

Ternary and quaternary metal nitrides: A new challenge for solid state chemistry

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Abstract: The crystal chemistry of ternary and quaternary phases of the systems A/AE - TE - N (A = alkali metal; AE = alkaline earth metal; TE = transition element) is predominantly characterized by the presence and formation of complex nitridometalate anions. A suitable classification of the nitrido-compounds is based on the correlation between coordination-numbers (TE), oxidation states (TE) and the specific structural characteristics of the anionic partial structures.

Introduction and preparative aspects

Compared with the large number of well-known and well-investigated oxometalates the crystal chemistry and physics of nitridometalates is rather young and just at the beginning. The particular interest in nitridometalate compounds is mainly raised by the high polarizability of the nitride ion which is expected to cause specific properties in structure and bonding relations.

After the early works of Robert Juza [1] the essential breakthrough in the field of nitridometalate chemistry was achieved by the development of suitable methods of preparation. A fundamental example in this connection is the reaction of intermetallic melts (A/AE-TE) with molecular nitrogen as an oxidizing agent [2]. Under these conditions nitrogen is generally reduced to the nitride stage but there are already indications that the reduction may also take place via the azide stage ($\text{Ba}_9\text{N}[\text{N}_3][\text{Ta}_4\text{N}_4]$ [3]).

Fragments and variations of the Li_3N type structure

The crystal structure of Li_3N [4] ($\hat{=}$ $\text{Li}_2[\text{LiN}]$ [5]) has been regarded as a unique structure type for a long time. Today, in addition to the substitution series $\text{Li}_2[(\text{Li}_{1-x}\text{TE}_x)\text{N}]$ (TE = Co, Ni, Cu [1,2,5]) we know the defect-superstructure $\text{Li}_4[\text{FeN}_2]$ ($\hat{=}$

$\text{Li}_2[\text{Fe}_{0.5}\text{N}]$) [6], the crystal structures of Li_4SrN_2 [7] (layered fragments of $\text{Li}_2[\text{LiN}]$) and LiSrN [8] ($\hat{=}$ $\text{Sr}[\text{LiN}]$), the intergrowth structure $(\text{Li}_{1-x}\text{Ni}_x)\text{Li}_4\text{Sr}_2\text{N}_3$ [9] ($\hat{=}$ Li_4SrN_2 . $\text{Sr}[(\text{Li}_{1-x}\text{Ni}_x)\text{N}]$) and the crystal structure of $\text{Ca}[\text{LiN}]$ [7] which is a modified fluorite type structure containing Li-N-ribbons which are also present in the $\text{Li}_2[\text{LiN}]$ type. Even $\text{Ba}_2(\text{Ni}_{1-x}\text{Li}_x)[\text{NiN}]_2$ [10] represents a variant of the $\text{Li}_2[\text{LiN}]$ crystal structure.

Structures related to binary TE-nitrides; CN(TE)=6, 5

Some of the ternary nitrides with elements of groups 4-6 in high (predominantly the highest) oxidation states contain the transition metal in octahedral (or trigonal prismatic) nitrido-coordination (CN=6): $\text{Li}_2[\text{ZrN}_2]$ and $\text{Li}_2[\text{HfN}_2]$ [11], $\text{Na}[\text{NbN}_2]$ [58] and $\text{Na}[\text{TaN}_2]$ [12]. $\text{Li}_2\text{Ta}_3\text{N}_5$ [13] and LiMoN_2 [14] can be described in terms of intercalation compounds. Zr(IV) in the crystal structure of $\text{Ba}[\text{ZrN}_2]$ [15] is in a tetragonal-pyramidal coordination (CN=5) by nitrogen.

Tetrahedral structures (Analogy to oxosilicates; CN(TE)=4)

A large number of nitridocompounds with elements of groups 4-7 (and 8, Fe) in high (in many cases the highest) oxidation states contain tetrahedral anions. Here, only a few but representative examples are presented: Isolated tetrahedra - $\text{Li}_7[\text{VN}_4]$ [1], $\text{Li}_6[\text{CrN}_4]$ [16] $\text{Ba}_5[\text{CrN}_4]\text{N}$ [17], $\text{Ba}_3[\text{MoN}_4]$ and $\text{Ba}_3[\text{WN}_4]$ [18], $\text{Li}_7[\text{MnN}_4]$ [1]; Dimers $[(\text{TE})_2\text{N}_7]$ - $\text{LiBa}_4[\text{Mo}_2\text{N}_7] \cdot \text{BaCl}_2$ [19] and $\text{LiBa}_4[\text{W}_2\text{N}_7]$ [20]; Rings - $\text{Ba}_{10}[\text{Ti}_4\text{N}_{12}]$ [21]; Chains $[(\text{TE})\text{N}_3]$ - $\text{Ba}_2[\text{Ta}_3\text{N}_3]$ and $\text{Sr}_2[\text{Ta}_3\text{N}_3]$ [22]; Framework $[(\text{TE})\text{N}_2]$ - $\text{Cs}[\text{Ta}_2\text{N}_2]$ [12]. The crystal structure of $\text{Li}_3[\text{FeN}_2]$ [23] contains infinite chains $\infty^1 [\text{FeN}_4/2]^{3-}$ of edge-sharing FeN_4 -tetrahedra.

