Supporting information figures

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

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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 higer than the other known group-14 elemental nitrides. Our results offer significant new progress on the solid-state chemistry of nitrides.

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Experimental Section

The pyrite-type group-14 elemental nitrides were synthesized by using a laser-heated diamond-anvil cell (LH-DAC) up to the pressure of approximately 60 GPa. The high purity elemental powder or foil (Si:99.9 %, Ge:99.999 %, Sn:99.95 %) was shaped with the dimension of ~80 × ~80 μm^2 and thickness of ~10 μm. The shaped starting element was located at the center of sample chamber that was prepared in the indented stainless steel gasket by using a pulsed infrared laser. Then, nitrogen was cryogenically loaded into the sample chamber in which small ruby chips were also loaded as the pressure marker.[1] The sample was heated under high pressure by an irradiation of infrared laser (λ=1090 nm) from both or one sides of the DAC. The heated sample was characterized by microscope observation, X-ray diffraction and Raman scattering measurements both at high and ambient pressures. High-pressure in-situ X-ray diffraction experiments were carried out at beam line of NE1, Photon Factory Advanced Ring (PF-AR) of a synchrotron facility of KEK, Tsukuba and at the Nagoya University beamline BL2S1 of Aichi Synchrotron Radiation Center (AichiSR), Aichi Science & Technology Foundation.[2] The monochromatic X-ray with the size of ϕ30 μm (at PF-AR) or ϕ100 μm (at AichiSR) was irradiated to the sample parallel to the compression axis. The diffracted X-rays were recorded on the imaging plate (at PF-AR) or charge coupled device detector (at AichiSR) with the exposure time of 20 and 3 min, respectively. For the ambient recovered sample, the synthesized samples were mounted on the polyamide capillary (SPIKA, Protein Wave Corporation) and the diffraction patterns were measured with the rotation of sample. The distance between sample and detector, wavelength of X-ray, tilting of detector etc. were calibrated based on the diffraction profile of standard material CeO_2 prior to the measurements. The 2-dimentional diffraction pattern was converted to the conventional 1-dimentional profile by using IPAnalyzer.[3] The phase identification and the crystal symmetry analysis were conducted by using dedicated software of PDIndexer and DICVOL06, respectively.[3,4] The Rietveld refinement was carried out by using RIETAN.[5] In addition to ruby pressure marker, the pressure dependence of diamond Raman band and the equation of state for nitrogen were also applied to determine the pressure in this study.[6,7] Argon ion laser with the wavelength of 488 nm was used as the excitation source for Raman spectroscopy. The incident laser was focused with the size of less than approximately 10 μm and was irradiated to the sample. The Raman signal was detected with the liquid nitrogen cooled CCD detector. After recovery of the sample into ambient pressure, the crystal morphology and chemical composition were examined by scanning microscope equipped with energy dispersive spectroscopy.

