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Plasma-Assisted Synthesis and Properties of Na_3N[†]

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Dark-blue sodium nitride, Na_3N, was prepared by the reaction of metallic sodium or liquid Na–K alloy with plasma-activated nitrogen at low pressure. The compound crystallizes in the cubic *anti*-ReO_3-type structure (space group $Pm\bar{3}m$ with $a = 4.73301(6)$ Å and $Z = 1$) according to powder and single-crystal X-ray diffraction data. Na_3N decomposes above 104 °C into the elements, with ΔH_f estimated at +64(2) kJ/mol.

Alkali metals, with the exception of lithium, react with elemental nitrogen neither under ambient conditions nor at higher temperatures. However, as sodium was used to purify nitrogen for spectroscopic investigations starting in 1872,[1] activation by electrical discharge was shown to lead to a reaction between sodium and nitrogen as reported by Salet in 1876,[2] followed by a number of investigations through the 1930s[3] including studies on the other alkali metals, arc discharge in liquid nitrogen,[3d] and thermal decomposition of the corresponding azides.[3f,j] Although compound formation and release of ammonia in subsequent hydrolysis were described in these studies, no solid analytical and structural evidence for nitride formation was presented. Only a few years ago, Na_3N[4a] and K_3N[4b] could be structurally characterized in 100−200-nm-thick films obtained by codeposition of atomized elements at low temperatures.

In 1911, Strutt (later Lord Rayleigh) coined the term *active nitrogen*[3e] in order to describe “a chemically active modification of nitrogen, produced by the electric discharge” with a specific yellow long-lived afterglow, also known as Lewis−Rayleigh afterglow. In the following years, the meaning of the term *active nitrogen* was extended to include any excited form of nitrogen, molecular or atomic, of sufficient lifetime so that its chemical and physical properties can be studied.[5]

Activation of nitrogen and other gases by means of electrical discharge received increasing attention in the 1960s because it was found useful for semiconductor applications, such as deposition of silicon nitride.[6] This technique underwent significant development under the term *plasma activation*.[7]

Though widely used industrially for thin film deposition of known nitrides, plasma activation of nitrogen was rarely employed in studies toward new compounds.[8] We could show recently that plasma-enhanced chemical vapor deposition, for example, can indeed lead to new compounds as in the case of Ta_2N_3.[9]

In this work, we report plasma-assisted synthesis of single-phase Na_3N on a laboratory scale, as well as its chemical and physical properties.

Na_3N was prepared in a reaction of elemental sodium (typically pieces of ca. 0.5 g) with gaseous nitrogen activated by capacitive high-frequency discharge (10−50 W and 13.6 MHz) at pressures of 0.1−4 mbar without external heating. Dark-blue film of the product forms within minutes on the metal surface at lower power. Use of higher power leads to heating of the metal, which at some point, presumably near the melting point of sodium, leads to growth of a microcrystalline dark-blue product on a 10 mg scale consisting to

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[†] Dedicated to Professor Roald Hoffmann on the occasion of his 70th birthday.

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over 90 wt % of cubic Na_3N contaminated predominantly by metallic sodium and NaN_3 according to powder X-ray diffraction analysis. External heating of sodium above its melting point appears to hinder the formation of the nitride; instead, only the azide is formed.

The formation of Na_3N can be further facilitated by the use of a liquid Na−K alloy as an alkali-metal source.[10] Typically, 2 g of such an alloy with compositions from $Na_{0.5}K_{0.5}$ to $Na_{0.2}K_{0.8}$ was used. The reaction progress could be followed by a pressure decrease down to 0.01 mbar, resulting in the disappearance of discharge when the system was closed. Qualitatively, the nitrogen pressure has little effect on the absorption rate, whereas the reaction rate scales nearly linearly with the power of the high-frequency source. The remaining liquid alloy was removed from the product by a pipet, and the product was washed with fresh alloy and separated from the liquid phase in a centrifuge. A typical experiment at 50 W over 8 h yields ca. 100 mg of Na_3N contaminated only by ca. 1 wt % of elemental sodium according to powder X-ray diffraction analysis. Single crystals of Na_3N up to 0.3 mm in size could also be isolated from the reaction products obtained with or without additional potassium.

The product is very air-sensitive. ***Caution!*** *Rapid exothermal oxidation of excess alkali metals on the surface of Na_3N particles can lead to decomposition of the nitride accompanied by a violent combustion. Samples of even a few milligrams should be disposed of carefully!*

Controlled oxidation of the alkali-metal excess by a small amount of dry oxygen followed by manual removal of the oxidized layer could also be used to purify the nitride. Na_3N itself appears to be stable with respect to pure oxygen.

