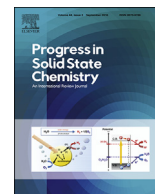




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# Itinerant nitrides and salt-like guanidates – The diversity of solid-state nitrogen chemistry

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## ABSTRACT

Recent advances in the chemistry of two peculiar nitrogen-based materials, that is, ternary itinerant iron nitrides and unsubstituted guanidate salts, are reviewed. Key to their synthesis is the versatile tool ammonia, either as a gas or as a liquid. For metallic nitrides  $M_x\text{Fe}_{4-x}\text{N}$  including transition-metal and main-group elements  $M$ , it is of paramount importance to follow an improved ammonolytic reaction for achieving both stable and metastable compounds; in addition, there is a magnetic effect acting on the crystal structure of  $\text{Ga}_x\text{Fe}_{4-x}\text{N}$ , and one also finds spin-glass behavior in main-group nitrides ( $M = \text{Ga}, \text{Ge}, \text{Sn}$ ). The guanidate review features an oxidation-controlled low-temperature synthesis of Yb salts, the first magnetic guanidates, and the doubly-deprotonated guanidates; the latter represent the all-nitrogen analogues of the ubiquitous carbonates. The covered guanidates adopt the compositions  $\text{MCN}_3\text{H}_4$ ,  $\text{M}(\text{CN}_3\text{H}_4)_2$ ,  $\text{M}(\text{CN}_3\text{H}_4)_3$  and  $\text{M}(\text{CNH})_3$  ( $M = \text{Li}-\text{Cs}, \text{Sr}, \text{Eu}, \text{Yb}$ ). We also cover the application of first-principles calculations at all levels to gain a deeper understanding of the studied materials.

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## 1. Introduction

Nitrogen-based materials have been enjoying a boom not only within fundamental research, but also with respect to applications. Their full potential can only be estimated by a comparison with the ubiquitous oxides: those compounds have dominated solid-state research from the inception of the field and still, new features and applications are being developed every day [1]. Nitrogen-based materials show an even richer variety when it comes to crystal structures [2], and a number of applications have already emerged [3]. We cannot imagine the world without N-based fertilizers [4] anymore, and equally important are explosives [5], high-performance steels (with their hardened nitride surfaces [6]), and nitride-based LEDs and transistors [7], to only name a few.

With increased effort in nitrogen-related chemical research, a number of thriving, specialized subfields have come to the surface. Here, we want to review recent advances of the last decade touching upon two subfields, ternary itinerant iron nitrides and salt-like guanidates. The focus is on their syntheses, their crystal structures and their properties, especially their magnetic behavior.

Synthetically, nitrogen-based compounds are demanding because a direct use of the elements is usually not possible – the molecule  $N_2$  is unreactive due to its  $N\equiv N$  bond [5]. Hence, key to many syntheses is the versatile chemical tool ammonia. For modern nitrides, an  $NH_3/H_2$  gas mixture is the nitrogen-source used in an improved ammonolytic synthesis. For the guanidates,  $NH_3$  is the solvent and the necessary medium for the other reduction agents. Whether in solid–gas or solid–liquid reactions, the conditions can be tuned to not only obtain thermodynamically stable compounds, but also even metastable phases under kinetically controlled conditions, as we will address at various points in the text.

Concerning the ternary iron nitrides, for reasons of brevity we focus exclusively on nitrides that are derived from ferromagnetic  $\gamma'$ - $Fe_4N$  and mainly on nitrides  $M_xFe_{4-x}N$  with main-group elements III and IV. In recent years, unusual structural properties were investigated, such as a magnetic effect acting on the crystal structure in  $Ga_xFe_{4-x}N$ , a nitrogen deficiency in  $Ge_xFe_{4-x}N_y$ , or a miscibility gap in  $Sn_xFe_{4-x}N$ . Furthermore, we describe that these nitrides exhibit a transition from ferromagnetism to spin-glass behavior upon substitution.

