Electronic Supplementary Information

High-Pressure Synthesis and Crystal Structure of Molybdenum Nitride Mo_3N_5 with Anisotropic Compressibility by Nitrogen Dimer

Takuya Sasaki[1], *Takuro Yamamoto*[2], *Shuto Asano*[1], *Ken Niwa*[1], and *Masashi Hasegawa*[1]

[1] Department of Materials Physics, Graduate School of Engineering, Nagoya University

Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603, Japan

[2] Department of Crystalline Materials Science, Graduate School of Engineering, Nagoya University

Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603, Japan

Corresponding Author

Takuya Sasaki & Ken Niwa

E-mail address: sasaki@mp.pse.nagoya-u.ac.jp (TS), niwa@mp.pse.nagoya-u.ac.jp (KN),

Department of Materials Physics, Graduate School of Engineering, Nagoya University

Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603, Japan

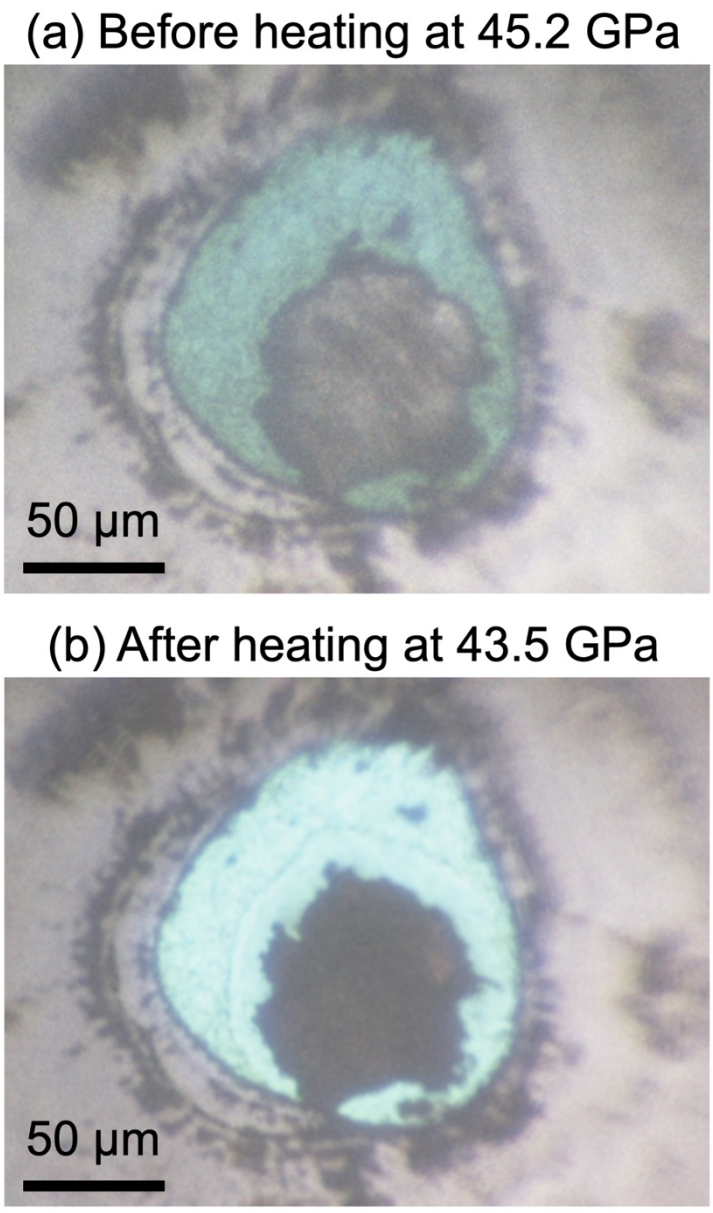

Figure S1. Optical photographs of the sample (a) before heating at 45.2 GPa and (b) after heating at 43.5 GPa.

