Preparation, Crystal Structure, and Properties of Barium Pernitride, BaN₂

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Stoichiometric barium pernitride, BaN₂, was prepared from the elements under N₂ pressure of 5600 bar in an autoclave at 920 K. The compound is isotypic to ThC₂ (space group $C2/c$, $Z = 4$) according to powder X-ray (neutron) diffraction data with $a = 7.1712(1)$, $b = 4.3946(1)$, $c = 7.2362(1)$ Å, and $\beta = 104.864(1)°$ ($a = 7.1745(1)$, $b = 4.3963(1)$, $c = 7.2393(1)$ Å, $\beta = 104.876(1)°$). The N−N distance of 1.221(4) Å (based on the neutron diffraction data) is indicative of a double bond in the N_2^{2-} dumbbells. BaN₂ is metallic according to magnetic susceptibility measurements and TB-LMTO band structure calculations.

Introduction

Consideration of the well-known compounds BaC₂ and BaO₂ raises a natural question of whether a similar compound exists in the barium (or alkaline earth metal in general)−nitrogen system, perhaps with the same stoichiometry, BaN₂. Deviations from the ideal, closed-shell $(Ba^{2+})_3(N^{3-})_2$ composition toward the metal-rich side have been shown to lead to the rich chemistry of alkaline earth metal subnitrides such as Ba₂N[1] and Ba₃N.[2] The nitrogen-rich side, on the other hand, could provide access to interesting N−N bonded species, specifically to the N_2^{2-} anion in BaN₂. This anion would be isoelectronic to the paramagnetic molecular oxygen and to the C_2^{4-} anion, which is thought to be responsible for superconductivity in rare earth metal carbides and carbide halides.[3,4]

The first report of a nitrogen-rich barium nitride dates from as early as 1892.[5] In 1934, the nitrides of M₃N₄ stoichiometry were reportedly obtained for Ba, Sr, and Ca by decomposing the respective amides in a vacuum.[6] In the 1950s, the first high-pressure experiments were attempted, which resulted in the preparation and characterization of BaN₂.[7] The equilibrium between the nitride and pernitride was investigated, indicating that no phases other than Ba₃N₂ and BaN₂ exist.[8] Another approach, namely decomposition of M(N₃)₂ azide by heating under organic solvents, was employed in 1966, leading again to the M₃N₄ composition.[9] These nitrides were investigated further;[10−14] though it was later shown that this method leads to a contamination by carbon and other impurities.[15] Although no good X-ray powder diffraction pattern suitable for a structure determination could be obtained in all of these studies, excess nitrogen by elemental analysis and the presence of hydrazine among hydrolysis products suggested N−N bonding in these materials. More recently, evidence for the formation of not fully reduced nitrogen species in reactions of barium with elemental nitrogen was found in IR[16] and photoelectron spectroscopy[17] investigations.

The existence of the N_2^{2-} anion was finally confirmed by preparation and structural characterization of $(Sr^{2+})_4(N^{3-})_2(N_2^{2-})$ = SrN and SrN₂.[18] We report below the preparation, structural characterization, and properties of the barium pernitride, BaN₂.

Experimental Section

Preparation of Samples in Belt Apparatus. Synthesis of Ba₂N has been described in detail earlier.[17] Distilled metallic Ba was first prereacted with a stoichiometric amount of nitrogen by slow heating in a cleaned Ta container to 570 K, then treated further at 670 K after adding distilled Na as a flux. Finally, sodium was removed by heating under vacuum to 710 K, leaving rhombohedral Ba₂N with X-ray powder diffraction pattern matching to literature data ($a = 4.031(1)$, $c = 22.532(4)$ Å).[19] Due to extreme sensitivity of the compounds involved to air

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and moisture, all operations were carried out in an argon-filled glovebox or on a vacuum line using Schlenk technique.

