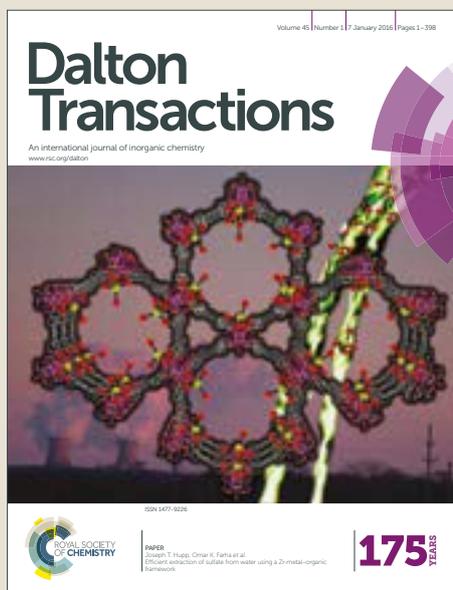


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Pyrite Form of Group-14 Element Pernitrides Synthesized at High Pressure and High Temperature

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Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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The chemical reaction of group-14 elements with molecular nitrogen at the pressures above 60 GPa successfully leads to the formation of pyrite-type pernitrides. These new crystalline group-14 elemental pernitrides were found to show the bulk modulus higher than the other known group-14 elemental nitrides. Our results offer significant new progress on the solid-state chemistry of nitrides.

The α - and β - A_3N_4 ($A=Si$ and Ge) have long time been known as crystalline group-14 (or “carbon group”) elemental nitrides such as widely used for hard material, heat insulator and photocatalyst.^[1-6] On the other hand, in 1999, cubic spinel(γ -) Si_3N_4 was successfully synthesized via a direct chemical reaction between silicon and molecular nitrogen at 15 GPa.^[7] Immediately after that, cubic spinel phase was also discovered in Ge_3N_4 under high pressure.^[8] Together with ambient-pressure synthesizable Sn_3N_4 ,^[9] the cubic spinel phase has been regarded as the 3rd structural polymorph of group-14 elemental nitride so far. The ambient-pressure quenchable γ - Si_3N_4 and γ - Ge_3N_4 show remarkable elastic and electronic properties in comparison with the ambient-pressure phases of α - and β - A_3N_4 .^[10-16] Therefore, γ - A_3N_4 has attracted much attention in the field of fundamental solid state chemistry and functional materials.

In this study, we report here the successful synthesis and characterization of novel group-14 elemental (Si , Ge and Sn) nitrides other than α -, β - and γ - A_3N_4 . Our newly discovered group-14 elemental nitrides were synthesized via direct chemical reaction between simple elements and molecular nitrogen at the pressure of approximately 60 GPa that is much higher pressure than the synthesis of spinel phase as reported in the previous studies. It was clearly found that they crystallize to the pyrite-type structure and quenchable into the

ambient pressure. In addition, they surprisingly show incompressible behavior than the γ - A_3N_4 . These superior physical properties including electronic ones that will be clear in the future, offer a new insight of the solid-state chemistry for group-14 elemental nitrides. The details of newly synthesized pyrite type group-14 elemental nitrides are described in this communication.

The high-pressure syntheses were carried out by using laser-heated diamond-anvil cell up to the pressure of approximately 65 GPa. The high purity group-14 element was loaded in the sample chamber together with molecular nitrogen and then, the sample was heated by the irradiation of infrared laser after the compression to the desired pressure. The detail is described in the Experimental section of supporting information. A laser heating immediately changed the elemental sample to be optically transparent as shown in Figure S1. The X-ray diffraction profiles of ambient pressure recovered samples that were synthesized at approximately 20 and 60 GPa are shown in Figure S2. The reaction between group-14 element and molecular nitrogen at approximately 20 GPa resulted in the formation of spinel phase with a small amount of residual group-14 element (e.g. $Sn-N_2$ experiment). On the other hand, the synthesis at pressure of approximately 60 GPa showed the XRD profile completely different from that of spinel phase. Newly additional peaks were detected together with those of spinel phase in the $Si-N_2$ and $Ge-N_2$ experiments whereas only new peaks were observed in the XRD profile of $Sn-N_2$ experiment. The peak indexing analysis found that all these newly appeared diffraction peaks are assigned to the cubic lattice. The chemical composition analyses by energy dispersive spectroscopy demonstrated that newly synthesized nitrides show a composition of $N/Si=2.3(6)$, $N/Ge=2.4(6)$ and $N/Sn=3.2(3)$ which are nitrogen-rich composition more than the spinel phase ($N/A=1.3$). Accordingly, the pyrite-type is strongly suggested as the model structure for newly synthesized group-14 elemental nitrides, although the nitrogen content of new tin nitride was somewhat greater than the expected values of stoichiometric composition of the pyrite-type compound. The surface