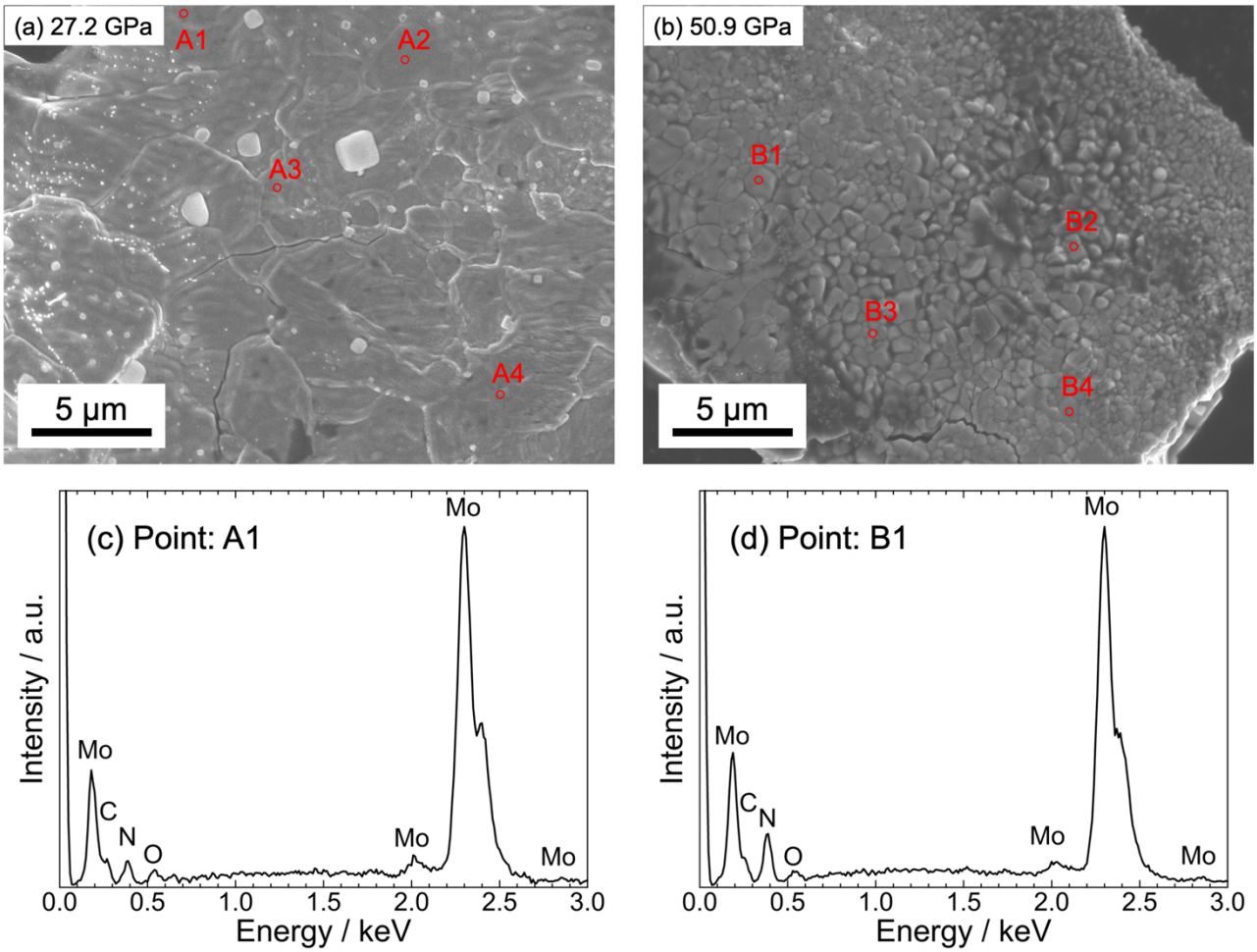

Figure S2. SEM image and different EDX measurement points on the surface of the sample synthesized at (a) 27.2 GPa and (b) 50.9 GPa. EDX spectra at point (c) A1 and (d) B1.

Table S1 Element content at different points as shown in Fig. S2.

