Stabilization of hexazine rings in potassium polynitride at high pressure

Yu Wang1, Maxim Bykov2,3, Ilya Chepkasov4, Artem Samtsevich5, Elena Bykova2, Xiao Zhang1, Shu-qing Jiang1, Eran Greenberg5,6, Stella Chariton5, Vitali B. Prakapenka6, Artem R. Oganov4 and Alexander F. Goncharov2,6

Polynitrogen molecules are attractive for high-energy-density materials due to energy stored in nitrogen–nitrogen bonds; however, it remains challenging to find energy-efficient synthetic routes and stabilization mechanisms for these compounds. Direct synthesis from molecular dinitrogen requires overcoming large activation barriers and the reaction products are prone to inherent inhomogeneity. Here we report the synthesis of planar N62- hexazine dianions, stabilized in KN6, from potassium azide (KN3) on laser heating in a diamond anvil cell at pressures above 45 GPa. The resulting KN6, which exhibits a metallic lustre, remains metastable down to 20 GPa. Synchrotron X-ray diffraction and Raman spectroscopy were used to identify this material, through good agreement with the theoretically predicted structural, vibrational and electronic properties for KN6. The N62- rings characterized here are likely to be present in other high-energy-density materials stabilized by pressure. Under 30 GPa, an unusual N20.75- -containing compound with the formula K2(CN)2, was formed instead.

Nitrogen-rich compounds are widely investigated as high-energy-density materials (HEDM)2,3. Their substantial energy storage or release capacity (up to 2.3 eV per atom) is related to the large energy difference of the single/double versus the triple bonds between nitrogen atoms. Numerous all-nitrogen species were predicted theoretically4–7; however, only a few such species have hitherto been reported8–10. One major obstacle is the low-order N–N bonds tend to be unstable at low pressures. They can be stabilized under pressure, however, providing a pathway for synthesis. At about 50 GPa, molecular diatomic nitrogen has been theoretically predicted to transform into an atomic solid with a single-bonded crystalline cubic gauche (cg-N) structure11, which was later experimentally demonstrated in the laser-heated diamond anvil cell (DAC) at 110 GPa and 2500 K (ref. 12). The high pressures required for formation of polynitrogens, however, as well as the difficulties in recovering these species under ambient (or practical) conditions, make this synthetic route challenging.

Theoretical calculations have previously predicted a number of high-pressure nitrogen-rich compounds with metals that form unusually few-bonded all-nitrogen groups as well as polymeric networks13–21. Stabilization of polynitrogen groups at ambient pressure commonly occurs in very complex compounds at the expense of the energy density yield22–25. Great progress has recently been made in synthesis and stabilization of various pentazole anion cyclo-N5- compounds26–28; however, their stability in common environments and energy yields still remain a matter of investigation. Application of pressure may allow stabilization of various nitrogen species in simple compounds with metals. A variety of compounds containing polymeric nitrogen chains were synthesized in several metal–nitrogen systems (for example, Be, Mg, Ta, Fe) at pressures between 50 and 100 GPa (refs. 21–24). BeN4 and MgN4 were found to be recoverable at atmospheric pressure, which suggests novel opportunities with regard to synthesis of HEDMs. Even more complex nitrogen rich compounds such as porous frameworks with transition metals (Re, Hf, W and Os), where the structure combines nitrogen low-order bonded chains and triply bonded nitrogen molecules have been synthesized above 100 GPa (refs. 19–21). A WN6 compound with a single-bonded N6 in a chair conformation ring has recently been synthesized above 126 GPa by laser heating tungsten in an N2 environment29.