Trigonal-planar anions $[(\text{TE}^{\text{III}})\text{N}_3]^{6-}$; CN(TE)=3

The compounds of general composition $(\text{AE})_3[(\text{TE})^{\text{III}}\text{N}_3]$ (TE = V, Cr, Mn, Fe) can be classified in two groups: i. crystal structures with space group Cmcm and C_{2v} -symmetry of the complex anions ($\text{Ca}_3[\text{VN}_3]$ [24], $\text{Ca}_3[\text{CrN}_3]$ [25], $\text{Ca}_3[\text{MnN}_3]$ [26]) and ii. crystal structures with space group $\text{P6}_3/\text{m}$ and D_{3h} -symmetry of the complex anions ($\text{Sr}_3[\text{CrN}_3]$ and $\text{Ba}_3[\text{CrN}_3]$ [27]; $\text{Sr}_3[\text{MnN}_3]$ and $\text{Ba}_3[\text{MnN}_3]$ [28]; $\text{Sr}_3[\text{FeN}_3]$ and $\text{Ba}_3[\text{FeN}_3]$ [29]). The differences in symmetry of the complex planar anions seem to be caused by the size and "hardness/softness" of the AE-cations rather than by a Jahn-Teller-distortion. The crystal structure of $(\text{Ca}_3\text{N})_2[\text{FeN}_3]$ [30] also contains planar anions with D_{3h} -symmetry. IR-spectra [29], Mössbauer-spectra [31] as well as calculations of the electronic structure of $\text{Ba}_3[\text{FeN}_3]$ [31] are consistent with the presence of a Fe(III)-low-spin-complex and with a Fe-N bonding order greater than one.

Nitridoferrates(II); CN(TE)=3, 2

The crystal structures of nitridoferrates(III) and (II) contain complex anions which are isostructural to main group systems [32]: $\text{Li}_3[\text{FeN}_2]$ [23] ($\infty^1 [\text{Fe}^{\text{III}}\text{N}_{4/2}^{3-}]/\text{SiS}_2$), $\text{Ba}_3[\text{FeN}_3]$ [29] ($[\text{Fe}^{\text{III}}\text{N}_3]^{6-}/\text{CO}_3^{2-}$), $\text{Ca}_2[\text{Fe}^{\text{II}}\text{N}_2]$ [33] ($[\text{Fe}_2^{\text{II}}\text{N}_4]^{8-}/[\text{In}_2\text{P}_4]^{6-}$), $\text{LiBa}_2[\text{Fe}_2\text{N}_3]$ [34] ($\infty^1 [\text{Fe}_2^{\text{II}}\text{N}_3]^{5-}/\text{B}_2\text{S}_3$) and $\text{Li}_4[\text{FeN}_2]$ [6] ($[\text{Fe}^{\text{II}}\text{N}_2]^{4-}/\text{CO}_2$). Fe(II) in the crystal structures of nitridoferrates(II) is in a distorted trigonal-planar arrangement (CN=3) and in a linear coordination by nitrogen (CN=2), respectively. The low oxidation state and the linear coordination of iron in the anions $[\text{Fe}^{\text{II}}\text{N}_2]^{4-}$ of the crystal structures of $\text{Li}_4[\text{FeN}_2]$ [6] and $\text{Sr}_2[\text{FeN}_2]$ [33] establish the bridge to the low-valency nitridocobaltates, nitridoniccolates and nitridocuprates.