Point Label	Mo at%	N at%	Point Label	Mo at%	N at%
A1	50.5	49.5	B1	30.0	70.0
A2	45.8	54.2	B2	25.9	74.1
A3	58.6	41.4	B3	24.4	75.6
A4	39.8	60.2	B4	30.8	69.2
Ave.	49(7)	51(7)	Ave.	28(3)	72(3)

Table S2 Diffraction index and *d* spacing of orthorhombic molybdenum nitride phase with lattice parameters of $a = 2.8619(2)$ Å, $b = 7.0727(4)$ Å, $c = 14.5971(9)$ Å, and $V = 295.46(3)$ Å^3.

h	*k*	*l*	$d_{obs.}$ / Å	$d_{cal.}$ / Å	$d_{obs.} - d_{cal.}$ / Å
0	0	2	7.2974	7.3015	-0.0042
0	0	4	3.6473	3.6500	-0.0028
0	2	0	3.5367	3.5370	-0.0003
0	2	1	3.4382	3.4376	0.0006
0	2	2	3.1827	3.1830	-0.0003
0	2	3	2.8614	2.8611	0.0003
1	1	1	2.6110	2.6105	0.0005
0	2	4	2.5394	2.5399	-0.0005
1	1	2	2.4940	2.4936	0.0004
0	0	6	2.4327	2.4332	-0.0005
1	1	3	2.3298	2.3295	0.0003
1	1	4	2.1462	2.1461	0.0001
0	0	8	1.8211	1.8248	-0.0037
1	3	0		1.8198	0.0013
1	3	1	1.8061	1.8058	0.0003
0	2	7	1.7959	1.7964	-0.0006
1	1	6		1.7932	0.0026
0	4	0	1.7669	1.7683	-0.0015
1	3	2		1.7658	0.0011
0	4	1	1.7557	1.7555	0.0002
0	4	2	1.7187	1.7186	0.0000
1	3	3	1.7046	1.7045	0.0001
0	4	3	1.6622	1.6620	0.0002
1	1	7	1.6394	1.6396	-0.0002
1	1	8	1.5034	1.5035	-0.0001

