

Redox-Intercalation of Hydrogen and Nitrogen in Alkaline-Earth Subnitrides

Gudrun Auffermann, René Chemnitz, Yurii Prots, and Rüdiger Kniep

The binary systems alkaline-earth metal-nitrogen and their intermediate compounds have been subject of numerous discussions for many years. At the beginning of the third millennium, the reactive gas high-pressure synthesis [1] led to single phase products of nitride-diazenides for the first time. Using this method it was possible to synthesize nitrogen rich compounds [2-4], which are free of impurities such as hydrogen, carbon and oxygen. The most important variable with regard to phase formation and composition is the reactive gas pressure. The formation of the different phases can be described in terms of reversible redox-intercalation processes, which are exemplified for the Sr-N system: Starting from Sr_2N as the host structure, diazenide-dumb-bells are inserted accompanied by simultaneous oxidation of an equivalent amount of strontium to Sr^{2+} . The stepwise intercalation proceeds with increasing the reaction pressure (up to 6000 bar) until the final state with the chemical composition SrN_2 is reached [2, 3].

Additional studies in the system Ba-N clearly show that starting from Ba_2N an insertion of nitrogen in the host structure succeeds in the same manner by increasing N_2 -reaction pressure, however, the pressure regions for obtaining pure intercalated phases are significantly lower and smaller. Thus, the pure diazenide BaN_2 [4] is already obtained at 200 bar N_2 reaction pressure, and reaction pressures in an even lower pressure range reveal the existence of Ba_4N_3 and BaN . The nitrogen content was ascertained by chemical analysis using the carrier gas hot extraction (CGHE) method (Fig. 1). For quantification the CGHE method was modified to allow controlled heating of the binary nitride diazenides in such a way that the determination of the thermal decomposition process was possible [5]. The crystal structures of the three compounds Ba_4N_3 , BaN [6] and BaN_2 [4] differ from that of the analogous strontium nitrogen compounds by different orientations of the $[\text{N}_2]$ dumb-bells. For a more detailed investigation of the intermediate crystal structures of the Ba-series, we intend to carry out synchrotron radiation studies. Obviously, the parameter gas pressure is a crucial tool for the

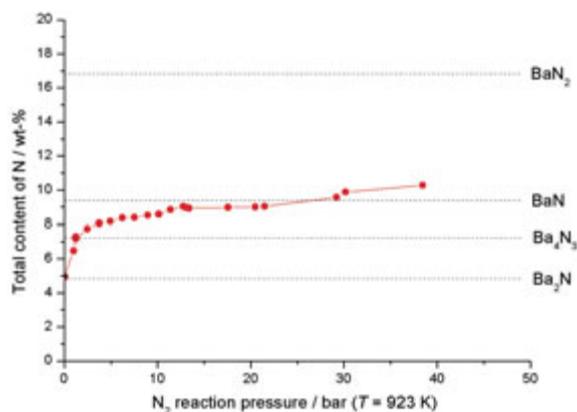


Fig. 1: Redox intercalation of Ba_2N with nitrogen at $T = 923$ K. The total content of intercalated nitrogen (wt-%) in reaction products plotted as a function of the reaction pressure (bar) of molecular nitrogen. The nitrogen content was ascertained by chemical analysis using the carrier gas hot extraction method.

selective synthesis of specific nitrogen compounds, in which the oxidation state is gained by adjusting the redoxpotential of the reaction gas by varying its pressure, thus increasing reaction pressures facilitate access to nitrogen rich compounds.

Recently, the investigations of the intercalation processes in the subnitride Sr_2N was extended to the reaction with molecular hydrogen [7]. The experimental results confirm that the pathway of gas pressure synthesis enables access to single phase products. The strontium-nitride-hydride (Sr_2N)H is obtained as brown-yellow single phase powder by the reaction of strontium subnitride (Sr_2N) with hydrogen (400 bar, 620 K) and subsequent treatment under vacuum (10^{-6} bar, 870 K). The structure determination was carried out by a combination of X-ray and neutron diffraction experiments on a deuterated sample, and the elemental composition of the ternary compound was confirmed by means of chemical analyses. Strontium (Sr^{2+}) in the crystal structure of (Sr_2N)D (Fig. 2) is arranged in a slightly distorted ccp-motif. Nitrogen (N^{3-}) and deuterium (D^-) occupy the octahedral voids of the strontium-matrix in an ordered manner resulting in an alternating

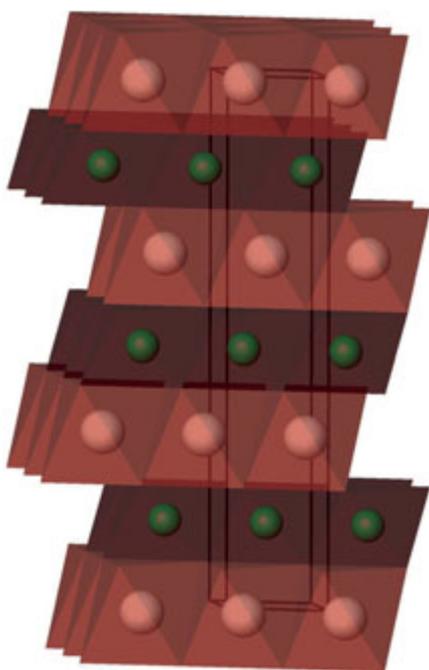


Fig. 2: Crystal structure of $(\text{Sr}_2\text{N})\text{D}$. Along $[001]$ the octahedral holes between the strontium layers (red) are alternatively filled with nitrogen (green in dark-colored octahedra) and deuterium (white in light-colored octahedra), respectively. The unit cell is outlined.

sequence of layers (anti- α - NaFeO_2 -type structure). Up to now, studies on the selective release of hydrogen from $(\text{Sr}_2\text{N})\text{H}$ result in partial decomposition of the sample.