Low-valency nitridocobaltates, -niccolates and -cuprates;CN(TE)=2

The main features of this class of compounds are the linear coordination of the transition elements (CN=2), their low oxidation states and the high covalency of the TE-N bond (bonding order greater than one). The connecting link between nitridoferrates, nitridocobaltates and nitridoniccolates/ - cuprates is clearly shown by the following sequence: Isolated dumb-bells $[\text{Fe}^{\text{II}}\text{N}_2]^{4-}$ ($\text{Li}_4[\text{FeN}_2]$ [6]) ---> dumb-bells $[\text{Co}^{\text{I}}\text{N}_2]^{5-}$ which are completed to infinite (linear) arrangements [...Li...[N-Co^I-N]...Li...] ($\text{LiSr}_2[\text{CoN}_2]$ [35]) ---> infinite (linear) chains $\infty^1 [(\text{TE})^{\text{I}}\text{N}_2/2]$ ($\text{Ca}[\text{NiN}]$ [2, 36], $\text{Ca}[\text{CuN}]$ [37]). Infinite chain anions $\infty^1 [\text{NiN}_2/2]$ are also present in the crystal structures of $\text{Ba}[\text{NiN}]$ [38] and $\text{Sr}[\text{NiN}]$ [2, 39]. However, these (planar) chains are angled with a change in direction at every fourth N-position along the chains which causes short Ni-Ni-contacts at the bend-positions. The particular conformation of the zig-zag-chains $\infty^1 [\text{CoN}_2/2]$ in the crystal structure of $\text{Ba}[\text{CoN}]$ [40] results in short Co-Co- as well as short Co-Co-Co-contacts alternating along the chains. Again, linear chains $\infty^1 [\text{NiN}_2/2]$ are present in the crystal structures of $\text{Sr}_3\text{Li}_3[\text{NiN}]_4$ [41] and $\text{Ba}_2(\text{Ni}_{1-x}\text{Li}_x)[\text{NiN}]_2$ [10], the crystal structure of $\text{Ba}_8\text{N}[\text{NiN}]_6$ contains infinite helical chain anions. The crystal structures of nitridocuprates are isotypes of the nitridoniccolate phases [37, 43]. The substitution of TE(Ni,Cu) against lithium (e.g. $\text{Ca}[(\text{Ni}_{1-x}\text{Li}_x)\text{N}]$ [44]) opens a way to modify the electronic properties of the low valency nitridometalates.

Subnitrides (Ternary Systems Ca-Ag,Au-N)

As reported above, the nitrido species participates as a strong ligand in the formation of covalent anionic complexes. At the same time, however, the nitrido nitrogen tends to occupy - as isolated (ionic) species - the centers of coordination polyhedra which are formed exclusively by alkaline earth metal cations. Such structural elements with an overall positive charge form $((EA)_6N)^-$ -octahedra which appear as "macro-cations": Isolated $(Ag_{16}Ca_6N)$ [47]), condensed to give one-dimensional columns $(NaBa_3N)$ [45]), two-dimensional layers $((Ca_3N)_2[FeN_3])$ [30]) and three-dimensional frameworks $(Ca_3XN; X = As, Sb, Bi, Ge, Sn, Pb)$ [46]), respectively. The subnitride $Ag_{16}Ca_6N$ [47] contains discrete $(Ca_6N)^{9+}$ -octahedra, the subnitride-auride Ca_3AuN ($\cong (Ca^{2+})_3Au^{-}N^{3-} \cdot 2e^-$) [48] crystallizes in the cubic perovskite type structure.

$Ca_2[ZnN_2]$ and selected nitridometalates of group 13

$Ca_2[ZnN_2]$ [49] is the only group 12 - nitridometalate which is known up to now. The structure completes the series of dumb-bell anions: $[Fe^I N_2]^{4-}$ [6], $[Co^I N_2]^{5-}$ [35], $[Zn^I N_2]^{4-}$. Even the crystal structure of the ternary nitridogallate $Sr_8Ga_3N_8$ ($\cong Sr_8[GaN_2][GaN_3]_2$ [50]) indicates the existence of dumb-bell anions $[GaN_2]$. The formation of intermediate compounds in the ternary systems (Ca,Sr,Ba)-Al-N is investigated only recently [37, 51]. The crystal structure of $Sr_3[Al_2N_4]$ [52] contains corrugated chains $[\infty AlN_{4/2}]^{3-}$ which consist of distorted AlN_4 -tetrahedra sharing common edges. At least three different modifications (α , β , γ -) were obtained with the composition $Ca_3[Al_2N_4]$ [53]; the γ -phase is an isotype of $Ca_3[Al_2As_4]$ [54]. The crystal chemistry of nitridogallates is of particular interest because of the well-known tendency of gallium to form homonuclear bonds, for example tetrahedral Ga_4 clusters ($Ca_{18.5}Ga_8N_7$ [55]), planar zigzag chains ($Ca_5[Ga_2N_4]$ [56]), or even layers of tetragonal pyramids ($Ca[GaN]$ [57]). The crystal structures of $(Sr_6N)[Ga_5]$ and $(Ba_6N)[Ga_5]$ [59] contain isolated octahedral cations $((EA)_6N)^{9+}$ and trigonal-bipyramidal cluster-anions $[Ga_5]^{7-}$; a simple model of the chemical bonding in these isotypic phases is given by the formula $\{((AE)_6N)^{9+}[Ga_5]^{7-} \cdot 2e^-\}$.

Concluding remarks and prospect

The basic idea for this short review was to give a comprehensive snapshot on the high activities which are just going on in nitridometalate chemistry. Together with the recent review article on the CRYSTAL CHEMISTRY OF INORGANIC NITRIDES [60] the state of the art is now well documented. "Nitrides are fascinating

materials" [60] and a new challenge not only for solid state chemistry but also for solid state research and materials sciences.

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