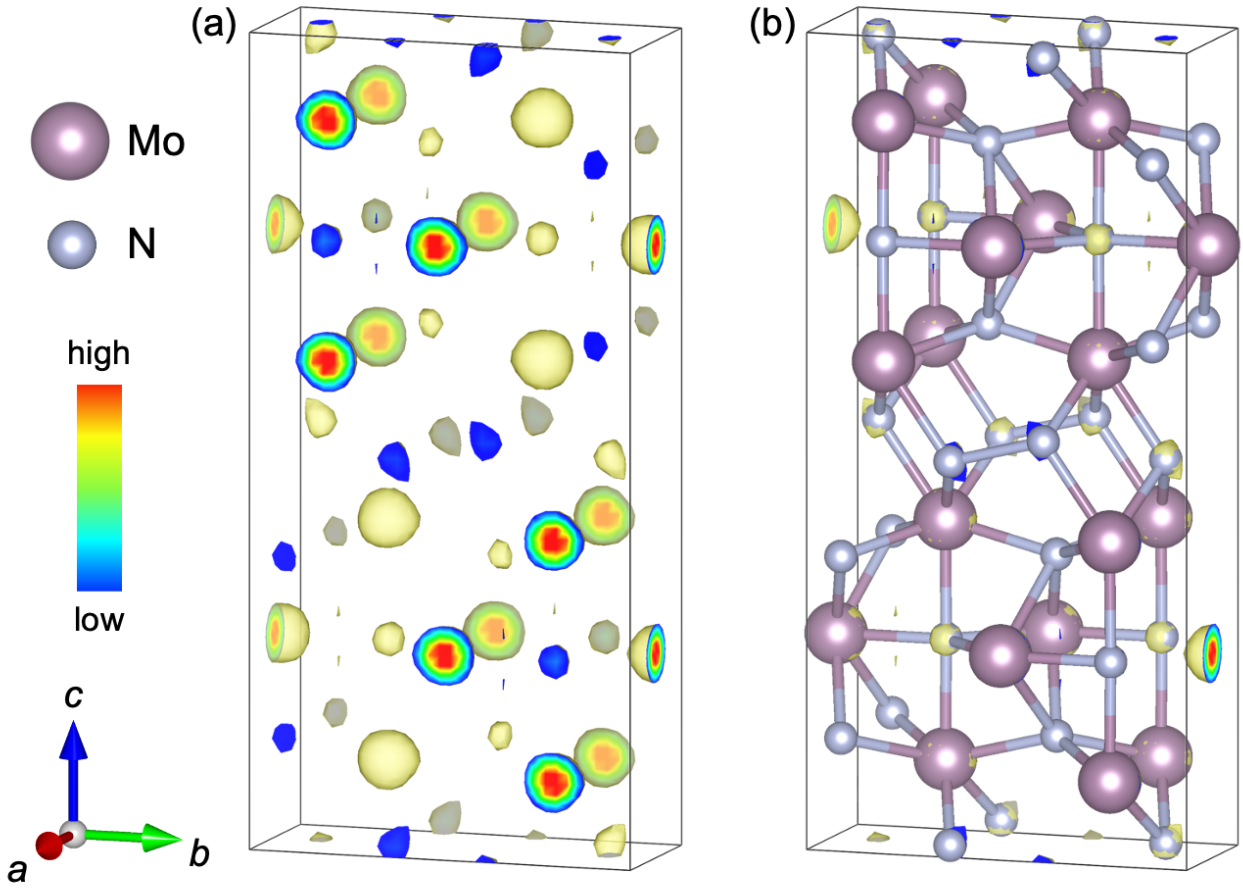

Figure S3. (a) Electronic density distribution obtained by Superflip. (b) Initial crystal structure of Mo_3N_5 with electronic density distribution determined based on electron density distribution by using JANA2006.

Table S3 Atomic coordinates for Mo_3N_5 optimized by DFT calculation with optimized lattice parameter a = 2.8802Å, b = 7. 0983Å, and c = 14. 6799Å.

Atom	site	*x*	*y*	*Z*
Mo1	8*f*	0	0.29722	0.10334
Mo2	4*c*	0	0.01010	1/4
N1	8*f*	0	0.09606	0.51159
N2	8*f*	0	0.57868	0.14315
N3	4*c*	0	0.30446	1/4

