Stabilization of pentazole anions in the high-pressure compounds Na₂N₅ and NaN₅ and in the sodium pentazole framework NaN₅·N₂†

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Synthesis and characterization of nitrogen-rich materials is important for the design of novel high energy density materials due to extremely energetic low-order nitrogen–nitrogen bonds. The balance between the energy output and stability may be achieved if polynitrogen units are stabilized by resonance as in cyclo-N₅⁻ pentazole salts. Here we demonstrate the synthesis of three oxygen-free pentazole salts Na₂N₅, NaN₅ and NaN₅·N₂ from sodium azide NaN₃ and molecular nitrogen N₂ at ~50 GPa. NaN₅·N₂ is a metal-pentazole framework (MPF) obtained via a self-templated synthesis method with nitrogen molecules being incorporated into the nanochannels of the MPF. Such self-assembled MPFs may be common in a variety of ionic pentazole compounds. The formation of NaN₅·N₂ demonstrates that the cyclo-N₅ group can accommodate more than one electron and indicates the great accessible compositional diversity of pentazole salts.

Introduction

The pentazole anion cyclo-N₅⁻, the recently discovered all-nitrogen structural unit, has attracted much attention due to potential application of nitrogen-rich compounds as high-energy density materials. Although this five-membered ring is formed with the high-energy nitrogen–nitrogen bonds, its aromaticity provides good thermal stability to pentazole salts. In 2017, the pentazole anion was generated by direct cleavage of the C–N bond in a multisubstituted arylpentazole using m-chloroperbenzoic acid and ferrous bisglycinate. Although this five-membered ring is formed with the high-energy nitrogen–nitrogen bonds, its aromaticity provides good thermal stability to pentazole salts. In 2017, the pentazole anion was generated by direct cleavage of the C–N bond in a multisubstituted arylpentazole using m-chloroperbenzoic acid and ferrous bisglycinate and stabilized by the compound [Na(H₂O)₂(N₅)₂]·2H₂O, [M(H₂O)₄(N₅)₂]·4H₂O (M = Mn, Fe and Co), and [Mg(H₂O)₆(N₅)₂]·4H₂O were synthesized. In 2018, all these salts containing the isolated cyclo-N₅⁻, large amounts of coordinated water molecules were present in the crystal structure, which played an irreplaceable role in stabilizing the cyclo-N₅⁻ anion through extensive hydrogen bond interactions. A series of pentazole frameworks like AgN₅, Cu[N₃](N₅) and Na₄6N₂40O15 were obtained in ion exchange reactions with [Na(H₂O)(N₅)]·2H₂O. In these water-free salts, the stabilization of cyclo-N₅⁻ is achieved by its coordination to metals and π–π stacking interactions. The Na₄6N₂40O15 compound has an unprecedented zeolitic architecture with Na₂0N₆0 and Na₂4N₆0 nanocages indicating a great potential for the synthesis of other metal-pentazole frameworks.

At the same time, the synthetic route to the pentazole anion was approached from a completely different perspective. Due to the great stability of cyclo-N₅⁻, this structural unit emerges in ionic high-pressure polynitrides. Steele et al. synthesized cesium pentazole CsN₅ in a one-step reaction between CsN₃ and N₂ in a diamond anvil cell at ~60 GPa. Similarly, LiN₅ was synthesized from elements at 45 GPa and appeared to be metastable under ambient conditions. Various metal pentazolates (pentazolates of Na, K, Rb, Be, Mg, Ba, Al, Ga, Sc, Y, and Zn) have been recently predicted using modern structure search algorithms, but have not yet been discovered experimentally. Here we studied the reactions between NaN₃ and nitrogen in laser-heated diamond anvil cells attempting to extend the series of water and oxygen-free alkali–metal pentazolates. Surprisingly, in addition to the...
expected simple sodium pentazolate salt NaN₅, we have also synthesized a never predicted complex pentazolate framework structure with incorporated dinitrogen molecules (NaN₅·N₂) and the sodium-rich pentazolate Na₂N₅. Synthesis of the complex NaN₅·N₂ demonstrates the high-pressure self-templated approach to polynitrides.

