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Pressure-induced Novel Nitrogen-Rich Aluminum Nitrides: AlN_6, Al_2N_7 and AlN_7 with Polymeric Nitrogen Chain and Ring

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Table S1. The unit-cell parameters and atomic positions of Al-N phases at different pressure.

structures	lattice parameters(Å)	atomic coordinates
Cm-AlN_2 P = 0 GPa	a = 9.76 b = 3.10 c = 5.91 α = 90.00 β = 154.08 γ = 90.00	Al1(0.098,0.000,0.866) Al2(0.113,0.000,0.360) Al3(0.598,0.500,0.866) Al4(0.613,0.500,0.360) N1(0.855,0.500,0.988) N2 (0.355,0.000, 0.988)
$P\bar{3}m1$-Al_2N P = 20 GPa	a = 2.81 b = 2.81 c = 8.67 α = 90.00 β = 90.00 γ = 120.00	Al1 (0.333, 0.667, 0.768) Al2 (0.667, 0.333, 0.232) Al3(0.000, 0.000, 0.500 Al4(0.000, 0.000, 0.000) N1 (0.667, 0.333, 0.632) N2(0.333, 0.667, 0.368)
$P\bar{3}m1$-Al_2N P = 40 GPa	a = 2.74 b = 2.74 c = 4.25 α = 90.00 β = 90.00 γ = 120.00	Al1 (0.333, 0.667, 0.768) Al2 (0.667, 0.333, 0.232) N1 (0.000, 0.000, 0.500)
*P*2/*m*- Al_2N P = 60 GPa	a = 3.90 b = 2.63 c = 2.65 α = 90.00 β = 96.75 γ = 90.00	Al1 (0.000, 0.000, 0.000) Al2 (0.500, 0.500, 0.500) N1 (0.500, 0.000, 0.000)
$P\bar{3}m1$-Al_2N P = 80 GPa	a = 2.64 b = 2.64 c = 4.13 α = 90.00 β = 90.00 γ = 120.00	Al1 (0.667, 0.333, 0.768) Al2 (0.333, 0.667, 0.232) N1 (0.000, 0.000, 0.500)
$P6_3mc$-AlN P = 0 GPa	a = 3.12 b = 3.12 c = 4.88 α = 90.00 β = 90.00 γ = 120.00	Al1 (0.333, 0.667, 0.250) Al2 (0.667, 0.333, 0.750) N1 (0.333, 0.667, 0.750) N2 (0.667, 0.333, 0.250)
$Fm\bar{3}m$-AlN P = 20 GPa	a = 3.04 b = 3.04 c = 3.75 α = 90.00 β = 90.00 γ = 120.00	Al1 (0.500, 0.000, 0.000) Al2 (0.500, 0.500, 0.500) Al3 (0.000, 0.000, 0.500) Al4 (0.000, 0.500, 0.000) N1 (0.000, 0.000, 0.000) N2 (0.000, 0.500, 0.500) N3 (0.500, 0.000, 0.500) N4 (0.500, 0.500, 0.000)
		Al1 (0.058,0.500, 0.236) Al2 (0.942,0.500,0.764)

$R\bar{3}m$-Al_2N_3 P = 0 GPa	a = 7.11 b = 2.75 c = 6.64 α = 90.00 β = 132.00 γ = 90.00	Al3 (0.558,0.000,0.236) Al4 (0.442,0.000,0.764) N1 (0.0662,0.000,0.462) N2 (0.434, 0.500,0.538) N3 (0.000,0.000,0.000) N4 (0.566,0.500,0.462) N5 (0.934,0.000,0.538) N6 (0.500,0.500,0.000)
$R\bar{3}m$-Al_2N_3 P = 20 GPa	a = 6.00 b = 6.00 c = 6.00 α = 27.04 β = 27.04 γ = 27.04	Al1(0.733,0.733,0.733) Al2(0.267,0.267,0.267) N1(0.461,0.461,0.461) N2(0.000,0.000,0.000) N3(0.539,0.539,0.538)
Cmmm-Al_2N_3 P = 40 GPa	a = 5.88 b = 4.91 c = 2.57 α = 90.00 β = 90.00 γ = 90.00	Al1(0.750,0.250,0.500) Al2(0.750,0.750,0.500) Al3(0.250,0.750,0.500) Al4(0.250,0.250,0.500) N1(0.118,0.000,0.000) N2(0.500,0.000,0.500) N3(0.882,0.000,0.000) N4(0.618,0.500,0.000) N5(0.000,0.500,0.500) N6(0.382,0.500,0.000)
$R\bar{3}m$-Al_2N_3 P = 60 GPa	a = 5.85 b = 5.85 c = 5.85 α = 26.63 β = 26.63 γ = 26.63	Al1(0.267,0.267,0.267) Al2(0.733,0.733,0.733) N1(0.461,0.461,0.461) N2(0.000,0.000,0.000) N3(0.539,0.539,0.539)
R3m-Al_2N_3 P = 80 GPa	a = 5.98 b = 5.98 c = 5.98 α = 25.32 β = 25.32 γ = 25.32	Al1(0.341,0.341,0.341) Al2(0.477,0.477,0.477) N1(0.948,0.948,0.948) N2(0.740,0.740,0.740) N3(0.874,0.874,0.874)
$R\bar{3}m$-AlN_2 P = 0 GPa	a = 3.89 b = 3.89 c = 3.89 α = 44.04 β = 44.04 γ = 44.04	Al1 (0.000, 0.000, 0.000) N1 (0.564, 0.564, 0.564) N2 (0.436, 0.436, 0.436)
C2/m-AlN_2 P = 20 GPa	a = 4.95 b = 2.82 c = 9.95 α = 90.00 β = 95.31 γ = 90.00	Al1 (0.000,0.500, 0.500) Al2 (0.371,0.500,0.730) Al3 (0.129,0.000,0.270) Al4 (0.500,0.000,0.500) Al5 (0.871,0.000,0.730) Al6 (0.629,0.000,0.730)