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Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x

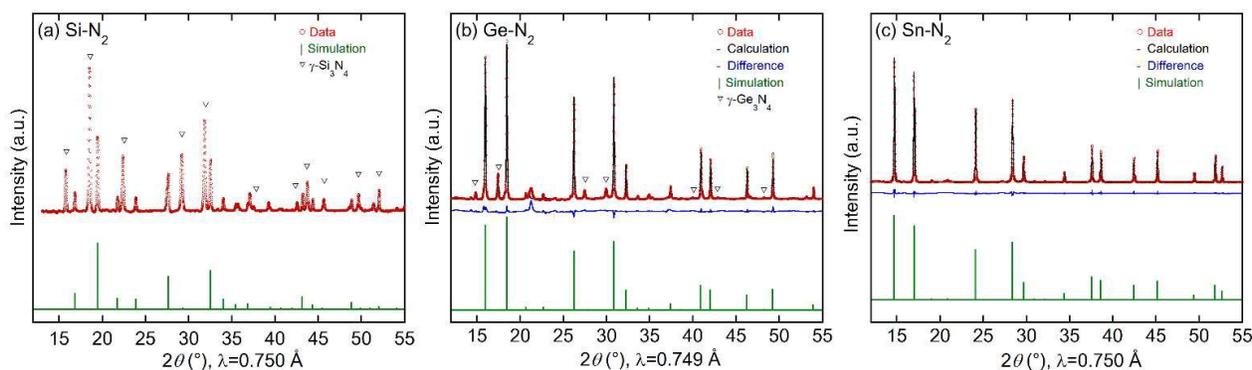


Figure 1 (a)-(c) Refined X-ray diffraction profiles of the pyrite-type group-14 elemental pnitrides synthesized in high pressure and high temperature. The XRD profiles are displayed after the subtraction of background. Open triangles represent the Bragg peak positions of spinel phase. The diffraction intensities of pyrite-type group-14 elemental pnitrides are simulated based on the refined parameters for GeN_2 and SnN_2 and theoretical calculation value for SiN_2 .^[18a]

roughness and excess molecular nitrogen captured in the lattice, might be considered as plausible factors to cause large uncertainties of the composition measurements. In addition, the coexistence with heavy elements possibly affects the detection of light elements. However, as discussed in later, the pyrite-type structure satisfied the observed XRD profile. The amount of impurity spinel phase of Si-N_2 experiment was larger than that of Ge-N_2 and Sn-N_2 experiments. This might be due to the difference of absorption coefficient to the wavelength of infrared laser for spinel and new cubic phase. The details are described in supporting information (see Figure S3). The experiments below the pressure of approximately 50 GPa showed no successful synthesis of these new nitrides. In addition, the synthesis pressures were no significant different among these nitrides. This indicates that the pressure at least approximately 60 GPa is required to synthesize the pyrite-type SiN_2 , GeN_2 and SnN_2 .

Figure 1(a)-(c) show the background subtracted XRD profiles of the recovered samples. Among these nitrides, SiN_2 showed low diffraction intensity mainly due to tiny sample

