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High-Pressure Synthesis and Behaviour of Sodium Orthonitrate \( \text{Na}_3\text{NO}_4 \)

R. Quesada Cabrera\(^a\), A. Sella\(^a\), E. Bailey\(^a\), O. Leynaud\(^b\), P.F. McMillan\(^a\)*

\(^a\)Department of Chemistry and Materials Chemistry Centre, Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ, United Kingdom
\(^b\)Department of Crystallography, Birkbeck College, Malet Street, London WC1E 7HX, United Kingdom

*Corresponding author. Fax:+442076797463.
E-mail address: p.f.mcmillan@ucl.ac.uk (P.F.McMillan).

Abstract

Sodium orthonitrate \( (\text{Na}_3\text{NO}_4) \) can be prepared rapidly and in high yield from \( \text{NaNO}_3 \) and \( \text{Na}_2\text{O} \) at high pressure in a multianvil press. The acceleration is atributed to a substantially negative molar volume of reaction, and provides a much faster route compared to the synthesis at ambient pressure. The high-pressure behaviour of sodium orthonitrate has been studied in a diamond anvil cell up to 64 GPa. At the upper end of the pressure ranges we see evidence for incipient pressure-induced amorphization. Similar processes are also discussed for \( \text{Na}_2\text{O} \) and \( \text{NaNO}_3 \).

Keywords

Sodium orthonitrate; sodium oxide; sodium nitrate; high-pressure synthesis; diamond anvil cell; pressure-induced amorphization.

Introduction

Structures based on tetrahedrally-bonded oxoanions form a wide range of important minerals and materials including sulphates, phosphates, and especially the orthosilicates containing isolated \( \text{SiO}_4^{4-} \) groups that are major components of the Earth's upper mantle. Such silicate anions are well known to polymerize to form chains, sheets, and three-dimensional network structures. The high-pressure behaviour of these tetrahedrally coordinated species has been studied extensively because of density-driven transitions to higher coordinated structures that are important for mantle mineralogy. For example, \((\text{Mg,Fe})_2\text{SiO}_4\) olivines transform to spinel structures containing silicon in octahedral coordination and this marks the passage between the upper and lower mantle within the Earth. Octahedrally coordinated silicon also occurs in other high-pressure mantle minerals including silicate perovskite, ilmenite, and garnet structures and \( \text{SiO}_2 \) polymorph stishovite. Unusual five-fold coordinated silicate species have been identified in glasses prepared at high pressure and these play an important role in the densification and viscous flow of the molten materials [1]. Compression of \((\text{Mg,Fe})_2\text{SiO}_4\) crystals and glasses results in pressure-induced amorphization and formation of such highly-coordinated species and linkages between the orthosilicate anions.

It is notable that tetrahedral oxoanion species are generally formed with atoms of the second or higher rows of the periodic table (\( \text{Si, P, S, Cl, Ge, As etc} \)). By contrast, the first row elements tend to form trigonal species (\( \text{BO}_3^{3-}, \text{CO}_3^{2-}, \text{NO}_3^- \)), behaviour attributed to their small size and to somewhat nebulous ideas such as octet expansion related to orbital
energies. However, a tetrahedral oxoanion chemistry does occur for boron, either co-polymerized with other species or as isolated B(OH)₄⁻ anions (e.g., LiB(OH)₄). A long-standing question in solid state chemistry and geochemistry has therefore been whether structures based on tetrahedral NO₃⁻ or CO₄³⁻ units can be prepared at all, and the extent of their thermodynamic or indeed kinetic stability. The occurrence of tetrahedral orthocarbonate species would have implications for carbon storage within mineral or melt species within the Earth.

*Ab initio* cluster calculations have indicated that tetrahedral units based on light element species should be thermodynamically stable with respect to decomposition to simpler ions [2]. For carbon, unambiguous proof of such structures has remained elusive. A tetrahedrally-bonded structure analogous to the SiO₂ polymorphs, was observed by high-P,T synthesis from CO₂ [3]. Other high-P,T studies on CO₂ have indicated formation of glassy "carbonia" that could contain even higher-coordinated carbonate species [4]. Recent experiments found that MCO₃ (M= Sr, Ca) can be transformed into polymeric chain structures containing linked CO₄ tetrahedra at high pressure [5]. Ionic orthocarbonate species containing CO₄⁺ groups have not been synthesized yet. Nonetheless, theoretical calculations [6] indicate that a very low energy barrier hinders the orthocarbonate structure from being a global minimum and molar volume considerations suggest the synthesis via high-pressure conditions, due to the smaller volume of the orthocarbonate structure as compared to the carbonate and oxide precursors mixture.

