Rare-Earth Nickel Nitridoborates with (BN) Anions: Characterized *RE*Ni(BN) and Anticipated *RE*M(BN) Compounds

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Received January 10th, 2006.

Professor Hans Georg von Schnering zum 75. Geburtstag gewidmet

Abstract. The compounds RENi(BN) with RE = Y, La, Ce, Pr, Tm and Yb were synthesized by solid state reactions from metal powders and α -BN at temperatures between 1000° and 1200 °C. In addition, the mixed phases (Ca,Yb)Ni(BN) and (Ca,Tm)Ni(BN) were synthesized. All products were characterized by powder XRD measurements and indexed isotypic with the structure of

Introduction

Nitridoborates represent a group of compounds containing different types of (BN_x) anions, such as [BN]ⁿ⁻, [BN₂]³⁻, $[B_3N_6]^{9-}$, $[B_2N_4]^{8-}$, and $[BN_3]^{6-}$ [1]. Compounds with the $[BN_2]^{3-}$ ion are well-known in combinations with alkaline and alkaline earth ions [2-14]. All the other nitridoborate ions are known from compounds containing rare-earth elements. These nitridoborates can occur as insulators $(La_3B_3N_6 [15])$, semiconductors $(La_3B_2N_4 [16])$, and as metals or superconductors (La₃Ni₂(BN)₂N [17, 18]). Compounds with the [BN]ⁿ⁻ anion are considered as being special, not only because the [BN]ⁿ⁻ ion can be contained in superconducting compounds, but also because there is no clear charge assignment available in compounds owing the [BN]ⁿ⁻ ion. In our present work we compare the electronic situation of $[BN]^{n-}$ with that of $[C_2]^{n-}$ where n can formally range between 2 and 6. In this context the B-N or C-C bond distances in compounds may serve as indicators for the respective ionic charge (n).

The first single-crystal XRD structure determination of a compound containing a [BN] anion was established for CaNi(BN) [19], revealing a B–N distance of 138 pm. For the superconducting compound $La_3Ni_2(BN)_2N$, the B–N CaNi(BN), consistent with the tetragonal space group P4/nmm. The bonding conditions of the (BN) anion are discussed in a perspective view on new nitridoborate compounds *REM*(BN) containing transition metal atoms (M) other than Ni.

Keywords: Nitridoborates; BN anion; Electronic structure; Syntheses

distance was refined at 143(2) pm (from single-crystal XRD) [18] and 143.7(4) pm (from neutron diffraction on powder) [17]. These distances are slightly longer than the B–N distance of approximately 135 pm, commonly assigned as a double bond in $[N=B=N]^{3-}$.

According to band structure calculations CaNi(BN) is expected as a small-gap semiconductor or a semi-metal, with the 3σ level of the [BN]²⁻ representing the highest occupied band, slightly below the (B–N-antibonding) π^* related bands. In comparison to this compound the *RE*Ni(BN) compounds with *RE*³⁺ ions contain one additional electron and are considered as metallic due to the partial occupation of π^* bands.

In this work we describe a number of isotypic RENi(BN) compounds with different RE atoms. In spite of several attempts to substitute nickel versus another transition metal atom (M), there is no other REM(BN) example known to date, but the calcium compound CaPd(BN). In order to provide an explanation for this experimental finding we have tried to inspect the electronic properties and bonding conditions of the [BN]ⁿ⁻ ion and its interactions in REM(BN) compounds containing transition metal atoms (M).

Experimental

Syntheses

All manipulations during the synthesis of *RE*Ni(BN) compounds were performed in an Ar filled dry-box (MBraun) using *RE* chunks or powders (Strem, 99.9 %), Ni powder (Strem, 99.9 %), and α -BN (ABCR, 99.8 %) as starting materials. In the case of Yb powder (Alfa Aesar, 99.9 %) a hydride was in fact present, approximately as YbH₂, according to XRD measurements. α -BN was degassed at 1000 °C under vacuum for three days prior use. Reactions were



