

Recent Developments in Nitride Chemistry

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The chemistry of ternary nitrides is reviewed with special focus on developments of the last two years (1996 and 1997). In particular, structures and properties of ternary and higher transition metal nitrides, main group nitrides, subnitrides, and nitride halides are compared, and a section on thermodynamics of ternary nitrides is included. Finally, methods for the preparation of gallium nitride single crystals are summarized.

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1. Introduction

Ternary nitrides were first systematically investigated by Juza et al.^{1,2} beginning in the 1940s. This work focused mainly on lithium compounds, due to their relatively easy preparation and mostly simple structures.^{1,2} In the following decades several groups started some work on a variety of ternary nitrides. But faster development of this field began in the 1980s, when several new preparation techniques were introduced and systematically exploited. Today, the class of ternary nitrides and the investigation of their properties is a rapidly growing topic; nevertheless, compared with ternary oxides or sulfides, even now relatively little is known about nitrides. This short review is intended to give an overview on developments of mainly the last two years (1996 and 1997). Several reviews appeared in 1996 and early 1997 that summarize accomplishments prior that time.^{3–10} Each review has a different focus, but together they do an excellent job of presenting the synthesis methods and the unusual chemistry of nitrides.

The majority of ternary nitrides contain electropositive elements, typically alkali or alkaline earth metals, serving as electron donors that stabilize nitridometalate ions by the inductive effect. The nitridometalate anions, MN_x^{n-} , are generally characterized by the coordination number (CN) of M. An overview on coordination behavior of metal atoms by nitrogen in ternary nitrides

with electropositive elements has been given by Kniep.⁵ When M is an early transition metal, high oxidation states are often achieved, accompanied with coordination numbers of 4–6. When M is a late transition metal, oxidation states of 0 to +2 are typical and the coordination number of M is often only 2. For ternary nitrides of main group metals, coordination numbers of 4 and 2 are dominant. In contrast to oxide or sulfide chemistry, Zintl phases with germanium(II) chains can be achieved in compounds that also contain nitridogermanate ions. The metal cation coordination in nitrides shows a wide variety, whereas the coordination number of nitrogen atoms is very frequently 6—often with different cations and bond lengths in the coordination sphere. These features are part of the unique chemistry of nitrides in the solid state.

In this review, we organize the discussion of ternary transition metal nitrides by coordination geometry and focus on condensation of the complex anions to form larger isolated anionic groups, which eventually lead to one-, two-, or three-dimensional extended structure anion networks. The section on main group nitrides has a similar focus, but is also structured by the main group element M. A brief summary then follows of recent developments in several other related compound classes and topics that have been growing rapidly the past few years; that is, subnitrides, nitride halides, and the thermochemistry of ternary nitrides. We conclude with a short overview on ongoing attempts to prepare suitable gallium nitride (GaN) single crystals for possible use as substrates for GaN-based devices.

Table 1 gives an overview of all ternary and higher nitrides discussed in this review. It is not a complete list of known nitrides, rather it is a survey of new nitride compounds discovered in the past few years and some related structures. The table contains information on the coordination of the metalate central atom by nitrogen, CN(M), or the nitrogen by metal atoms, CN(N), organized in the same sequence as in the following text. The dimensionality of the partial structure (the nitridometalate net) and some information on the overall structure type or structure features are also given. Compounds with the same composition in the same row do not necessarily have an identical structure, but the main structural features mentioned in the fourth column are similar.

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Table 1. Structural Features of Ternary Nitrides

compound	CN(M)	dimensionality	structural feature/type	ref
Octahedral Coordination				
Sr[MN ₂] M = Zr, Hf	6	2	α -NaFeO ₂ , layers of edge-sharing octahedra $^1_{\infty}$ [MN _{6/3}]	14
Na[MN ₂] M = Nb, Ta	6	2	α -NaFeO ₂ , layers of edge-sharing octahedra $^1_{\infty}$ [MN _{6/3}]	16, 17, 18
Ca[TaN ₂]	6	2	α -NaFeO ₂ , layers of edge-sharing octahedra $^1_{\infty}$ [MN _{6/3}]	19, 20
Ba[TaN _{2+x}]	4,5 (6)	3	HT-BaMnO ₃	31
Na _x Ta ₃ N ₅	6	3	filled Ta ₃ N ₅ /Ti ₃ O ₅	33
Li _{2-x} M _{2+x} O _y N _{4-y} M = V, Nb	6	3	rocksalt	34, 35
Li _{1-x} Nb _{3-3x} □ _{4x} O _y N _{4-y}	6	3	rocksalt	34, 35
Li ₂ Ta ₂ O _y N _{4-y}	6	3	rocksalt	34
Li _{1-x} V _{3+x} O _y N _{4-y}	6	3	rocksalt	34
Li _{2-x} Ta _{2+x} N ₄	6	3	rocksalt	36
Li ₂ Ta ₃ N ₅	6	3	ordered rocksalt	37
SrMoO _{2.5} N _{0.5}	6	3	perovskite	39
SrWO ₂ N	6	3	perovskite	39
ThTa ₃ N ₃	6	3	perovskite	41
(AE, Th)(N, O) AE = Ca, Sr	6	3	rocksalt	42
La _{1-x} Ca _x N _{1-x/3}	6	3	rocksalt	122
Trigonal Prismatic/Octahedral Coordination				
LiNb ₃ N ₄	6	2	filled MoS ₂	35, 38
Li _{1-x} Ta _{3+x} N ₄	6	2	filled MoS ₂	36
MnMoN ₂	6/6	2 (3)	layers of edge-sharing trigonal prisms $^2_{\infty}$ [M'N _{6/3}]	106
MWN ₂ M = Cr, Mn, Fe, Co, Ni	6/6	2 (3)	layers of edge-sharing trigonal prisms $^2_{\infty}$ [M'N _{6/3}]	105, 106, 107, 108, 115, 117, 120
(Fe _{0.8} M' _{0.2})M'N ₂ M' = Mo, W	6/6	2 (3)	layers of edge-sharing trigonal prisms $^2_{\infty}$ [M'N _{6/3}]	109, 110
M ₃ Mo ₃ N M = Fe, Ni		3	η -Fe ₃ W ₃ C	111, 112, 115, 117
M ₃ W ₃ N M = Fe, Co		3	η -Fe ₃ W ₃ C	116, 118
Transition Metal Nitrides, Tetrahedral Coordination				
Li ₃ Sr ₂ [MN ₄] M = Nb, Ta	4	0	Li ₃ Na ₂ [GaO ₄], isolated tetrahedra [MN ₄]	43
Li ₁₆ [MN ₄] ₂ O M = Nb, Ta	4	0	isolated tetrahedra [MN ₄]	64, 65, 68
Ba ₉ [MN ₄] ₂ N(N ₃) M = Nb, Ta	4	0	isolated tetrahedra [MN ₄]	72, 73
Ba ₅ [CrN ₄]N	4	0	isolated tetrahedra [MN ₄]	69
Ba ₃ [WNO ₃] ₂	4	0	Ba ₃ V ₂ O ₈ , isolated tetrahedra [MX ₄]	57
Na ₃ [MNO ₃] M = Mo, W	4	0	isolated tetrahedra [MX ₄]	59
Na ₄ [MN ₂ O ₂] M = Mo, W	4	0	isolated tetrahedra [MX ₄]	60
Li ₆ Ca ₁₂ [MN ₄] ₄ O ₃ M = Mo, W	4	0	isolated tetrahedra [MN ₄]	66
AE ₅₁ [WN ₄] ₁₂ N ₈ O ₃ AE = Ca, Sr	4	0	isolated tetrahedra [MN ₄]	75 (74)
Ba ₄ [WN ₄]Cl ₂	4	0	isolated tetrahedra [MN ₄]	77
A ₆ [M ₂ N ₄ O ₃] A = K, Rb, Cs; M = Mo, W	4	0	K ₆ Ti ₂ O ₇ , isolated units [M ₂ X ₇] of two-corner-sharing tetrahedra	61, 62
Li ₃ [FeN ₂]	4	1	infinite chains of edge-sharing tetrahedra $^1_{\infty}$ [MN _{4/2}]	156
AE ₂ [VN ₃] AE = Sr, Ba	4	1	chains $^1_{\infty}$ [MN ₂ N _{2/2}] of corner-connected tetrahedra	158
Na ₃ [MN ₃] M = Mo, W	4	1	chains $^1_{\infty}$ [MN ₂ N _{2/2}] of corner-connected tetrahedra	46-48
Na ₂ K[WN ₃]	4	1	chains $^1_{\infty}$ [MN ₂ N _{2/2}] of corner-connected tetrahedra	49
Na ₁₁ Rb[(WN ₃) ₄]	4	1	chains $^1_{\infty}$ [MN ₂ N _{2/2}] of corner-connected tetrahedra	49
Na ₅ A[(WN ₃) ₂] A = Rb, Cs	4	1	chains $^1_{\infty}$ [MN ₂ N _{2/2}] of corner-connected tetrahedra	50
NaA ₄ [(WN _{2.5} O _{0.5}) ₂] A = Rb, Cs	4	1	chains $^1_{\infty}$ [MX ₂ X _{2/2}] of corner-connected tetrahedra	63
K ₁₄ [W ₆ N ₁₆ NH]	4	1	ropes of corner-sharing tetrahedra	53
Na ₂ K ₁₃ [W ₇ N ₁₉]	4	2	layers of corner-connected tetrahedra	52
Cs[MN ₂] M = Nb, Ta	4	3	filled β -cristobalite, $^3_{\infty}$ [MN _{4/2}] framework	55, 56
Cs ₅ [Na{W ₄ N ₁₀ }]	4	3	ordered filled β -cristobalite, $^3_{\infty}$ [MN _{4/2}] framework	54
Main Group Element Nitrides, Tetrahedral Coordination				
Ca ₄ [GeN ₄]	4	0	isolated tetrahedra [MN ₄]	141
Ba ₅ [Si ₂ N ₆]	4	0	isolated units of two edge-sharing tetrahedra [M ₂ N ₆]	123

Table 1 (Continued)

compound	CN(M)	dimensionality	structural feature/type	ref
Main Group Element Nitrides, Tetrahedral Coordination (Continued)				
M ₃ M ^{III} [P ₃ O ₉ N] M ^I = Na, K; M ^{III} = Al, Ga, In, Ti, V, Cr, Mn, Fe	4	0	isolated units [(PO ₃ N _{1/3}) ₃] of three tetrahedra-sharing a common vertex at the nitrogen atom	178
Na ₂ M ^{II} [P ₃ O ₉ N] M ^{II} = Mg, Mn, Fe, Co	4	0	isolated units [(PO ₃ N _{1/3}) ₃] of three tetrahedra-sharing a common vertex at the nitrogen atom	178
Sr ₃ [Al ₂ N ₄]	4	1	infinite chains of edge-sharing tetrahedra ¹ _∞ [MN _{4/2}]	155
La ₂ [AlN ₃]	4	1	chains ¹ _∞ [MN ₂ N _{2/2}] of corner-connected tetrahedra	157
AE ₃ [(Ga ₂ N ₂) ₂] AE = Sr, Ba	4	1	infinite chains of edge-sharing tetrahedra ¹ _∞ [MN _{4/2}]	153, 154
Ca ₅ [(GeN ₃) ₂]	4	1	chains ¹ _∞ [MN ₂ N _{2/2}] of corner-connected tetrahedra	142
Mg ₂ [PN ₃]	4	1	Li ₂ SiO ₃ , ordered wurzite, chains ¹ _∞ [MN ₂ N _{2/2}] of corner-connected tetrahedra	159
Ca ₂ [PN ₃]	4	1	chains ¹ _∞ [MN ₂ N _{2/2}] of corner-connected tetrahedra	159, 160
γ-Ca ₃ [Al ₂ N ₄]	4	2	layers of edge- and corner-sharing tetrahedra ² _∞ [MN _{4/2}]	98
Ca ₃ [Ga ₂ N ₄]	4	2	layers of edge- and corner-sharing tetrahedra ² _∞ [MN _{4/2}]	153
Sr ₃ [Ga ₃ N ₅]	4	3	framework of edge- and corner-sharing tetrahedra ³ _∞ [M ₃ N ₅]	153
Ln ₃ [Si ₆ N ₁₁] Ln = Y, La–Nd, Sm	4	3	framework of corner-sharing tetrahedra	124, 125, 126, 129
Ln[Si ₃ N ₅] Ln = Y, La–Nd	4	4	framework of corner-sharing tetrahedra	125, 127–129
Y ₂ [Si ₃ N ₆]				129
Y ₂ [Si ₃ O ₃ N ₄]	4	3	framework of corner-sharing tetrahedra	130, 131
Nd ₂ [Si _{2.5} Al _{0.5} O _{3.5} N _{3.5}]	4	3	framework of corner-sharing tetrahedra	131
AEYb[Si ₄ N ₇] AE = Sr, Ba, Eu	4	3	framework of corner-sharing tetrahedra	133–135
Ba[Si ₇ N ₁₀]	4	3	framework of edge- and corner-sharing tetrahedra	132
AE ₂ [Si ₅ N ₈] AE = Sr, Ba, Eu	4	3	framework of corner-sharing tetrahedra	135, 136
Ba ₂ Nd ₇ [Si ₁₁ N ₂₃]	4	3	framework of corner-sharing tetrahedra	137
Ln _{(6+x)/3} [Si ₁₁ N _{20+x} O _{1-x}] Ln = Y, Gd–Lu	4	3	framework of corner-sharing tetrahedra	138
K ₃ [Si ₆ N ₅ (NH) ₆]	4	3	framework of corner-sharing tetrahedra	163
A ₃ [P ₆ N ₁₁] A = Na, K	4	3	framework of corner-sharing tetrahedra	162, 164
HPN ₂	4	3	β-crystalite	165
PON	4	3	β-crystalite	167
HP ₄ N ₇	4	3	framework of edge- and corner-sharing tetrahedra	166
α-P ₃ N ₅ /β-P ₃ N ₅	4	3	frameworks of edge- and corner-sharing tetrahedra	170, 171
M _{6+y/2-x} H _{2x} [P ₁₂ N ₂₄]X _y M = Mn, Fe, Co, Ni, Zn X = Cl, Br, I	4	3	sodalite	173–175
Zn ₈ [P ₁₂ N ₂₄]X ₂ X = O, S, Se, Te	4	3	sodalite	176
Square Planar Coordination				
Ln ₂ [MN ₃] M = Cr, Mn Ln = Ce, U, Th	4	1	U ₂ [CrN ₃], ¹ _∞ [MN ₂ N _{2/2}] chains of corner-sharing square planar units	78–80
Linear and Tetrahedral Coordination				
Si[CN ₂] ₂	4/2	3 (0)	isolated linear units [CN ₂] coordinate silicon atoms tetrahedrally leading to a cuprite-type structure	140
Square Pyramidal Coordination				
Ba[MN ₂] M = Zr, Hf	5	2	KCoO ₂ , layers of edge-sharing square pyramids ¹ _∞ [MNN _{4/4}]	21, 22
Trigonal Planar Coordination				
Ca ₆ [MN ₃]N ₂ M = Ga, Fe, Mn	3	0	isolated trigonal planar [MN ₃] units	70, 71
Ca ₃ [MN ₃] M = V, Cr, Mn, Co	3	0	isolated trigonal planar [MN ₃] units	86, 88, 89, 91
Sr ₃ [MN ₃] M = Cr, Mn	3	0	isolated trigonal planar [MN ₃] units	85, 90
Ba ₃ [MN ₃] M = Cr, Mn, Fe	3	0	isolated trigonal planar [MN ₃] units	85, 87, 90
Li[BeN]	3	2	layers of edge- and vertex-sharing trigonal planar [MN ₃]	179
Li _x Mn _{2-x} N	3	3	anti-Rutile (TiO ₂), framework of vertex- and edge-sharing trigonal planar units [MN ₃]	94
Two-Fold Coordination, Bent				
AE ₂ [GeN ₂] AE = Ca, Sr	2	0	bent dumb-bells [MN ₂]	142, 145
AE ₃ [GeN ₂][Ge] AE = Sr, Ba	2/0	0 (1)	bent dumb-bells [MN ₂] and Zintl-ionic chains of ¹ _∞ [Ge]	145, 147, 148