		N1 (0.0618,0.500,0.832) N2 (0.900, 0.500,0.036) N3 (0.938,0.500,0.168) N4 (0.186,0.000,0.615) N5 (0.314,0.500,0.385) N6 (0.100,0.500,0.964) N7 (0.562,0.000,0.832) N8 (0.400,0.000,0.036) N9 (0.438,0.000,0.168) N10 (0.686,0.500,0.615) N11 (0.814,0.000,0.385) N12 (0.600,0.000,0.964)
P6/mmm-AlN_2 P = 40 GPa	a = 2.66 b = 2.66 c = 4.90 α = 90.00 β = 90.00 γ = 120.00	Al1 (0.000, 0.000, 0.000) N1 (0.000, 0.000, 0.382) N2 (0.000, 0.000, 0.617)
Pnnm-AlN_2 P = 60 GPa	a = 4.45 b = 3.72 c = 2.54 α = 90.00 β = 90.00 γ = 90.00	Al1 (0.000, 0.000, 0.000) Al2 (0.500, 0.500, 0.500) N1 (0.596, 0.135, 0.000) N2 (0.404, 0.865, 0.000) N3 (0.904, 0.635, 0.500) N4 (0.096, 0.365, 0.500)
$R\bar{3}m$-AlN_2 P = 80 GPa	a = 4.45 b = 3.72 c = 2.54 α = 90.00 β = 90.00 γ = 90.00	Al1 (0.500, 0.500, 0.500) N1 (0.064, 0.064, 0.064) N2 (0.936, 0.936, 0.936)
P1-Al_2N_5 P = 0 GPa	a = 4.45 b = 3.72 c = 2.54 α = 90.00 β = 90.00 γ = 90.00	Al1(0.301,0.968,0.521) Al2(0.836,0.318,0.820) N1(0.146,0.111,0.179) N2(0.177,0.660,0.818) N3(0.955,0.278,0.057) N4(0.343,0.941,0.302) N5(0.654,0.308,0.570)
Cm-Al_2N_5 P = 20 GPa	a = 7.02 b = 2.77 c = 5.73 α = 90.00 β = 95.68 γ = 90.00	Al1(0.161,0.500,0.923) Al2(0.738,0.500,0.449) Al3(0.661,0.000,0.923) Al4(0.238,0.000,0.449) N1(0.791,0.500,0.111) N2(0.014,0.000,0.762) N3(0.837,0.000,0.680) N4(0.979,0.500,0.150) N5(0.038,0.500,0.375) N6(0.291,0.000,0.111) N7(0.514,0.500,0.762) N8(0.337,0.500,0.680)

		N9(0.480,0.000,0.150) N10(0.538,0.000,0.375)
$P\bar{1}$ -Al_2N_5 P = 40 GPa	a = 2.77 b = 2.77 c = 7.59 α = 99.69 β = 96.51 γ = 62.02	Al1(0.849,0.396,0.650) Al2(0.151,0.603,0.350) N1(0.815,0.178,0.046) N2(0.185,0.822,0.955) N3(0.500,0.000,0.501) N4(0.211,0.794,0.783) N5(0.789,0.206,0.219)
P1 -Al_2N_5 P = 60 GPa	a = 2.66 b = 2.70 c = 5.31 α = 93.30 β = 92.68 γ = 110.52	Al1(0.599,0.099,0.873) Al2(0.136,0.234,0.408) N1(0.428,0.839,0.335) N2(0.241,0.351,0.064) N3(0.944,0.812,0.706) N4(0.407,0.725,0.099) N5(0.765,0.455,0.631)
P1 -Al_2N_5 P = 80 GPa	a = 2.52 b = 3.88 c = 4.75 α = 99.64 β = 77.38 γ = 94.90	Al1(0.367,0.764,0.472) Al2(0.358,0.189,0.102) N1(0.809,0.832,0.102) N2(0.934,0.320,0.829) N3(0.950,0.666,0.833) N4(0.829,0.400,0.384) N5(0.886,0.143,0.556)
Cm-AlN_3 P = 0 GPa	a = 7.10 b = 7.01 c = 3.26 α = 90.00 β = 103.47 γ = 90.00	Al1(0.242,0.247,0.074) Al2(0.242,0.753,0.074) Al3(0.742,0.747,0.074) Al4(0.742,0.253,0.074) N1(0.355,0.181,0.636) N2(0.855,0.319,0.636) N3(0.401,0.500,0.121) N4(0.067,0.000,0.073) N5(0.527,0.098,0.784) N6(0.027,0.402,0.784) N7(0.855,0.681,0.636) N8(0.355,0.819,0.636) N9(0.901,0.000,0.121) N10(0.567,0.500,0.073) N11(0.027,0.598,0.784) N12(0.527,0.902,0.784)
$P\bar{1}$-AlN_3 P = 20 GPa	a = 2.80 b = 4.67 c = 4.90 α = 79.24 β = 92.58 γ = 94.22	Al1(0.256,0.226,0.803) Al2(0.744,0.774,0.197) N1(0.780,0.197,0.088) N2(0.727,0.215,0.540) N3(0.220,0.803,0.912) N4(0.748,0.348, 0.288) N5(0.273,0.785, 0.460) N6(0.252,0.652,0.712)
		Al1 (0.244, 0.876, 0.090)