Careful hydrolysis of the nitride yields only sodium hydroxide and ammonia, indirectly confirmed by X-ray diffraction analysis of the products after neutralization by HCl. Gravimetric analysis of the resulting NaCl and NH_4Cl confirmed the Na_3N stoichiometry.[12]

No signs of decomposition of Na_3N could be observed at room temperature over several weeks. X-ray diffraction analysis at higher temperatures using a Simon-Guinier camera[13] with a heating rate of 0.15 °C/min shows decomposition at 104 °C, which agrees well with the previously reported value of 96 °C.[4a] Upon cooling of these samples, metallic sodium was identified as the major decomposition product, contaminated by small amounts of NaN_3. Differential thermal analysis (DTA) measurements with a higher rate of heating (3 °C/min) indicate an onset of exothermal decomposition at ca. 140 °C. The latter analysis also yielded a preliminary value for $\Delta H_f(Na_3N)$ of +64(2) kJ/mol.

X-ray diffraction analysis of both single-crystal and powder samples of Na_3N obtained with or without additional potassium confirmed the previously reported *anti*-ReO_3-type structure[4a] (Figure 1) in the space group $Pm\bar{3}m$ with a = 4.73301(6) Å based on powder diffraction data [compared to the literature value of 4.7325(2) Å[4a]] and atoms in the special 1a 0,0,0 (N) and 3d $^1/_2$,0,0 (Na) positions. Nitrogen atoms are surrounded by octahedra of sodium atoms; the latter are each coordinated linearly by two nitrogen atoms with Na−N distances of 2.3665 Å. Anisotropic refinement of sodium thermal displacement parameters indicated preferred thermal motion perpendicular to the N−Na−N axis [$U_{22} = U_{33} = 0.0611(7)$ Å^2] compared to the direction along the Na−N contacts [$U_{11} = 0.0180(6)$ Å^2, values from single-crystal data]. However, no structural phase transition was observed for Na_3N down to −182 °C according to powder X-ray diffraction, in agreement with the earlier study.[4a] Only insignificant rest electron density (a peak of 0.275 e/Å^3) was found in the large void in the middle of the unit cell, ruling out possible occupation of the A site according to the perovskite ABX_3 structure type. Powder X-ray diffraction data collected on a single-phase sample of Na_3N could also be used for structure refinement (Figure 2), with the results in agreement with the single-crystal data.

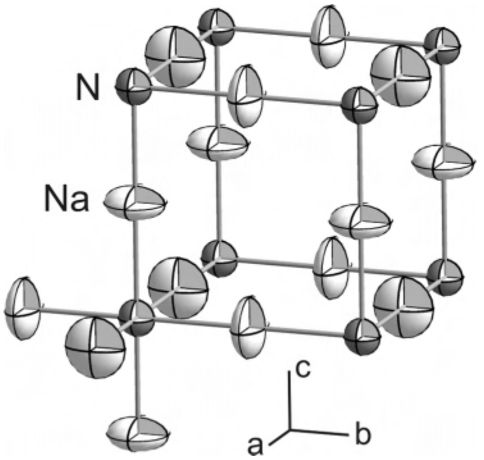

Figure 1. Crystal structure of Na_3N with thermal ellipsoids drawn at 90% probability.

Previous studies reported different colors for sodium nitride, ranging from gray, metallic, dark brown, dark blue to red, while single-phase films of Na_3N were observed to be red-brown.[4a] All of our samples are dark blue as prepared from sodium and nitrogen or after cleaning of the surface of the reaction product from the liquid Na−K alloy. During hydrolysis of the nitride, no color change is seen: dark-blue microcrystals could be observed for minutes under an optical microscope slowly evolving gas and finally disappearing in

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(10) A reaction between a liquid Na−K alloy and active nitrogen was already observed earlier, and the formation of sodium nitride and azide was reported without further characterization.[3b,k,l] Such a liquid alloy has also been shown to be an effective flux in the synthesis of Na−Ba subnitrides and suboxides.[11]

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(12) Hydrolysis of a 30 mg sample followed by absorption of the evolving NH_3 and neutralization by HCl yielded amounts of NaCl and NH_4Cl corresponding to 85(1) wt % of sodium and 14(1) wt % of nitrogen (expected 83.1 and 16.9 wt %). According to powder X-ray diffraction, NH_4Cl was phase-pure, while NaCl contained ca. 1−2 wt % of KCl, suggesting contamination of the Na_3N sample by a small amount of the Na−K alloy. See also the Supporting Information.