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3 Y. Seto, D. Nishio-Hamane, T. Nagai, N. Sata, *Rev. High Press. Sci. Tech.*, 2010, **20**, 269– 276. (Japanese article with English abstract).
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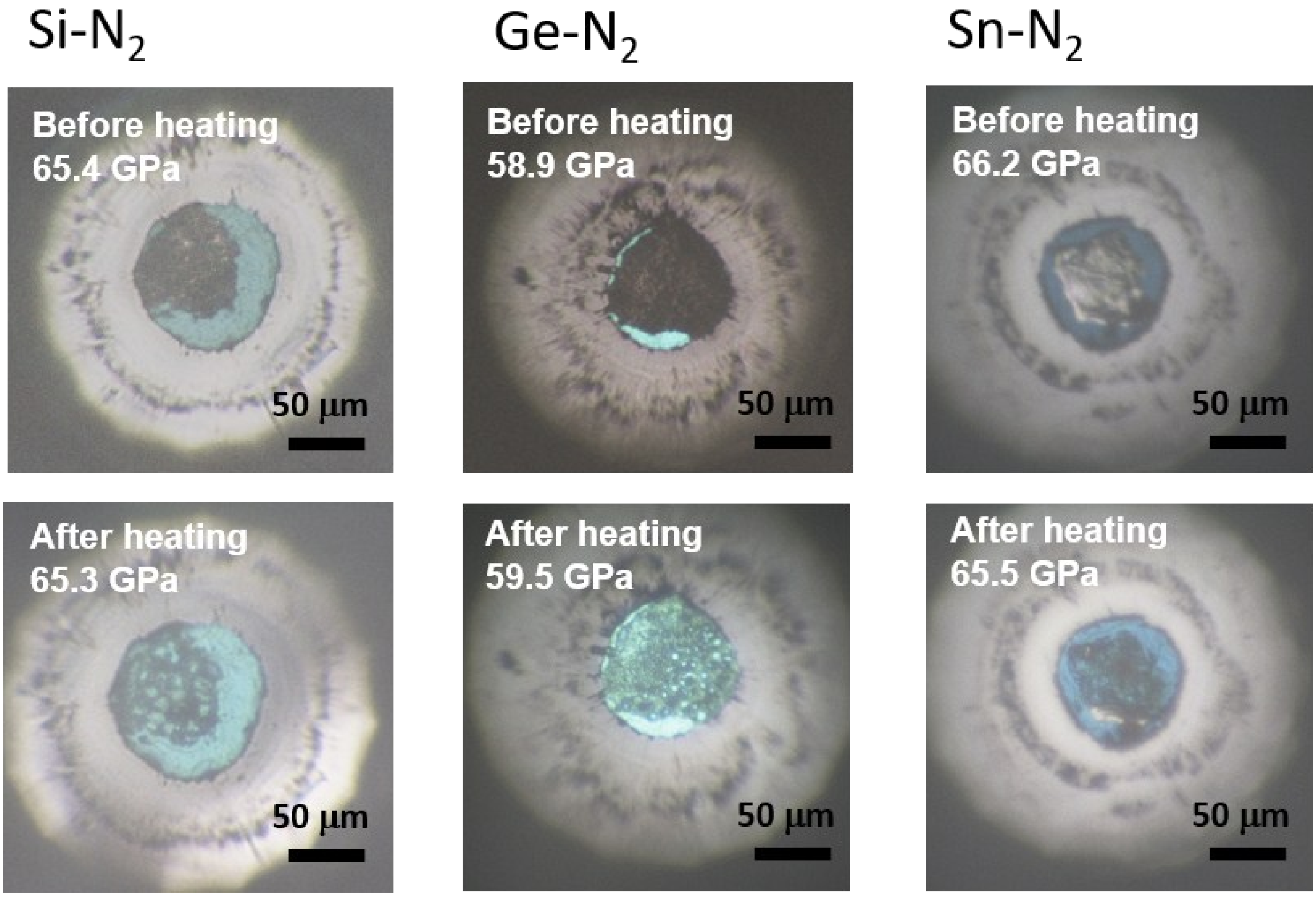
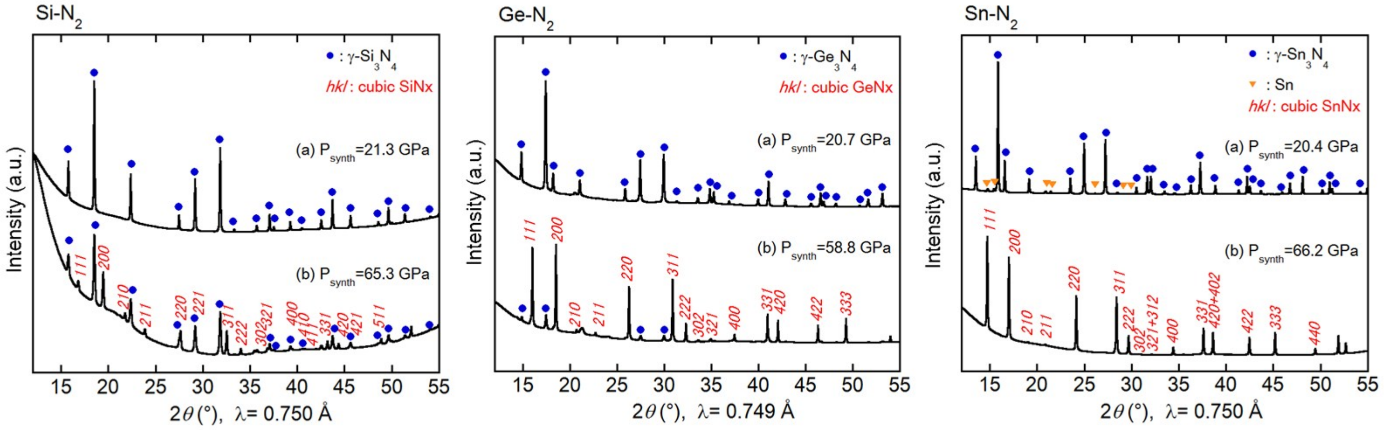
Figure S1. Examples of optical photographs of sample chamber before and after laser heating under high pressures.