For nitrogen on the other hand, the first solid-state orthonitrate was synthesised by Jansen [7], who obtained sodium orthonitrate Na₃NO₄ containing isolated NO₄⁻ units, by reaction of Na₂O with NaNO₃ at high temperature over a period of months (Fig. 1). This compound is therefore an attractive testing ground to explore the stability of high coordinate structures under extreme conditions.

In the present study, we have synthesized Na₃NO₄ via high-pressure conditions and investigated the high-pressure behaviour of Na₃NO₄ using synchrotron X-ray diffraction and Raman spectroscopy in the diamond anvil cell (DAC).

![Fig. 1. Two views of the orthorhombic (Pbca) Na₃NO₄ structure reported in ref. [3] at ambient conditions. View along a (left) and b axes (right). The NO₄⁻ groups are indicated by filled tetrahedra surrounded by Na⁺ ions (circles).](image-url)
Experimental

The ambient pressure synthesis of Na$_3$NO$_4$ was conducted by reaction between Na$_2$O and NaNO$_3$ as described in ref. [7]. The reactants (Na$_2$O 80%, Aldrich, main impurity Na$_2$O$_2$; NaNO$_3$ 99.9%, Aldrich) were ground together in an approximately 3:1 ratio under dry box conditions (<10 ppm O$_2$/H$_2$O, N$_2$ atmosphere) and loaded into a silver capsule that was crimped shut then transferred to a glass tube and sealed under vacuum before heating in a furnace at 380 °C (10 °C h$^{-1}$) for periods between 14-90 days.

For in situ high-pressure Raman and synchrotron XRD experiments, Na$_3$NO$_4$ samples were loaded into a screw-driven DAC without any pressure-transmitting medium under N$_2$ or Ar glove box conditions (H$_2$O/O$_2$ < 10 ppm). Diamond culet diameters were 300-150 μm. Pre-indentated rhenium gaskets were drilled with 80-μm diameter holes. Ruby chips were added to estimate the pressure inside the sample chamber [8].

The home-built Raman system is based on Kaiser supernotch filters, an Acton spectrograph and a LN$_2$ cooled back-thinned CCD detector [Soignard, Chem Mater]. An Ar$^+$ laser (514.5 nm, ~1 mW entering the cell) was focused onto the sample using a 50x Mitutoyo objective and Raman scattering was collected using backscattering geometry. Angle-dispersive X-ray diffraction data were obtained at station 9.5 HPHT, Daresbury SRS using $\lambda$ = 0.444 Å. Two-dimensional X-ray patterns were obtained and then integrated around the diffraction rings and converted into 1D plots using FIT2D software [9]. The X-ray beam was collimated and focused to 30 μm inside the cell using a Laue optical system [10]. Additional X-ray diffraction data were obtained at ESRF BM01A (Swiss-Norwegian beam Lines) using angle-dispersive techniques ($\lambda$ = 0.7 Å).

Results and Discussion

High-Pressure Synthesis of Na$_3$NO$_4$ from Na$_2$O + NaNO$_3$: characterisation by X-ray diffraction and Raman spectroscopy

The synthesis of Na$_3$NO$_4$ at room pressure allows the detection of Na$_3$NO$_4$ traces after 7-14 days [7]. According to these authors, a single crystal can be obtained only after 240 days. After several attempts, we obtained nearly pure Na$_3$NO$_4$ samples only after 90 days (Fig. 2). The main impurity was excess Na$_2$O, but traces of Na$_2$O$_2$ were sometimes detected by Raman spectroscopy. Runs carried out on samples containing Na$_2$O and NaNO$_3$ impurities allowed the X-ray patterns and Raman spectra of this antifluorite-structured compound to be obtained for the first time at high pressure.
Fig. 2 – Powder X-ray diffraction patterns at ambient P,T conditions from (a) precursors mixture, Na$_2$O (black) and NaNO$_3$ (grey), (b) calculated Na$_3$NO$_4$ from ref. [7], (c) pure Na$_3$NO$_4$ found after synthesis at 380°C/90 days at room pressure, (d) Na$_3$NO$_4$ after synthesis in the multianvil cell at 4 GPa/500°C/2 days. The pattern shown in (c) was obtained using $\lambda=0.7$ Å at BM01A, the Swiss-Norwegian Beam Lines (ESRF) but with 20 values recalculated for CuK$\alpha_1$ radiation for comparison with other patterns.