Table 1 (Continued)

compound	CN(M)	dimensionality	structural feature/type	ref
Two-Fold Coordination, Linear				
Sr ₃₉ [CoN ₂] ₁₂ N ₇	2	0	isolated linear units [MN ₂]	102
Sr ₂ [NiN ₂]	2	0	isolated linear units [MN ₂]	103
Sr[CuN]	2	1	Ba[NiN], infinite chains [MN _{2/2}], bent at some nitrogen atoms	98, 99
Sr ₆ [CuN ₂][Cu ₂ N ₃]	2	0	isolated units: linear [CuN ₂] and [Cu ₂ N ₃], at the central nitrogen atom bent	99
Ba[CuN]	2	1	infinite chain [MN _{2/2}], bent at some nitrogen atoms	101
Ba ₃ [ZnN ₂]O	2	0	isolated linear units [MN ₂]	67
Li ₃ [BN ₂]	2	0	isolated linear units [MN ₂]	186, 187
LiMg[BN ₂]	2	0	isolated linear units [MN ₂]	191, 192
LiAE ₄ [BN ₂] ₃	2	0	isolated linear units [MN ₂]	188–190
AE = Ca, Sr, Eu				
Ba ₄ [BN ₂] ₂ O	2	0	isolated linear units [MN ₂]	192, 194
AE ₂ Cl[BN ₂]	2	0	isolated linear units [MN ₂]	191
AE = Ca, Sr				
Ca ₁₅ [CBN] ₆ [C ₂]O		0	isolated linear units [CBN] next to [C ₂] and oxide ions	192
Ca _{9+x/2} [BN ₂] _{6-x} [CBN] _x		0	isolated linear units [MN ₂] and [CMN], disordered over the same position	193
La ₃ Ni ₂ B ₂ N ₃		2	Ni–B layers packed with LaN-type layers (rocksalt)	194
Li ₂ [CN ₂]	2	0	isolated linear units [MN ₂]	189
AE[CN ₂]	2	0	Ca[CN ₂], isolated linear units [MN ₂]	176, 177
AE = Mg, Ca				
AE[CN ₂]	2	0	isolated linear units [MN ₂]	176
AE = Sr, Ba				
AH[CN ₂]	2	0	isolated linear units [MN ₂]	178, 180
A = Na, K				
K ₅ H[CN ₂] ₃	2	0	isolated linear units [MN ₂]	179
AE ₂ [CN ₂][CN] ₂	2/1	0	isolated linear units [MN ₂] and [MN], disordered over the same position	181
AE = Sr, Ba				
Miscellaneous				
Ca[GaN]	1	1	¹ [Ga] chain, coordinated by nitrogen atoms	149
Ca ₅ [Ga ₂ N ₄]	2 + 2	1	¹ [GaN ₂] chain with Ga–Ga bonds	150
(AE ₆ N)[Ga ₅]		0	cluster [Ga ₅] and nitrogen atoms in AE octahedra	151
AE = Ca, Sr				
AE ₄ In ₂ N	0	(1)	¹ [In]-chain and NAE ₆ octahedra	152
AE = Ca, Sr				
Ba ₂ [GeGaN]	0/1	1	¹ [Ga _{2/2} GaN] chain with Ge–Ge bonds	148
Ti ₃ AlN			perovskite	115, 117
Subnitrides				
NaBa ₃ N	6	1	NBa ₆ cluster sharing faces to ropes ¹ [NBa _{6/2}]	203
Na ₅ Ba ₃ N	6	1	NBa ₆ cluster sharing faces to ropes ¹ [NBa _{6/2}]	204
A ₁₆ Ba ₆ N	6	0	isolated [NBa ₆] cluster	205
A = Na, Ag				
Na _x Ba ₁₄ CaN ₆	6	0	isolated [Ba ₁₄ CaN ₆] cluster with nitrogen in octahedra of one calcium and five barium atoms	206, 207
x = 14, 17, 21, 22				
Nitride Halides				
Li ₁₀ N ₃ Br	7	3	pentagonal bipyramids NLi ₇ sharing edges and corners to form a framework ³ [Li ₁₀ N ₃]	209
Li ₄ NCl	8	2	hexagonal bipyramids NLi ₈	210
Li ₅ NBr ₂	6	1	octahedra NLi ₆ connected by corners to chains	211
HT–Li ₅ NCl ₂	8	3	Li ₂ O	212
LT–Li ₅ NCl ₂	4	2	layers [Li ₄ N] and [LiCl ₂]	212
Li ₆ NBr ₃ (I)	6	3	anti-cryolite, Na ₃ AlF ₆	213
Li ₆ NBr ₃ (I')	6	3	anti-cryolite, Na ₃ AlF ₆	213, 214
Li ₆ NI ₃	6	3	anti-cryolite, Na ₃ AlF ₆	214
β-ZrNCl	6	2	β-ZrNCl, ZrN-slaps coordinated by chlorine layers	217
A ₂ ZrNCl	6	2	filled β-ZrNCl, alkali metals between chlorine double layers	215, 216
A = Li, Na, K				
Ce ₃ Br ₆ N	4	0	isolated units of two edge-sharing tetrahedra [(NLn ₂ Ln _{2/2}) ₂]	218
Ln ₃ Cl ₆ N	4	0	isolated units of two edge-sharing tetrahedra [(NLn ₂ Ln _{2/2}) ₂]	219, 220
Ln = Ce, Gd				
Ln ₂ Br ₃ N	4	1	infinite chains ¹ [NLn _{4/2}] of at opposite edges connected tetrahedra	221, 222
Ln = Ce, Gd				
Gd ₂ Cl ₃ N	4	1	infinite chains ¹ [NLn _{4/2}] of at opposite edges connected tetrahedra	223
Ce ₁₅ N ₇ I ₂₄	4,3	1,0	infinite chains ¹ [NLn _{4/2}] of at opposite edges connected tetrahedra and isolated trigonal planar units [NLn ₃]	224
Ln ₄ NS ₃ Cl ₃	4	0	isolated [NLn ₄] tetrahedra	225, 226
Ln = La–Nd, Gd				
Ln ₆ N ₃ S ₄ Cl	4	1	NLn ₄ tetrahedra connected to chains and double-tetrahedra ropes	227
Ln = La–Nd				
Pr ₅ N ₃ S ₂ Cl ₂	4	1	NLn ₄ tetrahedra connected to chains and double-tetrahedra ropes	228
ALa ₉ I ₁₆ N ₄	4	1	infinite chains ¹ [NLn _{4/2}] of <i>trans</i> -edge-sharing tetrahedra	229
A = Na, Rb, Cs				

Table 1 (Continued)

compound	CN(M)	dimensionality	structural feature/type	ref
Nitride Halides (Continued)				
Na ₂ Pr ₄ Br ₉ NO	4	1	infinite chains ${}^1_{\infty}[\text{NLn}_{4/2}]$ of trans-edge-sharing tetrahedra	231
Pr ₈ Br ₁₃ N ₃ O	4	1	infinite chains ${}^1_{\infty}[\text{NLn}_{4/2}]$ of <i>trans</i> -edge-sharing tetrahedra	231
ATh ₁₂ N ₆ X ₂₉	4	0	isolated cluster $[(\text{NThTh}_{3/3})_6]$ of cyclic <i>cis</i> -edge-sharing NTh ₄ tetrahedra	232, 233
A = Li, Na, Rb				
X = Cl, Br				

2. Transition Metal Nitrides with Electropositive Elements

Most newly reported transition metal nitrides were prepared by routes known for some time that are described elsewhere,^{3,6} so we do not discuss these synthesis methods here. However, one new, little-used preparation technique may soon lead to novel compounds; therefore, we want to briefly introduce it here. The application of microwave heating or microwave-generated nitrogen plasma led to a new preparation method for binary and ternary metal nitrides at reaction times of several hours.^{11,12} From reaction of metal powders with nitrogen, BN, AlN, GaN, α - and β -Si₃N₄, TiN, VN, NbN, Nb₂N, and Nb₃N₄ were prepared by this technique, but the products often were mixtures of two or more binary nitrides or still contained some unreacted metal. From reactions of Li₃N with metal powders or their binary nitrides under similar conditions, the known ternary nitrides Li₃MN₂ (M = Al, B, Fe), LiSi₂N₃, Li₂SiN₂, Li₅SiN₃, Li₁₈Si₃N₁₀, Li₇TiN₅, Li₇TaN₄ were also obtained. Additionally, a previously unknown lithium tantalum nitride phase seemed to have formed. A similar method of microwave-assisted carbothermal reduction and nitridation was used to prepare GaN, TiN, and VN powders.¹³

CN(M) = 6 and 5. The highest coordination numbers reached by M in ternary transition metal compounds containing electropositive elements are 5 and 6. These coordination numbers lead typically to rocksalt type structures, perovskites, or to layered structures.

The nitrides of the composition AE[MN₂] (AE = alkaline earth metal, M = transition metal), Sr[ZrN₂], and Sr[HfN₂]¹⁴ were prepared from their binary nitrides as diamagnetic grayish-green powders, crystallizing in the layered α -NaFeO₂ structure type¹⁵ isotypic to the compounds Na[MN₂] (M = Nb, Ta).^{16–18} The anions are close packed, and the alkaline earth and the transition metal atoms occupy octahedral holes in an ordered fashion leading to layers ${}^2_{\infty}[\text{MN}_{6/3}{}^{2-}]$ alternating with M = AE and M. A view in this structure is given in Figure 1. The metallic Ta(IV) compound Ca[TaN₂]^{19,20} (i.e., Ta *d*¹) crystallizes also in the α -NaFeO₂ structure type and shows a superconducting transition near 9 K.