Results and discussion

Synthesis of Na₂N₅ by high-pressure high-temperature decomposition of NaN₃

First, we discuss the high-pressure behavior of pure NaN₃ in the experiment where no molecular nitrogen was added to a sample chamber (sample #1). Non-heated NaN₃ at ~50 GPa produces a very weak diffraction pattern with a few broad peaks, which makes its unambiguous indexing impossible as has already been reported.²⁹ Although some high-pressure polymorphs of NaN₃ were predicted to be thermodynamically stable under these conditions, their formation can be prohibited by the large kinetic barriers.²⁰ It should be noted that NaN₃ is sensitive to hard X-rays, which is evidenced by the darkening of the sample and the appearance of new broad Raman bands (Fig. 1). X-ray exposure does not induce crystallization of the new product, which is apparently amorphous in nature (Fig. S1†) and may contain new types of N–N bonds formed because of the interactions between the azide ions. The Raman spectrum of the X-ray induced product agrees with the Raman spectrum of NaN₃ reported by Eremets et al.,²¹ who compressed NaN₃ without exposing it to hard X-rays. This suggests that X-ray and laser-induced photochemical processes are similar.

To overcome the kinetic barriers and to crystallize new compounds, the sample was laser-heated at ~50 GPa. At a high temperature of ~1800 K the strongest peaks on the diffraction pattern can be very well indexed with the hexagonal unit cell with \( a = 4.8380(6) \) Å and \( c = 2.6009(8) \) Å (Fig. 1c). Upon cooling the sharp peaks split indicating the symmetry lowering (Fig. 1e). Structure refinement against the single-crystal X-ray diffraction dataset of the temperature-quenched sample revealed the composition of the new phase as Na₂N₅. It crystallizes in the monoclinic space group \( Pn \) (No. 6) with \( a = 4.781(10) \) Å, \( b = 2.5873(7) \) Å, \( c = 4.934(12) \) Å, and \( \beta = 119.6(3)° \) at ~50 GPa. Nitrogen atoms form cyclo-N₅ rings stacked along the \( b \)-axis as shown in Fig. 2b. Sodium atoms form a hexagonal sublattice and define the pseudo-hexagonal symmetry of Na₂N₅. Due to the presence of only one N₂ ring in the unit cell, the sixfold rotation axis is a forbidden symmetry operation in Na₂N₅ at ambient temperature. Nevertheless, the lattice parameters show no monoclinic distortion at high temperature suggesting that hexagonal symmetry is fully restored, probably, due to the orientational disorder of N₅ groups.

Interestingly, the formal charge on the N₅ anion is ~2, which means that the Hückel \( 4n + 2 \) rule is not fulfilled. Therefore, it can be expected that an extra electron partially filling the antibonding orbitals of cyclo-N₅ will lead to the metallic properties of Na₂N₅. The calculated phonon dispersion curves for Na₂N₅ exhibit no imaginary frequencies demonstrating the dynamic stability of this compound (Fig. S2†).

Fig. 1  (a) Raman spectra acquired at different positions of the NaN₃ sample (sample #1) compressed up to ~50 GPa. Colour codes correspond to Fig. 1b. (b) Microscopic image of the sample chamber at ~50 GPa. Red circle shows an area, where the sample was laser-heated, and X-ray exposed before acquiring the Raman spectrum. Green area was laser-heated only, and the orange area was subjected to X-ray exposure for 20 min at 37 keV. (c) Le-Bail fit of the diffraction pattern obtained during laser-heating of NaN₃ at 1800 K \( (P6/m, a = 4.8457(6), \text{and } c = 2.6289(8) \text{ Å}) \). (d) Le-Bail fit of the diffraction pattern obtained after laser-heating of NaN₃ \( (Pm, a = 4.781(10) \text{ Å}, b = 2.5873(7) \text{ Å, } c = 4.934(12) \text{ Å, and } \beta = 119.6(3)°) \). (e) Comparison of the diffraction patterns of hot and temperature-quenched samples.
The Raman spectrum of Na$_2$N$_5$ is shown on the Fig. 1a. It is characterized by the disappearance of the strong peak around 1500 cm$^{-1}$ that corresponds to the stretching vibrations of the azide ion and the emergence of broad bands centered around 230, 440 and 1160 cm$^{-1}$ at $\sim$50 GPa.

