Effect of pressure on sodium azide studied by spectroscopic method

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Abstract

The high-pressure Raman and IR measurements of NaN₃ were performed at room temperature with pressure up to 35.0 and 26.0 GPa, respectively. Three phase transitions of β-NaN₃ → α-NaN₃ → γ-NaN₃ → δ-NaN₃ were revealed at 0.5, 14.0, and 27.6 GPa. All fundamental vibrational modes were analyzed based on experimental and theoretical methods. The phase transition from β-NaN₃ to ε-NaN₃ is attributed to the shearing distortion of unit cell and the rotation of the azide ions with increasing pressure. The abnormal symmetric evolution of bending modes observed in IR measurements reveals the rotational behavior of azide groups upon compression. Moreover, the azide ions might evolve into an energetically favorable arrangement under a higher pressure.

1. Introduction

The peculiar structures and physicochemical properties of inorganic azides make them play a particular role in practical and scientific application [1–3]. Their roles as propellants, explosives, and even photographic materials at low temperature have been used extensively in industry and military [4–7]. Additionally, the unique linear azide groups of these azides, three nitrogen atoms linked essentially by double bonds, make them the model system for studying the crystal structures, lattice dynamics, and electronic structures of solids with complex chemical bonding beyond alkali halides and cyanides [8–11]. Recently, the high-pressure studies about metal azides have attracted great attention due to their distinctive precursor role in the formation of polymeric nitrogen, an excellent high-energy-density material. This results from the lower bonding energy of N≡N bond (418 kJ mol⁻¹) in azides compared to that of N≡N bond (954 kJ mol⁻¹) in N₂ [5]. The promising application of azides in forming the polymeric nitrogen opened a new perspective for the high-pressure studies of these compounds.

Alkali azides are ideal precursor for synthesizing the polymeric nitrogen due to their more stable characteristic compared to heavy metal azides and covalent azides. In recent discoveries, we have extensively attempts at exploring the high-pressure structural stability, electronic structure, and evolution of azide ions of these azides [12–17]. A series of pressure-induced phase transitions were observed in these substances and the interlayered shearing of unit cell and rotation of azide ions were revealed as the pressure below 30.0 GPa [12–15, 17]. With increasing pressure, the azide ions were found to transform into chain like or ring structures then polymeric nitrogen nets [18–21]. Furthermore, the alkali metal cations were found to donate their electronic to change the electronic properties of nitrogen atom and compounds. Additionally, the ‘chemical precompression’ caused by these metal cations was found to lower the synthesis pressure of polymeric nitrogen [22–24]. In this respect, high-pressure investigations about these azides are beneficial for exploring the formation of polymeric mechanism.

Sodium azide (NaN₃), a typical alkali azide, has attracted considerable attention during the past several decades. At ambient conditions, NaN₃ possesses the rhombohedral structure with R-3m space group symmetry,
which is referred to $\beta$-NaN$_3$ [25–27]. The azide ion of NaN$_3$ linked through double bond is linear and symmetric and the azide-chains are orientated perpendicular to planes packed with Na-cations. During last century, a series of attempts have been conducted to exploring the stability, lattice dynamics, electronic structure, and optical properties of NaN$_3$, while the pressure was restricted to 4.0 GPa [28]. As reported that application of pressure below 1.0 GPa or temperature near 20 °C can initiate a phase transition from rhombohedral to monoclinic structure ($\alpha$-NaN$_3$), accompanied by the shearing of the Na-layers and the tilting of the azide chains [14, 25, 26, 28–31]. Recently, Eremets et al revealed two pressure-induced phase transitions of NaN$_3$ at 19.0 and 50.0 GPa respectively [32]. Additionally, they presented the successful transformation from azide ions into polymeric nitrogen net at pressure above 120.0 GPa. In 2013, three phases of NaN$_3$ with $I4/mcm$, $P6_3/m$, and $C2/m$ structure found to be stable above pressures of 6.5, 58.0, 152.0 GPa by theoretical method [22]. Pullham et al reported the structural characterization of NaN$_3$ at elevated pressures and temperature with the structure of $I4/mcm$ was revealed experimentally using neutron diffraction method [33]. In our recent experimental high-pressure x-ray diffraction (XRD) study of NaN$_3$, three phase transitions of NaN$_3$ were revealed at 0.3, 17.3, 28.7 GPa, respectively [14]. Moreover, Steele et al reported the structural and vibrational properties of NaN$_3$ under high pressure in their theoretical study with the Raman and infrared spectra are calculated [34]. Furthermore, they also reported the transformation from NaN$_3$ into sodium pentazolate under pressure [35]. The photochemical synthesis of NaN$_3$ studied by Goncharov et al revealed the formation of color centers in NaN$_3$ under pressure [36]. In this respect, a controversy about the high-pressure structures of NaN$_3$ was currently exists. Therefore, more in-depth high-pressure studies about this compound are significant. Additionally, the high-pressure spectroscopic studies about azides were found to play a significant role for exploring their mechanism of phase transitions and evolution of azide ions under pressure [16, 17, 37, 38]. Nevertheless, no experimental high-pressure IR studies about NaN$_3$ over these transition pressures have been reported.

