Synthesis and Structure of Na_3N

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One of the most pronounced violations of the homology principle in the periodic table is found in the binary nitrides of the alkali metals. While Li_3N forms spontaneously from the elements at room temperature,[1] the synthesis of the homologues Na_3N and K_3N has failed so far in spite of a multitude of attempts over many decades, and early claims of success reported in the literature have turned out to be irreproducible.[2]

To date, the methods employed for the synthesis of Na_3N or K_3N have been based either on a selective decomposition of the azides (in ammonia) or on a reaction of finely dispersed metal particles with nitrogen in an electrical discharge.[2–4] In particular, the latter route constitutes an attempt to perform the chemical reactions with already activated elements. Following this line of reasoning, one realizes that the highest possible activation is reached if single atoms of the elements are mixed on an atomic scale, in the desired ratio, before the reaction takes place. It is exactly this approach which we have chosen for the successful synthesis of Na_3N reported herein.

In a vacuum chamber atomic gas-phase species of the various components (here Na and N_2) are generated separately. The resulting atomic beams are codeposited onto a cooled substrate resulting in a statistical mixture of the atoms on the substrate. Subsequently, the samples are heated to room temperature (within 3 h for Na_3N) and analyzed by X-ray diffraction. After this short time, the X-ray powder diffraction patterns show remarkably well-resolved Bragg reflections with a very low background (Figure 1). Upon further heating, Na_3N decomposes above 360 K releasing nitrogen.

The diffraction patterns of Na_3N can be indexed according to a primitive cubic unit cell, with a refined lattice constant $a = 473.25(2)$ pm. The structure refinement, using the Rietveld profile-fitting method, clearly reveals the anti-ReO_3 structure type for Na_3N (Figure 1).[5] Thus, the structure of Na_3N consists of corner-sharing NNa_6 octahedra with an Na–N bond of 236.6 pm. This distance is in the expected range and compares well to those observed in the binary oxides and nitrides of Na and Li. The Na–Na and N–N separations are 334.6 and 473.3 pm, respectively. In Na_3N the coordination number of the nitrogen atom is lower (six) because of the higher effective radius of the alkali metal, than in Li_3N, in which eight Li atoms surround the nitrogen atom to form a hexagonal bipyramide (Li–N distances 194/211 pm).[1] As a result of the structure type the space filling in Na_3N is low, similar to ReO_3, WO_3, or Cu_3N. The calculated diffraction patterns of alternative structure models containing additional sodium or nitrogen atoms, which fill the vacancy in the center of the unit cell, show a considerably reduced intensity of the first Bragg reflection (100). However, all the measured powder patterns of Na_3N show (100) as the strongest reflection, even if texture-dependent intensity deviations are considered. Thus, we can conclude that no significant occupation of this position occurs. Similarly, a possible contamination with hydrogen can be excluded because no release of hydrogen was detected by mass spectrometry during the decomposition of Na_3N.

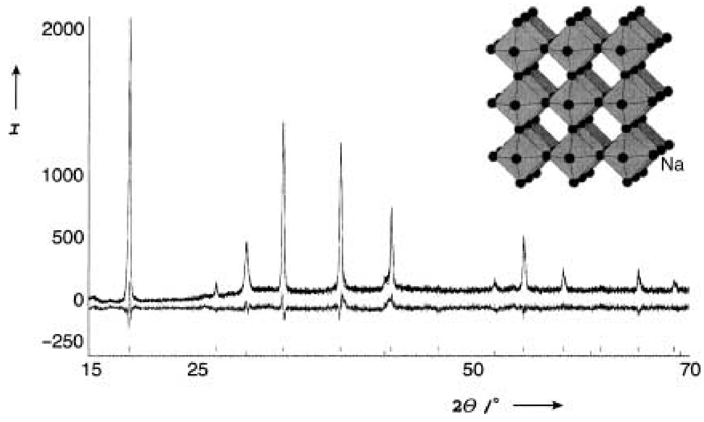

Figure 1. X-ray powder diffraction pattern (298 K) and crystal structure of Na_3N, measured (●), calculated (——), difference plot (gray), line diagram: top Na_3N and bottom Na.

In our new and versatile preparative approach,[8] the desired elements are deposited as an atomic-level dispersion resulting in an amorphous solid at liquid-nitrogen temperature. Upon heating ordered structures evolve, the order of appearance of which seems to follow Ostwald's rule, that is, at supersaturated conditions the low-density polymorphs crystallize first. Thus, the obtained polymorph of Na_3N is a metastable one and additional, denser modifications of Na_3N are expected to exist. This assumption is consistent with the results of the computational predictions of structure candidates for the alkali-metal nitrides.[6] A large number of (meta)stable structure candidates for Na_3N have been identified using global optimization and the energy-lid method. Ab initio calculations reveal the Li_3P-type to be the most stable modification followed by the Li_3N- and the anti-ReO_3-type (Figure 2), which differ only slightly in energy. However, out of these the anti-ReO_3 structure type possesses the lowest density, and thus this modification was not further considered at the time. According to these results, a phase transformation of Na_3N (anti-ReO_3 type) into the Li_3P- or Li_3N-type seems to be possible.

Temperature-dependent X-ray diffraction under high-vacuum conditions indicates that Na_3N (dispersed educt mixture) is amorphous at 77 K, orders at around 200 K into the anti-ReO_3 type, and is stable until 360 K with no further phase transformation (Figure 3).[7] Above 360 K Na_3N decomposes into Na and N_2 (demonstrated by mass spectrometry). Thus, increasing the temperature does not induce a phase transformation. Experiments to achieve a phase transformation through applying high pressure have not yet been performed.