$Ba(N_3)_2$ (98.5%, Schuchardt) was twice recrystallized from an aqueous solution by adding ethanol. Typically $Ba(N_3)_2 \cdot H_2O$ was formed, which began to lose water even at room temperature. However, if the aqueous solution of the azide was quickly added to an excess of ethanol, a solid product containing mostly anhydrous azide was obtained. The product was then dried in dynamic vacuum at 10^{-6} mbar. $Ba(N_3)_2$, purified in such a way, contains no water (<0.01 wt % O) and is stoichiometric according to elemental analysis. The powder X-ray diffraction diagram ($P2_1/m$ with $a = 9.617(2)$, $b = 4.395(1)$, $c = 5.438(1)$ Å, and $\beta = 99.78(3)°$) fits the existing literature data.[20] *CAUTION*: barium azide might explode upon rash heating.

Mixtures of Ba_2N and $Ba(N_3)_2$ with the overall stoichiometry of BaN_2 were loaded in cylindrical Au crucibles with an inner volume of about 25 mm³. The crucibles were surrounded by pyrophyllite and a cylindrical graphite heating element. Pressures up to $10-15$ kbar were applied in a standard belt apparatus over a period of several hours to a day. The temperature was raised slowly to prevent a sudden decomposition of the azide; samples were annealed at $570-670$ K.

Preparation of Samples at Low Nitrogen Pressure. The existing thermodynamic data for barium pernitride[8] indicate that a low pressure of nitrogen might be sufficient to keep the compound stable if the reaction temperature is low enough. For example, the equilibrium nitrogen pressure over the pernitride should be around 1 bar at 540 K. Accordingly, barium azide was slowly decomposed in a closed glass vessel which was evacuated or filled with Ar so that the resulting nitrogen pressure was around $1-3$ bar at temperatures of $470-530$ K. The samples were held at these final temperatures for about 10 days. The conversion of the azide to pernitride could be monitored optically, as the color changed from white through gray to dark-brown, and by measuring the nitrogen pressure. The color change occurred typically around $380-390$ K, while most of the nitrogen was released at slightly higher temperatures ($390-410$ K).

Preparation of Samples at High Nitrogen Pressures in an Autoclave. The autoclave experiments for the preparation of BaN_2 were carried out using modified high-pressure equipment,[18] which was originally developed by Bronger and Auffermann[21] for the synthesis of extremely sensitive hydrides and hydridometalates. Metallic barium (Alfa, 99.9%) was prereacted at 1120 K under ambient N_2 pressure. After cooling to room temperature, the N_2 pressure was increased to an initial pressure of 2800 bar, corresponding to a reaction pressure of 5600 bar at 920 K. A single-phase sample of BaN_2 (dark-brown powder) was obtained by holding the given temperature and pressure for a period of 72 h.

X-ray Investigations. The powder samples obtained in the belt apparatus, low N_2 pressure, and autoclave experiments were ground and sealed under argon in glass capillaries for X-ray diffraction investigations, which were carried out on a STADI-P STOE diffractometer with Cu $K\alpha_1$ radiation at room temperature. While only an approximate tetragonal model could be proposed for the former, the accurate monoclinic structure could be refined for the latter two samples using the CSD package[22] (Figures 1 and 2). Details of structure refinement are presented in Tables 1 and 2.