The barium analogues of these compounds, Ba[ZrN₂],²¹ Ba[HfN₂],²² and their solid solution Ba[Hf_{1-x}Zr_xN₂],²² however, crystallize in the layered KCoO₂²³ structure type. This structure type has rather few members (e.g., BaNiS₂,²⁴ K_xBa_{1-x}CoS₂,²⁵ and CsLiCl₂²⁶). In this structure, the transition metal is 5-fold coordinated in square pyramidal fashion. These polyhedra are edge connected at the bases to form ${}^2_{\infty}[\text{MN}_{4/4}\text{N}^{2-}]$ layers with the apical nitrogen ligands alternately above and below the layers. The barium atoms are located between these layers in a 1 + 4 + 4 coordination by nitrogen atoms. Ba[ZrN₂] was reported

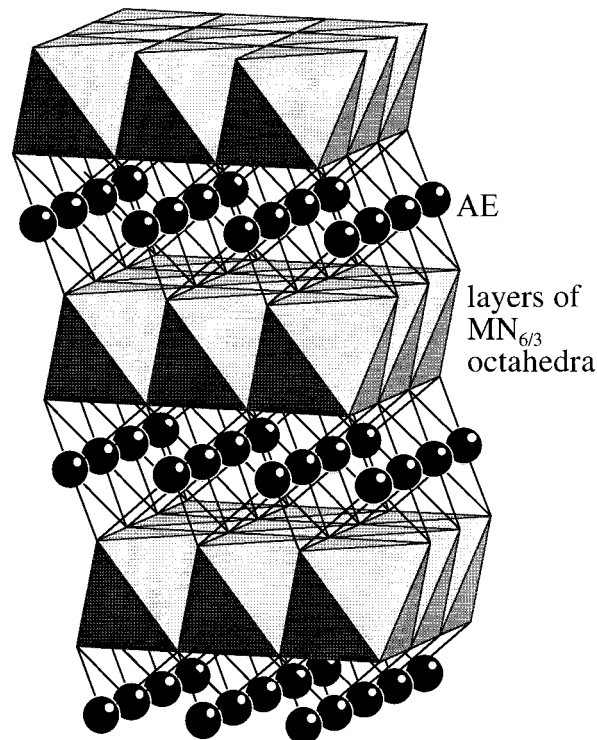


Figure 1. Structure of nitrides with α -NaFeO₂ type structure: Ca[TaN₂], Sr[ZrN₂], and Sr[HfN₂]. Layers of edge sharing octahedra MN₆ (M = transition metal) are stacked so that the alkaline earth atoms are also in octahedral coordination.

to exhibit temperature-independent paramagnetism above 20 K, even though zirconium is formally *d*⁰. So did the hafnium-containing samples, but these were reported to be superconducting below 8 K. Because neither the hafnium compound nor the zirconium–hafnium phases could be prepared as single-phase samples and the binary transition metal nitride impurities ZrN and HfN are known to become superconducting in the temperature region just mentioned, it seems probable that the superconductivity is not intrinsic to the ternary nitride. Recently, the structure of the long-known Zr₃N₄²⁷ was solved from powder X-ray diffraction data.^{28,29} The structure is related to that of Eu₃O₄ with three crystallographically distinct zirconium sites, two in octahedral and one in trigonal prismatic coordination by nitrogen atoms. These polyhedra share vertices, edges, and faces to form a three-dimensional framework. Further work by these authors illuminate the complex system of the zirconium nitride oxides.³⁰

The dark purple barium analogue of the Ca[TaN₂] compound shows a variable nitrogen stoichiometry BaTa_{2+x} (*x* ≤ 1/3) and a different structure.³¹ It adopts the hexagonal perovskite variant of the high-temperature BaMnO₃ structure type³² with disordered anionic vacancies. Due to the vacancies, the average CN of tantalum is 4.5 instead of 6. Two tantalum centered

octahedra share common faces to form double octahedra that are linked together in a three-dimensional network by all six remaining corners. Neutron and X-ray diffraction experiments indicate that the vacancies predominantly occur on the shared faces. It may be that the vacancies are arranged to give pseudo-tetrahedral symmetry to the neighboring tantalum atoms.

Reaction of metallic sodium with electrically insulating Ta_3N_5 at relatively low temperatures of 450 to 600 °C leads to the black intercalation phases $\text{Na}_x\text{Ta}_3\text{N}_5$ ($0 \leq x \leq 1.4$).³¹ In this reaction the connectivity of the Ta_3N_5 framework with tantalum atoms in octahedral coordination is preserved. The sodium ions have seven nitrogen neighbors in the open channels of the host compound. The unit cell volume increases only slightly (2.6%) for the nominal composition $\text{Na}_{1.0}\text{Ta}_3\text{N}_5$ compared with Ta_3N_5 . The low electrical resistivity of a pressed pellet (unsintered) at room temperature of 2.7 Ω cm and a nearly temperature independent paramagnetic susceptibility between 100 and 320 K both suggest metallic conductivity.

In contrast, lithium oxide nitrides of vanadium, niobium, and tantalum prepared by ammonolysis of the ternary oxides LiMO_3 and LiM_3O_8 ($M = \text{V}, \text{Nb}, \text{Ta}$) yield rocksalt type structures with random distribution of lithium and transition metal atoms, as well as disordered nitrogen and oxygen atoms, on the cationic and anionic sites, respectively.^{34,35} Because the oxygen–nitrogen ratio can vary with the oxidation state of the transition metal and the lithium–transition metal ratio in most cases is not fixed (due to lithium oxide loss during the reaction), the products are described as $\text{Li}_{2-x}\text{M}_{2+x}\text{O}_y\text{N}_{4-y}$ ($M = \text{V}, \text{Nb}$, $0 \leq x \leq 0.31$; $0.46 \leq y \leq 1.46$), $\text{Li}_{1-x}\text{Nb}_{3-3x}\square_{4x}\text{O}_y\text{N}_{4-y}$ ($0.08 \leq x \leq 0.16$; $0.73 \leq y \leq 1.20$); \square stands for a vacancy in the cationic lattice), $\text{Li}_2\text{Ta}_2\text{O}_y\text{N}_{4-y}$ ($0.28 \leq y \leq 1.22$), $\text{Li}_{2-x}\text{V}_{2+x}\text{O}_y\text{N}_{4-y}$ ($0.15 \leq x \leq 0.26$; $1.17 \leq y \leq 1.35$), and $\text{Li}_{1-x}\text{V}_{3+x}\text{O}_y\text{N}_{4-y}$ ($0.01 \leq x \leq 0.26$; $0.13 \leq y \leq 0.86$). Hence, these phases show structural similarities to the rocksalt type phase $\text{Li}_{2-x}\text{Ta}_{2+x}\text{N}_4$ ($0.2 < x < 1$)³⁶ and the ordered compound $\text{Li}_2\text{Ta}_3\text{N}_5$.³⁷

In a similar reaction at 1000 °C, LiNb_3N_4 was prepared from LiNb_3O_8 by ammonolysis.^{35,38} It crystallizes isotypic to $\text{Li}_{1-x}\text{Ta}_{3+x}\text{N}_4$ ($0 \leq x < 0.02$)³⁶ in a filled, layered MoS_2 structure. Lithium and niobium atoms occupy randomly octahedral holes between the layers, whereas the hexagonal prismatic voids in the layer are only filled with niobium atoms. Ammonolysis of ANb_3O_8 ($A = \text{Na}, \text{K}$) apparently does not lead to a ternary nitride. Depending on the reaction temperature the products are ternary oxoniobates, $\text{Nb}(\text{O},\text{N})$, or binary niobium nitrides.³⁵

Ammonolysis of SrMoO_4 and SrWO_4 leads to $\text{SrMoO}_{2.5}\text{N}_{0.5}$ and SrWO_2N , respectively.³⁹ Both blue-black compounds realize the perovskite structure type with probably complete disorder of oxygen and nitrogen atoms. In contrast to the perovskite type reddish-brown metallic conductor SrMoO_3 ,⁴⁰ the oxide nitrides show nearly temperature-independent resistivity between 60 and 300 K ($\rho \approx 0.2 \Omega$ cm for $\text{SrMoO}_{2.5}\text{N}_{0.5}$, $\rho \approx 1 \Omega$ cm for SrWO_2N). The temperature dependence of their magnetic susceptibilities, however, indicates Pauli paramagnetism, with possibly a spin glass such as antiferromagnetic transition at ~ 50 K for $\text{SrMoO}_{2.5}\text{N}_{0.5}$.

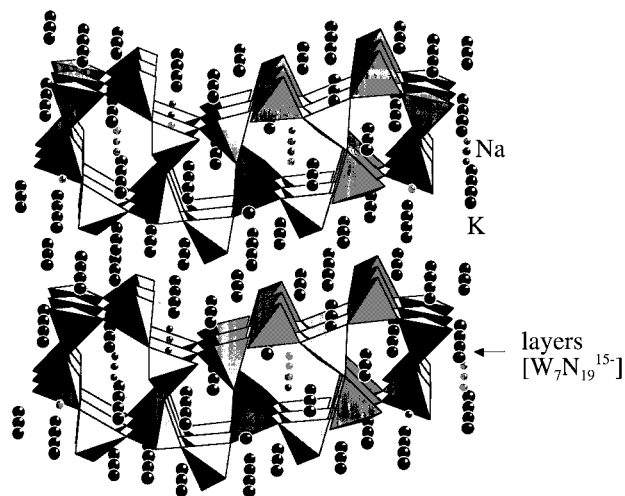


Figure 2. A view of the structure of $\text{Na}_2\text{K}_{13}[\text{W}_7\text{N}_{19}]$, showing the layers ${}^2[(\text{MN}_2\text{N}_{2/2})_3(\text{MNN}_{3/2})_4]^{15-}$ of corner-sharing WN_4 tetrahedra.

Some work concerning nitrides of thorium led to the perovskite type compound ThTa_3N_3 ⁴¹ and the oxide nitrides $(\text{Ca},\text{Th})(\text{N},\text{O})$ and $(\text{Sr},\text{Th})(\text{N},\text{O})$.⁴² The latter two crystallize in the rocksalt structure type with the metal atoms and the nonmetal atoms disordered on the cationic and anionic sites, respectively. Measurements of the electrical resistivity indicate semiconducting behavior.

CN(M) = 4. Tetrahedral coordination of a transition metal by nitrogen ligands is common and may result in isolated tetrahedra as observed in $\text{Li}_3\text{Sr}_2[\text{MN}_4]$ ($M = \text{Nb}, \text{Ta}$).⁴³ These compounds crystallize isotypic with the quaternary oxides $\text{Li}_3\text{Na}_2[\text{MO}_4]$ ($M = \text{Fe}, \text{Ga}$).^{44,45} The $[\text{MN}_4]^{7-}$ tetrahedra are arranged to produce tetrahedral coordination of the lithium atoms by nitrogen ligands as well. The LiN_4 tetrahedra share edges and corners. The strontium ions occupy channels within this lithium metalate framework, and are found in a distorted octahedral environment of nitrogen atoms.

With the right choice of electropositive metals, the nitridometalate tetrahedra can be linked with each other at vertices to form infinite chains ${}^1[\text{MN}_2\text{N}_{2/2}^{3-}]$ in $\text{Na}_3[\text{MN}_3]$ ($M = \text{Mo}, \text{W}$),^{46–48} $\text{Na}_2\text{K}[\text{WN}_3]$,⁴⁹ $\text{Na}_{11}\text{Rb}[(\text{WN}_3)_4]$,⁴⁹ and $\text{Na}_5\text{A}[(\text{WN}_3)_2]$ ($A = \text{Rb}, \text{Cs}$),⁵⁰ with quite different chain conformations, similar to what is known for the respective silicates.⁵¹ Layers with a complex linking scheme of corner connected tetrahedra ${}^2[(\text{MN}_2\text{N}_{2/2})_3(\text{MNN}_{3/2})_4]^{15-}$ were found in $\text{Na}_2\text{K}_{13}[\text{W}_7\text{N}_{19}]$.⁵² This layer is best described as composed of infinite ropes of rings of six tetrahedra $\text{W}_6\text{N}_{16}\text{N}_{2/2}$, like these reported recently for $\text{K}_{14}[\text{W}_6\text{N}_{16}\text{NH}]$.⁵³ In the structure of $\text{Na}_2\text{K}_{13}[\text{W}_7\text{N}_{19}]$, these ropes are connected by an additional tetrahedron to form the layers (Figure 2). With a high cesium content, the three-dimensional framework ${}^3[\text{MNN}_{3/2}^{1.5-}]$ in $\text{Cs}_5[\text{Na}\{\text{W}_4\text{N}_{10}\}]$ ⁵⁴ is reached. Every WN_4 tetrahedra is linked at three vertices to three other tetrahedra. The fourth nitrogen ligand of every tetrahedra coordinates a sodium ion leading to a distorted tetrahedral surrounding of these cations. If the tetrahedrally coordinated sodium atoms in $\text{Cs}_5[\text{Na}\{\text{W}_4\text{N}_{10}\}]$ are included in the framework description, the anionic part of the structure resembles an ordered variant of the β -cristobalite structure (SiO_2 modification) with a three-dimensional framework of all

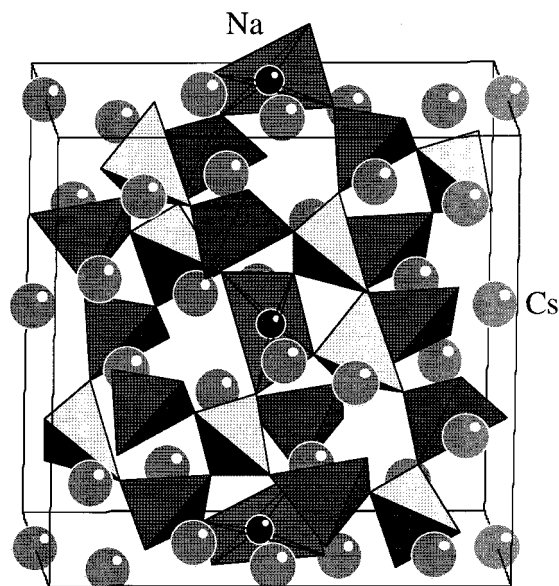


Figure 3. Unit cell of $\text{Cs}_5[\text{Na}\{\text{W}_4\text{N}_{10}\}]$. Solid gray WN_4 tetrahedra are linked at vertices to form a three-dimensional framework. Additional sharing of corners with distorted tetrahedra around sodium atoms leads to a β -cristobalite structural arrangement, filled with cesium atoms.

corner linked tetrahedra ${}^3[\text{MN}_{4/2}^-]$ ($M = \text{Na}$ and W). The unit cell of $\text{Cs}_5[\text{Na}\{\text{W}_4\text{N}_{10}\}]$ is shown in Figure 3. The cesium ions fill the large holes in this structure occupying somewhat distorted Friauf polyhedra with 12-fold coordination by nitrogen atoms, as is known for the filled β -cristobalite type nitrides $\text{Cs}[\text{MN}_2]$ ($M = \text{Nb}$, Ta).^{55,56} The coordination number of nitrogen in all these alkali metal nitridowolframates is frequently six, but often for one or several sites enlarged to seven or even eight in $\text{Cs}_5[\text{Na}\{\text{W}_4\text{N}_{10}\}]$.