Therefore, the purpose of this study was to carry out an intensive investigation of the high-pressure study of NaN$_3$ by spectroscopic method. Especially, the IR measurements are expected to reveal more information about the azide groups. The high-pressure Raman and IR measurements were performed using the diamond anvil cell (DAC) technique with the pressure up to 35.0 and 26.0 GPa, respectively. The mechanism of phase transitions and evolution of azide ions of NaN$_3$ under pressure were discussed.

2. Experimental section

The NaN$_3$ powder with a purity of 99% was purchased from Alfa Aesar Co. The pressure was generated by a symmetric DAC with flat anvil of 500 $\mu$m in diameter. A T301 stainless steel was selected as the gasket. The sample was placed in the chamber with 58 $\mu$m in thickness and 120 $\mu$m in diameter. The hydrostatic conditions were provided by the mixture of methanol and ethanol (volume ratio was 4:1), and a ruby ball was placed in the sample chamber as the pressure sensor according to its fluorescence of R1 line. All in situ Raman scattering spectra were recorded using a backscattering configuration. An 1800 groove mm$^{-1}$ was selected in the liquid nitrogen-cooled CCD camera of the Acton SpectraPro 500i spectrometer. The 532 nm wavelength of the excitation source was provided by the solid-state, diode-pumped Nd: Vanadate laser (Coherent Inc.). The laser output power on the sample was about 0.4 W and the acquisition time of each spectrum was 60 s.

In the high-pressure IR measurements, the DAC with flat anvils of 400 $\mu$m in diameter were selected to generate the appropriate pressure. The sample compartment (diameter: 100 $\mu$m, thickness: 60 $\mu$m) was preindented by the T301 steel gasket to loaded the sample. A ruby ball was placed in the sample chamber for pressure calibration. The powdery KBr was chosen to provide the hydrostatic pressure environment. All the IR absorption measurements were performed by a Bruker Vertex80V infrared spectrometer. All the IR signals were recorded using the liquid nitrogen-cooled CCD camera with a spectral resolution set at 2 cm$^{-1}$. The spectra ranged from 500 to 4000 cm$^{-1}$ and the acquisition time of each spectrum was 512 s.

The vibrational properties of $\beta$-NaN$_3$, $\alpha$-NaN$_3$, and $\beta$-NaN$_3$, were simulated based on the first-principle plane-wave pseudo-potential density functional theory. The generalized-gradient-approximation of Perdew–Burke–Ernzerhof was selected in the norm-conserving pseudopotential of the Cambridge Serial Total Energy Package (CASTEP) code. The convergence tests show the energy cutoff Ecutoff is 770 eV and the $\Gamma$-points of the electronic Brillouin zone integration is 0.03 Å$^{-1}$. In the geometry relaxation, the self-consistency convergence on the total energy was $5.0 \times 10^{-6}$ eV per atom. The atomic coordinates and structures of the unit cell used in computational sections are from [26] to [40]: $\beta$-NaN$_3$, rhombohedral structure, $R-3m$, $[a = b = c = 5.491 \text{ Å}, \alpha = 38.7^\circ, \text{Na}(0, 0, 0), \text{N}(0, 0, 0.5771), \text{N}(0, 0, 0.5)]$ and $\alpha$-NaN$_3$, monoclinic structure, $C2/m$, $[a = 3.646 \text{ Å}, c = 15.213 \text{ Å}, \beta = 108.4^\circ, \text{Na}(0, 0, 0), \text{N}(0.1016, 0.5, 0.7258), \text{N}(0.5, 0.5)]$. 