Neutron Investigations. Neutron diffraction experiments at ISIS, Rutherford Appleton Laboratory, Chilton, U.K. were carried out on the autoclave sample to determine the nitrogen positions precisely. The sample was placed under argon into a cylindrical vanadium container (diameter, 6 mm; length, 51 mm; wall thickness, 0.15 mm) and closed with a cap containing an indium seal. The first experiment was carried out at room temperature using the high-intensity time-of-flight diffractometer POLARIS (Table 3 and Figure 3). Additionally, neutron diffraction data were collected on the high-resolution time-of-flight
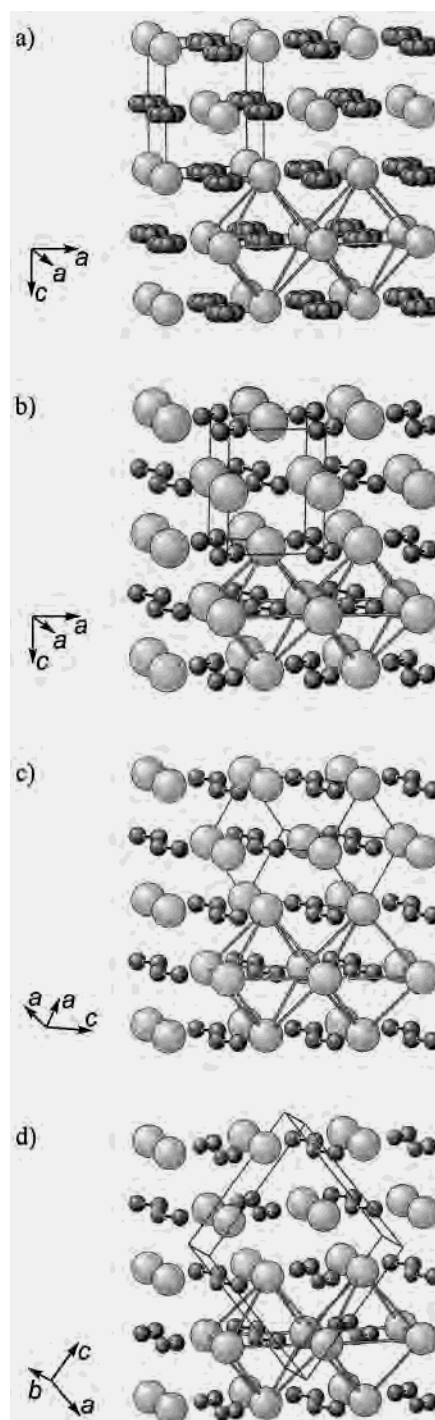
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Figure 1. Tetragonal model for the crystal structure of BaN_2 in space group $I4/mmm$. The positions of the nitrogen atoms are unknown, but they are likely to lie in the aa plane because the Ba octahedra are compressed along the c direction (a). Tetragonal crystal structure of MgC_2 in space group $P4_2/mnm$. The C_2 units lie in the aa plane along the diagonals of the Mg octahedra. The orientation of the C_2 units is the same in each layer, but alternates between the layers (b). Tetragonal crystal structure of SrN_2 in space group $I4/mmm$. All N_2 dumbbells are oriented along the c axis (c). Monoclinic crystal structure of BaN_2 in space group $C2/c$. The N_2 dumbbells lie horizontally along the diagonals of the Ba octahedra with alternating orientation within each layer (d).

diffractometer HRPD, at room temperature and at a temperature of 2 K, to look for additional splitting of the reflections. Hints for a deviation of the monoclinic cell and phase transitions at lower temperature were not observed (Table 3). The refinements were carried out using the program FULLPROF.[23]
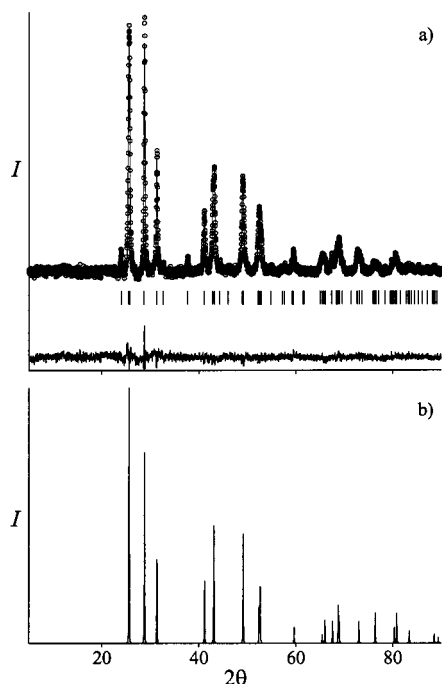
Figure 2. Rietveld refinement of powder X-ray diffraction data (with Cu Kα₁ radiation, room temperature) of a barium pernitride sample from a low N_2 pressure experiment. The measured data (circles) and the computed curve (solid line) are compared; the ticks mark the positions of the reflections. The difference curve is shown at the bottom (a). A calculated X-ray diffraction pattern based on the tetragonal structural model for BaN_2 (b).