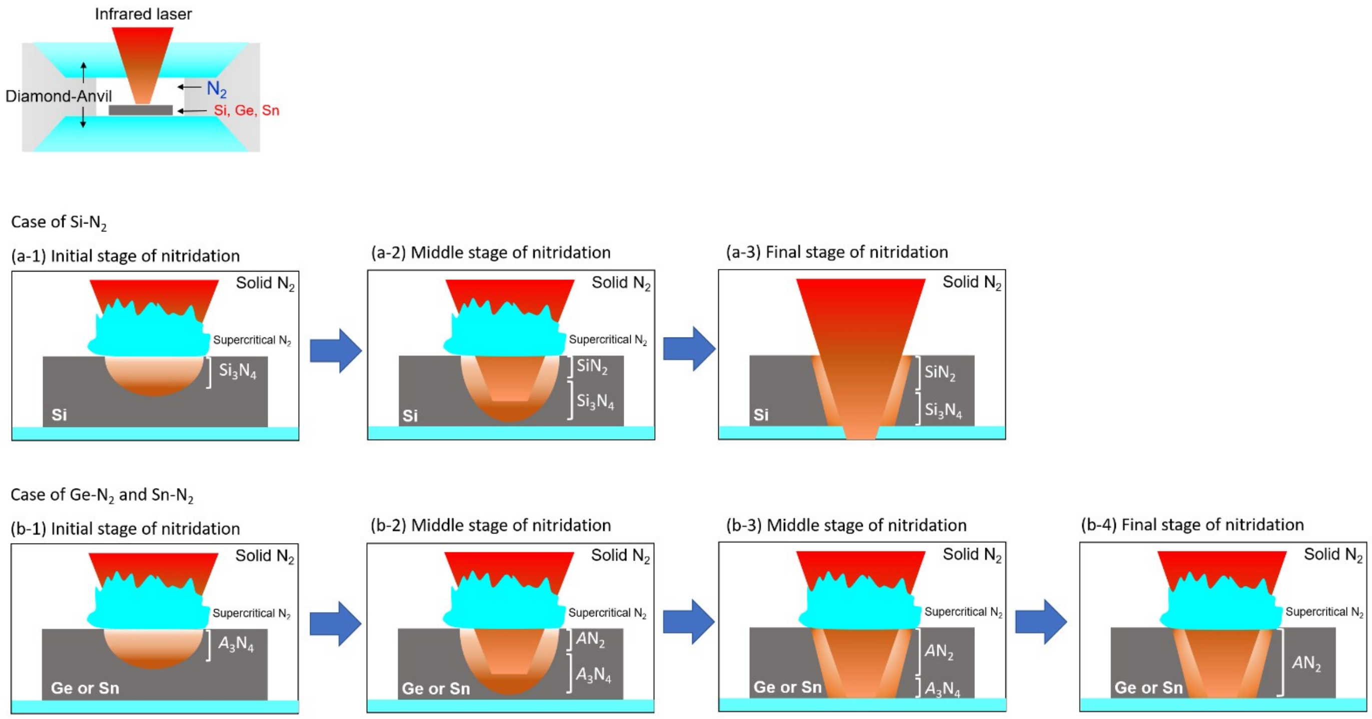
The group-14 elements show optically opaque before heating under high pressures while the color of the sample was changed to be transparent after heating.