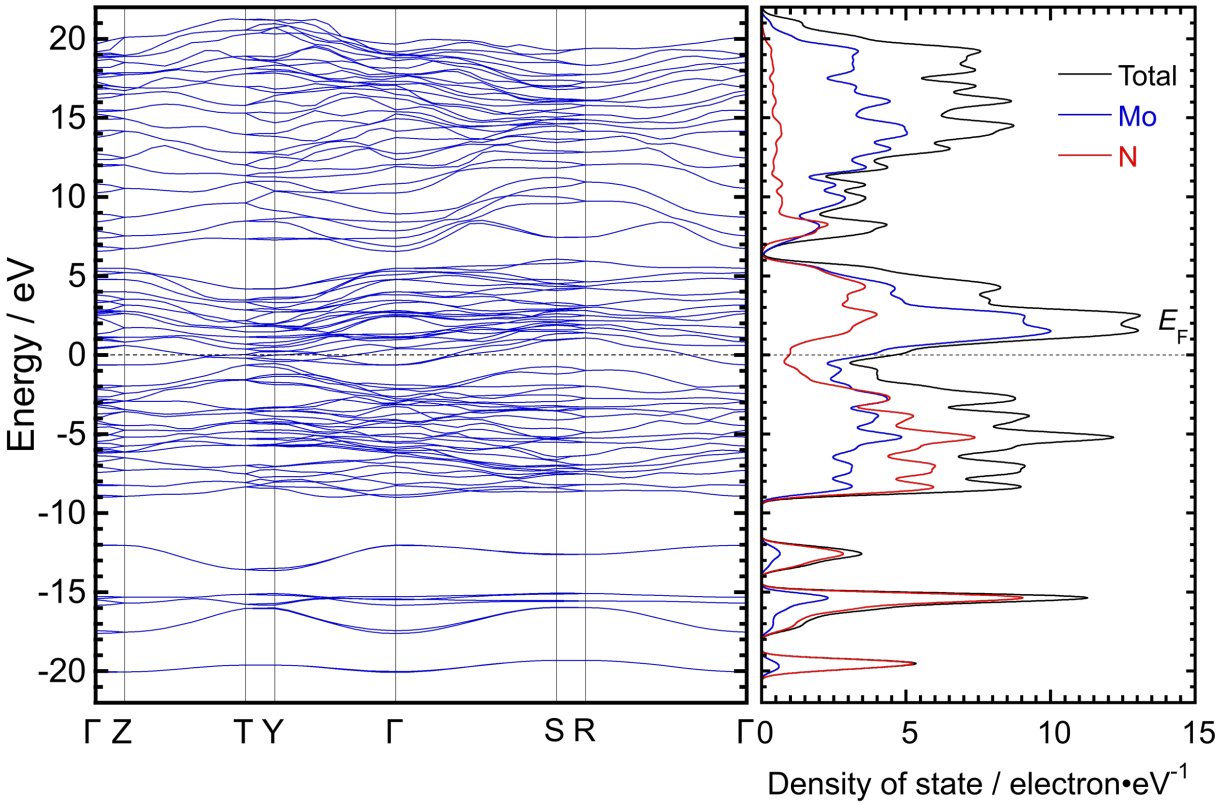

Figure S4 Electronic band structure and density of state (DOS) of Mo_3N_5.

