074
c (Å)	2.925	2.899

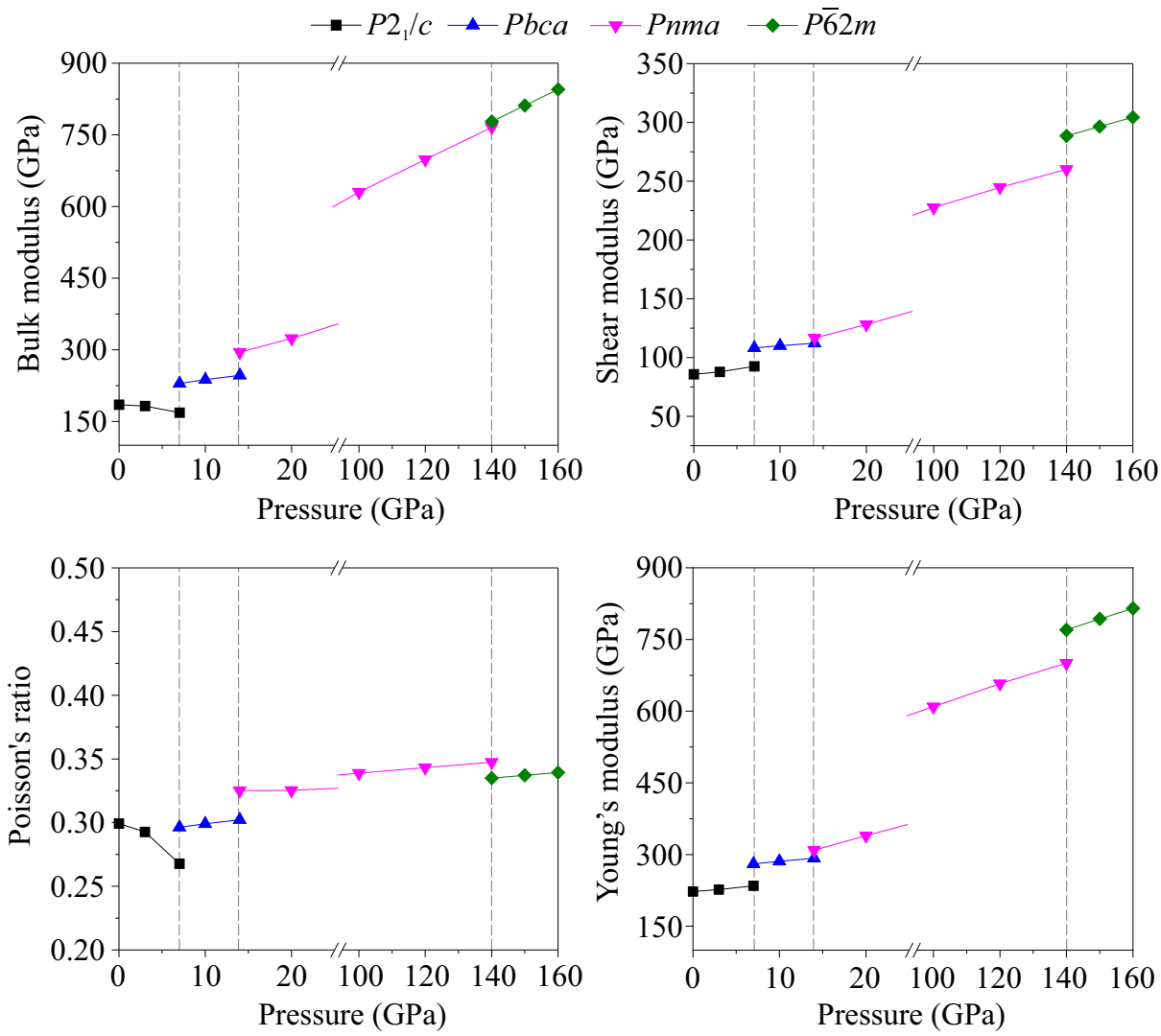

Figure S4: Pressure-dependence of B, G, ν, and E for ZrO_2 polymorphs.

