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Supporting Information of

High-Pressure Synthesis of PbN₂, the Missing Group 14 *A*N₂-type Compound Ken Niwa, ^{a,b,*} Hirokazu Ogasawara, ^c Takuya Sasaki, ^b Shunsuke Nomura, ^b Gendai Azuma, ^b Sylvain Pitié, ^d Gilles Frapper, ^d Masashi Hasegawa ^{a,b,*}

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Experimental details

Sample No.	Characterization methods
OH#45	XRD(BL2S1), Raman, Optical microscopy
OH#52	Raman, Optical microscopy
NS#1	XRD(BL2S1), Raman, Optical microscopy
AG#1	XRD(BL10XU, BL2S1), Raman, Optical microscopy
AG#2	Raman, Optical microscopy, Sem/EDS

OH#45

Lead was heated at approximately 50 GPa. The Raman spectroscopy measurements were made before and after laser heating. The heated sample was characterized based on the X-ray diffraction measurements at BL2S1, Aichi Synchrotron Center, Aichi, Japan, along with the decompression under room temperature.

OH#52

Lead was heated at approximately 50 GPa. The Raman spectroscopy measurements were made before and after laser heating. The Raman spectra was measured along with the decompression under room temperature without any laser heating anymore.

NS#1

Lead was heated at approximately 55 GPa. The Raman spectroscopy measurements were made before and after laser heating. The heated sample was characterized based on the X-ray diffraction measurements at BL2S1, Aichi Synchrotron Center, Aichi, Japan, along with the compression under room temperature.

AG#1

Lead was heated at 50.4 GPa. The pressure slightly increased by laser heating. The Raman spectroscopy measurements were made before and after laser heating. Then, the pressure decreased from 55.1 GPa to 43.2 GPa along with Raman spectra measurements. From 40.5 GPa to 14 GPa, the XRD profiles and Raman spectra were measured at BL10XU, SPring-8. Then, the sample was compressed again from 14 GPa to 32 GPa without heating along with measuring the XRD profiles. Due to the limitations of measurement conditions and experimental data, the fraction coordinates of nitrogen are preliminary optimized by using CASTEP software under fixing the experimentally determined lattice parameters. CIF is registered on the ICSD with Deposition Number 2441090.

AG#2

Lead was heated at approximately 50 GPa. The Raman spectroscopy measurements were made before and after laser heating. The Raman spectra was measured along with the decompression to ambient pressure under room temperature. After recovery of the sample, it was characterized by SEM/EDS.

Methodology Details

S1.1 DFT Framework

The calculations within the framework of density-functional theory (DFT) are performed using the projected-augmented-wave (PAW) method^{1,2} as implemented in VASP (version 6.4.2) and the exchange-correlation energy is treated using Perdew-Burke-Ernzerhof (PBE),^{3,4} within the generalized gradient approximation (GGA) PAW potentials. Pseudopotentials for the atoms used in this study are the one recommended by VASP team (POTCAR for VASP 6.4.2). A kinetic cutoff energy of 600 eV is used for the wavefunction expansion with a Monkhorst-Pack k-mesh grid with a spacing of $2\pi \times 0.02 \text{ Å}^{-1}$. All structures are optimized until the net forces on atoms are below 1 meV/Å, resulting in enthalpies that converged to better than 1 meV per atom (lower than a chemical accuracy of 1 kcal/mol, i.e., 43 meV/atom), and all forces on atoms are converged to less than 0.005 eV/Å.

S1.2 Phonon Dispersion Curves Calculations

In this work, first-principles phonon calculations using the finite displacements method at a quasiharmonic level are done using the open source package Phonopy (https://github.com/phonopy/phonopy).^{5,6} Supercell structures with displacements are created from a reference unit cell considering all possible crystal symmetry operations. In general, a supercell with cell parameters a, b, and c higher than 10 Å is sufficient, but larger ones can be required to avoid unphysical imaginary frequencies, especially at 0 GPa. Force constants are calculated using the optimized structure (VASP) at the PBE level of theory. In the table, S2 is given the supercell used for the phonon dispersion curves calculation of each Pb_xN_y phase.

	Pressure (GPa)	Space Group	Supercell Size
PbN ₂	0	I4/mcm	4x4x4
	25	I4/mcm	3x3x3
	50	I4/mcm	3x3x3
Pb(N ₂) ₃	10	<i>R</i> -3 <i>c</i>	2x2x2
	25	<i>R</i> -3 <i>c</i>	2x2x2
	50	<i>R</i> -3 <i>c</i>	2x2x2

Supercell Size Used for the Phonon Calculations of PbN_2 and $Pb(N_2)_3$ Phase at a GivenPressure.

S1.3 Vibrational properties computation (Raman Spectrum)

The phonopy extension (Phonopy Spectroscopy) was used to compute the Raman intensity.⁷ (https://github.com/skelton-group/Phonopy-Spectroscopy)

In order to estimate the Raman intensity of a phonon mode, it is first necessary to calculate the derivatives of the macroscopic dielectric tensor with respect to the normal mode coordinate:

$$I_{Raman}(\nu) \propto \frac{\delta \varepsilon^{\infty}}{\delta Q(\nu)}$$

Where ε^{∞} is the macroscopic high-frequency dielectric constant and $Q(\nu)$ is the normal mode coordinate of the ν th phonon mode. In practice, the derivative is replaced by the central difference, based on the evaluation of the macroscopic dielectric matrix at positive and negative displacement along the phonon mode Q(ν). Additionally, the macroscopic dielectric matrix is calculated by the DFPT method in the VASP code.

Structural Parameters of the Used PbN_2 and $Pb(N_2)_3$ Phases (distances in Å, angles in^o) at the PBE Level of Theory.