$P2_1/c$-AlN_3 P = 40 GPa	a = 11.56 b = 3.66 c = 11.22 α = 90.00 β = 165.99 γ = 120.00	Al2 (0.756, 0.124, 0.910) Al3 (0.756, 0.376, 0.410) Al4 (0.244, 0.624, 0.590) N1 (0.258, 0.755, 0.369) N2 (0.742, 0.245, 0.631) N3 (0.742, 0.255, 0.131) N4 (0.258, 0.745, 0.869) N5 (0.109, 0.656, 0.110) N6 (0.891, 0.344, 0.890) N7 (0.891, 0.156, 0.390) N8 (0.109, 0.844, 0.610) N9 (0.743, 0.957, 0.055) N10 (0.257, 0.043, 0.945) N11 (0.257, 0.457, 0.445) N12 (0.743, 0.543, 0.555)
P1-Al_2N_7 P = 0 GPa	a = 3.16 b = 5.24 c = 6.98 α = 101.35 β = 84.46 γ = 91.46	Al1(0.885,0.972,0.248) Al2(0.423,0.439,0.120) N1(0.657,0.196,0.687) N2(0.280,0.576,0.527) N3(0.173,0.693,0.676) N4(0.806,0.089,0.533) N5(0.918,0.617,0.174) N6(0.506,0.308,0.839) N7(0.404,0.114,0.188)
Cm-Al_2N_7 P = 20 GPa	a = 5.69 b = 4.77 c = 5.27 α = 90.00 β = 63.26 γ = 90.00	Al1(0.153,0.500,0.054) Al2(0.294,0.500,0.478) Al3(0.653,0.000,0.054) Al4(0.794,0.000,0.478) N1(0.243,0.202,0.749) N2(0.804,0.274,0.224) N3(0.304,0.226,0.224) N4(0.061,0.000,0.792) N5(0.159,0.000,0.305) N6(0.429,0.000,0.704) N7(0.243,0.798,0.749) N8(0.743,0.702,0.749) N9(0.304,0.774,0.224) N10(0.804,0.726,0.224)
Cm-Al_2N_7 P = 40 GPa	a = 5.69 b = 4.77 c = 5.27 α = 90.00 β = 63.26 γ = 90.00	Al1(0.153,0.500,0.054) Al2(0.294,0.500,0.478) Al3(0.653,0.000,0.054) Al4(0.794,0.000,0.478) N1(0.243,0.201,0.748) N2(0.804,0.273,0.223) N3(0.304,0.226,0.223) N4(0.060,0.000,0.791) N5(0.159,0.000,0.304) N6(0.429,0.000,0.703) N7(0.243,0.798,0.748)

		N8(0.743,0.701,0.748) N9(0.304,0.773,0.223) N10(0.804,0.726,0.223) N11(0.560,0.500,0.791) N12(0.659,0.500,0.304) N13(0.929,0.500,0.703) N14(0.743,0.298,0.748)
C2-Al_2N_7 P = 80 GPa	a = 8.18 b = 3.52 c = 4.88 α = 90.00 β = 127.29 γ = 90.00	Al1(0.728,0.832,0.209) Al2(0.771,0.332,0.790) Al3(0.228,0.332,0.209) Al4(0.271,0.832,0.790) N1(0.092,0.224,0.543) N2(0.569,0.197,0.863) N3(0.115,0.539,0.411) N4(0.500,0.452,0.000) N5(0.884,0.539,0.588) N6(0.907,0.224,0.456) N7(0.930,0.697,0.136) N8(0.592,0.724,0.543) N9(0.069,0.697,0.863) N10(0.615,0.039,0.411) N11(0.000,0.952,0.000) N12(0.384,0.039,0.588) N13(0.407,0.724,0.456)
P2/m-AlN_4 P = 0 GPa	a = 4.84 b = 2.96 c = 3.76 α = 90.00 β = 71.75 γ = 90.00	Al1(0.500,0.000,0.000) N1(0.062,0.000,0.343) N2(0.938,0.000,0.657) N3(0.521,0.500,0.325) N4(0.479,0.500, 0.675)
Pmcm-AlN_4 P = 20 GPa	a = 2.84 b = 4.11 c = 7.24 α = 90.00 β = 90.00 γ = 90.00	Al1(0.000,0.500,0.000) Al2(0.000,0.500,0.500) N1(0.500,0.602,0.835) N2(0.500,0.398,0.335) N3(0.000,0.895,0.329) N4(0.000,0.105,0.829) N5(0.000,0.895,0.171) N6(0.000,0.105,0.671) N7(0.500,0.398,0.165) N8(0.500,0.602,0.665)
$P\bar{1}$-AlN_4 P = 40 GPa	a = 2.86 b = 3.56 c = 3.74 α = 102.88 β = 111.13 γ = 93.98 a = 3.66	Al1 (0.500, 0.000, 0.500) N1 (0.956, 0.305, 0.366) N2 (0.044, 0.695, 0.634) N3 (0.843, 0.349, 0.996) N4 (0.157, 0.651, 0.004)
Cc2e-AlN_5 P = 0 GPa	a = 4.04 b = 3.78	Al1(0.000,0.272,0.000) Al2(0.000,0.772,0.500)

	c = 20.49 α = 90.00 β = 90.00 γ = 90.00	Al3(0.500,0.772,0.000) Al4(0.500,0.272,0.500) N1(0.000,0.770,0.000) N2(0.000,0.270,0.500) N3(0.865,0.867,0.808) N4(0.135,0.867,0.192) N5(0.635,0.867,0.308) N6(0.365,0.867,0.692) N7(0.881,0.972,0.859) N8(0.119,0.972,0.141) N9(0.619,0.972,0.359) N10(0.381,0.972,0.641) N11(0.500,0.270,0.000) N12(0.500,0.770,0.500) N13(0.365,0.367,0.808) N14(0.635,0.367,0.192) N15(0.135,0.367,0.308) N16(0.866,0.367,0.692) N17(0.380,0.472,0.859) N18(0.619,0.472,0.141) N19(0.119,0.472,0.359) N20(0.881,0.472,0.641)
Cm-AlN_5 P = 20 GPa	a = 6.46 b = 3.10 c = 20.49 α = 90.00 β = 107.36 γ = 90.00	Al1(0.408,0.000,0.532) Al2(0.908,0.500,0.532) N1(0.205,0.000,0.866) N2(0.772,0.129,0.267) N3(0.772,0.871,0.267) N4(0.112,0.250,0.925) N5(0.112,0.749,0.925) N6(0.705,0.500,0.866) N7(0.272,0.629,0.267) N8(0.272,0.371,0.267) N9(0.612,0.751,0.925) N10(0.612,0.249,0.925)
$P\bar{1}$-AlN_5 P = 40 GPa	a = 3.66 b = 4.41 c = 6.72 α = 85.02 β = 81.98 γ = 66.28	Al1(0.010, 0.890, 0.230) N1(0.510, 0.770, 0.660) N2(0.880, 0.770, 0.660) N3(0.850, 0.520, 0.290) N4(0.490, 0.530, 0.300) N5(0.330, 0.000, 0.000)
$I\bar{4}2d$-AlN_5 P = 60 GPa	a = 5.19 b = 5.19 c = 5.14 α = 90.00 β = 90.00 γ = 90.00	Al1(0.000, 0.000, 0.500) Al2(0.500, 0.000, 0.250) Al3(0.500, 0.500, 0.000) Al4(0.000, 0.500, 0.750) N1(0.680, 0.630, 0.650) N2(0.320, 0.370, 0.650) N3(0.630, 0.320, 0.350) N4(0.370, 0.680, 0.350) N5(0.820, 0.630, 0.100)