3. Results and discussion

3.1. The experimental and calculated vibrational spectra at ambient pressure

Under ambient conditions, sodium azide, referred to $\beta$-NaN$_3$, possesses the rhombohedral structure with $R-3m$ space group. The group theoretical analyses indicate that one $E_g$, one $A_{1g}$, two $A_{2u}$, and two $E_u$ are optic modes in $\beta$-NaN$_3$ [26]. The experimental and calculated Raman and mid-IR spectra of $\beta$-NaN$_3$ at ambient pressure were shown in figures 1(a) and (b). The double degenerate rotational $R(E_g)$ mode of azide groups were observed at 119.8 cm$^{-1}$ in experimental spectra while it locates at 110.2 cm$^{-1}$ in calculated results, in agreement with previous report [39]. The fundamental internal mode, $\nu_1$ ($A_{1g}$), with significant intensity at 1363.6 cm$^{-1}$ corresponds to the symmetric stretching of azide groups [39]. Additionally, the mode with weak intensity at 1342.3 cm$^{-1}$ is result from the symmetric stretching mode of the isotopic species N$_{15}$, (labeled as $\nu_1$($A_{1g}$)N$_{15}$ in this work) [39]. The calculated $\nu_1$($A_{1g}$) mode was detected at 1235.7 cm$^{-1}$. Additionally, two weak modes, observed at 1261.9 and 1272.6 cm$^{-1}$, were assigned to the overtone modes of 2$\nu_2$($A_{1g}$) [39]. The weak intensity of the 2$\nu_2$ also suggests that the fermi resonance between $\nu_1$ and 2$\nu_2$ is not appreciable. The mode at 1289.5 cm$^{-1}$ (labeled as DR) was assigned to the difference frequency of $\nu_1$($A_{1g}$) - $T(E_u)$ [39]. In the mid-IR measurements, the double degenerate bending modes $\nu_2$($E_u$) of the azide groups were observed at 638.8 and 605.6 cm$^{-1}$ in experiment and calculation, respectively [39]. Moreover, the calculated mode at 1956.9 cm$^{-1}$ with significant intensity was correspond to the asymmetric stretching mode $\nu_3$($A_{2u}$) of the azide groups. However, this mode locates at the multiphonon absorptinal region (1850–2500 cm$^{-1}$) of the diamond anvils in experimental spectra, hence, it can not be identified. The bending and asymmetric modes of azide groups are Raman–inactive indicates that azide groups of NaN$_3$ are linear and symmetrical. However, these two kinds of modes are Raman–active for nonlinear or as symmetrical azide groups in other azides, e.g., AgN$_3$ and SrN$_6$. Moreover, all the fundamental modes from calculations show lower frequencies than that of experimental results. This phenomenon can attribute to that the present temperature in calculations was 0 K while that was room temperature for the experiments. Moreover, both the experimental and calculated vibrational modes with their assignments are summarized in table 1.

![Figure 1](image.png)

Figure 1. (a) Raman and (b) IR spectra of $\beta$-NaN$_3$ from experimental (exp.) and calculated (cal.) methods. All assignments of vibrational modes are marked above each band. The DR mode represent difference frequency of $\nu_1$($A_{1g}$) - $T(E_u)$. The labels of $\times 5$ and $\times 10$ indicate a magnification of 5 and 10 times of the spectra. The shadow part in (b) corresponds to the multiphonon absorptinal region of the diamond.

3.2. The Raman spectra at high pressure

The high-pressure Raman spectra of NaN$_3$ were collected from ambient pressure up to 35.0 GPa at room temperature with the selected spectra demonstrated in figures 2(a) and (b). To show the evolution of all
vibrational modes, all their frequencies as a function of pressure were depicted in figures 3(a) and 3(b). As shown in figure 2, β-NaN3 is stable up to 0.5 GPa. Upon compression, the double degenerate $R(E_g)$ mode split into two modes at 0.5 GPa, which were labeled as 1 and 2 in figure 2(a). Meanwhile, the intensity of internal modes 3 and 4 started to reverse from this pressure point, as shown in figure 2(b). These phenomena indicate the occurrence of phase transition from β-NaN3 to α-NaN3 at 0.5 GPa, in agreement with the previous XRD study of NaN3 [14].