In this scheme also fit oxonitridometalates such as $\text{Ba}_3[\text{WNO}_3]_2$ ⁵⁷ prepared from ammonolysis of $\text{Ba}_3\text{W}_2\text{O}_9$. It crystallizes in a rhombohedral unit cell isotypic with $\text{Ba}_3\text{V}_2\text{O}_8$ ⁵⁸ by stacking together isolated $[\text{WNO}_3]^{3-}$ ions with barium atoms. Hence, the structure bears close similarities to these of $\text{Na}_3[\text{MNO}_3]$ ⁵⁹ and $\text{Na}_4[\text{MN}_2\text{O}_2]$ ($M = \text{Mo}$, W).⁶⁰ $\text{A}_6[\text{M}_2\text{N}_4\text{O}_3]$ ($A = \text{K}$, Rb , Cs ; $M = \text{Mo}$, W)^{61,62} contain dimetalate ions $[\text{M}_2\text{X}_7]^{6-}$ ($X = \text{N}$, O) formed by corner linking two tetrahedra, whereas $\text{NaA}_4[(\text{WN}_{2.5}\text{O}_{0.5})_2]$ ($A = \text{Rb}$, Cs)⁶³ are built of infinite chains of edge-sharing tetrahedra ${}^1[\text{WX}_2\text{X}_{2/2}^{2.5-}]$. In these compounds, the oxygen and nitrogen atoms probably are randomly distributed over the nonmetal sites. In contrast, in comparable oxide nitrides with the more polarizing cations lithium or the alkaline earth metals, the oxygen is normally found only surrounded by these elements, whereas the transition metal forms nitridometalate ions containing no oxygen. This latter feature was recently found in $\text{Li}_{16}[\text{NbN}_4]_2\text{O}$,^{64,65} $\text{Li}_6\text{Ca}_{12}[\text{MN}_4]_4\text{O}_3$ ($M = \text{Mo}$, W),⁶⁶ and the late transition nitridometalate oxide $\text{Ba}_3[\text{ZnN}_2]\text{O}$.⁶⁷ $\text{Li}_{16}[\text{NbN}_4]_2\text{O}$ crystallizes isotypic with $\text{Li}_{16}[\text{TaNa}_4]_2\text{O}$ ⁶⁸ and can be described as an ordered anti- CaF_2 type superstructure. Nitrogen and oxygen atoms together form the motif of a cubic close packing in which all tetrahedral sites are orderly occupied by niobium and lithium atoms so that niobium is exclusively coordinated by nitrogen. This ordering may be driven by the higher thermodynamic stability of binary lithium and calcium oxides compared with their ni-

trides,⁶⁶ whereas the heavier alkali metals seem not to be able to stabilize oxide ions not bonded to a transition metal atom in this kind of compound (see also Section 5: alkaline earth metal sodium subnitrides). Here we also mention nitrides with nitride ions coordinated only by alkaline earth elements and not a part of a nitridometalate ion in compounds such as $\text{Ba}_5[\text{CrN}_4]\text{N}$,⁶⁹ $\text{Ca}_6[\text{MN}_3]\text{N}_2$ ($M = \text{Ga}$, Fe , Mn)^{70,71} or the nitridometalate nitride azides $\text{Ba}_9[\text{MN}_4]_2\text{N}(\text{N}_3)$ ($M = \text{Nb}$, Ta)^{72,73} that have surprising thermal stability. Although the latter were prepared in a regime that included temperatures $> 700^\circ\text{C}$, they might have formed while cooling the reaction mixture down. The earlier reported compounds Ca_5MN_5 ⁷⁴ and $\text{Sr}_{27}\text{M}_5\text{N}_{28}$ ($M = \text{Mo}$, W)⁷⁴ were shown to be nitridotungstate oxide nitrides $\text{AE}_{51}[\text{WN}_4]_{12}\text{N}_8\text{O}_3$.⁷⁵ Tetrahedral nitridotungstate and alkaline earth ions are stacked together with isolated oxide and nitride ions, so that the latter two occupy tetrahedral holes formed only by alkaline earth atoms in possibly an ordered manner. The rhenium nitride with the composition $\text{Sr}_{27}\text{Re}_5\text{N}_{28}$ ⁷⁶ may hence also turn out to be such a nitridometalate oxide nitride. Analogously, $\text{Ba}_4[\text{WN}_4]\text{Cl}_2$ ⁷⁷ is one of only a few reported nitridometalate chlorides; the chloride ions are only coordinated by barium atoms.

Except for the black chromium(V) compound $\text{Ba}_5[\text{CrN}_4]\text{N}$ all the $M(\text{V})$ or $M(\text{VI})$ nitrides just mentioned form as colored (typically yellow, orange or red) transparent crystals, which would suggest diamagnetic and electrically insulating behavior. Hence, only in a few cases are the magnetic and electrical properties reported. Nevertheless, $\text{Li}_3\text{Sr}_2[\text{NbN}_4]$ ⁴³ and $\text{Li}_{16}[\text{NbN}_4]\text{O}$ ⁶⁵ show temperature-independent paramagnetism at $< 300\text{ K}$, as do the earlier reported $\text{Ba}[\text{ZrN}_2]$ ²⁵ and $\text{Ba}_2[\text{NbN}_3]$.²⁵ Presumably this result is due to Van Vleck paramagnetism and not Pauli paramagnetism.

$\text{Ce}_2[\text{MnN}_3]$ ⁷⁸ crystallizes isotypic to the recently reported $\text{Ce}_2[\text{CrN}_3]$,⁷⁹ the compounds $\text{Ac}_2[\text{MN}_3]$ ($\text{Ac} = \text{U}$, Th ; $M = \text{Cr}$, Mn),⁸⁰ and the cuprates Ca_2CuO_3 ,⁸¹ Sr_2CuO_3 ,⁸² and NaSrCuO_3 .⁸³ It realizes an unusual structure, with the transition metal coordinated nearly square planar by four nitrogen atoms. These square planar units share opposite vertices to form infinite chains ${}^1[\text{MnN}_2\text{N}_{2/2}]$, which are bridged via cerium atoms. Within these chains, manganese has shorter bonds to bridging nitrogen atoms than to terminal nitrogen atoms. Judging from the bond distances and comparing known values, the contact $\text{Mn}-\text{N}_{\text{terminal}}$ has to be assigned as a single bond, and the $\text{Mn}-\text{N}_{\text{bridging}}$ should have additional Π -interactions. This hypothesis was confirmed by extended Hückel band structure calculations. The cerium ions have $1 + 6$ coordination by nitrogen ligands with six distances comparable to that found in CeN ⁸⁴ of $d(\text{Ce}-\text{N}) \approx 2.51\text{ \AA}$ and one considerably shorter contact of $d(\text{Ce}-\text{N}) \approx 2.36\text{ \AA}$. Measurements of the electrical resistivity suggest metallic behavior ($\rho \approx 1.0 \times 10^{-3}\text{ }\Omega\text{ cm}$ at 270 K , $\rho \approx 1.8 \times 10^{-4}\text{ }\Omega\text{ cm}$ at 4 K). The data on the magnetic susceptibility indicate the absence of magnetic moments leading to oxidation state assignments of cerium(IV) and manganese(I). $\text{Ce}_2[\text{CrN}_3]$ might also be expected to be metallic, however, it so far has not been prepared as a single phase material.

$\text{CN}(\text{M}) = 3$. $\text{Sr}_3[\text{CrN}_3]^{85}$ and $\text{Ba}_3[\text{CrN}_3]^{85}$ were recently added to the series of $\text{AE}_3[\text{MN}_3]$ compounds ($\text{AE} = \text{Ca}, \text{Sr}, \text{Ba}$; $\text{M} = \text{Ga}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}$).^{86–91} A structure map of these compounds shows a clear dependence on bond distances. The calcium compounds crystallize in the orthorhombic space group $Cmcm$ and show shorter M–N distances than the strontium and barium compounds that crystallize in $P6_3/m$. All these compounds contain trigonal planar $[\text{MN}_3]^{3-}$ units. In the strontium and barium compounds, these exhibit ideal D_{3h} symmetry. A symmetry reduction in the calcium compounds is reflected in a distortion of the $[\text{MN}_3]^{3-}$ units to C_{2v} . It was suggested earlier that this distortion is due to a Jahn–Teller distortion of the low-spin Cr^{3+} ion,⁹² confirmed later by ab initio extended Hückel calculations.⁹³ However, the available data now suggest that the symmetry of this unit may be more dependent on the size of the alkaline earth metal cation than on the electron configuration of the transition metal.

The ternary phase $\text{Li}_x\text{Mn}_{2-x}\text{N}$ ($0.67 \leq x \leq 1$)⁹⁴ crystallizes in the anti-Rutile structure type with lithium and manganese atoms disordered on the anion site of the structure type. Hence, the metal atoms are in trigonal planar coordination by nitrogen atoms such as the transition metal atoms in the previously discussed compounds, but these polyhedra are connected into a three-dimensional network. Trigonal planar coordination of lithium is rare, but has been reported in a few nitride and oxide compounds (e.g. $\alpha\text{-Li}_3\text{N}$,⁹⁵ LiCaN ,⁹⁶ and LiKO ⁹⁷). The electrical resistivity measured on a pressed pellet increases slowly as the temperature is decreased (from $\rho \approx 8.5 \times 10^{-3} \Omega \text{ cm}$ at 250 K to $\rho \approx 1.0 \times 10^{-2} \Omega \text{ cm}$ at 4 K), suggesting activated behavior. Magnetic susceptibility and solid state ^6Li NMR show localized magnetic moments on the manganese atoms and probably a spin glass such as antiferromagnetic ordering at ~ 115 K.

$\text{CN}(\text{M}) = 2$. In contrast to the early transition metals, the late transition metals Fe, Co, Ni, Cu, and Zn prefer much lower coordination numbers in nitrides. For all these elements, 2-fold coordinated species are known. In the case of Co, Ni, Cu, and Zn, this arrangement is the preferred one, typically together with a low oxidation state, especially for Co(I), Ni(I) and Cu(I). In this group of compounds, the black $\text{Sr}[\text{CuN}]^{98,99}$ and the metallic-blue $\text{Sr}_6[\text{Cu}_3\text{N}_5]^{99}$ were recently reported. In the $\text{Sr}_6[\text{Cu}_3\text{N}_5]$ structure, isolated $[\text{CuN}_2]^{5-}$ units and isolated V-shaped $[\text{Cu}_2\text{N}_3]^{7-}$ units with a bond angle of $\sim 79^\circ$ at the bridging nitrogen atom were found. A two-point measurement of the electrical resistivity at room temperature on a single crystal suggests that this compound is an electrical insulator. The unit cell of $\text{Sr}_6[\text{Cu}_3\text{N}_5]$ and the two different, isolated nitridometalate ions are shown in Figure 4. The $\text{Sr}[\text{CuN}]$ structure ($\text{Ba}[\text{NiN}]$ structure¹⁰⁰) is built of one-dimensional infinite zigzag chains $[\text{CuN}_{2/2}^{2-}]$. These chains are bent at every third nitrogen atom with a bond angle of $\sim 82^\circ$, leading to relatively short copper–copper distances that may indicate $d^{10} - d^{10}$ bonding interactions. $\text{Ba}[\text{CuN}]^{101}$ is also built of infinite $[\text{CuN}_{2/2}^{2-}]$ zigzag chains, but these are alternately bent in an unequal zigzag manner: one up, two down, etc.

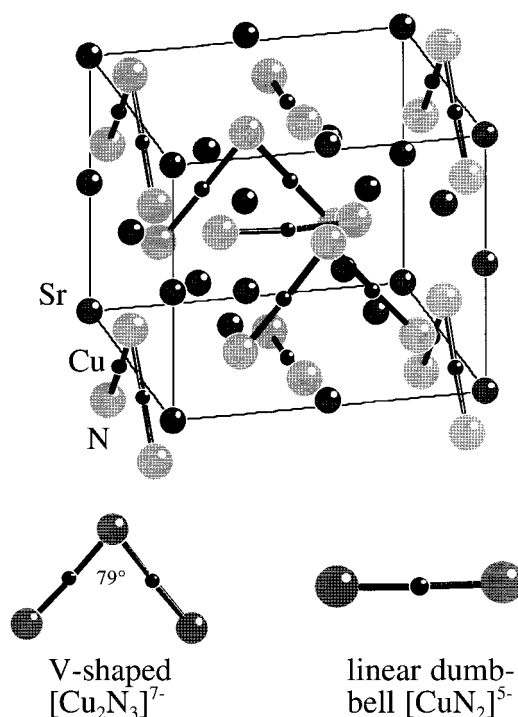


Figure 4. Unit cell of $\text{Sr}_6[\text{Cu}_3\text{N}_5]$ with the isolated nitridometalate ions $[\text{Cu}_2\text{N}_3]^{7-}$ and $[\text{CuN}_2]^{5-}$ depicted below.

Similar isolated $[\text{MN}_2]$ units were found in $\text{Sr}_{39}\text{Co}_{12}\text{N}_{31}$ ¹⁰² as well as isolated nitride ions only coordinated by strontium atoms in an octahedral fashion as already discussed. Hence, it is better to write the compound as $\text{Sr}_{39}[\text{CoN}_2]_{12}\text{N}_7$. It crystallizes in a relatively large cubic unit cell but with some disorder on one strontium site. Because the structure solution led to only one site for cobalt, it has a formal mixed valence of 1.25. Measurements of the magnetic susceptibility revealed an effective magnetic moment of $4.99 \mu_B$, which is considerably above the spin-only values calculated for Co(II) ($3.87 \mu_B$) and Co(I) ($2.83 \mu_B$), perhaps indicating significant spin–orbital contribution.