This product is not sensitive to X-rays like the starting material as the Raman spectra of X-ray exposed and non-exposed samples match very well (Fig. 1a).

**Synthesis of sodium pentazolate (NaN$_5$) and sodium pentazole framework (NaN$_5$·N$_2$)**

Laser-heating of the NaN$_3$ + N$_2$ sample (sample #2) at $\sim$52 GPa and 2200(200) K results in the formation of a series of novel Na–N compounds. Due to the intrinsic inhomogeneity of the sample, the Na : N ratio varies across the sample chamber. In the bulk of the NaN$_3$ piece, the Na : N ratio is close to 1 : 3, while on the border between NaN$_3$ and N$_2$ one can expect the formation of phases with N : Na $> 3$. This inhomogeneity, typical for high-pressure DAC experiments, makes the synthesis of phase-pure samples challenging, but at the same time allows to probe wide compositional interval in one experiment. In this study we combined high-resolution Raman mapping with X-ray diffraction analysis to spatially resolve various phases of the laser-heated sample. Already from the microscopic image one can recognize several visually distinct areas: the semi-transparent area close to the gasket (non-heated and non-X-ray exposed NaN$_3$), dark material (heated and X-ray exposed area), several transparent spots in the heated area looking like “holes” in the sample and the fully transparent area filled with nitrogen. The Raman spectra acquired from these areas have significantly different features. The Raman spectrum acquired from the bulk of the sample is similar to that of NaN$_2$N$_5$, while the Raman spectra acquired at the positions of transparent spots (Fig. 3g) contain numerous sharp Raman peaks which indicate the formation of well-crystallized compounds. Each region of the sample was probed by synchrotron X-ray diffraction, which allowed a detailed structural analysis of all novel phases.

**Sodium pentazolate (NaN$_5$)**

X-ray diffraction analysis at the positions of the transparent heated spots of sample #2 featuring sharp Raman peaks (Fig. 3b, e and g) revealed the formation of multiple well-crystallized single-crystal grains of new phases and it was possible to apply the methods of single-crystal X-ray diffraction to solve and refine the crystal structures of the new compounds (Fig. S3 and S4†). The first compound with a composition NaN$_5$ crystallizes in the orthorhombic space group $Pmm2_1$ (No. 31) with $a = 5.455(6)$, $b = 2.836(12)$, $c = 5.662(8)$ Å, and $V = 87.6$ (4) Å$^3$ at 52.9 GPa. Full crystallographic information is provided...
in the ESI and in Table S2.† Nitrogen atoms form five-membered planar rings with almost equal N–N distances (2 × 1.301 (7) Å, 1.286(8) Å and 1.290(7) Å). No restrictions on the shape or interatomic distances were applied during the structure refinement procedure. Slight differences between the N–N distances in aromatic cyclo-N₅⁻ rings are common in asymmetric or complex crystal environments.⁵,²⁷ The refined distances are only slightly shorter than the average N–N bond distances of the all reported cyclo-N₅ salts (e.g. [Na(H₂O)₃(N₅)]·2H₂O: 1.316 Å; [Mg(H₂O)₆(N₅)₂]·4H₂O: 1.316 Å; [Mn(H₂O)₆(N₅)₃]·4H₂O: 1.320 Å; [Fe(H₂O)₆(N₅)₃]·4H₂O: 1.329 Å; [Co(H₂O)₆(N₅)₂]·4H₂O: 1.314 Å; [Zn(H₂O)₆(N₅)₂]·4H₂O: 1.328 Å; and (N₅)₆(H₃O)₃(NH₄)₄Cl: 1.315 Å).¹ This demonstrates that the compression mechanism of pentazolate salts primarily affects the intermolecular distances leaving the N₅ units almost undistorted. The symmetric shape of the cyclo-N₅⁻ pentazolate anion agrees with its aromatic character: with 6 electrons in the delocalized π-system the Hückel rule is fulfilled. Each sodium atom is coordinated by seven pentazolate rings and each ring is coordinated with seven sodium atoms with the Na–N distances varying between 2.183(8) Å and 2.380(11) Å, as shown in Fig. 4. Pentazolate rings stack along the b-axis with an offset and with the distance of ~2.42(1) Å between the ring planes and 2.836(12) Å between the N₅ centroids. These distances are expected significantly shorter than the typical π–π stacking distances under ambient conditions (e.g. ~3.47 Å in AgN₅), but they may play a decisive role in the stabilization of this compound.²⁹