Table 1. Results of Powder X-ray Diffraction Studies on Barium Pernitride Samples.

	belt apparatus (tetragonal model)	low N_2 pressure	autoclave (high N_2 pressure)
space group, Z	$I4/mmm$, 2	$C2/c$, 4	
a, Å	4.386(1)	7.1591(6)	7.1712(1)
b, Å		4.3898(6)	4.3946(1)
c, Å	5.708(4)	7.2284(6)	7.2362(1)
β, °		104.910(7)	104.864(1)
cell volume, Å³	109.82(7)	219.52(7)	220.42(1)
refinement mode		full profile	
2θ (max), deg		88.62	99.64
R_{Bragg}, $R_{profile}$		0.066, 0.165	0.089, 0.140

Magnetic Susceptibility. Magnetic measurements were carried out on a MPMS-XL7 SQUID magnetometer (Quantum Design) at fields of 3.5 and 7 T in the 1.8–400 K range using a 115.0 mg pernitride sample from the autoclave experiments. The $\chi(T)$ data could be fitted by a sum of temperature-independent terms (Pauli paramagnetic and diamagnetic components), a quadratic Pauli paramagnetic term, and a paramagnetic impurity term. According to the latter, no more than 80 ppm mol of $S = 1/2$ impurity was present in the sample. Extrapolating χ_0 to infinite field strength yields the value 69×10^{-6} emu/mol, which, given the sum of atomic diamagnetic contributions (-39×10^{-6} emu/mol), allows one to estimate the temperature-independent Pauli paramagnetic component at 1.1×10^{-4} emu/mol using the $\chi(T) = C/T + \chi_0 + \chi_2 T^2$ relationship ($\chi_2 = 8.2 \times 10^{-11}$ emu/(mol K²), $C = 2.88 \times 10^{-5}$ emu·K/mol, $\chi_0 = 69 \times 10^{-6}$ emu/mol, see Figure 4).

Details of Band Structure Calculations. Electronic structure calculations were carried out using the TB-LMTO package[24] with the

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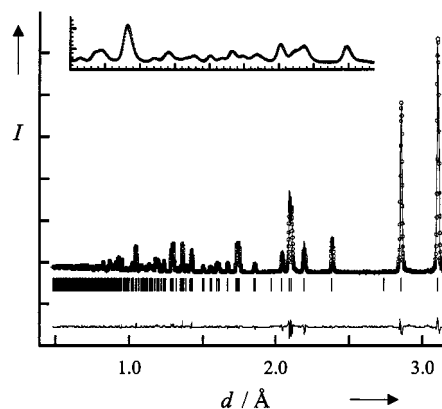
Figure 3. Neutron diffraction diagram (298 K, POLARIS) of BaN_2 (sample from the high N_2 pressure autoclave experiment). The observed (dots), calculated (solid line), and difference (lower solid line) profiles are shown. Ticks mark the positions of the Bragg reflections. In the upper part of the figure the d spacing region between 1.0 and 1.25 Å is magnified.

Table 2. Atomic Parameters in BaN_2 Based on Refinement of X-ray Diffraction Data.

belt apparatus sample, tetragonal model in $I4/mmm$				
	site	x	y	z
Ba	2a	0	0	0
N			unknown	

low-N_2 pressure sample, $C2/c$					
	x	y	z	$B_{iso/eq}$, Å²	occ.
Ba 4e	0	0.2009(8)	1/4	2.4(1)	
N 8f	0.311(4)	0.173(8)	0.060(4)	1.7(5)	0.97(2)

	B_{11}	B_{22}	B_{33}	B_{13}
B_{ij} for Ba	2.5(2)	2.7(3)	2.1(2)	0.7(2)

Autoclave sample, $C2/c$				
	site	x	y	z	B_{iso}, Å²
Ba	4e	0	0.1984(2)	1/4	1.04(1)
N	8f	0.291(1)	0.143(2)	0.032(1)	0.3(1)

Table 3. Results of Rietveld Refinement of Neutron Diffraction Data Collected on the Barium Pernitride Sample from Autoclave Experiments. The Space Group Is $C2/c$ with Ba Atoms in the 4e (0, y, 1/4) and N Atoms in the 8f (x, y, z) Positions.