Alkali metal–nitrogen compounds were proposed to reduce the pressure of synthesis and to improve the compound stability and energy density of HEDMs as they are predicted to form a wealth of materials with various structures and compositions at high pressures30–32. The structural motifs include penta-N5- salts, N62- hexazine dianions and polymeric chains, and some of them are predicted to be preserved at ambient conditions. Yet there are only a few experimental reports that support these findings. Steele et al. synthesized a penta-N5- salt of caesium40 by laser heating CsN4 azide in molecular N2 medium at 60 GPa in a DAC. The crystal structure of this CsN4 compound with six formula units in the unit cell is very complex and it was determined by comparing powder X-ray diffraction (XRD) and Raman spectroscopy results with theoretical calculations. Laniel and colleagues synthesized an LiN5 compound with penta-N5- ions by heating lithium in N2 medium at 45 GPa, but the precise atomic configuration could not be resolved due to powder nature of the sample33,34. They also documented the synthesis of lithium diazenide LiN3 at lower pressures. In a more recent work, Bykov and colleagues35 synthesized two pentazole (NaN5 and NaN5) and two diazenide (Na2(N2)4 and NaN4) structures at ~50, 28 and 4 GPa by laser heating sodium azide NaN3. Use of azides containing linear N5- groups as precursors allows to reduce substantially (for example, compared with molecular N2) the activation barrier for the reaction and provide more uniform reaction...
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Polymerization of various azides has been widely investigated in static DAC experiments\(^{44,47}\), mainly at room temperature, and theoretically. The experiments show a rich polymorphism at high pressures, but the azide group remains (meta)stable\(^{52}\) up to at least 60 GPa (in lithium azide); however, Raman spectroscopy in NaN\(_3\) azide above 19 GPa shows\(^{56}\) an appearance of additional Raman bands at 1800–2000 cm\(^{-1}\), which cannot be explained by the predicted K\(_2\)N\(_6\) compound at about 50 GPa; this compound features low-pressure low-temperature decompression behaviour via in situ Raman measurements. First-principles theoretical calculations (see Methods) have been performed on the previously predicted K\(_2\)N\(_6\) compound at about 50 GPa; this compound features planar hexazine dianions N\(_6^2\)^{2\(–\)}.

Results

The synchrotron XRD and Raman experiments in DAC are described in the Methods. In this work we focus on the experiments in which powdered potassium azide (KN\(_3\)) was investigated without any pressure medium/reagent, which gives preference to the formation of compounds with this composition. Further experiments in which molecular N\(_2\) was loaded together with KN\(_3\) are used to investigate the room-temperature compression and low-temperature decompression behaviour via in situ Raman measurements. First-principles theoretical calculations (see Methods) have been performed on the previously predicted I4/mcm, C2/m and P6/mmm KN\(_3\) structures\(^{44,47}\), and also explored the transition pathways between them.

It was previously shown that when compressed at room temperature, KN\(_3\) experiences phase transformations from I4/mcm to another structure at about 15 GPa (refs. 59,60), which is predicted by theoretical calculations\(^{44,47}\) to be C2/m. In this phase the linear N\(_3\) azide groups are aligned parallel to each other unlike the low-pressure I4/mcm, where they are alternately rotated by 90° with respect to each other. Our Raman spectroscopy data (Supplementary Fig. 1) do show a transformation above 15 GPa that is manifested by the splitting of the librational modes and appearance of new peaks, in good agreement with ref. 59. Above 30 GPa, the Raman spectra show a broad band near 1900 cm\(^{-1}\) that increases in intensity with pressure, similar to that reported previously in NaN\(_3\) (ref. 56). Our XRD data at ~50 GPa—which generally agree with the extrapolated results of ref. 60—reveal a poorly crystallized single crystal of KN\(_3\), with extremely broad diffracted peaks (Supplementary Fig. 2). The unconstrained lattice determination results in the following unit-cell parameters \(a = 5.4252(13)\), \(b = 5.487(11)\), \(c = 4.67(4)\) Å; \(a = 90.6(4)^\circ\), \(\beta = 92.2(4)^\circ\), \(\gamma = 90.22(17)^\circ\). This indexing suggests that this phase is just a heavily distorted I4/mcm ambient pressure structure. The refinement against single-crystal data using the undistorted I4/mcm model results in an \(R_I\) factor of ~11%, which clearly indicates that no major structural rearrangements take place, thus ruling out the predicted C2/m phase. The best refinement was obtained in a monoclinic space group I2/c (Supplementary Fig. 3 and Supplementary Table 1).

It is worth noting that KN\(_3\) is sensitive to X-ray exposure, as evidenced by a darkening of the sample (Fig. 1b), a distinct Raman spectrum (Fig. 2), and time-dependent XRD patterns (Supplementary Fig. 4). The irradiated product demonstrates a substantial reduction in intensity of the N\(_3\) azide Raman modes and sharpening and strengthening of the Raman peaks, which could be assigned to yet unidentified definitely polynitrogen configuration; however, time-dependent X-ray diffraction measurements do not show the appearance of new diffracted peaks, suggesting that the X-ray-induced phase is amorphous in nature (Supplementary Fig. 4).