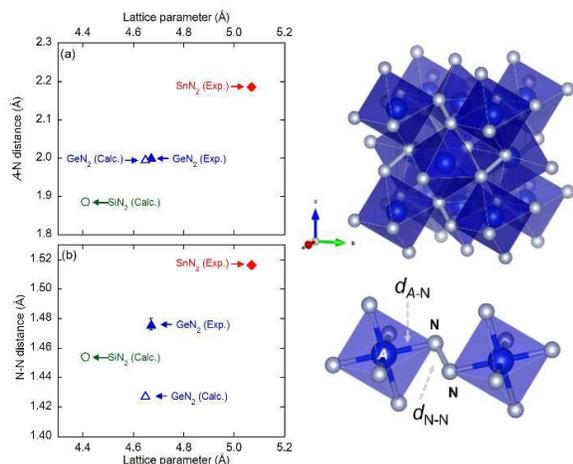


Figure 2 (a)(b) The lattice parameters dependence of A-N and N-N distances for pyrite-type group-14 elemental nitrides based on the present experimental results (solid symbols) together with those of previous theoretical calculations (open symbols).^[18a] The crystal structure of pyrite-type group-14 elemental pnitride and selected polyhedral connected by single bonded nitrogen (N-N).

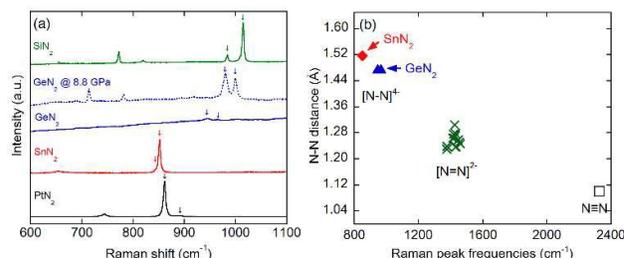


Figure 3 (a) Raman spectra of ambient recovered pyrite-type group-14 elemental pnitrides synthesized at high pressure and high temperature. The Raman spectrum of GeN_2 at 8.8 GPa and the pyrite-type PtN_2 were also shown for comparison. The arrows represent the frequencies associated with stretching vibration modes of A_g and T_g . (b) The relationship between Raman frequencies of A_g and T_g and nitrogens distances of nitrides or molecular nitrogen having the different bonding nature.^[19-21]

consisting of light elements and coexistence with the large amount of impurity phase (spinel phase). Further discussion is described in Figure S2. The large amount of high quality SiN_2 would allow refining the crystallographic parameters. Thus, only the lattice parameter was calculated for SiN_2 ($a=4.4371(3)$ Å) in this study. On the other hand, the structural refinement was performed for the other two new nitrides of GeN_2 and SnN_2 based on the pyrite-type structure. The refined crystallographic parameters are listed in Table 1. It was found from the XRD measurements that the lattice parameters of pyrite-type group-14 elemental pnitrides monotonically increase in order of SiN_2 , GeN_2 and SnN_2 , in which the experimental values are consistent with those of theoretical ones for SiN_2 and GeN_2 .^[18] The refined nitrogen position allows calculating the interatomic distance of N-N and A-N ($A=\text{Ge}$ and Sn). As shown in the Figure 2(a)(b) together with the results of theoretical calculation,^[18] it was found that the experimentally determined interatomic distances of N-N and A-N are found to increase with increasing the lattice parameters.

Raman spectroscopy is very useful method to investigate the state of nitrogen dimer in the structure. Several sharp Raman peaks were appeared after laser heating at the pressure of approximately 60 GPa (see Figure S4). The Raman spectra of the recovered SiN_2 , GeN_2 and SnN_2 are shown in Figure 3(a). Raman spectrum of the pyrite-type PtN_2 is also shown for comparison. As shown in Figure S5, it is clearly