		N6(0.180, 0.370, 0.100) N7(0.870, 0.320, 0.400) N8(0.130, 0.680, 0.400) N9(0.180, 0.130, 0.150) N10(0.820, 0.870, 0.150) N11(0.130, 0.820, 0.850) N12(0.870, 0.180, 0.850) N13(0.320, 0.130, 0.600) N14(0.680, 0.870, 0.600) N15(0.370, 0.820, 0.900) N16(0.630, 0.180, 0.900) N17(0.000, 0.500, 0.250) N18(0.500, 0.000, 0.750) N19(0.500, 0.500, 0.500) N20(0.000, 0.000,0.000)
$P\bar{1}$-AlN_6 P = 0 GPa	a = 4.82 b = 4.84 c = 4.11 α = 98.33 β = 107.99 γ = 109.76	Al1(0.000,0.000,0.500) N1(0.824,0.703,0.025) N2(0.876,0.697,0.765) N3(0.123,0.303,0.235) N4(0.595,0.017,0.436) N5(0.405,0.984,0.564) N6(0.176,0.297,0.975)
C2/m-AlN_6 P = 20 GPa	a = 11.83 b = 2.80 c = 3.72 α = 90.00 β = 82.39 γ = 90	Al1(0.000,0.000,0.000) Al2(0.500,0.500,0.000) N1(0.839,0.000,0.856) N2(0.661,0.500,0.144) N3(0.987,0.500,0.344) N4(0.682,0.500,0.427) N5(0.013,0.500,0.656) N6(0.817,0.000,0.573) N7(0.339,0.500,0.856) N8(0.161,0.000,0.144) N9(0.487,0.000,0.344) N10(0.182,0.000,0.427) N11(0.513,0.000,0.656) N12(0.317,0.500,0.573)
C2/m-AlN_6 P = 40 GPa	a = 5.11 b = 4.96 c = 4.30 α = 90.00 β = 63.03 γ = 90.00	Al1 (0.000, 0.500, 0.000) Al2 (0.500, 0.000, 0.000) N1 (0.261, 0.000, 0.775) N2 (0.739, 0.000, 0.225) N3 (0.289, 0.264, 0.334) N4 (0.789, 0.236, 0.334) N5 (0.211, 0.235, 0.666) N6 (0.711, 0.264, 0.666) N7 (0.761, 0.500, 0.775) N8 (0.239, 0.500, 0.225) N9 (0.789, 0.764, 0.334) N10 (0.289, 0.736, 0.334) N11 (0.711, 0.736, 0.666)

		N12 (0.211, 0.764, 0.666)
Pm-AlN_7 P = 0 GPa	a = 6.11 b = 8.07 c = 2.85 α = 90.00 β = 81.98 γ = 90.00	Al1(0.235,0.500,0.365) N1(0.915,0.500,0.453) N2(0.738,0.500,0.330) N3(0.562,0.500,0.210) N4(0.452,0.814,0.432) N5(0.452,0.186,0.432) N6(0.631,0.838,0.441) N7(0.631,0.162,0.441)
P6mm-AlN_7 P = 20 GPa	a = 5.19 b = 5.19 c = 3.49 α = 90.00 β = 90.00 γ = 120.00	Al1(0.000,0.000,0.672) N1(0.000,0.000,0.166) N2(0.500,0.000,0.666) N3(0.000,0.500,0.666) N4(0.500,0.500,0.666) N5(0.500,0.000,0.345) N6(0.000,0.500,0.345) N7(0.500,0.500,0.345)
*P*1-AlN_7 P = 40 GPa	a = 2.77 b = 4.58 c = 4.72 α = 112.39 β = 94.50 γ = 92.125	Al1(0.934, 0.460, 0.523) N1(0.348, 0.252, 0.968) N2(0.967, 0.046, 0.523) N3(0.388, 0.300, 0.251) N4(0.467, 0.492, 0.851) N5(0.840, 0.767, 0.313) N6(0.132, 0.992, 0.766) N7(0.622, 0.772, 0.068)
*P*1-AlN_7 P = 80 GPa	a = 3.47 b = 3.84 c = 4.12 α = 114.75 β = 91.28 γ = 101.68	Al1(0.311, 0.267, 0.965) N1(0.587, 0.355, 0.385) N2(0.967, 0.046, 0.523) N3(0.179, 0.719, 0.290) N4(0.796, 0.176, 0.782) N5(0.965, 0.920, 0.201) N6(0.429, 0.547, 0.671) N7(0.773, 0.121, 0.460)

Table S2. Calculated enthalpies of the predicted Al_xN_y compounds at different pressures.

Structure	Pressure (GPa)	Enthalpy (eV/atom)	Formation enthalpy(eV/atom)
Cm-Al_2N	0	-5.897	-0.628
$P\bar{3}m1$-Al_2N	20	-4.639	0.051
$P\bar{3}m1$-Al_2N	40	-3.323	-1.393
P2/m-Al_2N	60	-1.770	-1.203
$P\bar{3}m1$-Al_2N	80	-0.843	-1.820
$P6_3mc$-AlN	0	-7.445	-1.412
$Fm\bar{3}m$-AlN	20	-6.263	-2.036
$Fm\bar{3}m$-AlN	40	-5.304	-2.524
$Fm\bar{3}m$-AlN	60	-4.398	-2.913