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performed according to equation (1) in tantalum containers starting from mixtures with 1:1:1 molar ratios of *RE*, Ni, and BN, using total masses of about 400 mg in each reaction. Alternatively *RE* nitrides (made from *RE* metal chunks under nitrogen atmosphere) and nickel boride (made from nickel powder and β -rhombohedral boron (ABCR, 99.7 %) by arc melting) were used as starting materials, following equation (2). In attempt to synthesize mixed (Ca_{1/2}*RE*_{1/2})Ni(BN) compounds, dendritic calcium (Strem, 99.99 %) was used to substitute one-half of the *RE* metal.

$$RE + Ni + BN \rightarrow RENi(BN)$$
 (1)

$$REN + NiB \rightarrow RENi(BN)$$
 (2)

Reactions were performed as follows: Metal powders were thoroughly mixed with BN and then transferred into a carefully cleaned tantalum container. The tantalum container was sealed under Ar with an electric arc and then placed into a vacuum-sealed silica ampoule. The samples, as protected by two ampoules, were heated to temperatures between 1000 ° and 1200 °C in a (Carbolite) boxfurnace within one hour to three days, and remained at this temperature for two to fourteen days. After cooling the furnace by its natural cooling rate, black crystalline powders of *RE*Ni(BN) were obtained as reaction products.

Syntheses were successfully performed for the compounds YNi(BN), LaNi(BN), CeNi(BN), PrNi(BN), TmNi(BN), YbNi(BN), and for the mixed compounds (Ca,Yb)Ni(BN) and (Ca,Tm)Ni(BN) with the nominal compositions (Ca_{1/2} $RE_{1/2}$)Ni(BN). Reactions with metal chunks and BN powder involved the formation of *REN* as side phases. This side reaction can be in part suppressed by using finely divided metal (or metal hydride) powders instead of metal chunks, and through fine tuning the temperature conditions of reactions.

No attempts were made for the synthesis of other mixed phases or for ScNi(BN). Formations of remaining examples of *RE*Ni(BN) compounds were obviously hindered by competing stabilities of their respective binary nitrides (*RE*N), under conditions we have used. Again we note the disadvantage of direct solid state reactions, when compared with solid state metathesis reactions that were reported earlier for syntheses of other rare-earth nitridoborates [1, 20]. All *RE*Ni(BN) compounds remained stable in air for several days. Treatments with mineral acids lead to their decompositions.

Powder XRD studies

The reaction products were inspected with an X-ray powder diffractometer (STOE, StadIP) using monochromatic Cu-K α_1 radiation. The powder patterns were indexed with the aid of the program system WinXPOW (STOE). Lattice parameters were refined following a tetragonal indexing scheme (*P4/nmm*; *Z* = 2), isotypic with the crystal structure of CaNi(BN), displayed in Figure 1. Refined lattice parameters of *RE*Ni(BN) compounds are listed in Table 1. Lattice parameters previously reported for LaNi(BN) (a = 372.5(2) pm, c = 759.0(4) pm [21]) are in agreement with our results. The powder XRD patterns of LaNi(BN) and PrNi(BN) did not show any impurity reflections. A sample of CeNi(BN) contained traces of CeN. The amounts of *RE*N side phases in the samples of YbNi(BN), TmNi(BN) and in the mixed compounds were estimated between 10 and 20 %.



Figure 1 Crystal structure of *RE*Ni(BN) (left) and a section of the structure showing the environments of [BN] and nickel atoms (right).

Table 1 Calculated lattice parameters, c/a ratios, unit cell volumes, and number of indexed lines for CaNi(BN) and *RE*Ni(BN) compounds.

Compound	<i>a</i> /pm	c /pm	c la	Volume 1/10 ⁻⁶ pm ³	Number of indexed lines
CaNi(BN)	353.38(4)	763.76(1)	2.16	95.375(2)	31
YNi(BN)	347.81(3)	757.29(7)	2.18	91.61(2)	10
LaNi(BN)	371.96(3)	758.23(9)	2.04	104.9(2)	19
CeNi(BN)	358.49(3)	751.41(9)	2.10	96.57(2)	23
PrNi(BN)	363.05(2)	761.31(6)	2.10	100.34(1)	19
TmNi(BN)	344.06(6)	750.7(2)	2.18	88.86(4)	11
YbNi(BN)	343.10(2)	748.71(6)	2.18	88.14(1)	17
$Ca_xYb_{1-x}Ni(BN)$	346.9(2)	756.5(5)	2.18	91.0(1)	17
$Ca_{x}Tm_{1-x}Ni(BN)$	349.20(5)	759.5(1)	2.17	92.61(3)	25

Table 2Comparison of experimental, calculated (ab initio) C-Cand B-N distances and reduced overlap populations (extendedHückel).