The theoretically predicted phase transformations to another azide polymorph C2/m KN\(_3\) and hexazine P6/mmm K\(_2\)N\(_6\) (refs. 44,44,47,57) are reconstructive (which involves large rearrangements of the atoms and chemical bonds) and thus are kinetically hindered (impeded and delayed) due to the high kinetic barriers. The transformation barriers theoretically calculated in this work are high: 137 meV per atom for the transition from I4/mcm to C2/m KN\(_3\) at 30 GPa, and 426 meV per atom from I4/mcm to P6/mmm at 50 GPa (Supplementary Figs. 5 and 6). We performed high-temperature treatment of cold-compressed KN\(_3\) to overcome these barriers. At 49–53 GPa, laser heating of KN\(_3\) to 2500 K results in the formation of a new material that is clearly identified by shiny surfaces and a very distinct XRD pattern (Fig. 1 and Supplementary Fig. 7). The new phase was obtained in the form of fine-grain powder, as well as a part of the reconstructed (h k −1) precession image from the single-crystal XRD dataset of K\(_2\)N\(_6\) at ~50 GPa, demonstrating the crystal quality and the diffraction selection rules. The details of structural refinement are presented in Supplementary Table 2. A microphotograph of the sample in transmitted and reflected light at 50 GPa, which is transformed in the central more reflecting part. The crystal structure of K\(_2\)N\(_6\) at ~50 GPa.
as in the form of single crystals. The unit cell was indexed with a hexagonal unit cell ($a = 5.2855(9)$ Å, $c = 2.6186(5)$ Å for the powder sample; and $a = 5.281(3)$ Å, $c = 2.661(2)$ Å for the single crystals; see Fig. 1, Supplementary Fig. 7 and Supplementary Tables 2 and 3). This lattice is in a good agreement with the predicted high-pressure polymorphs of KN$_3$–K$_2$N$_6$ with P6/mmm symmetry. Indeed, structure refinement against single-crystal diffraction data based on this model converges with excellent agreement factors (Supplementary Table 2). In the P6/mmm structure, potassium and nitrogen atoms occupy Wyckoff sites 2a (1/3, 2/3, 0) and 6c (0.776(3), 0, 0.5), respectively (Supplementary Table 2). Nitrogen atoms are connected with each other, forming planar N$_6$ rings (Fig. 1c), whereas potassium atoms are twelve-coordinated by nearby nitrogen atoms, forming truncated triangular prisms. The refined N–N bond length of 1.184(13) Å is somewhat shorter than the theoretical predictions of vibrational frequencies of P6/mmm KN$_3$–K$_2$N$_6$. Observed P6/mmm KN$_3$–K$_2$N$_6$ Raman peaks are labelled according to the mode assignment based on comparison with theory. Structurally similar Pm Na$_2$N$_5$ Raman spectra are shown for comparison, supporting these assignments. The shaded area indicates the spectral ranges, where Raman peaks of the stressed diamond anvils appear.

Considering the oxidation state of potassium is +1, each N$_6$ ring must accommodate two electrons leading to an eight-$\pi$-electron system in N$_6^{2-}$. This system is therefore aromatic, with two extra electrons entering partially filled $\pi$ orbitals, leading to metallic character of this compound, in agreement with theoretical calculations of the electronic band structure (Supplementary Fig. 9). The intramolecular bond in the hexazine dianions ring is probably resonant; the bond order 1.33 can be calculated on the basis of the charge transfer of two electrons from potassium to the N$_6$ rings. Theoretical calculations predicted that P6/mmm KN$_3$ would be a stable polymorph above 40–50 GPa, which is mostly consistent with our observations.