Figure S2. The synchrotron X-ray diffraction profiles of group-14 element nitrides measured at ambient pressure.



The XRD patterns were measured at BL2S1, AichiSR, Japan. The upper profiles correspond to the nitrides that were synthesized at approximately 20 GPa. All the diffraction peaks are assigned to the spinel phase(γ-A_3N_4). The lower profiles correspond to the nitrides that were synthesized at approximately 60 GPa. The spinel phase is also detected whereas many new peaks are identified. The peak indexing analysis found that these newly appeared peaks can be assigned to the cubic symmetry. Further investigation combined with chemical analyses and crystal chemistry consideration gave a solution of crystal structure. The pyrite-type is strongly suggested as model structure for new cubic nitrides synthesized above the pressure of 60 GPa. The recovered sample was mounted on the polyamide capillary in order to reduce the background from the sample holder. However, the sample size in this study is very tiny and it seems difficult to eliminate the effect of scattering from the polyamide capillary especially the case of Si-N$_2$ experiments. As seen in the diffraction profile of Si-N$_2$ experiment that was recovered from approximately 60 GPa, the wavy background was detected in the 2θ region of around 20-25°. This is derived from the polyamide capillary. If the scattering factor of sample is intense as in the case of Ge-N$_2$ and Sn-N$_2$, this might be no significant effect on the analyses. However, silicon is light element in comparison with germanium and tin, and almost half of sample seems to be spinel phase and total amount of pyrite phase is quite small. These factors lead to the difficulty of refining the crystal structure of SiN$_2$ more precisely even though so-called low background sample holder was used. Thus, only the lattice parameter is calculated for SiN$_2$ in this study. However, the formation of GeN$_2$ an SnN$_2$ together with Raman scattering measurements for pyrite-type phases, allow giving a conclusion that pyrite-type SiN$_2$ is synthesized above the pressure of approximately 60 GPa.

Figure S3. The schematic illustration of laser heating experiments in DAC and nitridation of the group-14 elements



The schematic illustration of laser heating experiments in DAC is shown here. When infrared laser (λ=1090 nm) is irradiated to the group-14 element, the elements directly absorb the wavelength of infrared laser because group-14 elements are metallic at this pressure (a-1 and b-1). Then, the elements immediately reacted with supercritical molecular nitrogen to form the nitrides (probably spinel phase is formed at the initial state). The nitridation of elements is gradually proceeded into the inside of the elements. On the other hand, spinel phase of Si_3N_4 is transparent to the wavelength of infrared laser so as not to absorb the infrared laser furthermore and no nitridation seems expected. However, if the metallic silicon remains inside, the surface of Si_3N_4 further reacted with supercritical nitrogen due to the high temperature by thermal conductivity from the inside heated area. This results in the formation of nitrogen-rich phase pyrite-type SiN_2, although SiN_2 also exhibits no absorption of the wavelength of infrared laser (a-2). Further heating is likely to allow synthesizing the pure phase of SIN_2. However, when remaining silicon is completely reacted to form the spinel phase, there is no other laser absorber and further nitridation by laser heating is impossible, infrared laser is going through the sample (a-3). Thus, almost half of spinel Si_3N_4 coexists with pyrite-type SiN_2 in case of direct nitridation of silicon by infrared laser heating (a-3). Germanium and tin is also likely to exhibit same nitridation process (b-1, b-2). However, both elemental nitrides of spinel and pyrite phases allow absorbing the infrared laser wavelength and further heating can be made, although no pure element remain in the heated area (b-3). Finally, almost pure pyrite phase can be obtained for germanium and tin (b-4), although spinel phase can be detected for the Ge-N_2 experiment at approximately 60 GPa in this study due to the short heating time.