Hitherto, high-pressure alkali metal pentazolates were synthesized in the Cs–N and Li–N systems.⁵,¹⁰ The CsN₅ and LiN₅ phases lack a detailed structural analysis, but both clearly have structures different from NaN₅. LiN₅ crystallizes in the monoclinic P2₁ symmetry with a = 3.808(1) Å, b = 3.838(1) Å, c = 2.410 (1) Å, and β = 99.84(1)°, yielding a volume of V = 34.70(4) Å³ at 73.6 GPa. CsN₅ at 60 GPa is triclinic with V = 349.75 Å³. Apparently quite different atomic radii of alkali metals Li, Na and Cs lead to the stabilization of different structural types.

Steele et al. predicted that NaN₅ with symmetry Cm would be thermodynamically stable at 50 GPa. This does not agree with our result, but we should note that the predicted Cm structure has remarkably similar structural motifs with the experimental Pmn2₁ structure (Fig. S5†). Therefore, it is possible that these two structures can be energetically close to each other. In order to investigate this further, we have performed theoretical calculations within the framework of density functional theory, where the relative enthalpies of the experimental Pmn2₁ and predicted Cm NaN₅ were considered. The Pmn2₁ type structure appeared to be more stable than Cm-NaN₅ by ~0.15 eV per atom at 50 GPa. Recently Zhou et al. reported the formation of Cm-NaN₅ by room-temperature compression of NaN₅.³⁰ The compound was identified in a three-phase mixture by comparison of the theoretically predicted lattice and the experimental powder pattern, but the structure refinement was not performed. We cannot exclude the formation of metastable Cm-NaN₅ in the experiments of Zhou et al.: compression of the crystalline phases at low temperatures beyond their stability range often results in the formation of metastable materials.³¹

The Raman spectrum acquired from a sample area shown in Fig. 3g agrees with the expected modes of the pentazolate group. The strongest peak corresponding to the N₅ breathing mode is observed at 1319 cm⁻¹ at 48 GPa. This is in a very good agreement with the studies of LiN₅ (~1310 at 42 GPa (ref. 10)) and CsN₅ (1320 cm⁻¹ at 55 GPa (ref. 9)). The strong Raman peak observed at ~800 cm⁻¹ corresponds to the out-of-plane vibrations of nitrogen atoms. The theoretically calculated Raman spectrum of NaN₅ is shown in Fig. S6.† There is a fair agreement between the observed and calculated modes of the pentazolate groups, however an apparent complexity of the experimental Raman spectra compared to the calculated spectra and to LiN₅ and CsN₅ suggests that additional phases might be present in the same sample area as also confirmed by the XRD analysis (see below). It is worth noting that the Raman modes of N₅ rings in NaN₅ and Na₂N₅ differ substantially in the position and linewidth of the peaks (Fig. 1(a) and

Fig. 4 Crystal structure of NaN₅ at ~47 GPa shown in different projections. Yellow and blue spheres show the positions of sodium and nitrogen atoms, respectively. The lower portion of the figure shows the stacking geometry of the pentazolate rings, where stacked rings are color-coded for clarity. Distances are given in Å. E.s.d. values of bond distances can be found in the ESI.† Distances between the N₅ ring planes were calculated using Diamond 4.6.4 software.³²

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Sodium pentazolate framework NaN₅·N₂ compound

Another single-crystalline phase was found together with NaN₅ at 47 GPa. It crystallizes in the monoclinic space group P2₁/n with a = 10.321(3), b = 8.672(3), c = 11.0409(17) Å, β = 91.70(2)°, and V = 987.8(5) Å³. The structure contains two types of nitrogen species: pentazolate rings cyclo-N₅⁻ and dinitrogen units N₂. The unconstrained refinement of the crystal structure suggests the planar shape of the N₅ units, which was constrained to planar during the final refinement for the improvement of the data/parameter ratio. The N–N distances in pentazolate vary in the range of 1.26–1.32 Å and the Na–N₅ distances in the range of 2.1–2.4 Å, in agreement with NaN₅. Structure solution revealed the composition of this compound as NaN₇.