Comparable isolated $[\text{MN}_2]^{4-}$ units were also recently reported for $\text{Sr}_2[\text{NiN}_2]^{103}$ and the aforementioned $\text{Ba}_3[\text{ZnN}_2]\text{O}$,⁶⁷ but containing transition metals in the oxidation state II. Surprisingly $\text{Sr}_2[\text{NiN}_2]$ demonstrates metallic behavior as shown by measurements of the electrical resistivity on a single crystal ($\rho \approx 6 \times 10^{-3} \Omega \text{ cm}$ at 300 K) and by the paramagnetic susceptibility. Results of LMTO calculations are consistent with the observed metallic behavior, showing a finite density of states at the Fermi level. Some strontium orbital character of the wave functions at the Fermi level provides a pathway for conduction electrons between the $[\text{NiN}_2]^{4-}$ units.¹⁰⁴ In contrast, the zinc compound has a dark reddish-brown color and is probably an electrical insulator, as expected from the composition.

3. Ternary Nitrides Containing Two Transition Metals

In recent years ternary nitrides containing two transition metals have raised a lot of interest, especially after FeWN_2 ¹⁰⁵ was reported in 1993. Most of the new compounds have been prepared by ammonolysis of ternary oxide precursors at temperatures between 600

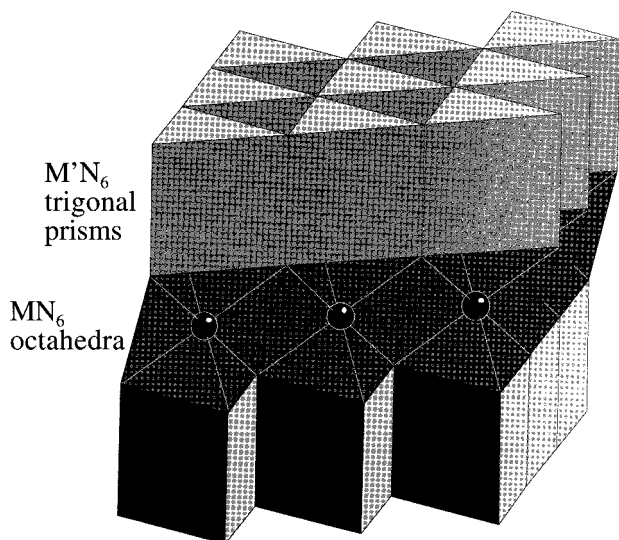


Figure 5. Most prominent stacking variant of $MM'N_2$ nitrides (e.g., $FeWN_2$), with $M' = Mo, W$ in trigonal prismatic coordination by nitrogen atoms, and the transition metal M (e.g., Mn, Fe, Co, Ni) coordinated octahedrally.

and 800 °C: MWN_2 from MWO_4 ($M = Mn, Fe, Co, Ni$),^{106–108} $MnMoN_2$ from $MnMoO_4$,¹⁰⁶ $(Fe_{0.8}W_{0.2})WN_2$ from $Fe_2(WO_4)_3$,¹⁰⁹ $(Fe_{0.8}Mo_{0.2})MoN_2$ from $Fe_2(MoO_4)_3$,¹¹⁰ Fe_3Mo_3N from $FeMoO_4$,^{111,112} and Ni_3Mo_3N from $NiMoO_4$.¹¹² A closer look at the ammonolysis reactions of MWO_4 ($M = Fe, Co, Ni$) to form MWN_2 nitrides revealed that it is probably a two-step reaction forming an intermediate phase at ~420 °C.¹¹³ $W_{0.62}(NO)$, with incorporated transition metal M , seems to be the parent phase of the intermediate.

The compounds $MM'N_2$ ($M' = Mo, W$) typically crystallize in layered structures with M' in trigonal prismatic coordination by nitrogen. These polyhedra are connected to each other forming layers ${}_2[M'N_{6/3}]$, which are stacked together, so that the second transition metal occupies octahedral voids between the layers. The most prominent stacking variant of this structure, realized by $FeWN_2$, for example, is drawn in Figure 5, showing the linking scheme of the polyhedra that leads to the layers. For these compounds it is not surprising to find the possibility for the formation of different stacking variants. In the compounds $(Fe_{0.8}M'_{0.2})M'N_2$ a partial occupation of the M site with 20% M' atoms is discussed. All these layered compounds show poor electrical conductivity ($\rho > 1.0 \Omega \text{ cm}$), with only a very small temperature dependence.

A similar treatment of the niobium and tantalum oxides $FeM'O_4$, FeM'_2O_6 , mixtures Fe_2O_3/M'_2O_5 ($M' = Nb, Ta$), or the intermetallic $FeTa$ with ammonia did not lead to ternary iron nitrides with M' , but to the phases $M'_5N_{6-6}O_y$ with M'_5N_6 structure.¹¹⁴ This structure is very similar to the previously discussed layered ternary nitrides. Alternating layers of trigonal prismatic and octahedral coordinated M' exist, but the octahedrally coordinated site is only 2/3 occupied. The experimental results suggest a catalytic role of iron in the formation of these phases.

Other compounds frequently obtained in these ternary systems of molybdenum and tungsten have the composition $M_3M'_3N$ ($M' = Mo, W$). The compounds Fe_3Mo_3N ,^{111,115} Fe_3W_3N ,¹¹⁶ Ni_3Mo_3N ,^{115,117} and Co_3W_3N ¹¹⁸

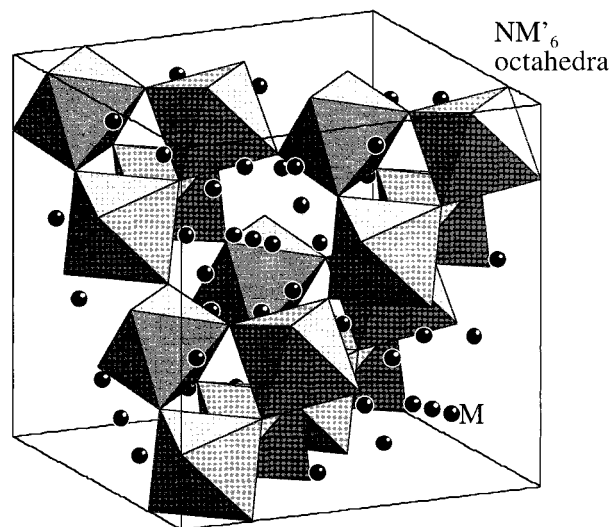


Figure 6. Unit cell of $M_3M'_3N$ compounds with a three-dimensional network of corner-sharing NM'_6 octahedra ($M' = Mo, W$).

have been reported. They exhibit the $\eta\text{-Fe}_3\text{W}_3\text{C}$ structure with nitrogen in octahedral coordination by M' only. The octahedra are connected at every corner to a three-dimensional network (Figure 6). Fe_3Mo_3N was found to possess metallic electrical conductivity ($\rho < 1.0 \Omega \text{ cm}$). This compound shows paramagnetic behavior and orders antiferromagnetically at 120 K.¹¹¹

Earlier it was suggested that the formation of $M_3M'_3N$ or $MM'N_2$ phases from ammonolysis of ternary oxides strongly depends on the structure of the oxide precursor, especially on the coordination of M' metal atoms.¹¹⁹ A different synthetic approach to prepare this kind of compound starts with the binary chlorides of both transition metals and treats them in a sol-gel like fashion. The chlorides are dissolved in acetonitrile and then complexed with triethylamine. After this step, an optional hydrolysis is sometimes performed. After removing the organic solvent an uncharacterized "polymeric" powder was obtained, which then was reacted with flowing ammonia gas at temperatures between 750 and 950 °C. In this way $CrWN_2$,¹²⁰ $FeWN_2$,^{115,117} Co_3W_3N ,¹¹⁸ Ni_3Mo_3N ,^{115,117} Fe_3Mo_3N ,¹¹⁵ Fe_3W_3N ,¹¹⁶ and Ti_3AlN ^{115,117} could be prepared. Other authors claim that Fe_3Mo_3N forms from reaction of nanoscale metal particles with flowing nitrogen or ammonia gas at temperatures $< 500 \text{ °C}$.¹²¹ However, they need to heat the samples to 700 °C to reach the necessary crystallite size to detect the compound by X-ray diffraction methods.

4. Nitrides of Main Group Elements

Recent years brought a considerable growth in the knowledge and understanding of ternary main group nitrides, especially of $Al, Ga, Si, Ge,$ and P . The large number of these new compounds is due mainly to the development and consequent use of new preparative techniques. Many of the new compounds were crystallized by reaction of alkaline earth metals with the main group metal in a flux of liquid sodium under medium nitrogen pressures of 10 to a 100 atm. For nitridosilicates, silicon diimide $[Si(NH)_2]$ was used successfully as starting material, whereas some nitridophosphates

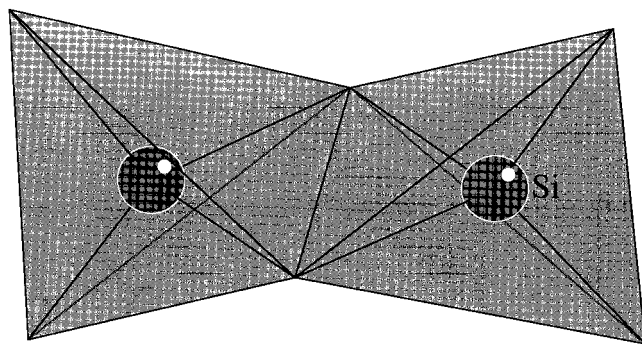


Figure 7. $[\text{Si}_2\text{N}_6]^{10-}$ unit of two edge-sharing tetrahedra in the structure of $\text{Ba}_5\text{Si}_2\text{N}_6$.

were prepared from more sophisticated precursors. Also important, mainly for many of the reported silicon and phosphorus compounds, are high temperature methods ($>1500\text{ }^\circ\text{C}$). Essentially all of these compounds satisfy the octet rule and are expected to be semiconducting or insulating.

CN(M) = 6. $\text{La}_{1-x}\text{Ca}_x\text{N}_{1-x/3}$,¹²² with two relatively electropositive metals, is considered here with the main group nitrides. In contrast to most known ternary nitride systems, Ca_3N_2 and LaN form a solid solution $\text{La}_{1-x}\text{Ca}_x\text{N}_{1-x/3}$ over a large range of compositions $0 \leq x < 0.7$. The phases adopt the rocksalt structure of LaN with the appropriate number of nitrogen vacancies.

Silicon Nitrides, CN(Si) = 4. All silicon nitrides contain silicon coordinated tetrahedrally by nitrogen. As discussed in the previous chapter for the transition metal nitrides with tetrahedral coordination, this chemistry bears some similarity to that of oxosilicates, but with the important extension of edge-sharing tetrahedra as well as nitrogen anions connecting three or even four silicon atoms.

The structure of $\text{Ba}_5[\text{Si}_2\text{N}_6]^{123}$ is built from isolated $[\text{Si}_2\text{N}_6]^{10-}$ units, best described as two edge-sharing tetrahedra of nitrogen atoms centered by silicon atoms, as shown in Figure 7. These units are stacked together with barium ions to form a distorted cubic closed packing of nitrogen atoms with most barium ions in octahedral holes. Silicon and, surprisingly, one barium site occupy tetrahedral holes.

$\text{Pr}_3[\text{Si}_6\text{N}_{11}]^{124}$ belongs to the family $\text{Ln}_3[\text{Si}_6\text{N}_{11}]$ ($\text{Ln} = \text{La, Ce, Pr, Nd, Sm}$).^{125,126} It contains a network of corner-connected SiN_4 tetrahedra of which one nitrogen ligand per tetrahedra is shared by three tetrahedra, whereas the other three nitrogen atoms connect only two tetrahedra. This network can be written as $^3_{}[\text{SiN}_{3/2}\text{N}_{1/3}^{1.5-}]$. Although the rare earth ions are eight coordinated by nitrogen atoms, nitrogen atoms are only four and five coordinated by silicon and rare earth metal atoms, respectively. In the structure of $\text{Ce}[\text{Si}_3\text{N}_5]$,¹²⁷ again belonging to a larger family $\text{Ln}[\text{Si}_3\text{N}_5]$ ($\text{Ln} = \text{La, Ce, Pr, Nd}$),^{125,128} the relations are a bit more complicated. One crystallographic type of tetrahedra shares one nitrogen atom with three other tetrahedra, the second type shares two, and the third shares three. The remaining nitrogen ligands connect only two tetrahedra, leading to the interesting network $^3_{}[(\text{SiN}_{3/2}\text{N}_{1/3})(\text{SiN}_{2/2}\text{N}_{2/3})(\text{SiN}_{1/2}\text{N}_{3/3})^{3-}]$. The rare earth ions in voids of this network are coordinated by nine nitrogen atoms. Yttrium silicon nitrides include three compositions so far. In addition to the $\text{Y}[\text{Si}_3\text{N}_5]$ and

$\text{Y}_3[\text{Si}_6\text{N}_{11}]$ compositions, $\text{Y}_2[\text{Si}_3\text{N}_6]$ has been reported. The latter was prepared from the binary oxides by a carbothermal reduction and nitridation method (CRN).¹²⁹ Unfortunately the structure of $\text{Y}_2[\text{Si}_3\text{N}_6]$ is not known, but ^{89}Y and ^{29}Si solid-state MAS NMR techniques indicate the presence of at least three crystallographically distinct silicon sites and at least two yttrium sites. In contrast to the alkali metal oxonitridometalates of transition metals discussed in a previous section, in yttrium nitrogen melilite ($\text{Y}_2[\text{Si}_3\text{O}_3\text{N}_4]$), hints of partial ordering of the nonmetal atoms in the tetrahedral coordination polyhedra of the silicon atoms were found from ^{15}N NMR studies.¹³⁰ Refinements of neutron diffraction data result in one nonmetal site exclusively occupied by oxygen atoms, whereas the other two sites are occupied to $\sim 80\%$ with nitrogen and 20% with oxygen atoms.¹³¹ Oxygen is mainly located on one site, which is bound to only one silicon atom, whereas the other two anion sites are bridging two tetrahedra. Very similar findings were also obtained for the melilite $\text{Nd}_2[\text{Si}_{2.5}\text{Al}_{0.5}\text{O}_{3.5}\text{N}_{3.5}]$.¹³¹

$\text{Ba}[\text{Si}_7\text{N}_{10}]^{132}$ has a highly condensed framework of SiN_4 tetrahedra that are partially edge and partially corner connected. The framework can be written as $^3_{}[(\text{SiN}_{1/2}\text{N}_{3/3})_4(\text{SiN}_{4/3})_3^{2-}]$. The barium ions are coordinated by 13 nitrogen atoms, sitting in the large voids formed by the nitridosilicate network with $d(\text{Ba}-\text{N}) \geq 2.91\text{ \AA}$ and an average distance $\bar{d}(\text{Ba}-\text{N}) = 3.27\text{ \AA}$, compared with, for example, $\bar{d}(\text{Ba}-\text{N}) = 2.86\text{ \AA}$ in $\text{Ba}_5[\text{Si}_2\text{N}_6]$.