	$[C-C]^{2-}$	Н-С-С-Н	CaC ₂ ^{a)}	$[B-N]^{2-}$	H-B-N-H
Experimental (pm)	_	120.0	119.5		123.8
Ab initio calc. [22] (pm)	127.1	119.0	-		122.7 [33]
ROP ^{b)}	1.81	1.83	1.85		1.34

^{a)} tetragonal modification

^{b)} all C-C and B-N distances set to 126 pm

Electronic Structure of the [BN] Anion

With the boron atom being slightly larger and the nitrogen atom being slightly smaller than carbon, one can expect similar bond distances in $[BN]^{n-}$ and $[C_2]^{n-}$ anions. According to *ab inito* (HF 6-31G*) calculations, B–N distances should range between 123 pm for HBNH (gas phase) and 130.4 pm for $[BN]^{2-}$ (Table 2) [22]. For $[N=B=N]^{3-}$ and $[C=C=C]^{4-}$ anions the corresponding B–N and C–C distances all amount to about 135 pm. Experimental data for $[BN]^{n-}$ are rarely available, with refined B–N distances of 138 pm in CaNi(BN) and 144 pm in La₃Ni₂(BN)₂N.



Figure 2 MO Scheme of [BN] and occupation with electrons corresponding to $[BN]^{2-}$ (at a bond distance of 126 pm). The molecular orbital overlap population (MOOP) is shown at right. The fermi energy $\varepsilon_{\rm f}$ is shown as a dashed line.

In order to compare the characteristics of [BN] and [C₂] anions we performed MO calculations using the CACAO program system [23]. As expected the principal MO picture appears quite similar for both species with the energy levels following the order 1σ , 2σ , π , 3σ , π^* as shown for [BN]ⁿ⁻ in the Figure 2. Considering a [BN]²⁻ ion the 3σ level is the HOMO, similar as for the acetylide ion in CaC₂ [24]. Any additional electron in will lead to the occupation of strongly antibonding π^* levels.

When the isolated [B-N] and [C-C] anions are compared with each other, two main differences in the bonding characteristics can be revealed on basis of extended Hückel calculations: The first difference is a comparable weak π bonding in [BN]²⁻ through weaker B(2p_{x,y}) – N(2p_{x,y}) orbital interactions due to the smaller overlap integral of the non-degenerate orbital interactions. The second difference is a change of the 3 σ orbital from slightly bonding in [C₂]²⁻ to slightly antibonding in [BN]²⁻, as shown by the MOOP (molecular orbital overlap population) in Figure 2. This nature of the 3 σ level in [BN]²⁻ is a result of orbital mixing of the strongly antibonding B(2s) – N(2p_z) interaction which exceeds the bonding B(2p_z) – N(2p_z) interaction. All this leads to a smaller value of the reduced overlap population (ROP) of 1.26 for $[BN]^{2-}$ compared with 1.81 for $[C_2]^{2-}$ (both calculated using B-N and C-C bond lengths of 1.26 pm).



Scheme 1

These results should let us expect slightly longer B-N distances compared with corresponding C-C distances. The bonding characteristics of the [BN] anion in compounds have been previously investigated and presented on basis of calculated band structures [1, 19].

Electronic picture of REM(BN) compounds containing a transition metal (M)

A projection of relevant energy states of different RE-(BN_x) and RE-Ni-(BN) compounds into a simple block scheme is given in Figure 3. The (5d) valence orbitals of RE atoms are the highest in energy. It can be seen that rare-earth nitridoborates RE-(BN_x) with different [BN_x] anions can occur as salt-like compounds (e.g. La₃B₃N₆) or as conductors, when excess electrons are present (e.g. La₃(B₂N₄)(e⁻) [1, 25]).