The structure of NaN₅·N₂ is shown in Fig. 5. The Na⁺ and N₅⁻ ions form a framework with wave-like channels running along the b-axis. Dinitrogen molecules fill these channels and possess several types of environments (Fig. 5d). Some molecules are embedded between the pentazolate rings and are aligned either almost parallel or perpendicular to them. Other molecules have quite short contacts with the Na atoms (starting at ~2.2 Å), but this interaction is not reflected in the elongation of the N–N bond, which remains around 1.1 Å. The refined N–N distances in the N₂ units (1.04–1.10 Å) are close to the distances typical for the triply bonded N≡N molecule. This suggests that no significant charge transfer occurs between Na and the N₂ units, and the formula of the compound may be presented as NaN₅·N₂. The Raman spectrum acquired at the position of the NaN₅ + NaN₇ mixture (Fig. S7†) has a peak at ~2190 cm⁻¹, which is ~200 cm⁻¹ lower in frequency than the Raman vibron of e-N₂ at this pressure. This indicates a very slight elongation of the N₂ molecule embedded into the channels. Apparently no π–π interactions between the pentazolate groups are present in NaN₅·N₂.

Therefore, the cyclo-N₅⁻ groups in this compound are mainly stabilized by sodium-pentazolate coordination.

Metal-inorganic frameworks with embedded dinitrogen units Hf₂N₂₀·N₂, WN₈·N₂, ReN₆·N₂ and Os₅N₂₈·3N₂ were recently synthesized at pressures above 1 Mbar²²,²⁴ and also predicted in several transition metal compounds. These compounds contain polymeric nitrogen chains that serve as linkers in the frameworks. With the example of NaN₅·N₂ we show that these framework compounds can appear in ionic polynitrides at high pressure too. Therefore, a complex inclusion compound is the natural and common form of all kinds of high-pressure polynitrides. The balance between the molecular and polymeric nitrogen at high pressure is defined by two factors: the triple N≡N bond is very stable and has a very large internal energy, while the single and double bonds are not that strong. At the same time, the dinitrogen molecule with its complete electronic shell usually remains non-bonded, and therefore, has a large volume defined by the van der Waals radius of N. This leads to a significant contribution of the PV term to the enthalpy as the pressure increases. Because of this, the polymerization of bulk nitrogen occurs at >100 GPa.³⁴ Below this pressure the nitrogen molecule is a stable structural unit and may serve as a template molecule for the self-assembly of framework structures.

Stability on decompression

To study the stability region of Na₂N₅, NaN₅ and NaN₇ the sample was gradually decompressed. NaN₇ could not be well resolved at pressures below 40 GPa. NaN₅ can be detected down to ~18 GPa by Raman spectroscopy, while at the next pressure point (~13.6 GPa) the broad band between 900 and 1200 cm⁻¹ disappears (Fig. S8†). The crystal quality of NaN₅ becomes worse with decreasing pressure, but the phase can be clearly detected by XRD down to ~25 GPa (Fig. 6a). The strongest Raman peak of NaN₅ (N₅⁻ breathing mode) remained until ~12 GPa (Fig. 6b).

In our previous studies of NaN₅₃, under high-pressure high-temperature conditions we performed laser-heating of the sample at around 27 GPa without the addition of extra nitrogen.³⁶ Under these conditions, an unusual compound Na₃[N₅]₄ which has a non-integer formal charge on the dinitrogen unit was formed. In that experiment one could not expect the formation of nitrogen-rich phases with a N:Na ratio sub-
stantially higher than 3. In the current experiment we explored the possibility of the formation of nitrogen-rich phases in this pressure region by heating NaN₃ with N₂ at around 34 GPa. Sample #2 was laser-heated at the very edge of the NaN₃ piece to ensure the excess nitrogen (Fig. 7a). Single-crystal diffraction analysis of the reaction products at the heated spot evidenced the formation of Na₃(N₂)₄ similar to that in the experiment without extra nitrogen (Table S2†). The unit cell volume of Na₃(N₂)₄ is in good agreement with the results of our previous studies (Fig. 7c). This allows us to conclude that pentazolates cannot be produced from NaN₃ + N₂ even with excess nitrogen at pressures below 35 GPa.