With further compression, modes 1 and 2 presented different pressure dependence, whereas, the relative intensity of modes 3 and 4 was reversed drastically as shown in figures 2(b) and 3(a). As the pressure increased to 14.0 GPa, three new Raman modes (labeled as 5–7) were observed in lattice mode region. Concurrently, a new mode (labeled as 8) began to burgeon in internal mode region. These phenomena consistently indicate the occurrence of the phase transition from α-NaN3 to γ-NaN3 at this pressure. The increased lattice modes indicate

Table 1. Raman and mid-IR frequencies and assignments of β-NaN3 obtained from experiments and calculations.

| Raman frequencies (cm⁻¹) | Mid-IR frequencies (cm⁻¹) | Assignments |
|--------------------------|---------------------------|-------------|
| Exp. | Cal. | Exp. | Cal. | $R(E_g)$ | $\nu_2 (E_u)$ | N=N=N bending |
| 119.8 | 110.2 | 638.8 | 605.6 | N$_3^-$ rotational mode |
| 1261.9 | 2$\nu_2 (A_{1g})$ | 1272.6 | 2$\nu_2 (A_{1g})$ | Overtone of N=N=N bending |
| 1289.5 | DR | 1342.3 | $\nu_1 (A_{1g})$ | N$_3$=N=N symmetric stretching |
| 1363.6 | 1235.7 | 1956.9 | $\nu_2 (A_{2u})$ | N$_3$=N=N symmetric stretching |
| 3309.3 | 3434.6 | 3526.7 | $2\nu_2 + \nu_3$ | Combinational frequencies |

Figure 2. Selected Raman spectra of NaN3 in (a) 30–450 cm⁻¹ and (b) 1230–1520 cm⁻¹ region up to pressure of 35.0 GPa. The solid diamonds (◆) denote the new bands with increasing pressure. The solid lines serve as visual guides, and the calculated spectra are labeled as cal.
that $\gamma$-NaN₃ has a lower structural symmetry than $\alpha$-NaN₃. With increasing pressure, modes 6 and 7 were gradually weakened then disappeared at 27.6 GPa. Simultaneously, another lattice mode (labeled as 9) was observed at this pressure as shown in figure 2(a). Additionally, significant broadening and strengthening of modes 1 and 5 were observed starting from 27.6 GPa as shown in the polygon of figure 2(a), which can be visually tracked up to the highest pressure of this work. From this perspective, we speculate that modes 1 and 5 were superposed over more Raman modes when pressure above 27.6 GPa, indicating a lower symmetry structure of $\delta$-NaN₃ than that of $\gamma$-NaN₃. All above changes of Raman spectra indicate that $\gamma$-NaN₃ was stable up to 27.3 GPa while $\delta$-NaN₃ appears at 27.6 GPa, which is in agreement with previous XRD study [14]. Of note, during $\gamma$-NaN₃ range, the internal mode 3 gradually split into double modes with increasing pressure as shown in figure 2(b). This phenomenon might due to the splitting of the in-phase and out-of-phase stretch modes of azide ions. Upon subsequent compression, the $\delta$-NaN₃ was stable up to the highest pressure of this work.