device	POLARIS	HRPD	HRPD
T, K	298	298	2
measuring time, h	4	10	12
reflns	995	294	109
a, Å	7.1745(1)	7.1708(2)	7.1431(2)
b, Å	4.3963(1)	4.3919(2)	4.3794(2)
c, Å	7.2393(1)	7.2344(2)	7.2079(2)
β, °	104.876(1)	104.858(1)	104.831(1)
Ba y	0.2004(6)	0.2016(7)	0.2003(6)
N x	0.2970(2)	0.2987(3)	0.2991(3)
N y	0.1463(4)	0.1485(4)	0.1487(4)
N z	0.0454(3)	0.0459(3)	0.0458(2)
Ba B_{iso}, Å²	0.40(4)	0.79(7)	−0.02(6)
N B_{iso}, Å²	0.87(1)	1.37(3)	0.68(3)
R_{Bragg}, $R_{profile}$	0.0235, 0.0444	0.0223, 0.0802	0.0233, 0.0691

crystal structure as refined from the room-temperature POLARIS neutron data (first column in Table 3). The program was allowed to insert somewhat smaller empty spheres than the default minimum value of 0.9 au. The k point set was extended to a 12 × 12 × 8 array (320 k points in the irreducible wedge) in order to properly describe the metallic compound. All other settings were kept at the default values; i.e., a scalar relativistic calculation with the Barth–Hedin local exchange-correlation potential[25] was carried out. A test spin-polarized
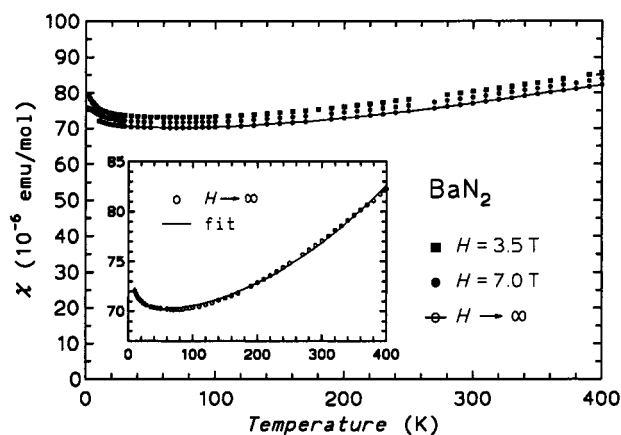
Figure 4. Susceptibility of a BaN_2 sample from the high N_2 pressure autoclave experiment, and the fitted curve using the $\chi(T) = C/T + \chi_0 + \chi_2 T^2$ relationship.
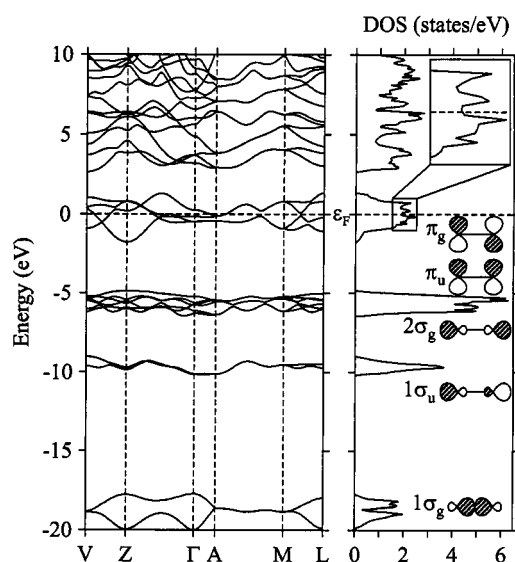

Figure 5. TB-LMTO band structure for BaN_2 (left). The special points of the Brillouin zone are defined in text. The total DOS for BaN_2 in states/eV per formula unit (right). The predominantly N bands are labeled with the iconic representations of the respective molecular orbitals of an isolated N_2 unit.

calculation with nonzero magnetic moments artificially placed on the nitrogen atoms converged back to the metallic state. The orbital character of the bands was analyzed using the so-called fat-band plots (not shown here); the resulting band structure and total density of states (DOS) plots are shown in Figure 5.