found that the Raman spectra of pyrite-type nitrides are completely different from those of spinel ones. The spectra among the pyrite-type SiN_2 , GeN_2 and SnN_2 are similar to each other while the recovered GeN_2 emitted intense fluorescence probably due to the change of optical absorption band during the decompression, because Raman scattering peaks at 8.8 GPa were clearly observed. It has been suggested that the vibration frequencies of nitrogen dimer strongly depend on the bonding nature.^[19-21] The Raman peak frequencies at approximately 800~1000, 1300~1500 and 2300~2400 cm^{-1} correspond to the stretching vibration modes of N-N ($d_{\text{N-N}} \approx 1.4$ Å),^[19] N=N ($d_{\text{N=N}} = 1.2 \sim 1.3$ Å)^[20] and $\text{N} \equiv \text{N}$ ($d_{\text{N} \equiv \text{N}} = 1.1$ Å),^[21] respectively. The pyrite type AX_2 allows five active Raman modes ($\Gamma = A_g + E_g + 3T_g$). The A_g and one T_g correspond to the stretching vibration modes of X-X dimer.^[22] The previous XRD measurements and advanced theoretical calculation for pyrite-type PtN_2 demonstrated that it consists of Pt^{4+} and the single bonded nitrogen $[\text{N-N}]^4$ having the interatomic distance of 1.42 Å.^[23,24] It was also reported that the pyrite-type PtN_2 shows two characteristic Raman peaks at around 850 cm^{-1} which correspond to the stretching vibration modes (A_g and T_g) of nitrogen dimer.^[23] The Raman peak frequencies associated with A_g and T_g modes for pyrite-type SiN_2 , GeN_2 and SnN_2 lie between 800 and 1000 cm^{-1} at ambient pressure. In addition, it is clearly found from Figure 3(b) that these Raman peak frequencies increase from SnN_2 , GeN_2 and SiN_2 . The interatomic distance of N-N for SiN_2 remains unidentified. However, the Raman peaks associated with A_g and T_g modes were appeared at the frequency lower than those of GeN_2 and SnN_2 . This strongly suggests that the interatomic distance of N-N for SiN_2 is shorter than those of GeN_2 and SnN_2 . As mentioned above, the shift to lower frequency corresponds to the longer interatomic distance of N-N. Thus, the results of Raman scattering measurements are consistent with those of XRD measurements. Present results demonstrated that the interatomic distance of both A-N and N-N increase with

increasing the ionic radius of group-14 elements (or lattice parameters of pernitrides). It is reasonably accepted that group-14 element in the pyrite type AN_2 adopts the valence state of A^{4+} and the charge density of A^{4+} increases with decreasing the ionic radius. This indicates that smaller cation ($r_{\text{Si}} < r_{\text{Ge}} < r_{\text{Sn}}$) readily attracts the electrons that occupy the anti-bonding state in the electron configuration of $[\text{N-N}]^4$ (see Figure S6). This results in the change of the bonding nature slightly from single to double bonding one from SnN_2 to SiN_2 . Thus, the interatomic distance of N-N for SiN_2 becomes shorter than those of GeN_2 and SnN_2 (see Figure S7).

Figure 4 shows the pressure dependence of the unit cell volumes that are normalized at the zero-pressure below the pressure of approximately 25 GPa. The pyrite-type phase was identified in the high pressure in-situ XRD patterns measured after laser heating at approximately 60 GPa (see Figure S8). On the other hand, the measured pressure-volume relation at higher pressure (40-50 GPa) show the anomalous behavior possibly due to the change of deviatoric stress in the sample chamber caused by the transformation of high pressure phase nitrogen along the decompression. Thus, the measured pressure and volume data below 25 GPa were fitted to the Birch-Murnaghan's equation of state to yield the zero-pressure bulk modulus K_0 . The K_0 are determined to be 354(13) GPa, 284(10) GPa and 219(11) GPa for SiN_2 , GeN_2 and SnN_2 , respectively (see Table 1). It was found that the bulk moduli of group-14 elemental pernitrides are higher than those of spinel phase (308(5) GPa, 296(4) GPa and 149(1.2) GPa for $\gamma\text{-Si}_3\text{N}_4$, $\gamma\text{-Ge}_3\text{N}_4$ and $\gamma\text{-Sn}_3\text{N}_4$, respectively),^[12,13,15] although K_0 of GeN_2 was comparative to that of spinel one. The $\gamma\text{-Al}_3\text{N}_4$ consists of AN_4 and AN_6 whereas the pyrite-type AN_2 consists of only AN_6 connected by a single bonded N-N. The packing of high coordinated polyhedral connected by single bonded N-N causes high density and higher bulk modulus than spinel nitrides.