At a pressure of 14 GPa laser-heating of NaN₃ with excess N₂ leads to the formation of P4/mmm NaN₂, previously synthesized at 4 GPa (Fig. 8). As discussed by Holtgrewe et al. and Bykov et al. in a low-pressure region both X-ray and laser radiation induce various photochemical transformations in sodium azide leading to amorphous phases. Therefore, in previous studies, it was challenging to distinguish between the Raman spectra of the photoinduced products and the Raman spectrum of NaN₂. Here using the combination of X-ray and Raman mapping we could solve this task (Fig. S9†). The Raman spectrum of NaN₂ is very simple with two active modes

![Fig. 6](image_url)  
(a) Pressure dependence of the unit cell volume of NaN₅. Red line corresponds to the 2nd order Birch–Murnaghan equation of state with V₀ = 148.0(4) Å³ and K₀ = 33.0(4) GPa. (b) Pressure dependence of the Raman peaks of NaN₅. With decreasing pressure some peaks could not be resolved anymore.

![Fig. 7](image_url)  
(a) Microscopic image of the sample heated at ~34 GPa. Newly heated areas are shown by red circles. (b) Crystal structure of Na₃(N₂)₄. (c) Pressure dependence of the unit cell volume of Na₃(N₂)₄. Red circle – data from this paper. Blue – from ref. 36. Orange line corresponds to the 3rd order Birch–Murnaghan equation of state with V₀ = 582(6) Å³, K₀ = 28.5(2.8) GPa, and K’₀ = 4.4(5).

![Fig. 8](image_url)  
(a) Microscopic image of the NaN₃ + N₂ sample laser-heated at ~14 GPa. Heated area is highlighted. The pressure slightly dropped after heating. (b) The crystal structure of NaN₂. (c) Pressure dependence of the unit cell volume of NaN₂. Red circle – data from this paper. Blue – from ref. 36. Orange line corresponds to the 2nd order Birch–Murnaghan equation of state with V₀ = 40.5(1) Å³ and K₀ = 29.1(5) GPa.
A1g and Eg. The most distinct Raman peak A1g corresponding to the N–N stretching vibration appears at 1960 cm\(^{-1}\) (Fig. S9†). The N–N stretching frequency is directly correlated with the N–N bond length according to Badger’s rule \(d_{NN} \sim A^{-2/3} + \delta\).\(^{18}\) The frequency of 1960 cm\(^{-1}\) agrees well with the refined bond distance of the \([N_2]^-\) unit of 1.16 Å at 4 GPa, demonstrating the charge transfer from Na to the \(N_2\) units.

**Conclusion**

In this study we discovered three novel high-pressure compounds in the Na–N system: Na\(_2\)N\(_5\), NaN\(_5\), and an unprecedented pentazolate framework NaN\(_5\)·N\(_2\). The transformation diagram in the NaN\(_3\) + N\(_2\) system is shown in Fig. 9. The formation of metal-pentazolate frameworks through a high-pressure self-templated synthesis method constitutes a major advance in cyclo-pentazolate chemistry.