To explore more information about the phase transitional mechanism, vibrational properties of $\alpha$-NaN₃ were calculated using the CASTEP code (labeled as cal. in figure 2(a)). The calculated results show that the rotation mode $R(E_g)$ of azide ions in $\beta$-NaN₃ evolved into mode $R(B_2)$ and $R(A_g)$ in $\alpha$-NaN₃. Moreover, the eigenvectors of mode $R(E_g)$, $R(B_2)$, and $R(A_g)$ of the two phases were simulated as demonstrated in figure 4(a). The mode $R(E_g)$ in $\beta$-NaN₃ presents the double degenerate rotation mode of azide groups. In $\alpha$-NaN₃, the mode $R(B_2)$ and $R(A_g)$ correspond to the rotational vibrations of azide groups parallel to $yz$ and $xz$ plane, respectively. This phenomenon is agreement with the group theoretical analyses about $R-3m$ of $\beta$-NaN₃ and $C2/m$ of $\alpha$-NaN₃ [26]. This evolution of the rotational vibrations from double degenerate mode into nondegenerate one can attributed to the deformation of unit cell during the phase transition. As the schematic diagram shown in figure 4(b), compression leads to the shearing distortion of Na-layers parallel to $ab$ plane and rotation of azide ions perpendicular to $ab$ plane as the arrows shown, which, consequently, result in the structural phase transition from rhombohedral to monoclinic structure. The phase transformation mechanism was also well established in previous works about NaN₃ [26, 30, 31]. Additionally, the rotation process may also be accompanied with tilting of the azide ions. This phenomenon was also observed in previous optical and XRD studies of NaN₃ [14, 26]. Moreover, the tilt angle of the azide ions was found become larger than the shear angle of the unit cell in the low temperature studies of NaN₃ [29, 31, 37, 38]. Analogously, we speculate that the rotation angle of azide groups will become larger than the shear angle of the unit cell in the process of $\beta$-NaN₃ to $\alpha$-NaN₃. In this respect, the terminal $N^-$ atom of one azide ion become closer to the central $N^+$ atom in a neighboring azide ion, resulting in an energetically more favorable arrangement of azide ions in $\gamma$-NaN₃ or $\delta$-NaN₃. Additionally, the calculated results shown that the symmetric stretching mode $\nu_1(A_{1g})$ in $\beta$-NaN₃ was found to evolve into $\nu_1(A_g)$ mode in $\alpha$-NaN₃ as shown in figure 2(b). The gradual reversion of intensity of modes 3 and 4 (both correspond to the symmetric stretching mode of azide ions) might due to the charge-transfer of N atom induced by the compression.

Figure 3. The pressure dependence of Raman modes in region of (a) 30–450 cm⁻¹ and (b) 1230–1520 cm⁻¹. The vertical dashed lines imply the proposed phase boundaries.
3.3. The IR spectra at high pressure

The bending and asymmetric stretch modes of azide groups are Raman inactive but IR active in azides with linear symmetric azide ions. Therefore, IR measurements are of benefit to reveal more information about azide groups of NaN₃ upon compression. Additionally, series of interesting behaviors about azide groups and phase transitional mechanism of RbN₃, CsN₃, and AgN₃ have revealed in our previous high-pressure IR studies [16, 17, 38].

The high-pressure IR spectra of NaN₃ were collected from ambient pressure up to 26.0 GPa at room temperature with the selected spectra demonstrated in figure 5(a). Upon compression, the double degenerate mode \( V_2(E_g) \) split into two nondegenerate modes at 0.8 GPa. Their split trend was gradually strengthened up to the highest pressure. Simultaneously, a series of new combinational modes labeled as 3–6 were observed in region of 3200–3500 cm⁻¹. All the spectral characteristics mentioned above due to the phase transition from \( \beta \)-NaN₃ to \( \alpha \)-NaN₃ at 0.8 GPa. The calculated mid-IR spectra of \( \alpha \)-NaN₃ (labeled as cal. in figure 5(a)) show that the double degenerate mode \( V_2(E_g) \) split into nondegenerate modes \( V_2(A_u) \) and \( V_2(B_u) \) in \( \alpha \)-NaN₃, which is in agreement with the group theoretical analyses about \( R-3m \) of \( \beta \)-NaN₃ and \( C2/m \) of \( \alpha \)-NaN₃ [26]. Additionally, we simulated the eigenvectors of \( V_2(E_g) \), \( V_2(A_u) \), and \( V_2(B_u) \) modes using CASTEP code. As demonstrated in figure 6, the \( V_2(E_g) \) mode of \( \beta \)-NaN₃ includes the bending modes of azide groups in \( xz \) and \( yz \) planes. Upon
compression, their degenerate behavior is eliminated due to the deformation of unit cell and the rotation of azide ions as shown in figure 4(b). Therefore, the monoclinic structure with C2/m of α-NaN₃ is further confirmed by the IR results, in agreement with the Raman and XRD studies.