$Fm\bar{3}m$-AlN	80	-3.528	-3.238
$R\bar{3}m$-Al_2N_3	0	-7.033	-0.542
$R\bar{3}m$-Al_2N_3	20	-6.153	-1.454
$Cmmm$-Al_2N_3	40	-4.978	-1.688
$R\bar{3}m$-Al_2N_3	60	-4.260	-2.224
$R3m$-Al_2N_3	80	-3.154	-2.272
$R\bar{3}m$-AlN_2	0	-7.203	-0.407
$C2/m$-AlN_2	20	-6.156	-0.519
$P6/mmm$-AlN_2	40	-5.160	-1.530
$Pnnm$-AlN_2	60	-4.295	-1.892
$R\bar{3}m$-AlN_2	80	-3.350	-2.073
$P1$-Al_2N_5	0	-7.233	-0.218
Cm-Al_2N_5	20	-6.089	-0.852
$P\bar{1}$ -Al_2N_5	40	-5.175	-1.302
$P1$ -Al_2N_5	60	-4.124	-1.458
$P1$ -Al_2N_5	80	-3.322	-1.7631
Cm-AlN_3	0	-6.970	0.209
$P\bar{1}$-AlN_3	20	-6.151	-0.277
$P2_1/c$-AlN_3	40	-5.372	-1.317
$P2_1/c$-AlN_3	60	-4.500	-1.637
$P2_1/c$-AlN_3	80	-3.668	-1.898
$P1$-Al_2N_7	0	-7.403	-0.097
Cm-Al_2N_7	20	-6.010	-0.474
Cm-Al_2N_7	40	-6.035	-1.838
Cm-Al_2N_7	60	-4.198	-1.182
$C2$-Al_2N_7	80	-3.452	-1.517
$P2/m$-AlN_4	0	-7.436	-0.029
$Pmcm$-AlN_4	20	-6.259	-0.242
$P\bar{1}$-AlN_4	40	-5.300	-0.990
$P\bar{1}$-AlN_4	60	-4.464	-1.326
$P\bar{1}$-AlN_4	80	-3.430	-1.364
$Cc2e$-AlN_5	0	-7.582	-0.022
Cm-AlN_5	20	-6.124	-0.013
$P\bar{1}$-AlN_5	40	-5.247	-0.767
$I\bar{4}2d$-AlN_5	60	-4.224	-0.903
$I\bar{4}2d$-AlN_5	80	-3.623	2.398
$P\bar{1}$-AlN_6	0	-7.511	0.158
$C2/m$-AlN_6	20	-6.243	-0.065
$C2/m$-AlN_6	40	-5.370	-0.493
$C2/m$-AlN_6	60	-4.509	-1.056
$C2/m$-AlN_6	80	-3.692	-1.288
Pm-AlN_7	0	-7.282	0.469
$P6mm$-AlN_7	20	-5.757	0.472
$P1$-AlN_7	40	-5.185	-1.317

*P*1-AlN_7	60	-4.246	-0.695
*P*1-AlN_7	80	-3.615	-1.105

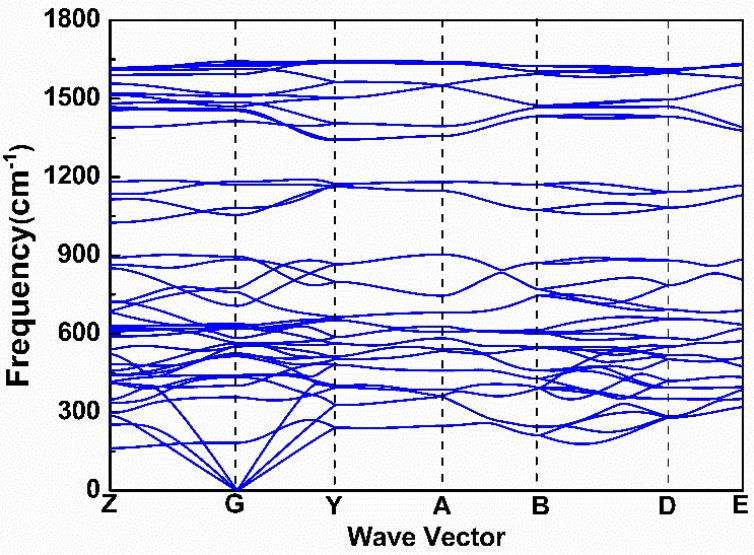

Fig. S1 Phonon dispersion curves of C2/m-AlN_6 at 30 GPa.

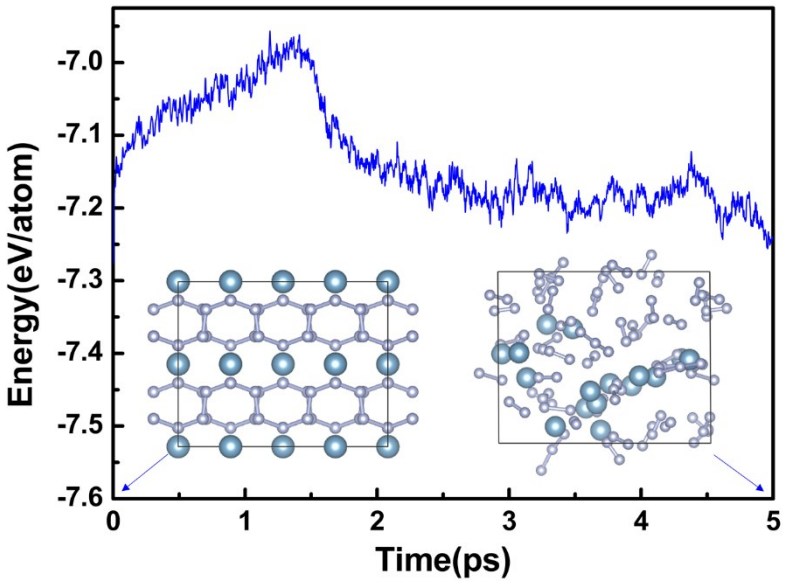

Fig. S2 Fluctuations of the total energies obtained by molecular dynamics simulation under the NPT ensemble at ambient pressure at 1500 K and for *C*2/*m*-AlN_6 phase.