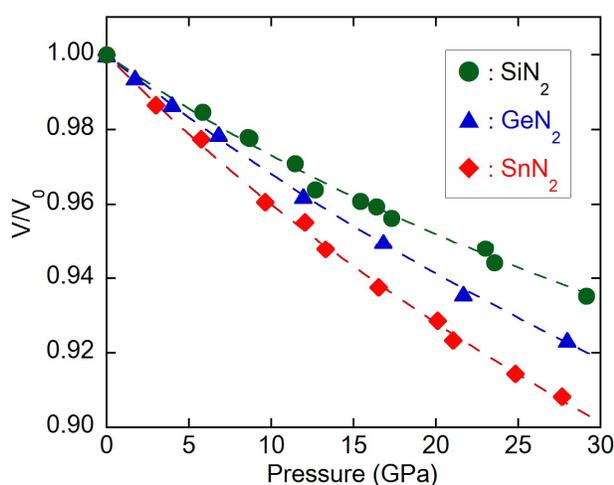


Figure 4 Pressure-volume data for pyrite-type group-14 elemental pernitrides. The dashed lines represent the results of fitting to the 3rd order Birch-Murnaghan equation of state.

Table 1. Summary of the pyrite-type group-14 elemental pernitrides

	$a / \text{\AA}$	u	$B / \text{\AA}^2$	$d_{\text{A-N}} / \text{\AA}$ $d_{\text{N-N}} / \text{\AA}$	K_0 / GPa K_0'
GeN_2	4.6702(1)	0.4087(3)	Ge: 0.49(1) N: 1.2(1)	2.001(1) 1.476(4)	284(10) 4.9(2.2)
SnN_2	5.06860(8)	0.4136(2)	Sn: 0.68(1) N: 0.71(9)	2.186(1) 1.516(1)	219(11) 5.7(1.3)

*The atomic coordinate sites of pyrite-type AN_2 ; $A(4a) = (0, 0, 0)$, $N(8c) = (u, u, u)$

* $R_{\text{wp}} = 1.351\%$, $R_e = 3.003\%$, $R_B = 6.101\%$ and $R_f = 5.546\%$ for GeN_2

* $R_{\text{wp}} = 1.170\%$, $R_e = 4.163\%$, $R_B = 1.775\%$ and $R_f = 1.547\%$ for SnN_2

*The zero-pressure bulk modulus and its pressure derivative of SiN_2 were determined to be 354 (13) GPa and 6.4(1.4), respectively.

Silicon, germanium and tin have been commonly known to form the dioxides (AO_2).^[25] The high-pressure phase with the space group of $Pa-3$ has been discovered for all these dioxides.^[26-28] The space group of $Pa-3$ is same as that of pyrite-type compound however, there seems no covalent bonding between nearest oxygens in these cubic phase of SiO_2 , GeO_2 and SnO_2 , because the interatomic distance between

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oxygens are much longer than that of MO_2 ($M=Na, Mg$ and Zn etc.)^[29-31] that have covalent bonding oxygens (O-O) in the structure. Thus, SiO_2 , GeO_2 and SnO_2 with the space group of $Pa-3$ are called as the high-pressure form of PdF_2 .^[26-28, 32] In addition, these cubic dioxides are unquenchable into ambient pressure and the transition pressure is largely different among SiO_2 ($P>260$ GPa), GeO_2 ($P>80$ GPa) and SnO_2 ($P>21$ GPa),^[26-28] which is completely different from the present results for pyrite-type SiN_2 , GeN_2 and SnN_2 . The comparison between group-14 elemental dioxides and pernitrides having the space group of $Pa-3$ indicates that the chemical bonding between anions plays an very important role for stabilizing the high pressure phase, even though both compounds (dioxides and pernitrides) show the same crystal symmetry.

In conclusion, we have succeeded in the synthesis of pyrite-type AN_2 ($A=Si, Ge$ and Sn) via a direct chemical reaction between group-14 elements and molecular nitrogen above the pressure of 60 GPa. The pyrite-type AN_2 are quenchable into ambient condition. The XRD structural analyses and Raman scattering measurements found that the interatomic distance of N-N increases in order of SiN_2 , GeN_2 and SnN_2 . This indicates that the bonding nature is gradually changed from single to rather double bonding from SnN_2 to SiN_2 due to the difference of charge density among Si^{4+} , Ge^{4+} and Sn^{4+} . The pyrite-type AN_2 shows the bulk modulus higher than that of $\gamma-A_3N_4$ due to the consist of only AN_6 octahedra connected by the single bonded N-N. The α -, β - and γ - A_3N_4 have long time been known as the group-14 elemental nitrides whereas we have succeeded in the synthesis of new 4th group-14 elemental pernitrides by means of the high-pressure experiments at the pressure of above 60 GPa. The further investigation would offer deep insight of these pyrite-type group-14 elemental pernitrides especially with respect to the electronic properties.

