



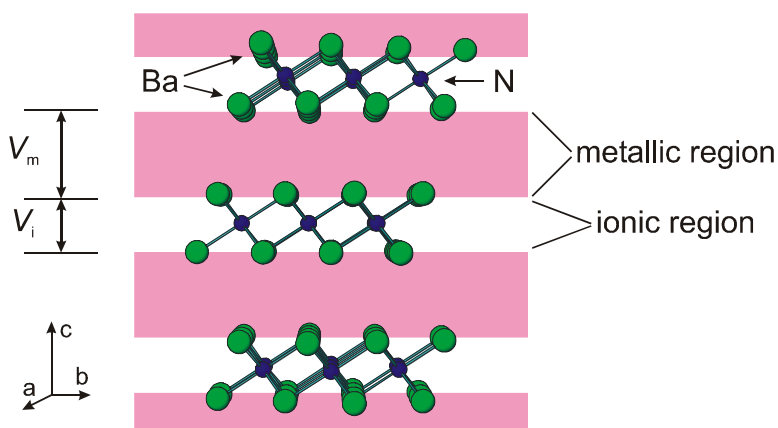
	Experiment title: Group IA and IIA metal subnitrides and suboxides under pressure	Experiment number: CH-1115
Beamline: ID09	Date of experiment: from: 03.10.2001 to: 08.10.2001	Date of report: 26.02.2002
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Report:

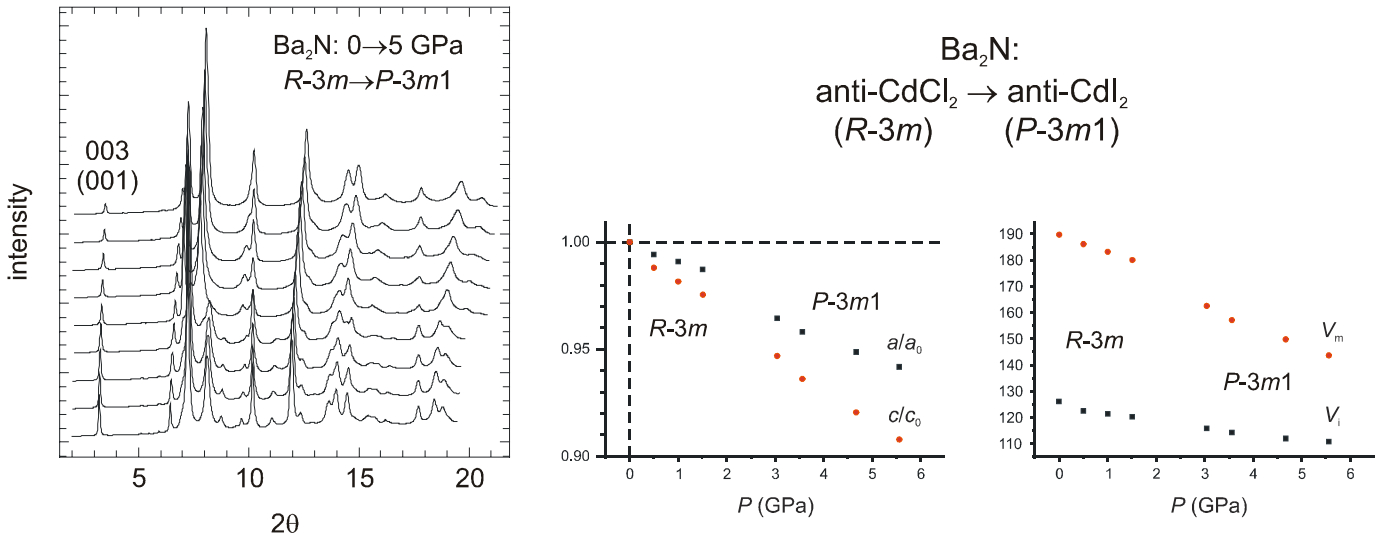
High pressure experiments were carried out in a diamond anvil cell on several samples of alkali and alkaline earth metal subnitrides and suboxides using the beam line ID09 ($\lambda = 0.416 \text{ \AA}$). Observed structural changes under pressure, deduced from Rietveld refinement of the collected diffraction data, provided an experimental tool to probe a unique combination of metallic and ionic bonding, which co-exist in these compounds. Simultaneous presence of anions (O^{2-} and N^{3-}) and nearly free electrons results in a spacial separation of ionic and metallic regions. This, in turn, often leads to low-dimensional anisotropic crystal structures. Furthermore, electrostatic repulsion between the anions and the remaining valence electrons leads to rather open structures, susceptible to application of external pressure. Below we present the results of high pressure investigations on alkaline earth subnitrides and related compounds.