The Raman spectra measured concomitantly with XRD change drastically following the transformation (Fig. 2), where all of the X-ray-exposed and -unexposed azide peaks disappear and thus all of the observed Raman peaks correspond to a pure N$_6^{2-}$ hexazine dianion K$_2$N$_6$ compound. The P6/mmm KN$_3$ synthesized in this work shows distinctive Raman bands in the spectral range characteristic for the stretching vibrations of a few-bonded nitrogen (1000–1300 cm$^{-1}$), and two low-frequency modes in the spectral range of the N–N bending modes and lattice vibrations. Weak peaks at ~700 cm$^{-1}$ can also be seen. We have been able to trace the Raman spectrum of this phase down to approximately 20 GPa on unloading (Supplementary Fig. 8), thus establishing their pressure behaviour and allowing comparison with theoretical calculations of vibrational frequencies of P6/mmm KN$_3$ at 100 GPa (Fig. 4) and a hypothetical N$_6$ hexaazabenzen molecule, where the ring is out-of-plane distorted with the D$_3$ symmetry. These data provide very important clues for assigning the observed Raman modes of synthesized here P6/mmm KN$_3$ (Fig. 4). Moreover, we have performed first-principles calculations of the vibrational and electronic properties of P6/mmm K$_2$N$_6$ and Pm Na$_2$N$_5$ (ref. 52;...
Methods), which allow the direct comparison of the experimental and theoretical Raman mode frequencies at 50 GPa.

The group theory predicts four $A_{1g}$, $2E_{2g}$ and $E_{1g}$ Raman-active modes for the $N_6^{2−}$ rings and one $E_{1g}$ mode for potassium vibrations of $P6\overline{3}m/m$ $K_2N_6$. No translation or rotation modes are expected from the $N_6^{2−}$ hexazine dianions, which is some 17% denser. However, $I4\overline{1}/amd$ $K_2(N_6)_2$, diazenide (synthesized at 30 GPa, also assisted by laser heating), which is slightly deficient in nitrogen, has about the same density as $I4/c$ azide. To take into account the difference in composition we added a volume of nitrogen in molecular and monatomic (cg-N) compounds at the same pressure determined from their equations of states$^{64,65}$. The theoretical volumes of $I4/mcm$ and $C2/m$ (which we do not observe) $K_{2N_2}$ and $P6/m/m$ $K_2N_2$ are shown for comparison$^{44,47}$.

Fig. 3 | Volumes per formula unit of K–N compounds investigated here. KN, azide—the $I4/mcm$ structure of which was determined up to 15 GPa (ref. 49)—develops a monoclinic distortion with the space group $I2/c$ (determined at 53 GPa; Supplementary Figs. 2 and 3, and Supplementary Table 1) where it transforms on laser heating into a $P6/m/m$ $K_2N_6$ compound with $N_6^{2−}$ hexazine dianions, which is some 17% denser. However, $I4/\overline{1}/amd$ $K_2(N_6)_2$, diazenide (synthesized at 30 GPa, also assisted by laser heating), which is slightly deficient in nitrogen, has about the same density as $I4/c$ azide. To take into account the difference in composition we added a volume of nitrogen in molecular and monatomic (cg-N) compounds at the same pressure determined from their equations of states$^{64,65}$. The theoretical volumes of $I4/mcm$ and $C2/m$ (which we do not observe) $K_{2N_2}$ and $P6/m/m$ $K_2N_2$ are shown for comparison$^{44,47}$.

Fig. 4 | Vibrational frequencies of $P6/m/m$ $K_2N_6$. The results deduced from the Raman spectra are compared with the theoretically calculated Raman frequencies for $P6/m/m$ $K_2N_6$ and $Pm$ $K_2N_6$. Brillouin zone centre vibrational modes of $P6/m/m$ $K_2N_6$ (ref. 47) and the Raman-active modes of a $N_6^{2−}$ ring isomer in the twist-boat $D_2$ structure$^{46}$. The error bars for the Raman frequencies are smaller than the symbol size. Above 80 GPa, the $A_{1g}$ mode cannot be observed as it interferes with the Raman signal from diamond anvils. These results support the presented here vibrational modes assignment of $P6/m/m$ $K_2N_6$. can be assigned to the coupling with the carriers. The frequencies of the characteristic $N$–$N$ stretching deformation modes decrease with pressure release and these dependencies extrapolate reasonably well to the theoretically calculated values of the twist-boat $N_6^{2−}$ isomer at ambient pressure. Note that the frequencies and the pressure dependencies of the fundamental modes of the $N_6^{2−}$ ring are close to those of pentazole rings measured previously$^{45,53}$ in CsN$_5$ and LiN$_5$ (Supplementary Fig. 11). Moreover, the calculated here Raman modes of $Pm$ $K_2N_6$ with pentazole rings are also close in frequency (Fig. 4), albeit the number of predicted Raman modes is much larger than observed (Fig. 4). Nonetheless, the Raman spectra of $P6/m/m$ $K_2N_6$ and $Pm$ $K_2N_6$ are clearly distinct in the spectral range of the fundamental modes of the nitrogen rings (Fig. 2), especially for the stretching-deformation modes at 1100–1300 cm$^{-1}$, supporting the presence of $N_6^{2−}$ rings in $P6/m/m$ $K_2N_6$.