Especially remarkable are the structures of $\text{AEYb}[\text{Si}_4\text{N}_7]$ ($\text{AE} = \text{Sr, Ba}$)^{133,134} and $\text{EuYb}[\text{Si}_4\text{N}_7]$,¹³⁵ where four tetrahedra are condensed on one nitrogen atom. It follows that there is a formal positive charge at this nitrogen ligand. The remaining three nitrogen ligands per tetrahedra connect only two silicon atoms. The resulting framework $^3_{}[\text{SiN}_{3/2}\text{N}_{1/4}^{1.25-}]$ provides voids and channels sufficient in size for alkaline earth and (Eu(II)) ions ($\text{CN} = 12$), respectively, and ytterbium atoms ($\text{CN} = 6$). Figure 8 shows a section of this structure. $\text{EuYb}[\text{Si}_4\text{N}_7]$ and $\text{Eu}_2[\text{Si}_5\text{N}_8]$ ¹³⁵ are the first Eu(II)-containing nitridosilicates. The latter one crystallizes isotypic to the compounds $\text{AE}_2[\text{Si}_5\text{N}_8]$ ¹³⁶ ($\text{AE} = \text{Sr, Ba}$). The nitridosilicate network is built from vertex-sharing tetrahedra. SiN_4 units with three nitrogen atoms link three tetrahedra to form layers. Every fourth nitrogen ligand of each of this tetrahedra is connected to only one other tetrahedra, of which all four nitrogen are shared by only two silicon atoms. These tetrahedra connect the layers in the third dimension, leading to the framework $^3_{}[(\text{SiN}_{1/2}\text{N}_{3/3})_4(\text{SiN}_{4/2})_4^{4-}]$. Alkaline earth or Eu(II) atoms occupy positions that are eight or nine coordinated by nitrogen atoms.

Dark blue $\text{Ba}_2\text{Nd}_7[\text{Si}_{11}\text{N}_{23}]$ is the first nitridosilicate with a zeolite-like structure.¹³⁷ The complex structure of corner-connected SiN_4 tetrahedra provides channels for barium and neodymium ions. Remarkable is the high coordination number of 16 for one barium site, leading to unusually long bond distances $d(\text{Ba}-\text{N})$ in the range 3.37–4.41 \AA , again compared with those in $\text{Ba}_5[\text{Si}_2\text{N}_6]$ with the range 2.61–3.40 \AA and barium in tetrahedral and octahedral coordination.

The structures in the system $\text{RE}_{6+x/3}[\text{Si}_{11}\text{N}_{20+x}\text{O}_{1-x}]$ ($\text{RE} = \text{Y, Gd-Lu}$)¹³⁸ with the ideal compositions

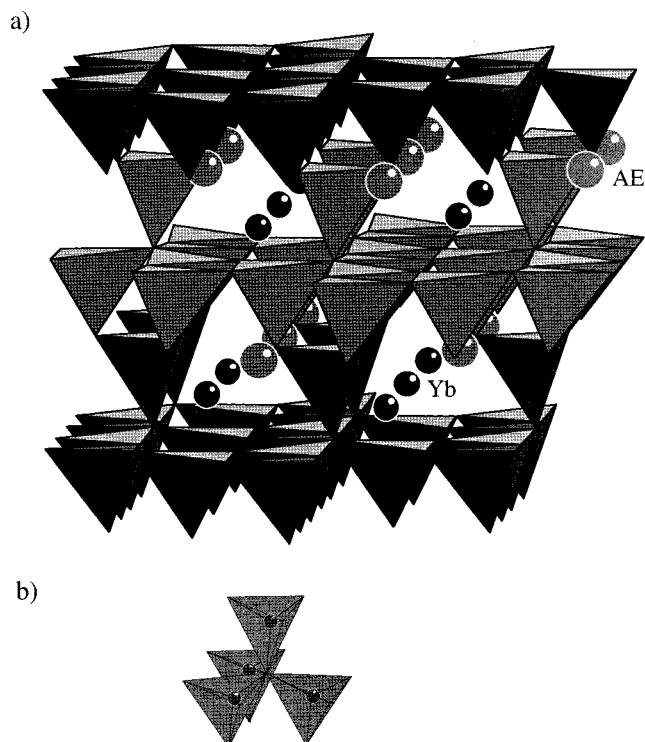


Figure 8. (a) A part of the structure of $\text{AEYb}[\text{Si}_4\text{N}_7]$ ($\text{AE} = \text{Sr}, \text{Ba}, \text{Eu}$) compounds with the three-dimensional framework of vertex-sharing SiN_4 tetrahedra. (b) A section with one central nitrogen atom linking four tetrahedra at their corners.

$\text{Re}_6[\text{Si}_{11}\text{N}_{20}\text{O}]$ and $\text{RE}_{6+1/3}[\text{Si}_{11}\text{N}_{21}]$ at the borders, are quite complicated. The silicon is again coordinated tetrahedrally by nitrogen atoms. These tetrahedra share some corners, forming a complex three-dimensional framework. Two rare earth metal sites are fully occupied and, depending on the oxygen content, a third one is partially occupied. For $x = 0$, the third rare earth metal site is not occupied, for $x = 1$ it is occupied to 1/3. Also, one silicon position depends on the oxygen or rare earth metal content. For example at $x = 0$, one SiN_4 tetrahedron is connected at four corners to the nitrido-silicate network, leaving one nonmetal ion (N or O) isolated. On the other hand, at $x = 1$, the silicon has moved to bond to the previously isolated anion, now forming a tetrahedra SiN_4 with one terminal atom.

For the first time, Si_3N_4 microtubes¹³⁹ were obtained from silicon diimide $[\text{Si}(\text{NH})_2]$ in the presence of cobalt powder. These microtubes have a regular hexagonal morphology and are sometimes filled with cobalt silicide (Co_2Si).

A similar breakthrough was achieved with the preparation of the first crystalline solid in the Si–C–N system. Silicon dicarbodiimide $(\text{Si}[\text{CN}_2]_2)$ ¹⁴⁰ directly forms from the reaction of silicon chloride with $\text{Me}_3\text{Si}-\text{N}=\text{C}=\text{N}-\text{SiMe}_3$ at 100 °C in the presence of pyridine. The structure can be described as an anti-cuprite type (two independent, interpenetrating β -cristobalite structures) with silicon on the oxygen sites of the structure parent type. Linear $[\text{CN}_2]^{2-}$ ions occupy the copper sites of the cuprite structure such that the nitrogen ends are pointing toward the silicon atoms. In this way the silicon atoms are again tetrahedrally coordinated by four nitrogen, as shown in Figure 9.

Germanium Nitrides, $\text{CN}(\text{Ge}) = 4, 2, 0$. In contrast to silicon, germanium exhibits a much broader

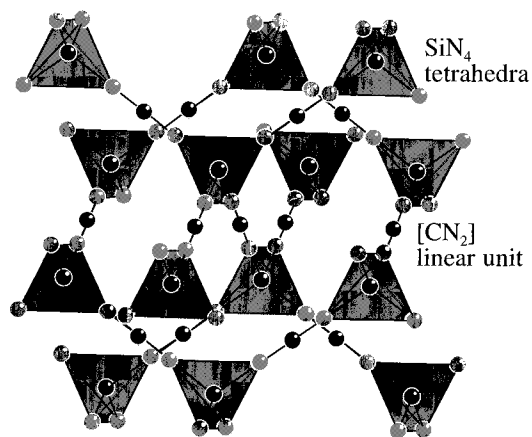


Figure 9. Anti-cuprite-like structure of $\text{Si}[\text{CN}_2]_2$ with silicon atoms in tetrahedral coordination by nitrogen ligands of the linear $[\text{CN}_2]$ units. This arrangement results in two independent interpenetrating networks.

coordination chemistry and oxidation states of +4, +2, and even –2 in nitrides. The oxidation state of +4 for germanium leads to tetrahedral coordination by nitrogen in $\text{Ca}_4[\text{GeN}_4]$ ¹⁴¹ and $\text{Ca}_5[(\text{GeN}_3)_2]$.¹⁴² $\text{Ca}_4[\text{GeN}_4]$ contains isolated tetrahedra $[\text{GeN}_4]^{8-}$ stacked together with 5-fold coordinated calcium atoms. Quite similar to some nitridometalate structures already discussed, $\text{Ca}_5[(\text{GeN}_3)_2]$ is built from one-dimensional infinite chains $[\text{GeN}_2\text{N}_{2/2}^{2.5-}]$ of corner-connected tetrahedra. The chains have a conformation and are stacked together in a manner similar to that found in the pyroxene structures of the oxosilicates ortho- and clinoenstatite (both MgSiO_3 modifications).^{143,144} Calcium ions are coordinated by six nitrogen atoms, so that nitrogen atoms possess six or seven metal neighbors. Recently reported ternary Ge(II)-nitrides include $\text{Ca}_2[\text{GeN}_2]$ ¹⁴² and $\text{Sr}_2[\text{GeN}_2]$,¹⁴⁵ both containing five coordinated alkaline earth ions and isolated $[\text{GeN}_2]^{4-}$ dumb-bells. Because these $[\text{GeN}_2]^{4-}$ units are isoelectronic to SO_2 it is not surprising to find that they are bent with an angle of $(\text{N}-\text{Ge}-\text{N}) \approx 113^\circ$. This geometry is also expected from extended Hückel molecular calculations.¹⁴⁶ Also there are $\text{Sr}_3\text{Ge}_2\text{N}_2$,¹⁴⁵ $\text{Ba}_3\text{Ge}_2\text{N}_2$,¹⁴⁷ and their solid solution $(\text{Ba}_x\text{Sr}_{1-x})_3\text{Ge}_2\text{N}_2$ (reported with $x \approx 0.8$)¹⁴⁸ that contain the bent $[\text{GeN}_2]^{4-}$ dumb-bell as well as an infinite germanium zigzag chain. Hence, they are best described as Ge(II)Ge(–II) Zintl compounds, $\text{AE}_3[\text{GeN}_2][\text{Ge}]$. Although the nitrogen ligands are octahedrally coordinated by the germanium atoms of the dumb-bells and the alkaline earth ions, the barium sites have only low coordination numbers by nitrogen atoms between two and five. The coordination sphere of the alkaline earth atoms is completed by the anionic germanium atoms of the Zintl anion. Figure 10 gives a view of the structure. Nitride compounds with metal–metal bonds were previously reported for gallium and indium; for examples, in $\text{Ca}[\text{GaN}]$,¹⁴⁹ $\text{Ca}_5[\text{Ga}_2\text{N}_4]$,¹⁵⁰ $(\text{AE}_6\text{N})[\text{Ga}_5]$,¹⁵¹ and $\text{AE}_4\text{In}_2\text{N}$ ¹⁵² ($\text{AE} = \text{Ca}, \text{Sr}$). The indium compounds contain similar infinite zigzag chains $[\text{In}^{2.5-}]$, whereas the nitrogen ions are coordinated by octahedra of alkaline earth metal atoms: $(\text{AE}_2\text{AE}_{4/2}\text{N})\text{In}$. Finally, the compound Ba_2GeGaN ¹⁴⁸ also exhibits infinite zigzag metal chains, but every second germanium atom in the $[\text{Ge}^{2-}]$ chain just mentioned is replaced by a GaN unit leading to $\text{Ba}_2[\text{Ge}^{\text{II}}\text{Ga}^{\text{I}}\text{N}]$. The

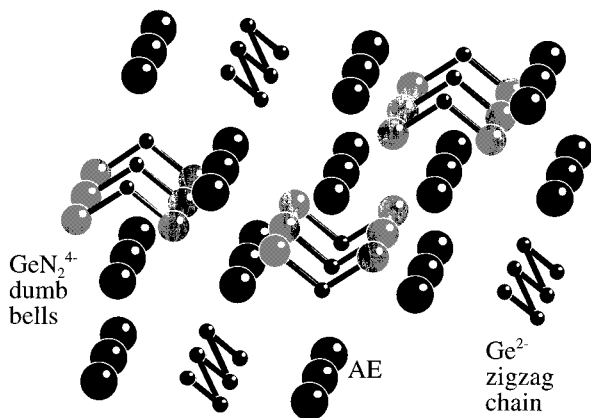


Figure 10. A segment of the structure of $\text{AE}_3\text{Ge}_2\text{N}_2$ (AE = Sr, Ba) with infinite ${}^1[\text{Ge}^{2-}]$ zigzag chains and isolated $[\text{GeN}_2]^{4-}$ dumb-bells.