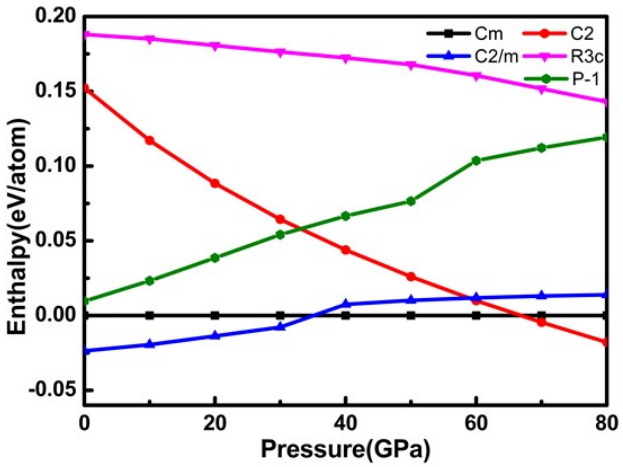

Fig. S3 Enthalpy difference between Cm-Al_2N_7 and other phases of Al_2N_7.

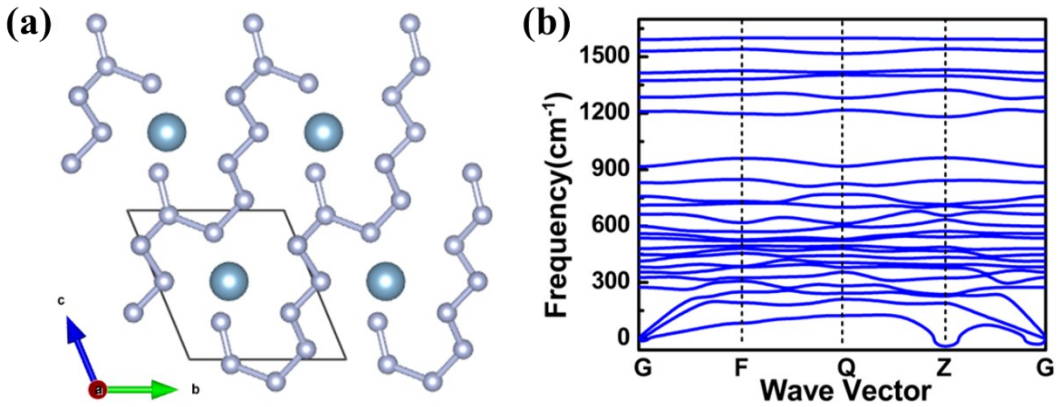

Fig. S4 (a) Crystal structure and (b) phonon dispersion relation of P1-AlN_7 at 40 GPa.

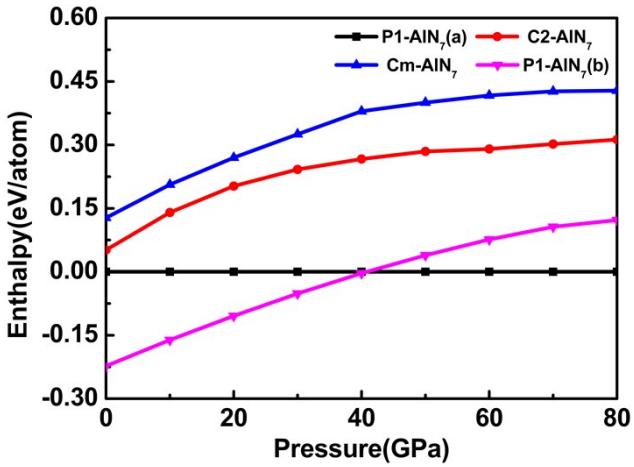

Fig. S5 Enthalpy difference between P1-AlN_7 and other phases of AlN_7. The black line represents the metastable P1-AlN_7 searched under 80 GPa, and the pink line represents the structure searched under 40 GPa.

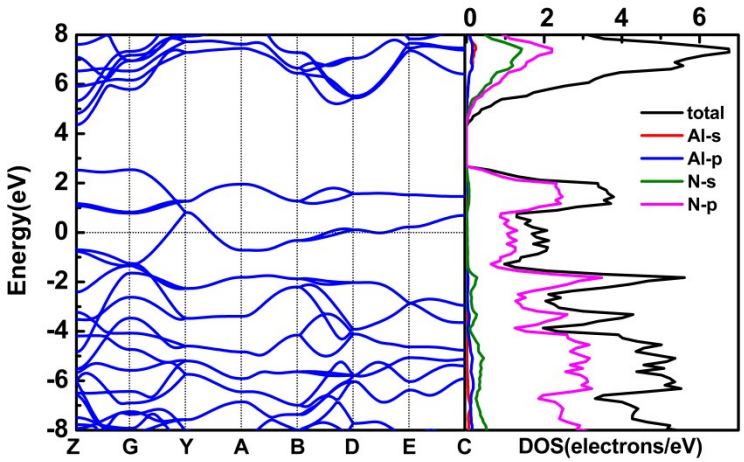

Fig. S6 Band structure and density of states (DOS) of *C*2/*m*-AlN_6 at 30 GPa.

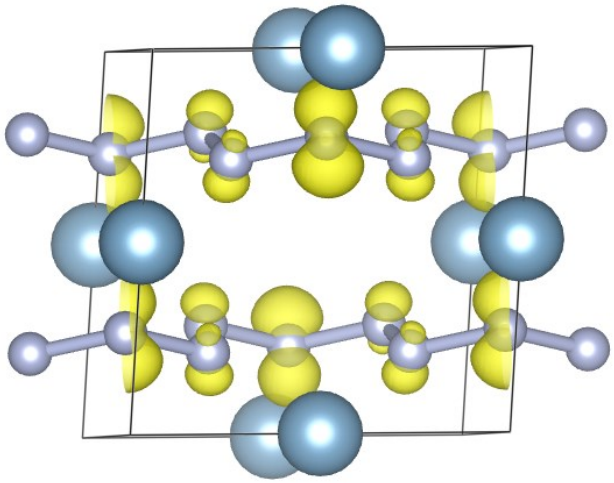

Fig. S7 Three-dimensional partial charge density distribution of an energy band crossing Fermi energy for *C*2/*m*-AlN_6 at ambient condition. The value of isosurface is 0.01.