On unloading of $P6/m/m$ $K_2N_6$ at room temperature, we find that the structure is preserved down to 21 GPa and no X-ray decomposition was detected. On unloading at 78 K, the Raman spectra show clear signs of deterioration of this compound at 22 GPa, where the characteristic bands become weaker and other broad bands at 400, 1800, 2100 and 2300 cm$^{-1}$ increase in intensity (Supplementary Fig. 8). The product is difficult to identify; it is definitely not azide as there is no sign of the characteristic N–N stretching mode of the linear $N_5$ groups. Based on observations of a number of high-frequency modes this product is probably a highly disordered state with elongated $N_2$ molecules. The Raman spectrum of this material is qualitatively similar to that of the cold compressed azide (Fig. 2).

Laser heating to 2500 K of laser- and X-ray-unexposed KN, azide, first pressurized to 50 GPa and then unloaded at room temperature to 30 GPa, results in the formation of a shiny material that looks similar to $K_2N_6$ but is different in structure and composition judging from single-crystal XRD and Raman spectroscopy measurements (Fig. 5). Similar results were obtained in the loading cycle probed by Raman. The reaction products tend to be textured and
single crystals of good quality and sufficient sizes can be selected by mapping the heated sample area. This material is stable to X-ray irradiation, unlike the initial KN₃ azide. The structure and composition of the synthesized material were directly solved to be I₄/a/amd K₃(N₂)₄ (which is isostructural with Na₄(N₂)₄; Supplementary Table 4). This material has been synthesized in similar P-T conditions in our previous work.⁶²

Discussion

Past experiments on various azides at high pressures showed the stability of the linear N₃⁻ ion to at least 60 GPa, judging from vibrational spectroscopy.⁶⁴–⁶⁶. Theoretical calculations predict a major phase transformation within this chemical structure to a monoclinic C2/m, where the linear N₃⁻ groups become collinear on forming the C2/m structure. LiN₃ at ambient pressure and α-NaN₃ at 0.3–17 GPa have the same structure.⁶⁷–⁷⁰,⁷¹ However, our experiments show that this transformation does not occur in potassium azide up to at least 50 GPa. At room temperature, KN₃ is reported to transform under pressure to another phase with linear N₃⁻ groups, but the structure of this phase is not monoclinic C2/m. Instead our data (Supplementary Figs. 2–4) show that it prefers to remain in an only slightly distorted I₄/mcm structure, preserving the original lattice to at least 50 GPa; however, the azide ion becomes chemically unstable in this regime as manifested by formation of other yet-unidentified polynitrogen species above 30 GPa (as evidenced via emergence of a 1900 cm⁻¹ Raman band; Supplementary Fig. 1) a process that is accelerated by X-ray radiation exposure.

These results show that the azide ion N₃⁻ configuration becomes unstable at high pressures. Our high-pressure laser heating experiments revealed two new classes of compounds that become stable at these conditions. The structural and vibrational spectroscopy data provide concerted consistent data identifying their physical and chemical structure.

The N₃⁻ hexazine dianion ring compound discovered here represents a previously unobserved polynitrogen configuration with low-order nitrogen–nitrogen bonds. The energy yield for this prototypic material can be estimated from the enthalpy versus pressure curves extrapolated to ambient pressure. This yields about 160 kJ mol⁻¹ (1.7 eV), which is comparable to that of a common explosive. Although this material cannot be recovered to ambient pressure, we hope that this study will help with the search and synthesis of other polynitrogens, which are potentially energetic and recoverable.