Results and Discussion

High-pressure experiments in a belt apparatus resulted initially in dark-brown samples with $BaN_{1.3-1.6}$ composition according to elemental analysis, typically contaminated by oxygen. Similar samples were obtained by slow decomposition of barium azide in closed vessels, whereby an oxygen impurity could be excluded (NO-analyzer NOA, Leybold–Heraeus). The content of nitrogen in the autoclave sample was analyzed using a temperature ramping during the carrier gas hot extraction method (NO-analyzer TC-436DR, LECO). These studies led to the composition $BaN_{2.00(3)}$, indicating the existence of N_2^{2-} dumbbells by taking the SrN_2 and SrN data as a reference.[18] The X-ray diffraction pattern could be approximately described by a tetragonal body-centered subcell used as the starting model

(see Tables 1–2 and Figure 1), suggesting structural similarity to dicarbides of the alkaline earth metals. The unit cell volume per formula unit (54.9 Å^3) lies between the respective values for the tetragonal BaC_2 (68.8 Å^3)[26] and BaO_2 (49.5 Å^3).[27] The c/a ratio (1.30) is significantly smaller than that for tetragonal BaC_2 (1.62),[26] indicating that the N_2 units are perpendicular rather than parallel to the c axis,[28] much like in the structure of MgC_2 with the c/a ratio of 1.28.[29,30]

The tetragonal model had to be rejected, as a better fitting of the powder X-ray diffraction pattern could be achieved when the structure was refined in the space group $C2/c$ (isotypic to ThC_2[31,32] and low-temperature alkaline earth metal dicarbide modifications[26,34]). Independently, the monoclinic unit cell could also be used to refine X-ray and neutron diffraction data collected on samples prepared in the high-pressure autoclave. By this, the composition BaN_2 was confirmed (Table 2). Although the stoichiometry of the other two samples were nitrogen deficient with respect to the idealized BaN_2 composition, the occupancy refinement of the nitrogen position resulted in practically full occupation (Table 2). A poorly crystallized cubic Ba_3N_2 impurity, possibly present in the two samples according to X-ray diffraction, could be responsible for the deviations from the ideal stoichiometry.

The N–N bonding distance is 1.221(4) Å (based on PO-LARIS neutron diffraction data), which is comparable to the N–N distances of 1.225(5) Å and 1.224(2) Å in SrN and SrN_2,[18] respectively. These distances are indicative of a double bond, as seen from a comparison to transition metal complexes[18] and to *cis*- (1.209 Å) and *trans*-N_2F_2 (1.224 Å).[35] A comparable interatomic distance of 1.21 Å is found in the O_2 molecule.[36]

Electronic structure calculations (TB-LMTO) on the obtained crystal structure suggest that the compound should be metallic and exhibit only Pauli paramagnetism, despite a possible triplet on the N_2^{2-} units. The Fermi level was found to cross the 3 eV wide block of the N–N antibonding bands based on the π_g (π^*) orbitals of the dumbbell. The Ba 5d orbitals were found to be responsible for the significant width of the π^* band due to substantial Ba 5d–N 2p interactions, thus also being responsible for the metallic nature of the pernitride. In other words, one can speak of a partial charge transfer of the π^* electrons from the N_2^{2-} unit to the Ba^{2+} cations, much like in rare earth metal carbides containing the isoelectronic C_2^{4-} unit. The density of states at the Fermi level was computed to be 1.9 states/eV per formula unit (see Figure 5), leading to the expected value of 1.2×10^{-4} emu/mol for χ_0(Pauli). The latter is in a good agreement with the experimentally observed value of 1.1×10^{-4}

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emu/mol. Additionally, the positive quadratic Pauli contribution to $\chi(T)$ indicates that the condition $g(E)g''(E) > (g'(E))^2$ is satisfied at the Fermi level, where $g(E)$ is the density of states and $g'(E)$ and $g''(E)$ are the first and second derivatives, respectively. This implies that the Fermi level is near a minimum of $g(E)$, which also agrees with the results of our calculations (see Figure 5).

Supporting Information Available: Details of crystal structure refinements based on X-ray and neutron diffraction data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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