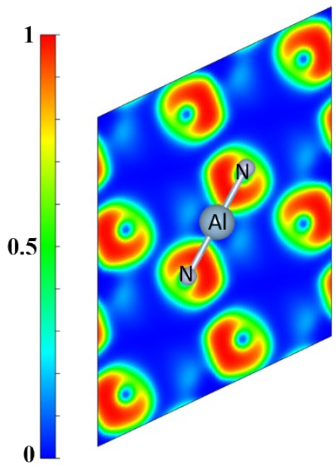

Fig. S8 Two-dimensional ELF distribution diagram on (010) crystal plane.

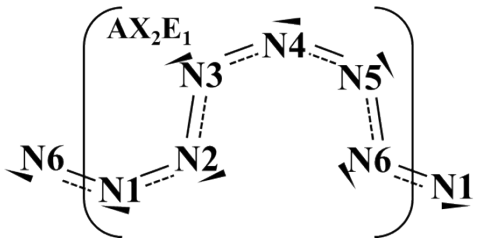

Fig. S9 The Lewis crystal structure with VSEPR notation for C2/m-AlN_6.

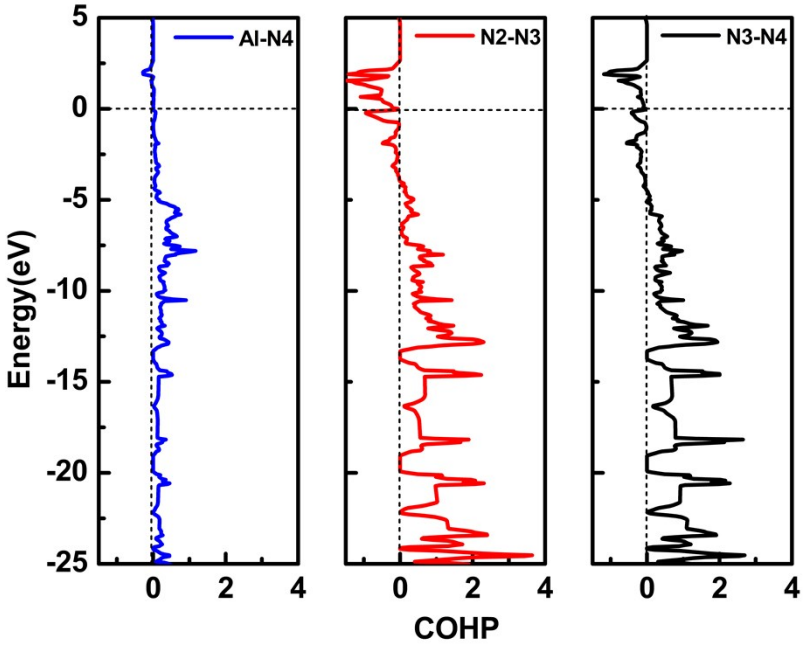

Fig. S10 COHPs between Al-N4, N2-N3 and N3-N4 pairs for *C2/m*-AlN_6 phase at 30 GPa. Fermi levels are set at zero energy and marked by dotted lines.

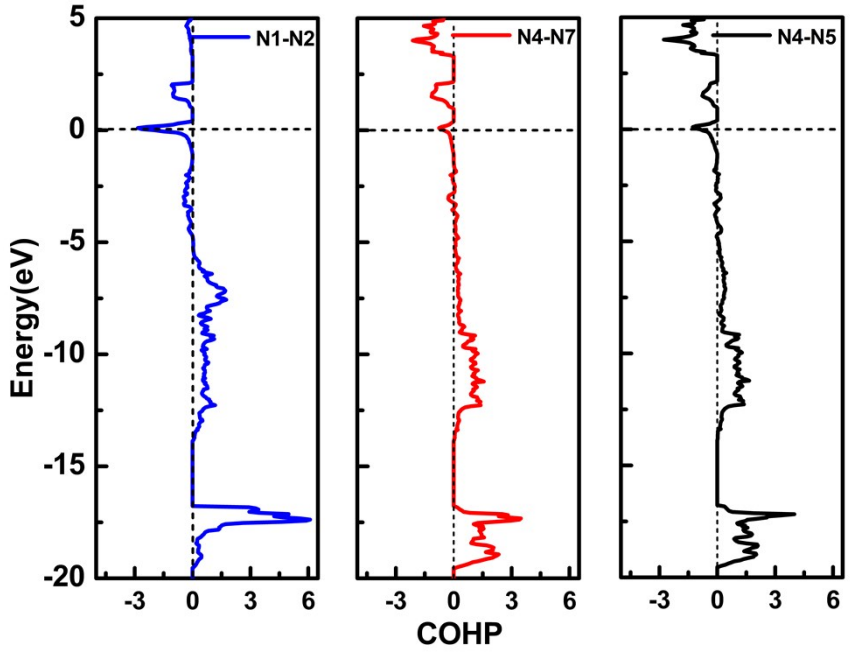

Fig. S11 COHPs between N1-N2, N4-N7 and N4-N5 pairs for *C*2*m*-Al_2N_7 phase at 40 GPa. Fermi levels are set at zero energy and marked by dotted lines.