Laser heating of KN₃ azide at 30 GPa results in the formation of an unexpected diazenide I₄/a/amd K₃(N₂)₄ with a complex structure, which contains potassium atoms and elongated N₄⁻ polyanions with different site symmetries, and a very large unit cell. The theoretically predicted C2/m azide polymorph is not obtained even though the transformation barrier (Supplementary Fig. 5) is not very high and can definitely be overcome with laser heating assistance. It is interesting that the diazenide structure does not seem to reveal more efficient packing than azide as the specific volume of K₃(N₂)₄ is very similar to that of KN₃ azide (Fig. 3). It is likely that synthesis of this structure is at least partially due to its high entropy.
stemming from rotating dinitrogens. By contrast, the formation of K3N6 with hexazine diannions rings at 50 GPa is accompanied by a large volume contraction (about 17%), which explains the importance of pressure in its synthesis. This transformation leads to the formation of few-bonded polynitrogen species, at relatively low pressure compared to monatomic polymeric nitrogen.

Varying the reagent compositions during the synthesis (for example, by providing an excess of nitrogen) would lead to the formation of compounds other than the ones explored here. Our preliminary experiments suggest that laser heating of K3N6 in N2 results in a wealth of new compounds, including various polyatomic/nitrogen species, with different compositions and structures; these results will be presented in detail elsewhere.

Conclusions

Our experiments show that the azide group N3− is prone to chemical destabilization under pressure, as evidenced by a loss of crystallinity of the compressed sample at 300 K, spontaneous emergence of extra Raman bands, and sensitivity to X-ray radiation. The reaction products likely comprise modified variety of nitrogen species such as, for example, dinitrogen-containing compounds and/or square planar D3h N6+ (ref. 34); however, the lack of crystallinity hinders their identification. Depending on the pressure of the synthesis, two new crystalline materials form following laser heating: hexazine diannions ring stabilized in K3N6 above 45 GPa, which remains metastable down to 20 GPa, and an unusual K(N3)2 diazidine at 30 GPa. Neither compound, however, was stable under ambient conditions. The high-pressure synthesis of polynitrogen compounds from azides may be scalable, and may promote the formation of various polyatomic/nitrogen species with different compositions and structures.

Online content

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Methods
DAC experiments. The high-pressure, high-temperature behaviour of KN₃ was studied on two samples intended for combined XRD/Raman measurements and another four samples for Raman measurements. BX90-type DACs, equipped with Bowles-Almac type seats and conical diamond anvils, and symmetrical-type DACs, with standard design seats and diamond anvils (Almax, EasyLab), were used for single-crystal/powder diffraction and Raman measurements, respectively. A powder sample of potassium azide KN₃ was placed in sample chambers of DAC equipped with diamond anvils with the culets of 100–300 μm in diameter for single-crystal and powder-diffraction XRD and Raman experiments. Rhenium foil preindented to a thickness of 30 μm was served as a gasket. Ruby chips were placed inside the sample chambers for pressure measurement.

The XRD sample had no pressure-transmitting medium. All of the Raman samples were loaded with nitrogen gas at a high pressure of 0.15 GPa at room temperature. Raman samples 1 and 2 were quenched to below 2 GPa with different gaskets: DACs served as a gasket. Raman samples 2 and 4 were quenched to below 4 GPa at liquid-nitrogen temperature using a continuous flow He/N₂ cryostat. All samples were compressed up to the target pressures and laser-heated (λ = 1064 nm) using double-sided laser-heating systems of the GSECARS (APS, Argonne) or ISSP (Heife) beamlines (see below). Laser heating of KN₃ in the DAC was performed without any absorber by directly coupling near infrared laser radiation with the sample. KN₃ is a weak absorber at 50–60 GPa; however, it can be coupled to the laser via grain boundaries and other defects, although care must be taken as it tends to run away once the temperature becomes higher than approximately 1000 K. Thus the temperature at which the reported below reactivity is reported should be considered cautiously. The heat-exchanger system becomes non-transparent; we performed XRD and Raman mapping of these areas where available.

X-Ray diffraction measurements were performed at the GSECARS beamline (13IDD, APS, Argonne). We used monochromatic X-ray beam (λ = 0.2952 Å) focused down to 3 × 3 mm² by a Kirkpatrick–Baez mirror system and diffraction patterns were collected on a Pilatus 1M detector (CdTe). For the single-crystal XRD measurements, samples were rotated around a vertical ω axis within a ±35° range. The diffraction images were collected with an angular step Δω = 0.5° and an exposure time of 1 s or 2 s per frame. Please see below for details on the single-crystal X-ray diffraction analysis and structural solution.