In conclusion, with the aid of a novel and complex synthesis method the elusive compound Na_3N has been prepared for the first time. The crucial advantage of this new approach is the use of educts dispersed on an atomic scale. Thus, the

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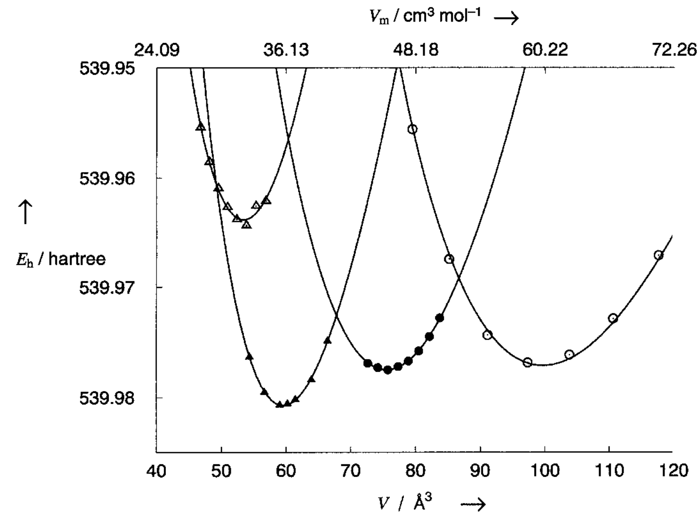

Figure 2. Energy of the structure candidates in the system Na_3N as a function of the volume (△ Li_3Bi type, ▲ Li_3P type, ● Li_3N type, ○ ReO_3 type).[9]

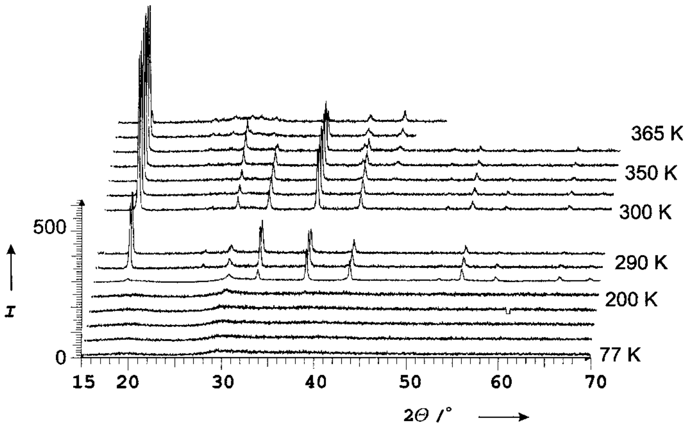

Figure 3. Temperature-dependent X-ray diffraction measurements of Na_3N under high vacuum. The sample is amorphous in the range from 77–200 K, Bragg reflections of Na_3N are present between 200–360 K, and Na_3N decomposes into Na and N_2 above 360 K. Two different samples are used (sample of the high-temperature study shows texture-dependent intensity deviations). The temperatures of the single scans are: (from bottom to top) 77, 110, 140, 170, 200, 200–273, 290, 295, 300, 320, 330, 350, 360, 365, 370 K.

transport distances during the subsequent solid-state reactions are reduced to atomic scales, and crystalline products are formed at unrivaled low temperatures and within extremely short times.[8] Besides its conceptual singularity, a particular advantage of this synthesis method is its ability to allow the synthesis of extremely labile or metastable solids. This feature is convincingly demonstrated by the synthesis of Na_3N, the decomposition of which at 360 K almost certainly precludes a preparation by classical solid-state reactions.

Experimental Section

Na_3N was prepared using an evaporation system consisting of an ultra-high-vacuum (UHV) chamber, for further details see ref. [8]. Segregated sodium was evaporated from a PBN crucible using an effusion cell, at 473 K. Nitrogen (purity 5.0; Westfalen, Münster) mass flow was controlled to 1.6 $cm^3 min^{-1}$ and the stream into the chamber passed through a microwave plasma source (2.45 GHz, 80 mA). Sodium and nitrogen (100-fold excess) were codeposited for a period of 3–9 h onto sapphire substrates (0001) both sides of which were epitaxial-polished; TBL-Kelpin, Neuhausen) in the temperature range 77–300 K (process pressure: 5×10^{-5} mbar).

The samples obtained at 77 K have a reflecting, metallic appearance. At room temperature all the samples are red-brown. Samples of Na_3N are very hygroscopic, and after storage in a glove box (Ar, $H_2O < 0.04$ ppm) for 14 days, the X-ray diffraction patterns indicate a considerable decomposition to NaOH. Even freshly prepared samples sometimes exhibit small amounts of NaOH. However, most samples contain metallic sodium as an impurity, which presumably was formed by partial decomposition of Na_3N during the preparation process.

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[5] Crystallographic data of Na_3N at 298 K (X-ray powder diffraction analysis): cubic, space group $Pm\bar{3}m$ (No. 221) $a = 473.25(2)$ pm, $Z = 1$, Na in (3d), N in (1a), $R_p = 8.0\%$ $R_{wp} = 10.3\%$, $R_{Bragg} = 5.3\%$, $B_{eq} = 4.5$, 11 reflections. The program Topas (Bruker AXS, Karlsruhe) was used for the refinement of the lattice constant and of the structure (Rietveld). Further details on the crystal structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number (number CSD-412313).

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[7] X-ray investigations: All powder diffraction patterns were measured on a theta/theta D8-Advance powder diffractometer (Bruker AXS) with parallel beam (Göbelmirror, $Cu_{K\alpha}$) in an X-ray chamber under high vacuum (5×10^{-7} mbar) with incidence angles of 2 to 10°, step 0.02°. The temperature of the samples was controlled by the sample holder. The residual gas was recorded by a mass spectrometer (C-100M, Leybold-Inficon).

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