The most comprehensive set of data was obtained for the Ae_2N ($Ae =$ alkaline earth metal, that is Ca, Sr, or Ba) family of isostructural compounds. These subnitrides, which can be formally described as $(Ae^{2+})_2N^{3-} \cdot e^-$ in ionic formalism, have strongly anisotropic two-dimensional structure held together by both ionic and metallic bonding. While the 2D Ae_2N layers are held together by ionic bonding between the Ae^{2+} and N^{3-} ions, the bonding between the neighboring Ae_2N layers can be viewed as metallic due to the remaining valence electron per formula unit. This bonding situation is presented schematically on the right using rhombohedral Ba_2N as an example:

Such model description of the Ae_2N compounds suggests anisotropic compressibility due to the presence of alternating ionic (hard) and metallic (soft) layers in the crystal structures. This was confirmed by the results of Rietveld refinement of the collected diffraction



data. Moreover, several phase transitions were observed in Ba_2N . In the first phase transition at 2 GPa merely the mutual orientation of the Ba_2N layers changes from the anti- CdCl_2 -type stacking in $\text{Ba}_2\text{N-I}$ to the anti- CdI_2 -type arrangement in $\text{Ba}_2\text{N-II}$. It is clear in the series of powder diffraction patterns below that the 003 peak of the space group $R-3m$ transforms into the 001 peak of the space group $P-3m1$; these peaks correspond to the separation between the adjacent Ba_2N layers:



Further increase of the pressure induced at first another phase transition at 6 GPa to a defect cubic anti- Th_3P_4 -type phase in the space group $I-43d$ ($\text{Ba}_2\text{N-III}$), followed by a transition at 8 GPa to $\text{Ba}_2\text{N-IV}$ with a yet unknown structure, which, according to the powder diffraction pattern, is likely to be a distorted variant of the cubic $\text{Ba}_2\text{N-III}$ phase. The last observed $\text{Ba}_2\text{N-IV}$ phase appears to be stable up to 40 GPa.

The behavior of Ca_2N and Sr_2N follows that of Ba_2N : analogous anisotropic compressibility is observed, with the c -direction being softer as the ab -directions, and with a larger compressibility of the metallic region compared to the ionic region, based on Rietveld refinement. However, only one phase transition was observed for each compound in the 0–40 GPa range. In both cases the high-pressure phase appears to be isostructural to the $\text{Ba}_2\text{N-IV}$ phase. The transitions take place at *ca.* 12 GPa for both Ca_2N and Sr_2N .

Two further compounds, related to the layered Ae_2N subnitrides, were also investigated: ionic nitride hydrides Ca_2NH and Ba_2NH . Their high pressure behavior is important for a comparison with the subnitrides because the remaining valence electron of metallic (Ae^{2+}) $_2\text{N}^{3-} \cdot e^-$ is now bound as hydride anion in purely ionic (Ae^{2+}) $_2\text{N}^{3-} \text{H}^-$. Moreover, the arrangement of barium and nitrogen atoms in Ba_2NH is practically the same as that in Ba_2N , with the hydrogen atoms being between the 2D- Ba_2N layers.

Cubic Ca_2NH ($Fd-3m$) was found to transform into a rhombohedral structure (isotypic to Ba_2NH at ambient pressure) at *ca.* 2 GPa. A typical result of Rietveld refinement is shown on the right. Ba_2NH , on the other hand, turned out to have two phase transitions at *ca.* 6 and 13 GPa, though the crystal structure of the two new phases could not yet be solved.

The up to now obtained structural results on the Ae_2N and Ae_2NH compounds are being prepared for publishing.