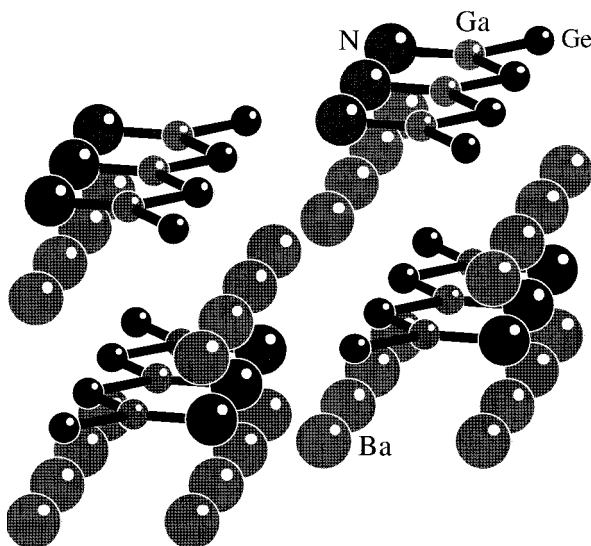


Figure 11. A view in the structure of $\text{Ba}_2[\text{GaGeN}]$ with infinite chains ${}^1[\text{Ge}_{2/2}\text{GaN}^{4-}]$.

resulting infinite chains ${}^1[\text{Ge}_{2/2}\text{GaN}^{4-}]$ are depicted in Figure 11. Again, nitrogen is coordinated octahedrally by barium and gallium atoms, whereas the barium ions are only coordinated by two or three nitrogen atoms. Additional gallium and germanium atoms complete the coordination of the barium atoms.

Gallium and Aluminum Nitrides, CN(M) = 4. Ga(I) and Ga(III) show a broad variety of different coordination possibilities by nitrogen in inorganic solid-state compounds, but in the recently reported structures of Ga(III) nitrides, tetrahedrally coordinated is the rule. $\text{Sr}_3[(\text{GaN}_2)_2]^{153}$ and $\text{Ba}_3[(\text{GaN}_2)_2]^{154}$ crystallize isotypic with $\text{Sr}_3[\text{Al}_2\text{N}_4]^{155}$ and contain infinite chains ${}^1[\text{GaN}_{4/2}^{3-}]$ of edge-sharing tetrahedra. These chains are found in a similar form in $\text{Li}_3[\text{FeN}_2]^{156}$. In the gallium nitrides the alkaline earth ions are surrounded octahedrally by nitrogen atoms, whereas nitrogen is coordinated by six or seven metal atoms. $\text{Ca}_3[\text{Ga}_2\text{N}_4]^{153}$ is isotypic with $\gamma\text{-Ca}_3[\text{Al}_2\text{N}_4]^{98}$ forming layers ${}^2[\text{GaN}_{4/2}^{3-}]$ of edge- and corner-sharing tetrahedra. The nitrogen ligands are again 6- or 7-fold coordinated by metal atoms. Finally, $\text{Sr}_3[\text{Ga}_3\text{N}_5]^{153}$ is built of a framework of edge- and corner-linked tetrahedra ${}^3[\text{Ga}_3\text{N}_5^{6-}]$ that can be written as ${}^3[(\text{GaN}_{3/2}\text{N}_{1/3})\text{-(GaN}_{2/2}\text{N}_{2/3})(\text{GaN}_{1/2}\text{N}_{3/3})^{6-}]$. This structure looks the

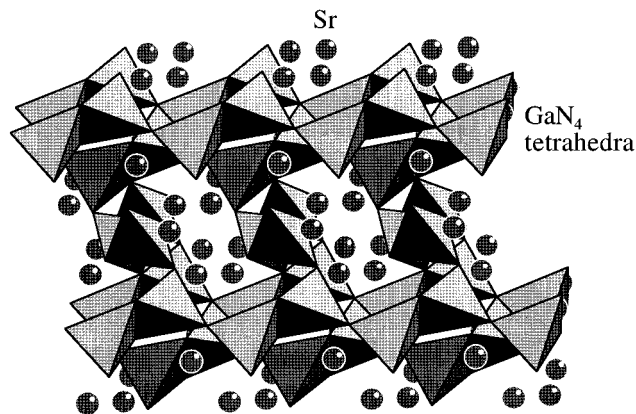


Figure 12. A section of the three-dimensional framework structure of $\text{Sr}_3[\text{Ga}_3\text{N}_5]$ built from edge- and corner-sharing tetrahedra GaN_4 .

same as that for $\text{Ln}[\text{Si}_3\text{N}_5]$, but in the structure of the silicate, the tetrahedra are only corner connected, no edge sharing occurs. The strontium atoms in the voids of this framework are six and seven coordinated, also leading to 6- and 7-fold coordination of nitrogen ligands by metal atoms. Figure 12 shows a section of this structure.

With aluminum, $\text{La}_2[\text{AlN}_3]^{157}$ was recently discovered, containing infinite chains ${}^1[\text{AlN}_2\text{N}_{2/2}^{6-}]$ of corner-sharing tetrahedra. The coordination number of lanthanum is seven. $\text{La}_2[\text{AlN}_3]$ crystallizes isotypic with the transition metal nitrides $\text{Sr}_2[\text{VN}_3]^{158}$ and $\text{Ba}_2[\text{NbN}_3]^{21}$. It was prepared from lanthanum amide and aluminum powder in a sodium flux, which was produced by thermal decomposition of sodium amide. Surprisingly, it also forms as a minor byproduct using aluminum oxide instead of the aluminum powder.

Phosphorus Nitrides, CN(P) = 4. The structural chemistry of phosphorus nitrides has many similarities with that of silicon nitrides. Phosphorus in all known nitrides is coordinated tetrahedrally by nitrogen atoms. These tetrahedra can be isolated, corner connected with one nitrogen atom linking two or three tetrahedra (nitrogen ligands bridging four phosphorus atoms such as in the nitridosilicates $\text{EaYb}[\text{Si}_4\text{N}_7]$ (Ea = Sr, Ba, Eu)¹³³⁻¹³⁵ have not been encountered yet) or edge connected. $\text{Ca}_2[\text{PN}_3]^{159,160}$ (isotypic with $\text{Ba}_2[\text{VN}_3]^{158}$) and $\text{Mg}_2[\text{PN}_3]^{159}$ contain infinite chains ${}^1[\text{PN}_2\text{N}_{2/2}^{4-}]$ of corner-connected tetrahedra. The calcium atoms in $\text{Ca}_2[\text{PN}_3]$ are 7-fold coordinated in a pentagonal bipyramidal arrangement, whereas the magnesium atoms in $\text{Mg}_2[\text{PN}_3]$ are tetrahedrally coordinated by nitrogen atoms. The latter compound is isotypic with $\text{Li}_2\text{SiO}_3^{161}$ and hence can be described as a superstructure of the wurtzite structure type, with magnesium and phosphorus atoms ordered at the site of the metal atoms in the structure type. $\text{K}_3[\text{P}_6\text{N}_{11}]^{162}$ crystallizes similar to the earlier reported $\text{K}_3[\text{Si}_6\text{N}_5(\text{NH})_6]^{163}$ and $\text{Na}_3[\text{P}_6\text{N}_{11}]^{164}$ in a cubic unit cell. The PN_4 tetrahedra are corner connected, but one nitrogen ligand of every phosphorus atom connects three tetrahedra, whereas the other three connect two. These connections result in a complicated three-dimensional network ${}^3[\text{PN}_{3/2}\text{N}_{1/3}^{0.5-}]$ with potassium ions in 8- and 9-fold coordination by nitrogen ligands.

HPN_2^{165} was recently synthesized by ammonolysis of P_3N_5 at an ammonia pressure of 6 Kbar. This compound

crystallizes in a distorted variant of the β -cristobalite type structure built up by corner-connected $\text{PN}_2(\text{NH})_2$ tetrahedra linked on all corners ${}^3[\text{PN}_{2/2}(\text{NH})_{2/2}]$. It was found to possess remarkable thermal proton conductivity.¹⁶⁶ High-pressure investigations revealed a phase transition between 14 and 24 GPa that is not accompanied with a change in the coordination number of the phosphorus. Similar behavior is also known for β -cristobalite type PON.¹⁶⁷ However, for the latter compound, the experimental data in the recent literature are not clear because other authors did not observe a phase transition at <48 GPa.¹⁶⁸ HP_4N_7 ¹⁶⁶ can be prepared by reaction of P_3N_5 with ammonium chloride, but was not obtained single phase in this way. The neat powder was produced by pyrolysis of the precursor $(\text{NH}_2)_2\text{P}(\text{S})\text{P}(\text{NH}_2)_3$.¹⁶⁹ Rietveld structure refinements reveal a three-dimensional framework of corner- and edge-connected tetrahedra. The hydrogen atoms seem to be statistically disordered over nitrogen ligands that connect three PN_4 tetrahedra.

P_3N_5 was found to possess two different modifications, α - P_3N_5 ¹⁷⁰ and β - P_3N_5 .¹⁷¹ α - P_3N_5 resembles the structure of HP_4N_7 with PN_4 tetrahedra sharing corners and edges ${}^3[\text{PN}_{2/2}\text{N}_{2/3}]$. It was prepared by pyrolysis of $[\text{P}(\text{NH}_2)_4]\text{I}$.¹⁷² β - P_3N_5 has a superstructure of that of the α -type, produced by different stacking of identical layers.

To complete the possibilities known for corner connection of tetrahedra, nitridophosphates also form sodalites. After the nitridosodalites $\text{M}_{6+y/2-x}\text{H}_{2x}[\text{P}_{12}\text{N}_{24}]\text{X}_y$ ($\text{M} = \text{Zn, Fe, Co, Ni, Mn}$; $\text{X} = \text{Cl, Br, I}$; $0 \leq x \leq 4$; $y \leq 2$)¹⁷³⁻¹⁷⁵ were reported some time ago, the chalcogenide analogues $\text{Zn}_8[\text{P}_{12}\text{N}_{24}]\text{X}_2$ ($\text{X} = \text{O, S, Se, Te}$)¹⁷⁶ were prepared. All of the chalcogenide analogues are built from a three-dimensional framework of $[\text{P}_{12}\text{N}_{24}]$ β -cages that contain XM_4 tetrahedra. In the former halides, the metal atoms are statistically distributed over seven of eight possible sites, whereas the latter chalcogenides do not show disorder. The similarly formed $\text{Zn}_6[\text{P}_{12}\text{N}_{24}]$ (from $[\text{P}_{12}\text{N}_{24}]$ β -cages) has the ability to encapsulate molecular hydrogen up to 8.6 cm^3/g .¹⁷⁷ This procedure is reversible and reproducible.

The interesting structures of the compounds $\text{M}^{\text{I}}_3\text{M}^{\text{III}}[\text{P}_3\text{O}_9\text{N}]$ ($\text{M}^{\text{I}} = \text{Na, K}$; $\text{M}^{\text{III}} = \text{Al, Ga, In, Ti, V, Cr, Mn, Fe}$) and $\text{M}^{\text{I}}_2\text{M}^{\text{II}}_2[\text{P}_3\text{O}_9\text{N}]$ ($\text{M}^{\text{I}} = \text{Na}$; $\text{M}^{\text{II}} = \text{Mg, Mn, Fe, Co}$) have cubic symmetry containing $[(\text{PO}_3)_3\text{N}]^{6-}$ units in which the nitrogen atom is shared by three $[\text{PO}_3\text{N}_{1/3}]^{2-}$ tetrahedra.¹⁷⁸

Beryllium Nitrides, $\text{CN}(\text{Be}) = 3$. $\text{Li}[\text{BeN}]$ ¹⁷⁹ crystallizes in a new structure type. The beryllium atoms are trigonal planar coordinated by nitrogen ligands. These units are linked by corners and edges to form layers ${}^2[\text{BeN}_{3/3}]$ between which the lithium ions are located, surrounded nearly tetrahedrally by four nitrogen atoms. Figure 13 depicts the ${}^2[\text{BeN}_{3/3}]$ layers in this structure.