Band structure calculations on *RE*Ni(BN) compounds feature the fermi level above a density of state peak of the nickel 3d bands [1], so that Ni 3d states fall into the region of B-N bonding states. We may note that the states near the fermi level are of mixed (BN) π^* -Ni(4s,4p,3d)-*RE*(5d) nature, rather than pure *RE* states, as shown in the simplified block scheme in Figure 3.

Results and Discussion

Compounds with the formula *RE*Ni(BN) have been synthesized on different ways, by direct combinations of metal



Figure 3 Approximate density-of-states projection for RE-(BN_x) (salt-like), RE-(BN_x)(e⁻) (metal-like), and RE-Ni-(BN)(e⁻) (metal-like) compounds. Note the energetically low-lying Ni 3d energy states.

powders with α -BN, and by reactions of *RE*N and NiB. Products were obtained as black powders. The XRD patterns of compounds *RE*Ni(BN) with *RE* = Y, La, Ce, Pr, Tm, and Yb were indexed isotypically with the known pattern of CaNi(BN) (space group P4/nmm) as listed in Table 1. Their intensity profiles were in good agreement with the calculated ones. However, attempts to refine crystal structures on basis of powder XRD data did not provide accurate results for the light atoms, and are therefore not reported here. A comparison of lattice parameters and cell volumes shows the expected trend of the lanthanide contraction. A slightly smaller cell volume was obtained for the cerium compound. This kind of deviation has been often referred as being due to the presence of some Ce⁴⁺ (besides Ce³⁺).

Syntheses of mixed metal compositions (Ca, RE)Ni(BN) were designed to prove the existence of such phases. Structure parameters and unit cell volumes of (Ca, Yb)Ni(BN) and (Ca, Tm)Ni(BN) suggest compositions near the starting compositions (Ca_{1/2} $RE_{1/2}$)Ni(BN) when graphically extrapolated between CaNi(BN) and RENi(BN), and we may expect a significant phase width possible. No signs of superstructure reflections were obtained for these mixed phases from the powder XRD patterns.

The crystal structures of *RE*Ni(BN) compounds (Figure 1) contain square planar layers of nickel atoms with Ni–Ni distances at $(a \sqrt{2})/2$. Boron atoms of [BN] anions are situated above and below the square centers in an alternating fashion. The approximate tetrahedral coordination of Ni with four [BN] anions suggests a relation of this fragment with Ni(CO)₄.

Electronic structure calculations on $[BN]^{n-}$ and $[CC]^{n-}$ ions revealed some differences between these ions, such as a weaker B–N bonding in $[BN]^{n-}$. However, the bonding characteristics of the [BN] anions can be viewed as being closely related with those of $[C_2]$ anions in $REM(C_2)$ compounds (M = Co, Ni) [26–28], or with [BC] anions in RENi(BC) compounds [29–30]. Another series of related compounds involves the $REM_2(BCB)$ compounds with M = Ni, Pd, Pt, Co, Rh, or Ir [31–32] crystallizing related with the ThCr₂Si₂ type structure. We note that all these compounds are known by a whole series of RE elements but mostly with nickel or a group 8 transition element (M).

Considering the electronic situation in the *REM*(BN) system, the intrinsic problem for the stability of such a compound will be the (H_{ii}) energy of the d levels of M relative to the $(3\sigma - \pi^*)$ HOMO-LUMO gap of [BN]²⁻. Will the d energy of M be high, lets say as high as the 5d of the rare earth elements, the d electrons will populate strongly antibonding (π^*) levels of [BN]ⁿ⁻, and possibly decompose it into a nitride-boride. Will the d energy of M be energetically low, such as for nickel, the d states will drain bonding (3σ and so on) electrons from [BN]ⁿ⁻ to achieve a d¹⁰ electron count (if not already owned). Hence, the formation of a stable *RE*Ni(BN) compound will depend on the d energy and the d electron count of M. As shown in the block scheme in Figure 3, the 3d energy states of nickel are clearly

below fermi level, and below the 3σ HOMO of [BN]²⁻. The 3d energies of elements in the periodic table decrease from Ti to Cu, and the further right ones are energetically below the (3σ) HOMO of [BN]²⁻. We may therefore assume that group 8 elements with d electron counts near d¹⁰ are feasible candidates for new *REM*(BN) compounds.

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