Phases	Space Group	P (GPa)	Z	Lattice Parameters	Atomic Coordinates (fractional)	
PbN ₂	<i>I4/mcm</i> (140)	0	4	a=5.271, b=5.271, c=6.965 α=90.0 β=90.0 γ=90.0	Pb(0.000,0.000,0.250); N(0.419,-0.081,0.000)	
		25	4	a=4.790, b=4.790, c=6.302 α=90.0 β=90.0 γ=90.0	Pb(0.000,0.000,0.250); N(0.409,-0.091,0.000)	
		50	4	a=4.600, b=4.600, c=6.030 α=90.0 β=90.0 γ=90.0	Pb(0.000,0.000,0.250); N(0.404,-0.096,0.000)	
Pb(N ₂) ₃	<i>R</i> -3 <i>c</i> (167)	10	6	a=7.460, b=7.460, c=10.550 α=90.0 β=90.0 γ=120.0	Pb(0.000,0.000,0.000); N(- 0.077,0.534,0.125)	
			25	6	a=7.062, b=7.062, c=10.052 α=90.0 β=90.0 γ=120.0	Pb(0.000,0.000,0.000); N(- 0.078,0.530,0.127)
		50	6	a=6.710, b=6.710, c=9.605 α=90.0 β=90.0 γ=120.0	Pb(0.000,0.000,0.000); N(- 0.078,0.525,0.129)	



Fig.S1 (AG#1) Raman spectra measured along the decompression from 55.1 to 43.2 GPa



Fig.S2 Results of structure search



Fig.S3 (AG#1)_Unrolled 2-D image and corresponding 1-D profile



Fig.S4 (AG#1) XRD profiles measured along the decompression at BL10XU (SPring-8) and recompression at BL2S1 (AichiSR) under room temperature.



Fig.S5 Pressure dependence of normalized lattice parameters



Fig.S6 (OH#52)_ Raman spectra measured using Ar ion laser



Fig.S7 (AG#2)_ Raman spectra from other positions



Fig.S8 (AG#2)_ Raman spectra of whole wavenumber regions with enlargement of Diamond Raman band



Figure S9 The pressure dependence of the Raman-active wavenumbers of R-3c Pb(N₃)₂ at 0 K. The pressure dependence of the atomic motions along A_{1g} vibrational mode v₉ at Γ k-point are illustrated.



Fig.S10 Evolution of the N₂ interatomic distance (in Å) in function of the pressure (in GPa) of I4/mcm PbN₂ in blue and R-3c Pb(N₂)₃ in red (PBE level of theory).



Fig.S11 (AG#2)_SEM image of recovered sample (a) Left side: unheated region, Right side: heated region (b) Magnified image of heated area



Fig.S12 Illustration of pyrite (a1, a2) and $CuAl_2$ (b1, b2, b3) type structures. Large and small balls correspond to group 14 elements and nitrogen, respectively.

hkl	d _{obs}	d _{calc.}	d_{obs} - $d_{calc.}$	$2\theta_{obs}$	$2\theta_{calc.}$	$2\theta_{obs}$ - $2\theta_{calc.}$
100	3.3133	3.3140	-0.0006	7.2504	7.2490	0.0014
001	3.1074	3.1036	0.0038	7.7315	7.7410	-0.0095
110	2.3382	2.3398	-0.0016	10.2809	10.2738	0.0071
101	2.2598	2.2621	-0.0023	10.6389	10.6281	0.0109
111	1.8649	1.8662	-0.0013	12.9004	12.8911	0.0093
200	1.6533	1.6528	0.0005	14.5597	14.5643	-0.0047
002	1.5477	1.5481	-0.0004	15.5588	15.5548	0.0040
210	1.4787	1.4779	0.0008	16.2900	16.2989	-0.0089
201	1.4591	1.4577	0.0015	16.5100	16.5266	-0.0166
102	1.4019	1.4016	0.0003	17.1891	17.1923	-0.0031
211	1.3341	1.3334	0.0006	18.0702	18.0788	-0.0086
112	1.2882	1.2901	-0.0020	18.7197	18.6910	0.0287
220	1.1689	1.1678	0.0011	20.6499	20.6689	-0.0190
202	1.1291	1.1291	0.0001	21.3852	21.3866	-0.0014
300	1.1008	1.1009	-0.0001	21.9420	21.9401	0.0018
221	1.0934	1.0925	0.0009	22.0929	22.1118	-0.0189
212	1.0700	1.0683	0.0017	22.5822	22.6194	-0.0372
310	1.0438	1.0443	-0.0005	23.1569	23.1449	0.0120
301	1.0346	1.0371	-0.0025	23.3660	23.3082	0.0578
003		1.0313	0.0033		23.4423	-0.0763
311	0.9896	0.9894	0.0002	24.4443	24.4493	-0.0051

Table.S1 Peak indexing results

a=3.297(1) Å and c=3.089(2) Å

	$v(cm^{-1})(\Gamma)$						
Ir. Rep.	0 GPa	10 GPa	20 GPa	30 GPa	40 GPa	50 GPa	50 GPa Exp.
Eg	48.9	85.0	99.9	111.8	121.9	129.8	~200
Eg	383.0	450.8	477.3	501.5	525.6	543.1	~550
B _{1g}	392.6	475.9	511.4	547.9	579.0	609.3	~600
B _{2g}	1467.5	1351.7	1293.4	1321.3	1354.0	1368.8	ND
A _{1g}	1592.3	1541.3	1507.5	1493.9	1488.2	1474.7	ND

Table S2 Value at Γ of Raman Active Bands (cm⁻¹) of *I*4/*mcm* PbN₂ at given pressure (GPa).

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