Recently, our interests in the intercalation processes were extended to single crystals [8]. In these studies single crystals of Sr_2N react with molecular nitrogen and hydrogen, respectively, using the gas pressure method. The results show that the optimum reaction conditions for the preparation of homogeneously intercalated single crystals differ from those for single phase powders in the way that higher reaction pressures are needed for the implementation of the same amount of nitrogen and hydrogen, respectively, in a single crystal. The development of the intercalation process was monitored by SEM and single crystal X-ray diffraction. The intercalation process proceeds from the border area to the core of the single crystal, which is exceedingly visible for the intercalation of hydrogen in the strontium subnitride (Fig. 3). These observations also confirm the preservation of the topochemical host – guest relations for intercalation and deintercalation in the formation of the

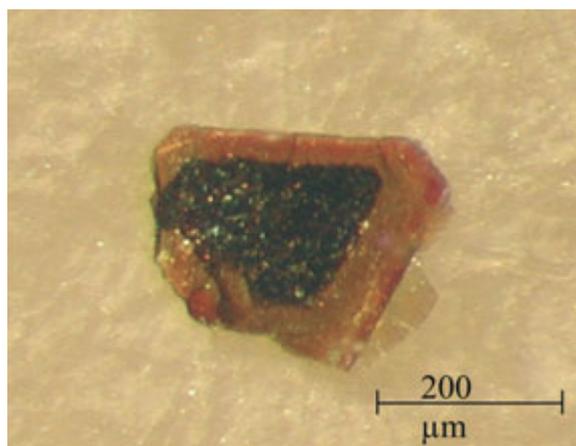


Fig. 3: LM-micrograph from a single crystal of Sr_2N after reaction with molecular hydrogen. For the visualization of the progress of the redox intercalation process reaction conditions were chosen, which were only optimized for preparation of single phase powders. Under these conditions only a partial intercalation of hydrogen in the single crystal takes place as indicated by dark and light-colored parts.

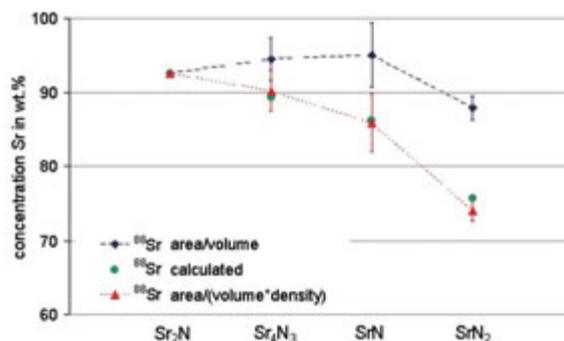


Fig. 4: Results of the LA-ICP-MS analysis of the intercalation series in the system Sr-N taking into account two different quantification strategies. The experimental data were collected on pressed pellets of Sr_2N , Sr_4N_3 , SrN and SrN_2 with single spot ablation (Ø 50 μm , 3 J/cm^2 , 5 Hz, 50 pulses, 20 ms DwellTime). The time resolved signals were integrated, normalized to Sr_2N and corrected on the basis of the ablated volume (blue) and in the second case, the densities of the compounds are additionally considered (red). The calculated concentrations (green) result from the empirical formula. The dotted lines serve for a better visualization of the trend of the concentration of Sr.

strontium nitride-diazenides. Finally, investigations with LA-ICP-MS were carried out for spatially resolved chemical analyses (see “Spatially Resolved Chemical Analyses with Laser Ablation ICP-MS”). Pre-investigations on single phase pow-

ders (pressed pellets) of the intercalation series Sr_2N , Sr_4N_3 , SrN and SrN_2 were carried out to develop a quantification strategy for precise analyses of the content of strontium in single crystals. Reproducible and reliable results could only be obtained when the ablated volumes of the samples as well as their densities were determined and considered (Fig. 4). With respect to the spatial resolved analysis of single crystals concerning the proceeding of the intercalation process these facts still hamper the investigations. However, first studies on single crystals confirmed the expected tendency that the intercalation proceeds from the borders to the core.

References

- [1] G. Auffermann, R. Kniep and W. Bronger, *Z. Anorg. Allg. Chem.* **632** (2006) in press.
- [2] G. Auffermann, Yu. Prots and R. Kniep, *Angew. Chem. Int. Ed.* **40** (2001) 547.
- [3] Yu. Prots, G. Auffermann, M. Tovar and R. Kniep, *Angew. Chem. Int. Ed.* **41** (2002) 2288.
- [4] G. V. Vajenine, G. Auffermann, Yu. Prots, W. Schnelle, R.K. Kremer, A. Simon and R. Kniep, *Inorg. Chem.* **40** (2001) 4866.
- [5] G. Auffermann, U. Schmidt, B. Bayer, Yu. Prots and R. Kniep, *Anal. Bioanal. Chem.* **373** (2002) 880.
- [6] G. Auffermann, Yu. Prots and R. Kniep, unpublished.
- [7] R. Chemnitzer, G. Auffermann and R. Kniep, *Z. Anorg. Allg. Chem.* **631** (2005) 1813.
- [8] R. Chemnitzer, Thesis, TU Dresden, in preparation.