Figure S4. High pressure in-situ Raman scattering spectra before and after laser heating at approximately 60 GPa.

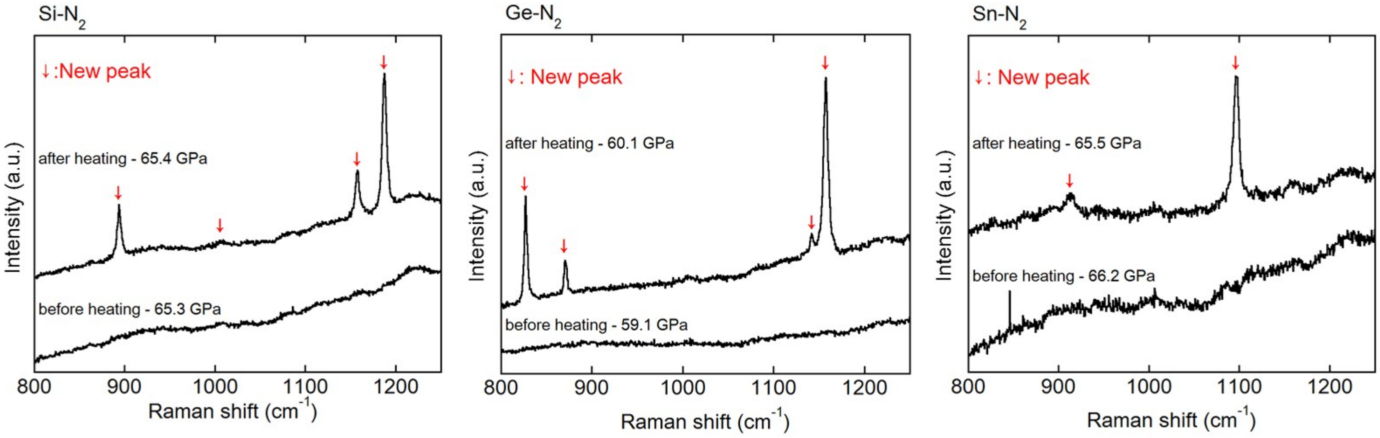
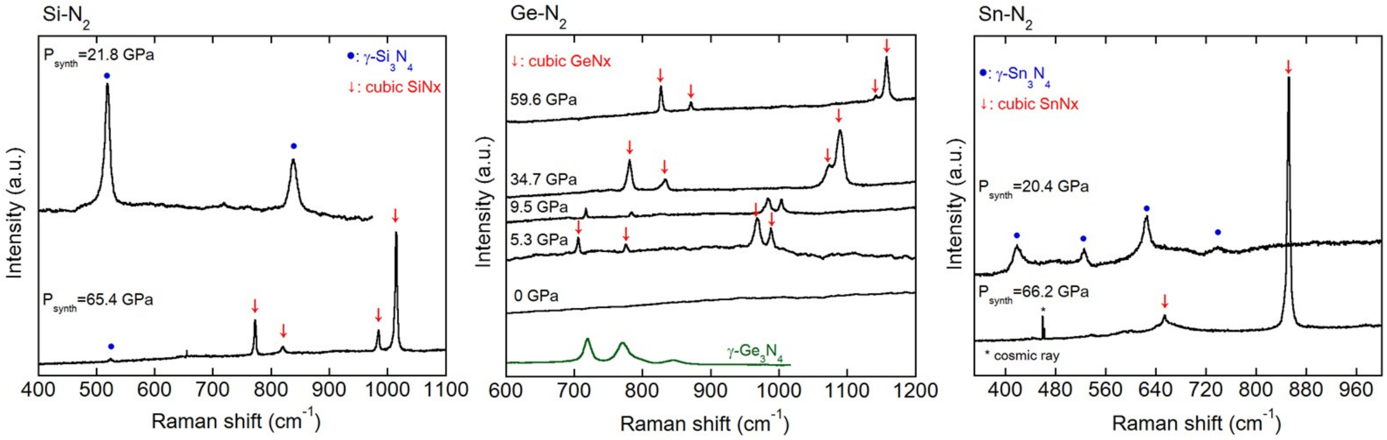
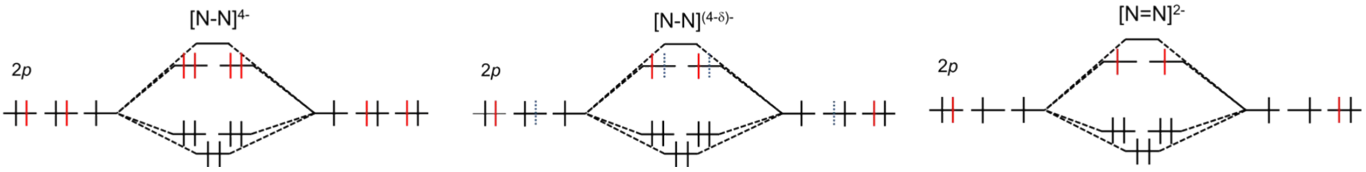