Raman spectra of the sample studied at GSECARS using XRD combined with laser heating were measured concomitantly using the GSECARS Raman system with the excitation wavelength of 532 nm in the spectral range of 10 to 4000 cm⁻¹ with a 4 cm⁻¹ spectral resolution (see below). The Raman spectra of the laser heated at ISSP samples were examined with 532 and 660 nm excitation lines using a similar custom system coupled to a continuous flow cryostat (see below).

Laser heating and cryogenic cooling systems. The double-sided laser-heating systems of GSECARS (APS, Sector 13, Argonne)¹⁰ features the flat top focal spot of 10 μm in diameter. The sample temperature was measured radiometrically (grey body approximation). The thermal radiation was recorded with a Princeton grating spectrometer (300 mm focal length) combined with PIXIS and PiMx charge-coupled detector array detectors.

The double-sided laser heating system at ISSP (Heife) is combined with the Raman confocal system thus making concomitant Raman probing of the heating area very convenient. Another similar Raman system coupled to a continuous flow He/N₂ cryostat was used for Raman experiment, where the sample was investigated following unloading at room and low (78 K) temperatures.

Raman systems. The full description of the confocal GSECARS Raman systems, which has been used concomitantly to XRD measurements, has been published elsewhere.¹⁰ It features five excitation laser lines from the ultraviolet to the infrared, which can be automatically changed and double-sided laser heating.

Two Raman systems at ISSP (Heife) are described in the previous sections.

Single-crystal XRD analysis. We used the CrysAlis software package for the analysis of the single-crystal diffraction data (indexing, data integration, frame scaling and absorption correction). To calibrate an instrumental model in the CrysAlis software, that is, the sample-to-detector distance, detector's origin, offsets of goniometer angles, and rotation of both X-ray beam and the detector around the instrument axis, we used a single crystal of orthoenstatite (Mg_(1.93)Fe_(0.06))(Si_(1.93), Al_(0.06))O₆, Pbca space group, a = 8.81172(2), b = 5.18320(10) and c = 18.2391(3) Å). Using the Olex2 crystallography software package, the structures were solved with the SHLEXT structure solution program utilizing Intrinsic Phasing and refined with the SHELXL refinement package using least-squares minimization. The single-crystal diffraction images were integrated to powder patterns with Dioptas software.¹⁰ Le-Bail fits of the diffraction patterns were performed with the Jana2006 software.¹⁰ A- and B-level alerts of the IUCr's CheckCIF routine are related to data incompleteness, which is unavoidable in a high-pressure diffraction experiment.

Structural analysis of cold-compressed KN₃. Most of the cold-compressed KN₃ sample produces weak powder diffraction pattern, as shown in Supplementary Fig 2; however, we were able to locate the grain that produces the poor-quality single-crystal diffraction pattern. The diffraction patterns collected at the positions of the powder-like and single-crystal samples demonstrate that the same phase is present in both collection spots. The peak positions are only slightly different, which can be explained by pressure gradients in the sample without a pressure-transmitting medium. The differences in the distribution of intensities are clearly related to the strong preferred orientation of the single-crystal sample.

The unconstrained lattice determination from the single-crystal XRD dataset reveals the I-centered lattice with a = 5.425(3), b = 5.487(1), c = 4.67(4) Å, α = 90.64(2)°, β = 92.2(4)°, γ = 90.22(17)°. These parameters are close to the parameters expected for the I₄/mcm KN₃, compressed to ~50 GPa; however, the structure is clearly distorted. The refinement of the I₄/mcm KN₃ structure using our single-crystal dataset resulted in the good agreement factor Rᵢ = 11.03% for 32/5 data to parameter ratio. This agreement demonstrates that we indeed deal with the distorted I₄/mcm structure rather than with a completely different structure type, like predicted C2/m KN₃. The unconstrained lattice refinement suggests either monoclinic or triclinic symmetry. By a group–subgroup transformation we have generated the I2/c model of KN₃, from the high-symmetry I₄/mcm. The refinement converged with a slightly worse Rᵢ = 13.73% at a 56/8 data/parameter ratio. Although this value is higher than for the I₄/mcm model, the use of monoclinic symmetry is justified by the lattice parameters. We provide the structure model of I2/c KN₃ below (Supplementary Table 1) with a notice that the quality of the dataset allows to distinguish main structural motifs, while it should not be used for the judgement about specific structure details. For example, although the refined N–N distances in the azide group are reasonable (1.17(1) Å) these should not be considered when comparing these parameters with other azides at similar conditions. Similarly, further symmetry reduction to triclinic does not provide additional reliable structural information.