The precursors mixture (3:1 molar ratio, ~5 mm$^3$) was sealed inside a Pt capsule in the glove box and pressurized up to 4 GPa in a 1,000-ton Walker-type multianvil press (Fig. 3). W/Re thermocouples were used for temperature measurement and control. Then, the mixture was heated up to 500 °C (10 °C h$^{-1}$) and held for 50 hours before quenching by turning off the furnace power.

Fig. 3. Multianvil assembly. The capsule containing the precursors mixture was sealed by welding at one end, with a combination of Pt disc and BN plug at the other. This allowed easy loading in the glove box. The Pt disc had a slightly larger diameter than the capsule and was bowed slightly before assembly. Careful assembly produced gas tight sample environments without the need for welding at both ends. This greatly facilitates loading of temperature and atmosphere sensitive samples.
Simple molar volume considerations for the reaction:

$$\text{Na}_2\text{O} + \text{NaNO}_3 \rightarrow \text{Na}_3\text{NO}_4$$

($$\text{Na}_3\text{NO}_4 (V_m = 57.20 \text{ cm}^3 \text{ mol}^{-1})$$, $$\text{Na}_2\text{O} (V_m = 27.31 \text{ cm}^3 \text{ mol}^{-1})$$ and $$\text{NaNO}_3 (V_m = 36.95 \text{ cm}^3 \text{ mol}^{-1})$$) suggest a significantly negative value volume of reaction ($$\Delta V = -7.06$$) associated with the reaction. Hence the equilibrium is strongly shifted in favour of orthonitrate at high pressure. This is also reflected in the rate of the reaction – peaks associated with $$\text{Na}_3\text{NO}_4$$ could be seen within 2 days at 500°C (Fig. 2). Thus the application of pressure provides a useful route to the orthonitrate material.

The presence of $$\text{Na}_3\text{NO}_4$$ following syntheses at ambient and high pressure was first observed by Raman spectroscopy (Fig. 4). The Raman spectrum of $$\text{Na}_3\text{NO}_4$$ at room conditions is dominated by a strong peak at 843 cm\(^{-1}\) ($$\nu_1$$) due to symmetric NO\(_4^3-\) stretching vibrations. The antisymmetric N–O stretching bands are observed at ~1000 cm\(^{-1}\) ($$\nu_3$$). Symmetric and antisymmetric O–N–O bending modes appear between 650-670 cm\(^{-1}\) ($$\nu_4$$) and at 540 cm\(^{-1}\) ($$\nu_2$$), respectively [7]. The Raman studies also demonstrate the presence of $$\text{Na}_2\text{O}$$ and $$\text{NaNO}_3$$ remaining within the samples. The band at 240 cm\(^{-1}\) corresponds to the triply degenerate stretching mode of $$\text{Na}_2\text{O}$$, whereas the band at 1058 cm\(^{-1}\) along with a shoulder at 1067 cm\(^{-1}\) are due to the dominant NO\(_3^2-\) stretching vibrations of $$\text{NaNO}_3$$ (Fig. 4).

Fig. 4 - Raman spectra of $$\text{Na}_3\text{NO}_4$$ at ambient conditions after synthesis at (a) 380°C/90 days at room pressure and (b) 4 GPa/500°C/2 days. The corresponding vibrational modes are indicated [7]; the extra bands indicate the presence of precursors, $$\text{Na}_2\text{O}$$ and $$\text{NaNO}_3$$.

Raman spectroscopy at high pressure

The high-pressure behaviour of $$\text{Na}_3\text{NO}_4$$ was monitored by Raman spectroscopy up to 61 GPa (Fig. 5). Using our microbeam technique (3-4 μm) we could obtain spectra of $$\text{Na}_3\text{NO}_4$$ alone from regions where $$\text{Na}_2\text{O}$$ or $$\text{NaNO}_3$$ grains were absent. Little change was observed in the $$\text{Na}_3\text{NO}_4$$ spectrum throughout the pressure range studied, indicating that the orthonitrate structure is remarkably resistant to compression. The vibrational frequencies plotted versus pressure show that a new band is clearly observed among the $$\nu_4$$ bending modes above 21 GPa (Fig. 5), which indicates minor structural changes occurring within
this pressure range. Compression above 40 GPa results in the appearance of additional weak spectral features in the region between 300-450 cm$^{-1}$. However, all these spectral changes are fully reversible upon decompression at room temperature.