The authors would like to thank Mr. T. Inagaki, Dr T. Kikegawa, Dr T. Nagae, and Prof. N. Watanabe for their technical support with the high-pressure in-situ synchrotron radiation XRD measurements. We also appreciate Mr. E. Hirose, Prof. K. Soda and Dr Y. Shirako for the valuable discussions and help of data analysis. The synchrotron radiation XRD measurements were performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2012G567) and carried out at Aichi Synchrotron Radiation Center (Proposal No. 2016N1001, 2016N3001). This research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

Notes and references

- 1 P. Popper, S.N. Ruddlesden, *Nature*, 1957, **179**, 1129.
- 2 D. Hardie, K.H. Jack, *Nature*, 1957, **180**, 332-333.
- 3 S.N. Ruddlesden, P. Popper, *Acta Crystallogr.*, 1958, **11**, 465-468.
- 4 G. Ziegler, J. Heinrich, G. Wötting, *J. Mater. Sci.*, 1987, **22**, 3041-3086.
- 5 F.L. Riley, *J. Am. Ceram. Soc.*, 2000, **83**, 245-265.
- 6 K. Maeda, N. Saito, Y. Inoue, K. Domen, *Chem. Mater.*, 2007, **19**, 4092-4097.

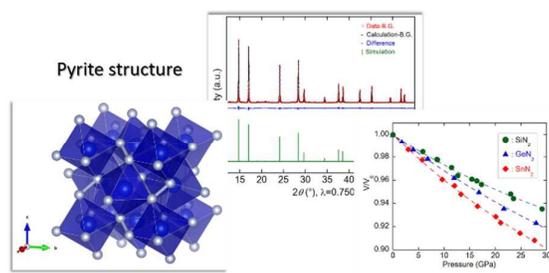
- 7 A. Zerr, G. Miehe, G. Serghiou, M. Schwarz, E. Kroke, R. Riedel, H. Fueß, P. Kroll, R. Boehler, *Nature*, 1999, **400**, 340-342.
- 8 G. Serghiou, G. Miehe, O. Tschauner, A. Zerr, R. Boehler, *J. Chem. Phys.*, 1999, **111**, 4659-4662.
- 9 a) N. Scotti, W. Kockelmann, J. Senker, St. Traßel, H. Jacobs, *Z. Anorg. Allg. Chem.*, 1999, **625**, 1435-1439; b) M.P. Shemkunas, G.H. Wolf, K. Leinenweber, W.T. Petuskey, *J. Am. Ceram. Soc.*, 2002, **85**, 101-104.
- 10 M.B. Kruger, J.H. Nguyen, Y.M. Li, W.A. Caldwell, M.H. Manghnani, R. Jeanloz, *Phys. Rev. B*, 1997, **55**, 3456-3460.
- 11 Y.M. Li, M.B. Kruger, J.H. Nguyen, W.A. Caldwell, R. Jeanoz, *Solid. State. Commun.*, 1997, **103**, 107-112.
- 12 J. Z. Jiang, H. Lindelov, L. Gerward, K. Stahl, J.M. Recio, P. Mori-Sanchez, S. Carlson, M. Mezouar, E. Dooryhee, A. Fitch, D. J. Frost, *Phys. Rev. B*, 2002, **65**, 161202.
- 13 M.P. Shemkunas, W.T. Petuskey, A.V.G. Chizmeshya, K. Leinenweber, G.H. Wolf, *J. Mater. Res.*, 2004, **19**, 1392-1399.
- 14 E. Soignard, P.F. McMillan, C. Hejny, K. Leinenweber, *J. Solid. State. Chem.*, 2004, **177**, 299-311.
- 15 G.K. Pradhan, A. Kumar, S.K. Deb, U.V. Waghmare, C. Narayana, *Phys. Rev. B*, 2010, **82**, 144112.
- 16 T. D. Boyko, A. Hunt, A. Zerr, A. Moewes, *Phys. Rev. Lett.*, 2013, **111**, 097402.
- 17 F. Izumi, K. Momma, *Solid State Phenom.*, 2007, **130**, 15-20.
- 18 a) R. Wehrich, V. Eyert, S.F. Matar, *Chem. Phys. Lett.*, 2003, **373**, 636-641; b) Y.C. Ding, A.P. Xiang, X.J. He, X.F. Hu, *Physica B*, 2011, **406**, 1357-1362; c) C. Chen, Y. Xu, X. Sun, S. Wang, F. Tian, *RSC Adv.*, 2014, **4**, 55023.