Theoretical calculations. First-principles calculations were conducted using the Vienna ab initio simulation package (VASP).¹¹ The structure was optimized using the density-functional theory within gradient approximation.¹² The cutoff energy of plane waves was set to 600 eV. The partition of the first Brillouin zone into a grid of k-points was carried out with a resolution 2 × 0.03 Å⁻¹. To calculate thephonon dispersion and Raman-active vibration modes of I point the PHONONI program was used with VASP interfaces.¹³ The electronic density of state and band structure were calculated at a resolution 2 × 0.015 Å⁻¹. Electron dispersion curves and density of states were plotted using the SUMO software.¹⁴ The crystal structures of I₄/mcm-KN₃, C2/m-KN₃, and P6/mmm-KN₃, were relaxed at 30 and 50 GPa. Using the relaxed structures, we constructed likely transition paths (20 for each transition) and optimized them, which allowed us to find the lowest energy path for each transition. At the first stage, the most convenient representations of the initial and final structures are sought; it allows one to determine the optimal representation of unit cells of these structures.¹⁵ At this stage, two unit cells are transformed to have the same number of atoms taking into account the total symmetry of non-equivalent supercells whose number is determined within the Hart–Fock–Fandely theory.¹⁶ For each of two structures, we work only with lattices and seek such unit cell settings (among all possible choices of the unit cell) that are closest to each other. At the second stage, atoms are placed back into two generated supercells and the algorithm finds such correspondence, or mapping, between the two structures such that the total distance travelled by all of the atoms, from the initial to the final structure, is minimal.¹⁷ It is important to note that the mapping algorithm is not commutative; thus, for each pair of structures, the algorithm produced the ten likeliest A → B and B → A paths, respectively. The above-mentioned initial paths of phase transitions were optimized using the variable-cell nudged-elastic-band method as implemented in USPEX.¹⁸ Each path consisted of 20 intermediate structures (images). The I₄/mcm-KN₃ has 16 atoms in the unit cell, whereas C2/m-KN₃, and P6/mmm-KN₃, have eight atoms. According to the mapping algorithm, two end structures must be extended to the cell with an equal number of atoms. Thus, the transitions from I₄/mcm-KN₃, to C2/m-KN₃, at 30 GPa and from I₄/mcm-KN₃, to P6/mmm-KN₃, at 50 GPa were simulated in cells with 16 atoms. The transition from C2/m-KN₃, to P6/mmm-KN₃, at 50 GPa was simulated in cells with 8 atoms. In order to obtain accurate determination of transition states and intermediate minima corresponding to metastable transition states, we used the climbing image–descending image technique.¹⁸ The spring constants for the variable-cell nudged-elastic-band method were varied from 3 to 6 eV Å⁻¹. The halting criterion for the calculation was set as root mean square forces on images that are less than 0.003 eV Å⁻¹. All calculations were based on density functional theory within the generalized gradient approximation (PBE functional), and the projector augmented wave method as implemented in the VASP package.¹⁹ The plane–wave energy cutoff of 600 eV was used, ensuring excellent convergence of total energies, forces and stresses.

Crystal structures were relaxed until the maximum net force on atoms became less than 0.01 eV Å⁻¹. The Monkhorst–Pack scheme was used, ensuring excellent convergence of total energies, forces and stresses.

Data availability
The datasets generated during and/or analysed during the current study are available at https://doi.org/10.6084/m9.figshare.19236573 (ref. 18).
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Author contributions

Y.W., M.B. and A.F.G. conceived the research and designed the experiments. Y.W., M.B., X.Z., E.G., S.C., B.B. and S.-q.J performed the experiment. E.B., Y.W., M.B. and A.F.G. analysed the data. I.C., A.S. and A.R.O. performed and analysed the calculations. A.F.G., Y.W., M.B. and A.S. wrote the manuscript. All authors reviewed and discussed the manuscript during preparation.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to Alexander F. Goncharov.

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