Fig. 5 - Raman spectra of Na$_3$NO$_4$ during compression at room temperature. We typically avoided those regions contaminated with any precursor in this study, but illustrate in some spectra the presence of Na$_2$O and NaNO$_3$ in the sample (symbols).

Fig. 6 - Raman shifts of Na$_3$NO$_4$ during compression (full circles) and decompression (empty circles) runs. All pressure-induced changes were found to be fully reversible.
Synchrotron X-ray diffraction at high pressure

The X-ray diffraction experiments sampled a much larger volume of the material within the DAC compared with the microbeam Raman results described above. The X-ray beam could only be collimated to 30 μm and the diameter of the DAC gasket hole was ~80 μm, so features from Na₂O and NaNO₃ were present along with the Na₃NO₄ reflections in the patterns and these had to be taken into account during the analysis of the data. The diffraction patterns are dominated by Na₂O reflections. The absence of a pressure-transmitting medium meant that compression was non-hydrostatic and peak broadening for all phases was expected to occur arising from pressure gradients and internal strains in the sample. Selected X-ray diffraction patterns of the reaction components upon compression are shown in Fig. 7.

There are no significant changes between the patterns recorded at 7 and 10 GPa, except for an intensity increase of the NaNO₃ peaks, which reflects the inhomogeneity across the sample (Fig. 7). However, a closer observation of intensity ratios suggest that the peak at 2θ~10.3° may arise from a superposition of reflections from NaNO₃ and Na₃NO₄, as it can be confirmed in the diffraction pattern obtained at 13 GPa. Indeed, above 10 GPa reflections associated with Na₂O broadened and vanished while a broad signal was observed at 2θ~13.5°. The NaNO₃ features also seem to undergo dramatic peak broadening and intensity decrease. The broadening and vanishing of the peaks from the precursors mixture will be discussed below. The peak at 10.3° in the pattern at 13 GPa must now correspond to the [023] reflection from Na₃NO₄ as its intensity is comparable with other peaks from the ambient-pressure structure (Fig. 7).

A minor rearrangement of the Na₃NO₄ structure seem to occur between 13-25 GPa, as suggested by the changes observed within the 11-13° region of the corresponding patterns (Fig. 7). This is consistent with our Raman results (Fig. 6). Unfortunately, the broadening of the peaks was so severe as to preclude structure solution for any possible high-pressure modification.

Beyond 25 GPa, the diffraction patterns are dominated by the broad peak due to Na₂O. However, the Na₃NO₄ diffraction peaks are still visible up to 64 GPa although they are significantly broadened, that might be due to the non-hydrostatic pressurization conditions, or could indicate the initial steps of some disordering mechanism operating at higher pressure.
Fig. 7. Powder X-ray diffraction patterns from Na$_3$NO$_4$ upon pressure under non-hydrostatic conditions. The symbols mark those reflections corresponding to NaNO$_3$ (■) and Na$_2$O (†).

The broadening and/or vanishing of those reflections due to the precursors may seem to contradict theoretical studies on alkaline oxides predict a very rich landscape for pressure-induced phase transitions in pure Na$_2$O [11] or experimental observations in which pure NaNO$_3$ remained crystalline beyond the pressure range observed in this work [12]. However, it is plausible that both compounds undergo pressure-induced amorphization due to geometrical instability in the mixture. The reduced diffusion of atoms in the mixture at high pressure may hinder the rearrangement of the corresponding structures into new crystalline phases, and thus a phase transition would be kinetically impeded. This is consistent with the pressure-induced amorphization process observed for Ca(NO$_3$)$_2$/NaNO$_3$ mixture above 9 GPa [13].

**Conclusion**

We saw no evidence for pressure-induced amorphization or appearance of new bands that might signal a coordination increase or polymerization among the orthonitrate groups within the pressure range studied. On the other hand, the broadening or vanishing of precursor peaks above 13 GPa have been explained in terms of pressure-induced amorphization in the sample mixture, as a consequence of a possible kinetically-hindered phase transition.
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