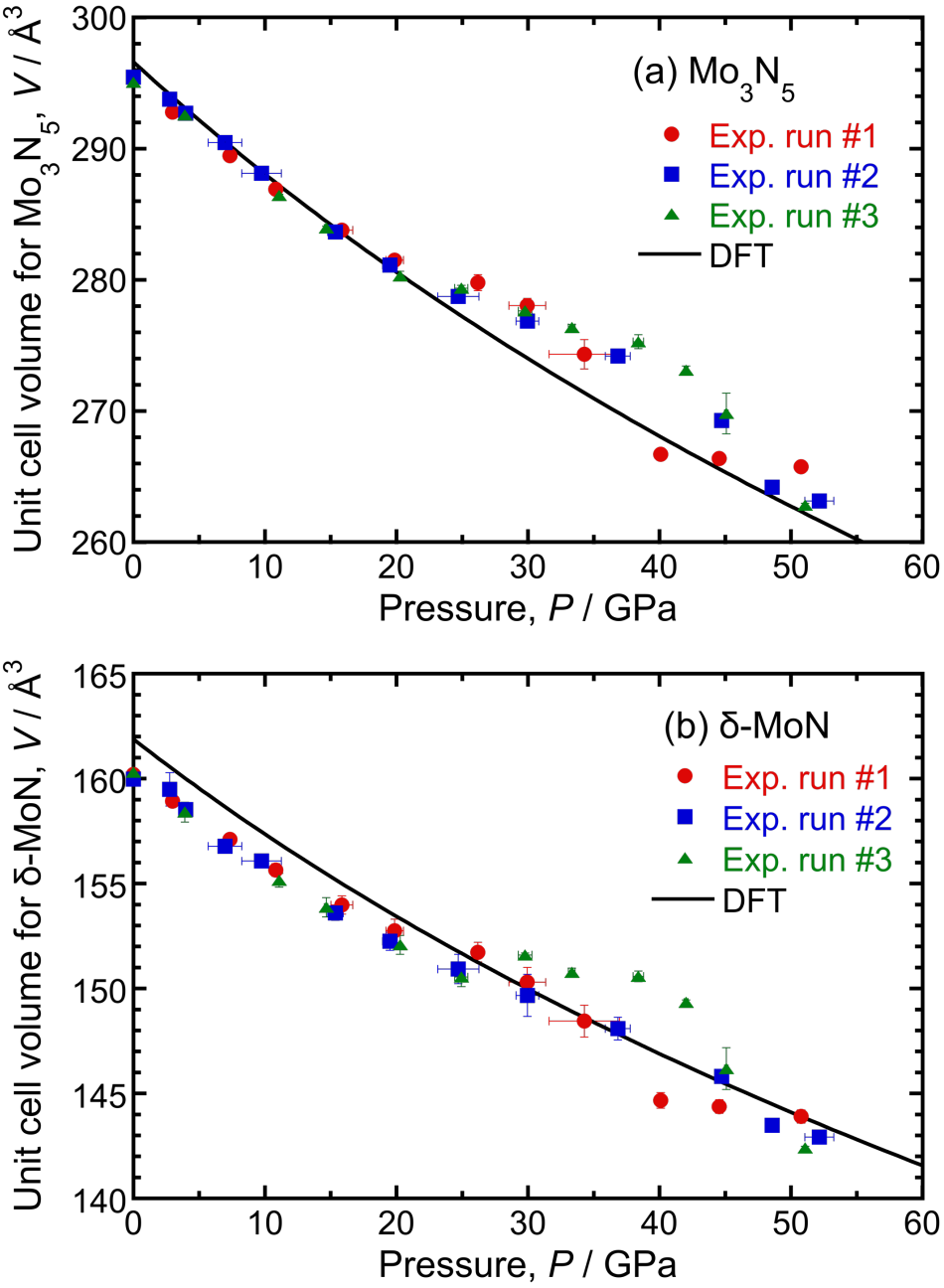

Figure S5. Pressure dependence of lattice volume of (a) Mo_3N_5 and (b) δ-MoN in different experimental runs (#1, #2, and #3). The data points plotted in red circles (#1) and blue squares (#2) were measured at PF-AR NE1. The data points plotted in green triangle (#3) were measured at AichiSR BL2S1. The solid lines represent the DFT results of fitting to the third-order Birch–Murnaghan equation of state.