**Experimental**

**Synthesis**

In all the experiments discussed in this article, powder NaN\(_3\) (Sigma Aldrich, ≥99.5%, kept in a dry box) was placed inside the sample chamber of a BX90 diamond anvil cell. Sample #1 did not contain any pressure-transmitting medium, while sample #2 was loaded with nitrogen that served as a pressure-transmitting medium and as a reagent. Both samples were compressed up to ~50 GPa and laser heated (\(\lambda = 1064\) nm) using a double-sided laser-heating system of GSECARS (13IDD, APS, Argonne, USA). The typical heating time was around 10 s at each heating spot. The experimental conditions are presented in Table S1.†

**X-ray diffraction**

The reaction products contained multiple good-quality single-crystalline domains of novel phases and they were studied by synchrotron single-crystal X-ray diffraction at the beamline GSECARS 13IDD (APS, Argonne, USA) with the following beamline setup: \(\lambda = 0.2952\) or 0.3344 Å, beam size ~3 x 3 \(\mu\)m\(^2\), Pilatus CdTe 1 M detector. For the single-crystal XRD measurements samples were rotated around a vertical \(\omega\)-axis in the range ±33°. The diffraction images were acquired at an angular step \(\Delta\omega = 0.5^\circ\) and an exposure time of 2–5 s per frame. For analysis of the single-crystal diffraction data (indexing, data integration, frame scaling and absorption correction) we used the CrysAlisPro software package. To calibrate an instrumental model using the CrysAlisPro software, i.e., 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 \(((Mg_{1.93}Fe_{0.06})(Si_{1.93}Al_{0.06})O_6, Pbcn space group, a = 8.8117(2), b = 5.18320(10), and c = 18.2391(3) Å)\). Powder diffraction measurements were performed either without sample rotation (still images) or with continuous rotation in the range ±20°/ao. The images were integrated to powder patterns using the DIOPTAS software.\(^{18}\) Le-Bail fits of the diffraction patterns were performed using the Jana2006 software.\(^{20}\) The structure was solved based on the single-crystal XRD data using the ShelXT structure solution program\(^{41}\) by intrinsic phasing and refined using the Olex2 program.\(^{42}\) CSD 2051780, 2051781 and 2075304† contain the supplementary crystallographic data for this paper.

**Raman spectroscopy**

The Raman spectra of the samples were acquired using a GSECARS (Advanced Photon Source, Chicago, USA) Raman system with an excitation wavelength of 532 nm in the spectral range of 10 to 3000 cm\(^{-1}\) and a 4 cm\(^{-1}\) spectral resolution. Technical details of the system are described elsewhere.\(^{43}\)

**Calculations details**

The structures found in the experiment and in previous publications were recalculated with the norm conserving projector augmented waves (PAWs)\(^{44}\) and energy cut-off values of 750–830 eV using the DFT code CASTEP.\(^{45}\) CASTEP calculates finite basis set corrections by determining the total energy at three cut-off energies, and then numerically evaluating the derivative required in the correction term. Variational density functional perturbation theory (DFPT)\(^{46}\) was used to calculate the Raman spectra. Thirty irreducible k-points were used for electronic Brillouin zone integration and vDW-DF2 dispersion corrections were enabled.\(^{47}\) The band structure was calculated using the PBE functional.\(^{48}\) The k-point separation was 0.03 Å\(^{-1}\) for conducting and 0.06 Å\(^{-1}\) for insulating systems. The structures were considered converged when the force on each atom was less than 0.002 eV Å\(^{-1}\) and total energy tolerance was less than 10\(^{-8}\) eV. Deviation of the stress tensor from that defined by the target pressure was less than 0.001 GPa. The phonon dispersion calculations were performed using linear response and finite displacement methods implemented in the CASTEP\(^{45}\) code. Linear response provides an analytical way of computing the second derivative of the total energy with respect to a given perturbation. Spatial derivatives of the macroscopic polarization are calculated numerically along the eigenvectors of each Raman active phonon mode by calculating the polarization for each displacement. The Raman cross-section was calculated through appropriate space averaging of the spatial derivatives according to the formalism presented in ref. 49.
Author contributions

MB and AFG: conceptualization; MB: data curation; MB and IB: formal analysis; AFG and MFM: funding acquisition; MB, EB, SC, VBP, and AFG: investigation; MB and AFG: writing.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was sponsored by the Army Research Office and was accomplished under the Cooperative Agreement Number W911NF-19-2-0172. This research used the resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. We acknowledge the support of GeoSoilEnviroCARS (Sector 13), which is supported by the National Science Foundation – Earth Sciences (EAR-1634415). Use of the GSECARS Raman Lab System was supported by the NSF MRI Proposal (EAR-1531583).

Notes and references