The guanidates, on the other side, are deprotonated salts of the strong base guanidine,  $CN_3H_5$ . Interestingly, guanidine can be deprotonated not only once, but twice. The synthetic challenges and their solutions are reviewed in depth. Today, guanidates of the alkali metals, a single alkaline-earth metal, and several rare-earth metals have been characterized. We will evaluate the role of hydrogen-bonding and ionic forces in their crystal structures. Finally, the first magnetic guanidates,  $Eu(CN_3H_4)_2$  and  $Yb(CN_3H_4)_3$ , have been found.

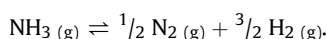
We also cover the application of first-principles calculation including the planning of synthesis, the analysis of crystal structures, and the interpretation of properties.

## 2. The synthesis of ternary iron nitrides

### 2.1. The classical ammonolytic reaction

Many ternary iron nitrides were already synthesized five decades ago. The method of choice was the nitridation of intermetallic precursors in an ammonia–hydrogen gas flow at intermediate temperatures around 600 °C. Among the first accessible nitrides were  $Ni_xFe_{4-x}N$ ,  $Pd_xFe_{4-x}N$ , and  $Pt_xFe_{4-x}N$  [8,9]. As of today, many more nitrides  $M_xFe_{4-x}N$  with a transition metal or a metalloid  $M$  have been synthesized and characterized ( $M = Mn$  [10],  $Co$  [11],  $Cu$  [12],  $Zn$  [13],  $Ru$  [14],  $Rh$  [15,16],  $Ag$  [17],  $Os$  [14],  $Ir$  [14], and  $Au$  [17] as well as  $Ga$  [18–21],  $Ge$  [18,22],  $In$  [13,18,23], and  $Sn$  [18,24–26]).

This solid–gas reaction has the advantage of forming mostly single-phase products that are necessary for characterizing structural and magnetic properties. The most relevant parameter of the ammonolytic reaction is the nitridation temperature because it influences the equilibrium of the ammonia dissociation (i.e., the reverse Haber–Bosch equilibrium)



At high temperatures, the dissociation of ammonia into the elements is almost complete so that inert  $N_2(g)$  accumulates in the gas phase. The nitridation of iron, iron(III) oxide or intermetallic precursors is only possible in the temperature range between 300 and 700 °C [27]. The nitrogen activity  $a_N$  of the aforementioned gas-phase reaction is given by the following formula:

$$a_N = \sqrt{a_{N_2}} = K \cdot \frac{a_{NH_3}}{a_{H_2}^{3/2}} \approx K \cdot \frac{p_{NH_3}}{p_{H_2}^{3/2}}$$

Thus, the exact nitride stoichiometry can be controlled by the supplied gas atmospheres. For illustration, the archetype of  $M_xFe_{4-x}N$ , the binary nitride  $\gamma'$ - $Fe_4N$ , is formed in an atmosphere of 50%  $NH_3$  in  $H_2$ . Phases such as  $\epsilon$ - $Fe_3N$  and  $\zeta$ - $Fe_2N$ , however, are obtained in atmospheres of 80–90%  $NH_3$  in  $H_2$  or 100%  $NH_3$ , respectively [27]. To conclude, the composition of the  $NH_3/H_2$  atmosphere determines which nitrides are accessible.

### 2.2. The improved two-step ammonolytic reaction

In recent years, chemists have combined synthesizing an intermetallic alloy with the nitridation in a single (at least formally) reaction (Fig. 1) [15,16]. This drastically improves the reaction efficiency (time) and the quality of the nitride. The first step is a coupled reduction reaction developed by Klemm and co-workers [28,29], in which the reduction of a metal oxide is accompanied by the simultaneous formation of an intermetallic alloy. The term *sintering reaction* has been established to describe this step even though a chemical reaction takes place. The second reaction step, the nitridation of the intermetallic alloy, depends on the nitridation temperature and the stoichiometry of the  $NH_3/H_2$  gas mixture, just as the classical ammonolytic reaction. Introducing a temperature

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