At 11.1 GPa, another new mode (labeled as 7) was observed in bending vibrational region. Moreover, intensity of this mode was continuously strengthened up to highest pressure as shown in figure 5(a). Additionally, this mode was also observed and identified to the symmetry of Bu which involves a distorted azide bending in Steele et al.’s theoretical study of NaN₃ [34]. Moreover, the combinational modes of 3–5 were weakened significantly then disappeared with increasing pressure. These phenomena were associated with phase transition from α-NaN₃ to γ-NaN₃ at this pressure. Additionally, the phase transitional sequence was revealed by the pressure dependence of all IR modes as shown in the figure 5(b). The splitting of mode V2(Eu) and the disappearance of modes 3–6 revealed the phase transition from β-NaN₃ to α-NaN₃ at 0.8 GPa. The appearance of mode 7, pressure dependence’s inflections of modes 1, 2, and 6, and the disappearance of modes 3–5 collectively indicate the α-NaN₃ to γ-NaN₃ phase transition at 11.1 GPa.

Interestingly, the frequencies’ pressure dependences of V2(Au) and V2(Bu) mode present the symmetric behavior about their center symmetrical line throughout the entire α-NaN₃ and γ-NaN₃ range. As shown in the polygon of figure 5(b), the V2(Au) mode presented the abnormal softening behavior, while the V2(Bu) mode shown the hardening character in the whole compression process. This symmetric phenomenon of azide ions’ bending modes has also been observed in high-pressure studies of RbN₃, CsN₃, and AgN₃. Moreover, the bending behaviors in these azides are all related to the rotational behaviors of azide groups upon compression [16, 17, 38]. In this respect, the symmetric behavior of V2(Au) and V2(Bu) mode of NaN₃ can attribute to the rotation of azide ions upon compression. As figure 4(b) shown, the shearing of the Na-layers and the tilting of the azide ions induce the azide ions’ rotation on the axis through the central nitrogen atom collectively. As a result, all the distances between the terminal N− and the central N+ of the adjacent azide ion are changed (increased or decreased), consequently, their corresponding vibrational acting forces are changed. Therefore, lead to the softening and hardening of mode V2(Au) and V2(Bu) respectively. As shown in figure 5(b), the symmetric character of V2(Au) and V2(Bu) mode can be tracked throughout the α-NaN₃ and γ-NaN₃ range, indicating the rotation of azide ions is maintained in the whole process. In addition, we speculate that the parallel arrangement of azide ions in α-NaN₃ will might, ultimately, evolve into a perpendicular arrangement due to their rotation behavior with increasing pressure. As the recent study found that I4/mcm structure of NaN₃ with perpendicular arrangement of azide groups is dynamically stable [22, 33]. Additionally, the perpendicular arrangement of azide groups was also found to be energetically favorable under pressure in RbN₃ and AgN₃ [16, 17].

Figure 6. Simulated eigenvectors of V2(Eu) in β-NaN₃ and V2(Au) and V2(Bu) in α-NaN₃. The purple and blue spheres denote Na and N atoms, respectively.
4. Conclusions

In this study, the high-pressure Raman and IR measurements of NaN₃ were performed using the DAC technique with pressure up to 35.0 and 26.0 GPa, respectively. All of the fundamental vibrational modes at ambient pressure were analyzed based on experimental and theoretical results. Upon compression, the Raman and IR spectroscopic analyses collectively revealed the phase transitional sequence of $\beta$-NaN₃ → α-NaN₃ → γ-NaN₃ → δ-NaN₃ at 0.5, 14.0, and 27.6 GPa. The shearing distortion of unit cell and rotation of the azide ions were revealed during phase transition of $\beta$-NaN₃ to α-NaN₃. The fundamental vibrational modes of α-NaN₃ were calculated by CASTEP code. With increasing pressure, the splitting of internal mode of azide ions was revealed in γ- NaN₃. In the high-pressure IR measurements, the symmetrical evolution of bending modes $V_2(A_1)$ and $V_2(B_3)$ of azide groups was observed, which reveals the rotation of azide groups upon compression. Moreover, the azide ions might evolve into an energetically favorable perpendicular arrangement under higher pressure due to their rotation during their formation behavior. Generally, our spectroscopic studies provide more insights into the structural evolution and behavior of azide group of NaN₃ under high-pressure.

Acknowledgments

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