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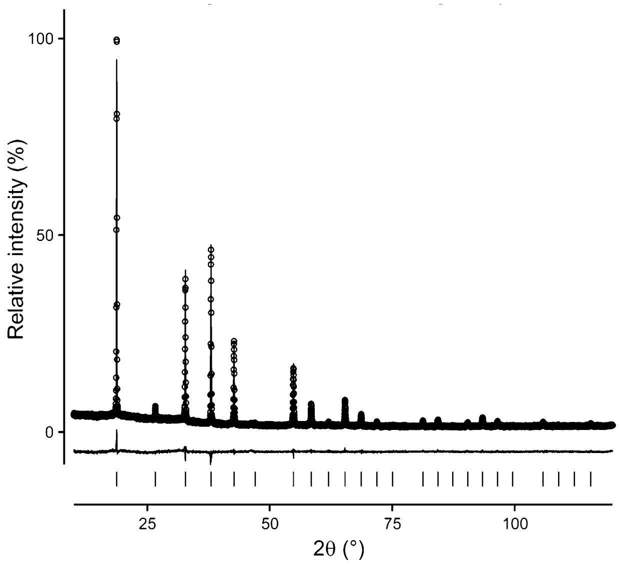

Figure 2. Results of Rietveld refinement for a single-phase sample of Na_3N: a comparison of measured (open circles) and calculated intensities with a difference curve below and vertical lines marking the reflection positions.

a colorless surrounding of wet sodium hydroxide. These observations lead us to conclude that the deep color of the Na_3N samples is not due to nonstoichiometry or alkali-metal dispersion in Na_3N but rather is likely to be an intrinsic property.

Such deep coloring of a supposedly strongly ionic compound between electropositive sodium and electronegative nitrogen might seem counterintuitive at first. However, the formal ionic description $(Na^+)_3N^{3-}$ assumes a nitride anion, for which the lattice energy should compensate the sum of the first three (negative) electron affinities. Electron−electron repulsion in the highly charged anion leads to high-lying filled N 2p states comprising the valence band with only a relatively small band gap to the empty Na 3s states of the conduction band.

A comparison of ionic lithium and sodium compounds is useful here. Excitation of an electron across the band gap may be simplistically viewed as a charge transfer from anion to cation with the energy cost of the electron affinity and lattice energy reduced by the ionization energy of the cation.[14] In pairs of related compounds, LiF/NaF, Li_2O/Na_2O, and Li_3N/Na_3N, the effect of the anion's electron affinity is cancelled, while the first ionization energies of lithium (5.39 eV) and sodium (5.14 eV)[15] are quite similar. Consequently, the reduction of the band gaps in the first two pairs from lithium to sodium compounds (14.5 eV in LiF[16] to 11.7 eV in NaF[17] and from ~7 eV in Li_2O[14,18] to ~4 eV in Na_2O[14]) can be qualitatively explained by higher lattice energy and thus better electrostatic stabilization of the 2p anion states in the case of lithium compared to the isostructural sodium compounds with longer cation−anion distances. Because red α-Li_3N has a band gap of 2.1 eV,[19] one could also expect a smaller band gap and thus a deeper color for Na_3N, even though the two are not isostructural.

An interesting correlation between the band gap and enthalpy of formation has been pointed out recently for binary oxides: more negative ΔH_f° is usually accompanied by a larger band gap.[20] Though no similar study for binary nitrides has appeared so far, a comparison of the ΔH_f° values for Li_3N (−164.56 kJ/mol[21]), Cu_3N (+74.4 kJ/mol[21]), and Na_3N (+64 kJ/mol) suggests that the band gap in Na_3N should be closer to the value for Cu_3N (~0.5 eV according to theoretical estimates[22] compared to the optical band gap of 1.5−1.65 eV in thin films[23]) rather than to that for Li_3N (2.1 eV[19]).

Preliminary band structure calculations on Na_3N at the density functional theory (DFT) level result in an unrealistic overlapping of the valence and conduction bands by 0.6 eV. Because DFT is known to underestimate band gaps by ca. 1−2 eV,[24] a band gap of around 0.5−1 eV can be expected for Na_3N.

Na_3N is likely to be the most ionic binary nitride stable at room temperature, yet it appears to have a band gap typical for a semiconductor. The open *anti*-ReO_3-type structure suggests the possibility of intercalation, Na^+ diffusion, and structural transitions under high pressure. The metastable compound might act as an efficient nitride anion donor in exchange reactions. Plasma-assisted synthesis gives access to Na_3N in amounts sufficient for further study of its physical and chemical properties, which are being currently investigated.

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Supporting Information Available: Experimental details, X-ray diffraction data on single-crystal and powder samples, a CIF file for Na_3N, DTA investigations, and further results of chemical analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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