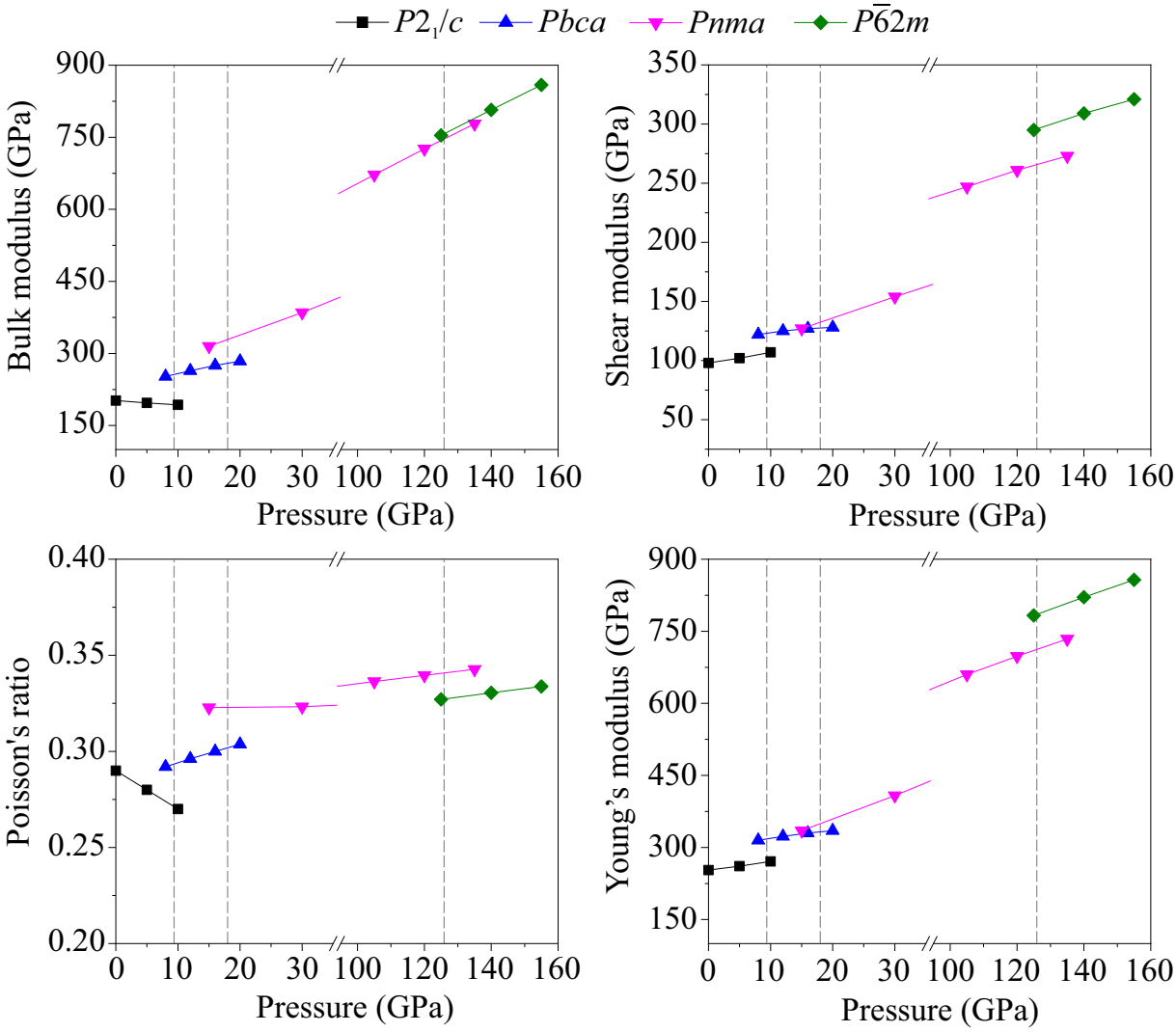

Figure S5: Pressure-dependence of B, G, ν, and E for HfO_2 polymorphs.

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