- 19 M.I. Eremets, A.G. Gavriliuk, I.A. Trojan, D.A. Dzivenko, R. Boehler, *Nat. Mater.*, 2004, **3**, 558.
- 20 a) G.V. Vajenine, G. Auffermann, Y. Prots, W. Schnelle, R.K. Kremer, A. Simon, R. Kniep, Preparation, *Inorg. Chem.*, 2001, **40**, 4866-4870; b) G. Auffermann, Y. Prots, R. Kniep, S.F. Parker, S.M. Bennington, *CHEMPHYSICHEM*, 2002, **9**, 815-817; c) S.B. Schneider, R. Frankovsky, W. Schnick, *Inorg. Chem.* 2012, **51**, 2366-2373; d) M.E. Fieser, D.H. Woen, J.F. Corbey, T.J. Mueller, J.W. Ziller, W.J. Evans, *Dalton Trans.*, 2016, **45**, 14634-14644.
- 21 H. Schneider, W. Häfner, A. Wokaun, H. Olijnyk, *J. Chem. Phys.*, 1992, **96**, 8046-8053.
- 22 a) H. Vogt, T. Chattopadhyay, H.J. Stolz, *J. Phys. Chem. Solids* 1983, **44**(9) 869-873; b) C. Sourisseau, R. Cavagnat, M. Fouassier, *J. Phys. Chem. Solids*, 1991, **52**(3), 537-544; c) T.P. Mernagh, A.G. Trudu, *Chemical Geology*, 1993, **103**, 113-127; d) K. Kleppe, A. P. Jephcoat, *Mineral. Mag.*, 2004, **68**(3), 433-441.
- 23 a) J.C. Crowhurst, A.F. Goncharov, B. Sadigh, C.L. Evans, P.G. Morrall, J.L. Ferreira, J. Nelson, *Science*, 2006, **311**, 1275-1278; b) A.F. Young, J.A. Montoya, C. Sanloup, M. Lazzeri, E. Gregoryanz, S. Scandolo, *Phys. Rev. B*, 2006, **73**, 153102; c) H.R. Soni, S.D. Gupta, S.K. Gupta, P.K. Jha, *Physica B*, 2011, **406**, 2143-2147.
- 24 W. Wessel, R. Dronskowski, *J. Am. Chem. Soc.*, 2010, **132**, 2421-2429.
- 25 R.W.G. Wyckoff in *Crystal Structure*, Second Edition Vol. 1, Robert E. Krieger Publishing Company Malabar, Florida, 1982, Chapter IV
- 26 a) Y. Kuwayama, K. Hirose, N. Sata, Y. Ohshi, *Science*, 2005, **309**, 923-925; b) Y. Kuwayama, K. Hirose, N. Sata, Y. Ohshi, *Phys. Chem. Minerals*, 2011, **38**, 591-597.
- 27 S. Ono, T. Tsuchiya, K. Hirose, Y. Ohishi, *Phys. Rev. B*, 2003, **68**, 014103.
- 28 a) J. Haines, J.M. Léger, O. Schulte, *Science*, 1996, **271**, 629-631; b) J. Haines, J.M. Léger, *Phys. Rev. B*, 1997, **55**, 11144-11154.
- 29 G.F. Carter, D.H. Templeton, *J. Am. Chem. Soc.*, 1953, **75**, 5247-5249.

Journal Name

COMMUNICATION

- 30 N.G. Vannerberg, *Ark. Kemi*, 1959, **14**, 99–105.
31 N.G. Vannerberg, *Ark. Kemi*, 1959, **14**, 119–124.
32 Tressaud, J.L. Soubeyroux, H. Touhara, G. Demazeau, F. Langlais, *Mat. Res. Bull.*, 1981, **16**, 207–214.

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Incompressible pyrite form of group 14 elemental pnitrides synthesized at high pressures and high temperature