Figure S5. Raman spectra of group-14 elemental nitrides.



The Raman spectra of the recovered nitrides synthesized at approximately 20 and 60 GPa were shown for the experiments of $Si\text{-}N_2$ and $Sn\text{-}N_2$ systems. The Raman peaks corresponding to the spinel and new cubic phases are represented with the solid circle and down-direction arrows, respectively. In the $Ge\text{-}N_2$ experiment, the Raman spectra measured in-situ high pressures show sharp peaks along the decompression whereas the recovered GeN_2 showed intense fluorescence probably due to the change of optical absorption band during the decompression.

Figure S6. Schematic illustration of electronic configuration for nitrogen dimer with different bonding nature.



The electronic configuration of [N-N]$^{4-}$ proposed for pernitrides $A^{4+}(N_2)^{4-}$. The lower and upper level correspond to the bonding and anti-bonding orbital, respectively. The anti-bonding orbital occupied by electron leads to the reduction of chemical bonding. Small ionic radius of A^{4+} readily attracts the electron that occupied the anti-bonding state and this result in the bonding state slightly close to double bonding one.

Figure S7. The relationship among ionic radius, charge density and interatomic distance of N-N

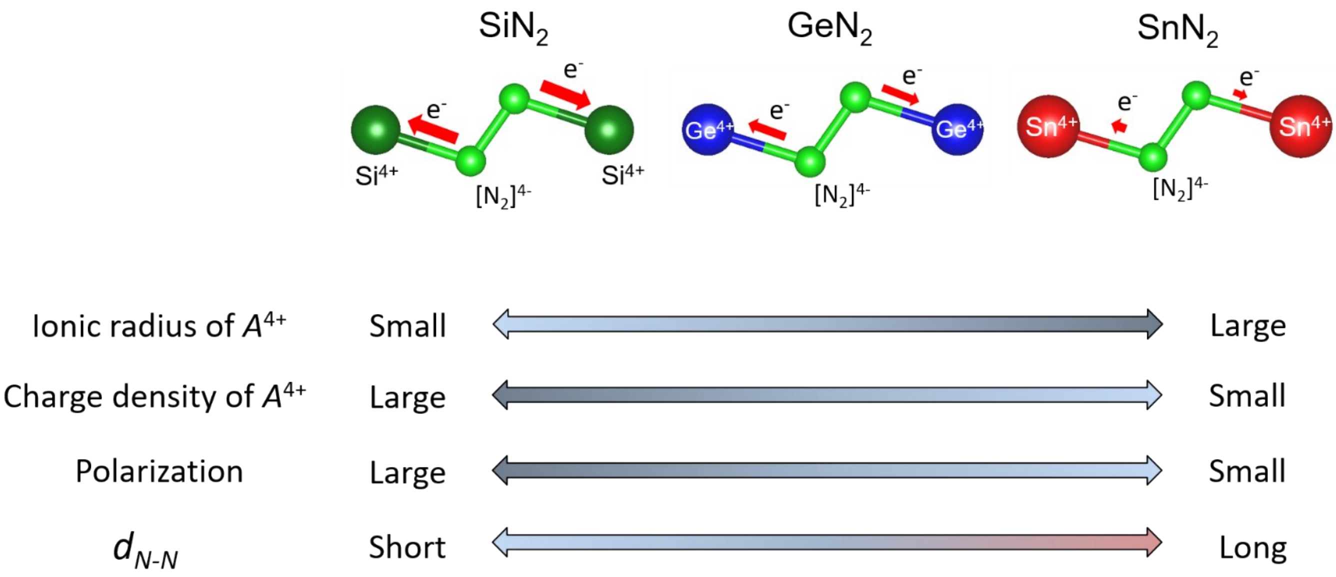
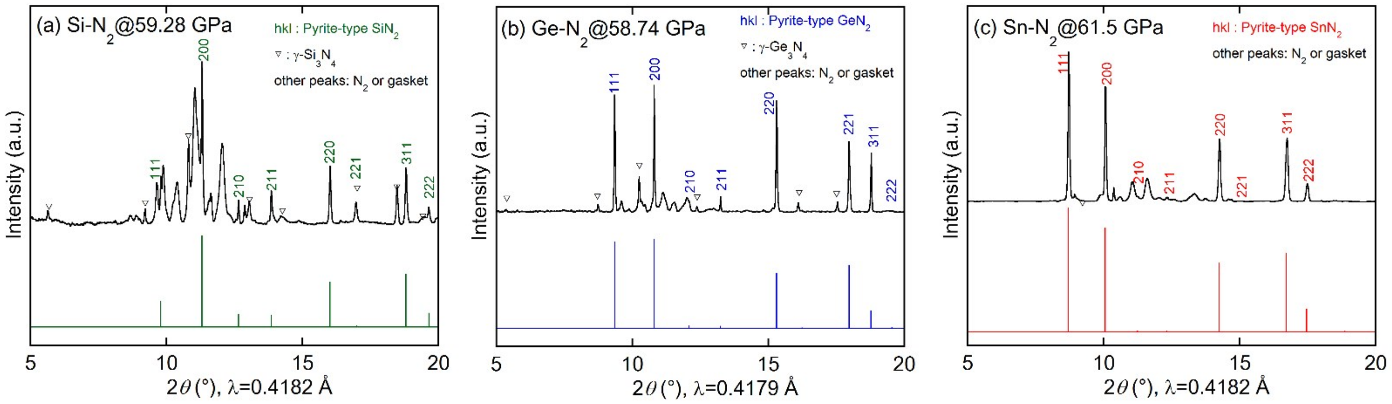


Figure S8. The high pressure in-situ XRD profiles of heated samples



The XRD patterns were measured by using synchrotron radiation X-ray source at Photon Factory, KEK (Tsukuba, Japan). The measurements were performed after the laser heating at approximately 60 GPa. Newly appeared peaks are assigned with cubic phase which does not correspond to the spinel one and recovered into ambient pressure. The peaks detected at around 10-15˚ are derived from the high-pressure phase of molecular nitrogen or gasket.