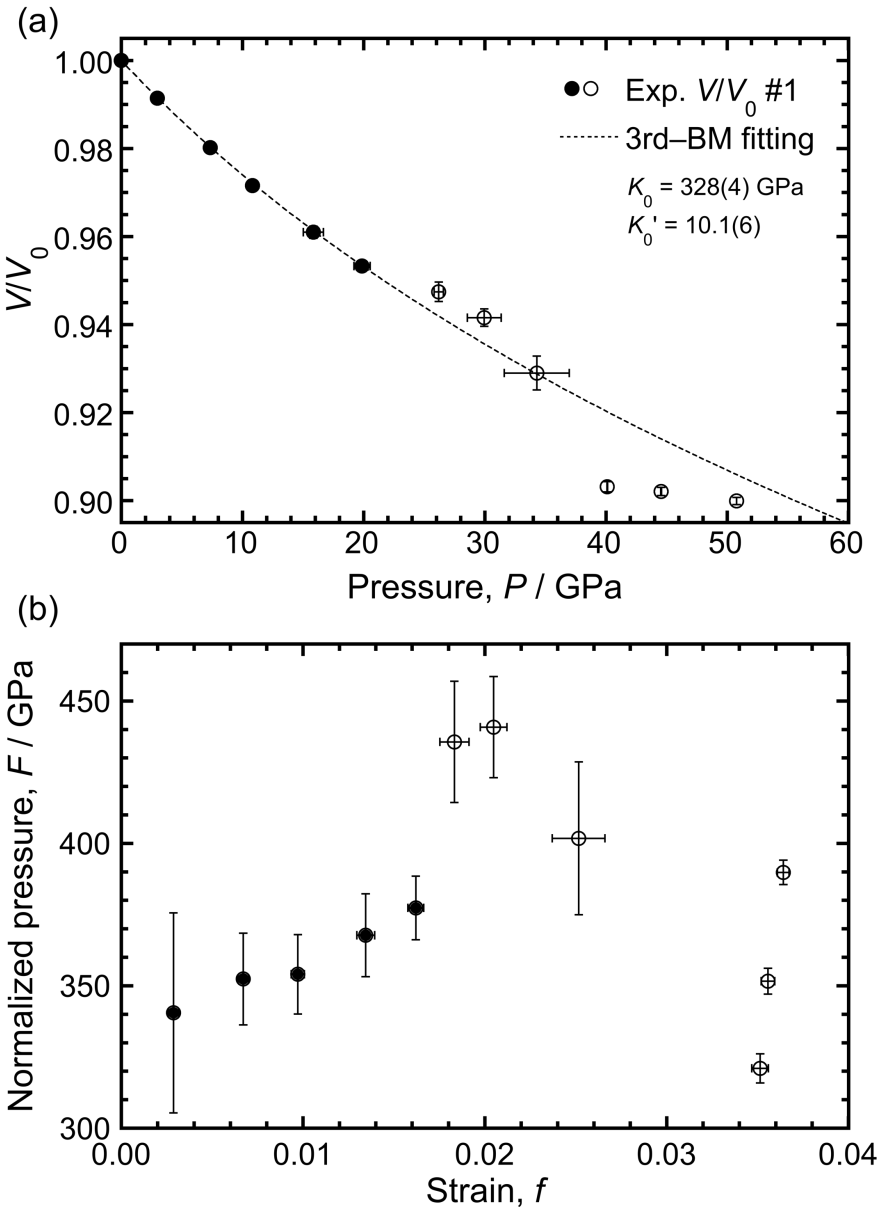

Figure S6. (a) Pressure dependence of normalized lattice volume of Mo_3N_5. The open and closed circles represent experimental data for run #1. The dotted lines represent the results of fitting experimental data up to 20 GPa, indicated by the closed circles, to the third-order Birch–Murnaghan equation of state. (b) The relationship between the strain f and the normalized pressure F corresponding to run #1. Strain f and normalized pressure F are defined as:

$$f = \frac{\left(\frac{V}{V_0}\right)^{-2/3} - 1}{2} \tag{S1}$$

$$F = \frac{P}{3f(2f+1)^{5/2}} = K_0\left[1 + \frac{3}{2}(K_0' - 4)f\right] \tag{S2}$$

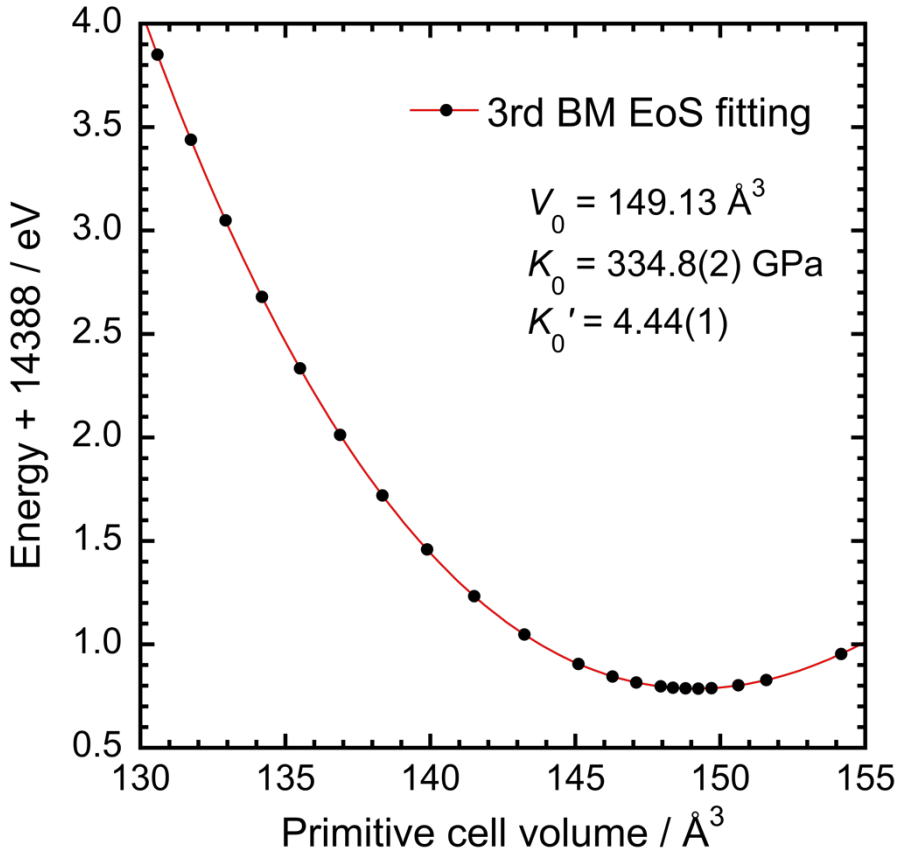

Figure S7 Energy E as a function of primitive lattice volume V for Mo_3N_5. The red line represents the results of fitting to the 3rd order Birch–Murnaghan equation of state as following.

$$E(V) = E_0 + \frac{9V_0K_0}{16}\left\{\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^3 K_0' + \left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^2 \left[6 - 4\left(\frac{V_0}{V}\right)^{\frac{2}{3}}\right]\right\} \qquad \text{(S3)}$$

Table S4 Elastic stiffness constants for Mo_3N_5 by DFT calculation.

C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
436(1)	703(4)	495(5)	233(1)	200(1)	131(4)	222(2)	257(1)	187(3)