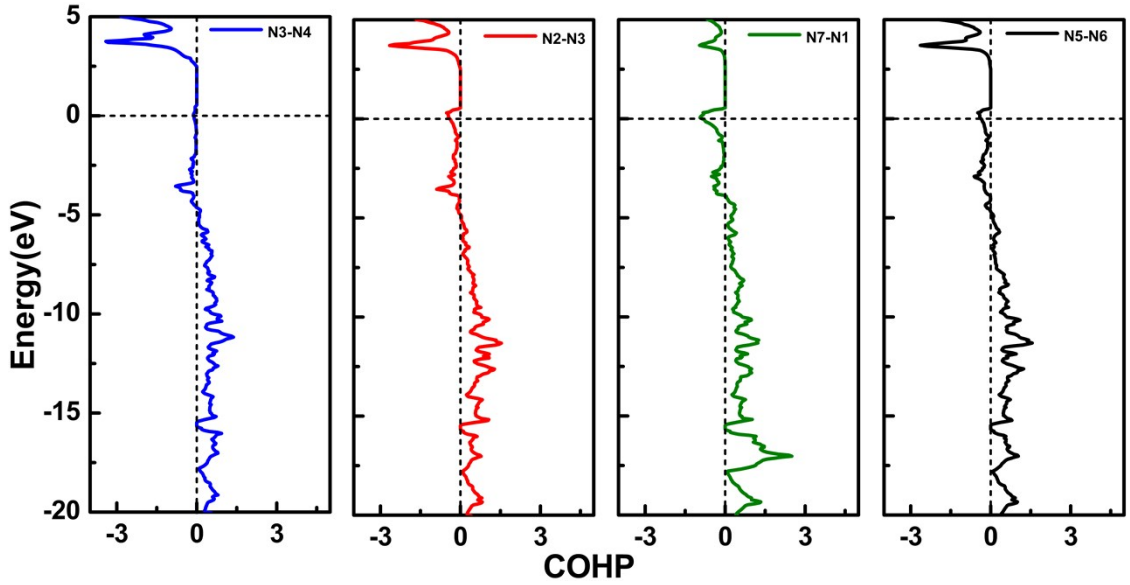

Fig. S12 COHPs between N3-N4, N2-N3, N7-N1 and N5-N6 pairs for *C*2-Al_2N_7 phase at 80 GPa. Fermi levels are set at zero energy and marked by dotted lines.

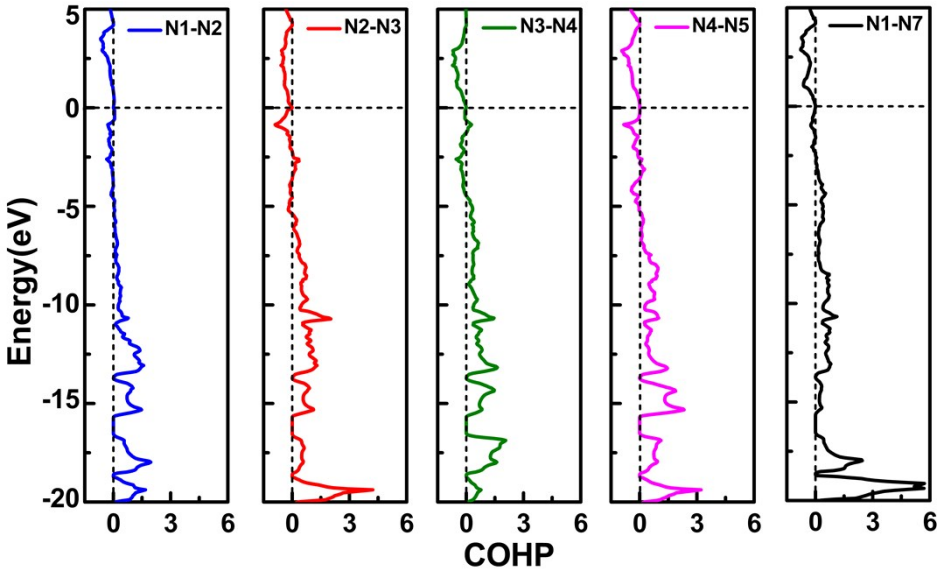

Fig. S13 COHPs between N1-N2, N2-N3, N3-N4, N4-N5 and N1-N7 pairs for *P*1-AlN_7 phase at 80 GPa. Fermi levels are set at zero energy and marked by dotted lines.

Table S3. The calculated bond parameters and hardness of C2/m-AlN_6, Cm-Al_2N_7, Cm-Al_2N_7 and P1-AlN_7.

Structure	V(Å^3)	bond	n^{μ}	d^{μ}(Å)	P^{μ}	V_b^{μ}	H_v^{μ}	H_v(GPa)
*C*2/*m*-AlN_6	99.79	N-N	4	1.34	0.70	1.91	176.19	43.86
		N-N	8	1.37	0.69	2.04	155.51	
		Al-N	4	1.99	0.32	6.25	11.15	
		Al-N	8	2.00	0.36	6.35	12.24	
*C*m-Al_2N_7	127.65	N-N	4	1.30	0.77	1.29	374.43	39.32
		N-N	4	1.36	0.67	1.47	260.00	
		Al-N	4	1.86	0.41	3.77	33.25	
		Al-N	2	1.86	0.48	3.77	38.93	
		Al-N	2	1.87	0.35	3.83	27.63	
		Al-N	2	1.94	0.34	4.28	22.34	
		Al-N	2	1.94	0.35	4.28	23.00	
		Al-N	4	1.98	0.40	4.55	23.73	
		Al-N	4	2.03	0.23	4.90	12.05	
		Al-N	4	2.07	0.34	5.19	16.15	
		Al-N	2	2.09	0.23	5.35	10.41	
*C*2-Al_2N_7	111.78	N-N	4	1.30	0.77	1.07	507.27	63.96
		N-N	4	1.36	0.67	1.23	352.25	
		N-N	4	1.37	0.61	1.25	309.17	
		Al-N	4	1.86	0.41	3.14	45.05	
		Al-N	2	1.86	0.48	3.14	52.74	
		Al-N	2	1.87	0.35	3.19	37.44	
		Al-N	4	1.94	0.35	3.56	31.16	
		Al-N	4	1.98	0.4	3.79	32.15	
		Al-N	4	2.04	0.23	4.14	15.92	
		Al-N	2	2.10	0.23	4.52	13.78	
		Al-N	4	2.07	0.34	4.33	21.88	
*P*1-AlN_7	48.49	N-N	1	1.25	0.98	2.79	131.08	33.58
		N-N	1	1.28	0.76	3.00	90.29	
		N-N	1	1.30	0.80	3.14	87.95	
		N-N	1	1.30	0.77	3.14	84.65	
		N-N	1	1.31	0.75	3.21	79.35	
		N-N	1	1.32	0.71	3.29	72.32	
		N-N	1	1.33	0.70	3.36	68.66	
		Al-N	1	1.83	0.17	8.76	3.38	
		Al-N	1	1.83	0.69	8.76	13.72	
		Al-N	1	1.85	0.06	9.05	1.13	