Carbon and Boron Nitrides, $\text{CN}(\text{M}) = 2$. Because cyanamide ions $[\text{NCN}]^{2-}$ can also be considered as nitridocarbonate units, we should mention new developments in this area. $\text{AE}[\text{CN}_2]$ ($\text{AE} = \text{Mg, Sr, Ba}$)¹⁸⁰ were prepared by reaction of melamine ($\text{C}_3\text{N}_3(\text{NH}_2)_3$) with the binary metal nitrides Mg_3N_2 , Sr_2N , and Ba_3N_2 , respectively. All three compounds contain the linear $[\text{CN}_2]^{2-}$ unit. $\text{Mg}[\text{CN}_2]$ crystallizes isotypic with $\text{Ca}[\text{CN}_2]$ ¹⁸¹ in

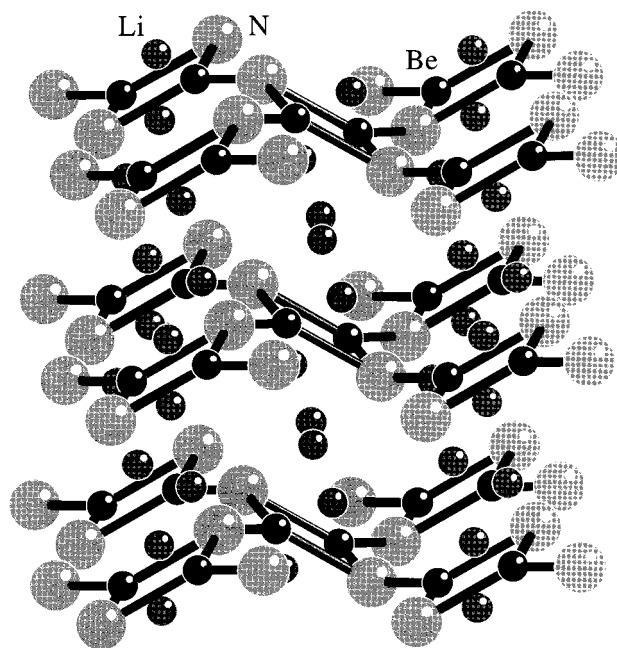


Figure 13. A part of the structure of $\text{Li}[\text{BeN}]$ with ${}^2[\text{BeN}_{3/3}]$ layers of connected BeN_3 triangles.

a layered structure. The magnesium atoms are coordinated by six nitrogen atoms of six different $[\text{CN}_2]^{2-}$ ions. These octahedra form layers by edge sharing. The $[\text{CN}_2]^{2-}$ units connect these layers in the third dimension; the two nitrogen atoms of every ion belongs to the upper or lower layer. In this way, the $[\text{CN}_2]^{2-}$ ion is surrounded by an elongated octahedron of magnesium atoms, leading to tetrahedral coordination of the nitrogen ligands by one carbon and three magnesium atoms. A similar arrangement takes place in $\text{Sr}[\text{CN}_2]$ with the SrN_6 octahedra now vertex sharing. In $\text{Ba}[\text{CN}_2]$, the barium atoms are surrounded rather irregularly by six nitrogen ligands, resulting in a three-dimensional arrangement. Although the existence of $\text{Na}_2[\text{CN}_2]$ and $\text{K}_2[\text{CN}_2]$ seems to be uncertain, $\text{KH}[\text{CN}_2]$ ¹⁸² and $\text{K}_5\text{H}[\text{CN}_2]_3$ ¹⁸³ were recently prepared from reactions of potassium amide with melamine ($\text{C}_3\text{N}_3(\text{NH}_2)_3$). The NCN groups of the HNCN^- ions in $\text{KH}[\text{CN}_2]$ are not entirely linear ($(\text{N}-\text{C}-\text{N}) \approx 174^\circ$) like earlier reported for $\text{NaH}[\text{CN}_2]$.¹⁸⁴ On the other hand, the NCN groups in $\text{K}_5\text{H}[\text{CN}_2]_3$ show an angle of 180° given by symmetry. Reacting Ba_2N or Sr_2CO_3 with HCN is reported to lead to the compounds $\text{Ba}_2[\text{CN}_2][\text{CN}]_2$ and $\text{Sr}_2[\text{CN}_2][\text{CN}]_2$, respectively, with cyanamide ions next to cyanide ions disordered on the same position in the crystal structure.¹⁸⁵ Considering the different dimensions of the anions, this result is quite surprising. $\text{Si}(\text{CN}_2)_2$ ¹⁴⁰ was already mentioned with the silicon nitrides, and with its linear $[\text{CN}_2]^{2-}$ units connecting the silicon atoms, it fits also in this discussion.

The newly reported nitrides of boron show the known isolated linear unit $[\text{BN}_2]^{3-}$, first reported in $\text{Li}_3[\text{BN}_2]$.^{186,187} $\text{LiSr}_4[\text{BN}_2]_3$ ¹⁸⁸ crystallizes in a cubic unit cell, isotypic with $\text{LiCa}_4[\text{BN}_2]_3$ ¹⁸⁹ and $\text{LiEu}_4[\text{BN}_2]_3$.¹⁹⁰ The earlier reported $\text{LiMg}[\text{BN}_2]$ ¹⁹¹ was now thoroughly described.¹⁹² It crystallizes isotypic with $\text{Li}_2[\text{CN}_2]$ ¹⁹³ with complete disorder of lithium and magnesium atoms on one crystallographic site and distorted tetrahedral coordination by nitrogen ligands. In this way, nitrogen is coordinated square pyramidal with lithium and

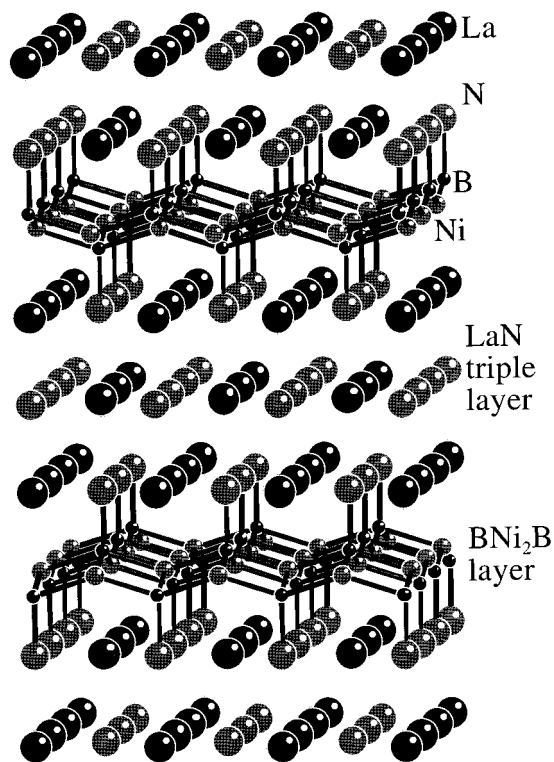


Figure 14. View in the structure of $\text{La}_3\text{Ni}_2\text{B}_2\text{N}_3$ showing B–Ni₂–B layers between LaN triple layers.

magnesium atoms at the base and boron atoms at the apex of the pyramid. Likewise, the earlier reported $\text{Ba}_4[\text{BN}_2]_2\text{O}$ ^{192,194} is best described as a nitridoborate oxide. As discussed in Section 2, the oxide ions are coordinated in an octahedral fashion exclusively by barium atoms. The essentially linear $[\text{BN}_2]^{3-}$ unit exhibits an angle of (N–B–N) $\approx 173^\circ$.

Similar findings with basically linear, isolated $[\text{BN}_2]^{3-}$ units are reported for the nitridoborate halides $\text{Ca}_2\text{Cl}[\text{BN}_2]$ and $\text{Sr}_2\text{Cl}[\text{BN}_2]$.¹⁹⁵ However, the nitrogen ligands at both ends of the $[\text{BN}_2]^{3-}$ unit are not crystallographically equivalent. One is coordinated by four, and the other by three alkaline earth atoms, resulting in different B–N bond lengths.

The $[\text{CBN}]^{4-}$ ion found in $\text{Ca}_{15}[\text{CBN}]_6[\text{C}_2]_2\text{O}$,¹⁹⁶ which also contains oxide and $[\text{C}_2]^{2-}$ ions, also falls in this group of anions. As expected from the composition, the structure is built by a fairly complicated stacking of the ions. In $\text{Ca}_{9+x/2}[\text{BN}_2]_{6-x}[\text{CBN}]_x$ ($0 \leq x \leq 2$)¹⁹⁷ the $[\text{CBN}]^{4-}$ ion partially replaces the isoelectronic $[\text{BN}_2]^{3-}$ ion in the cubic parent structure of $\text{Ca}_3[\text{BN}_2]_2$.

The superconducting nitride boride $\text{La}_3\text{Ni}_2\text{B}_2\text{N}_3$ ($T_c \approx 13$ K),¹⁹⁸ originally prepared by arc-melting of the metal elements under nitrogen gas, consists of triple layers of LaN alternately stacked together with B–Ni₂–B layers.¹⁹⁹ The latter layers are related to those found in boride carbides $\text{LnNi}_2\text{B}_2\text{C}$.²⁰⁰ The LaN-triple layer forms a section of the rocksalt structure, which is also adopted by lanthanum nitride. The different layers are stacked so that the boron atoms face nitrogen atoms, but at a long distance of $d(\text{B–N}) = 2.02$ Å (for comparison in $[\text{BN}_2]^{3-}$ $d(\text{B–N}) \approx 1.36$ Å). Hence, in contrast to the nitridoborates, already discussed, the compound is better described as a nitride boride and has boron in a 4 + 1-like coordination by four nickel atoms and the nitrogen atom at a fairly long distance. Figure 14 gives

a view of the structure. This compound was more recently prepared from lanthanum, nickel, and polyborazylene $[\text{B}_3\text{N}_3\text{H}_{\approx 4}]_x$ in a pyrolysis reaction at 1000 °C.²⁰¹ A theoretical study on $\text{La}_3\text{Ni}_2\text{B}_2\text{N}_3$ showed that its superconductivity is related to the three-dimensional linking of the B–Ni₂–B layers through the lanthanum atoms of the LaN layers.²⁰²

5. Sodium Alkaline Earth Subnitrides

Several metallic sodium subnitrides containing one or two alkaline earth metals were discovered by Simon⁹ within the last six years. They all contain octahedral $[\text{NAE}_6]$ (AE = Ca, Ba) clusters centered by a nitrogen atom like those known from some ternary transition metal nitrides [e.g., the compounds $\text{Ba}_5[\text{CrN}_4]\text{N}$ ⁶⁹ or $\text{Ca}_6[\text{Mn}_3]\text{N}_2$ (M = Ga, Fe, Mn)^{70,71} discussed in Section 2. These clusters are embedded in different metallic sodium matrices that allow different compositions. Because the parallels of these subnitrides with the alkali metal suboxides recently were discussed in reviews^{7,9} we want to concentrate only briefly on their structures.

The first compounds reported were NaBa_3N ²⁰³ and $\text{Na}_5\text{Ba}_3\text{N}$,²⁰⁴ which contain the aforementioned octahedral $[\text{NBa}_6]$ cluster. These share common faces to form infinite chains $^1_\infty[\text{NBa}_{6/2}]$, which are stacked together according to a hexagonal rod packing, isolated by the variable amount of sodium. In $\text{Na}_{16}\text{Ba}_6\text{N}$ ²⁰⁵ (and $\text{Ag}_{16}\text{Ca}_6\text{N}$, which has a metallic resistivity), isolated $[\text{NAE}_6]$ octahedra are situated in a cubic body-centered arrangement.

The recently discovered mixed calcium barium subnitrides are of the general composition $\text{Na}_n\text{Ba}_{14-n}\text{CaN}_6$,^{206,207} with $n = 14, 17, 21$, and 22. They contain the discrete $[\text{Ba}_{14}\text{CaN}_6]$ unit that is again isolated by a variable amount of sodium. The calcium atom is located in the center, surrounded by an octahedra of six nitrogen atoms. The outer hull is formed from 14 barium atoms in a way that every nitrogen atom is octahedrally coordinated by five barium atoms and the calcium atom in the centers. An analogous description is that of six $[\text{NBa}_5\text{Ca}]$ octahedra sharing common faces, so that all octahedra have a common corner at which the calcium atom is bound. In $\text{Na}_{14}\text{Ba}_{14}\text{CaN}_6$, these units are packed together in a face-centered cubic arrangement, in $\text{Na}_{17}\text{Ba}_{14}\text{CaN}_6$ the units are packed together in a nearly trigonal prismatic array and in $\text{Na}_{21}\text{Ba}_{14}\text{CaN}_6$ the units are packed in nearly a body-centered cubic fashion. In $\text{Na}_{22}\text{Ba}_{14}\text{CaN}_6$, the $[\text{NBa}_5\text{Ca}]$ units alternate with Na_6 rings to form chains. Diffuse scattering of the obtained crystals ($\text{Na}_{22}\text{Ba}_{14}\text{CaN}_6$) revealed an orientation disorder of these chains relative to each other:²⁰⁸ two of these chains pack best if the $[\text{NBa}_5\text{Ca}]$ cluster of one chain is located next to a Na_6 unit of the neighboring chain. The third chain in triangular packing then has an orientation problem relative to the two other chains resulting in “packing-frustration” and chain disorder. Figure 15 views this structure along these chains.

6. Nitride Halides

This section deals with nitride halides that were not mentioned in the previous sections (e.g., $\text{Ba}_4[\text{WN}_4]\text{Cl}_2$ in Section 2). Because the following nitrides are mostly

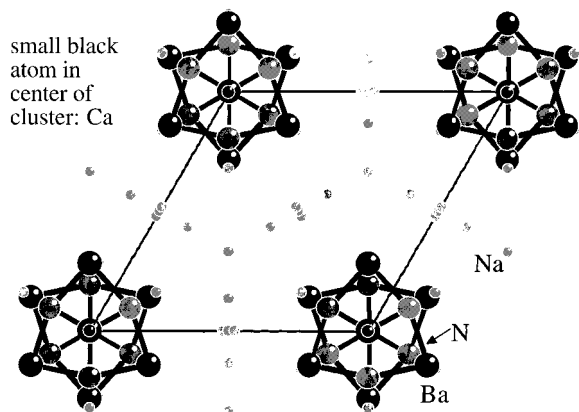


Figure 15. Structure of $\text{Na}_{22}\text{Ba}_{14}\text{CaN}_6$ viewed along the hexagonal c -axis. Infinite chains of stacked $[\text{Ba}_{14}\text{CaN}_6]$ units running along this direction are emphasized.

metal rich relative to their nitrogen content, they are best classified by the coordination polyhedra around nitrogen and the way these are linked together.

Lithium Nitride Halides, $\text{CN}(\text{N}) = 2-8$. Lithium nitride halides show a large variety of polyhedra and coordination numbers of nitrogen by lithium atoms. They were originally investigated by Sattler and Hahn in the 1960s. In the meantime they attracted some attention as lithium ion conductors. Newer work in these systems elucidate structures and structural relationships of compounds that can be described with the general composition $\text{Li}_{3-2x}\text{N}_{1-x}\text{X}_x$. In general, the structures can be understood as products of acid-base reactions in which the framework structure of Li_3N is broken down to units of lower dimensionality.²⁰⁹⁻²¹⁴ The normal pressure structure of $\alpha\text{-Li}_3\text{N}$ ⁹⁵ consists of flat hexagonal layers ${}^2[\text{Li}_2\text{N}^+]$ with nitrogen atoms in 6-fold coordination by lithium atoms. The nitrogen atoms are also coordinated linearly above and below through apical lithium atoms that connect the layers, resulting in hexagonal bipyramids of lithium atoms around nitrogen. In this way, the lithium atoms within the layers are surrounded in a trigonal planar fashion by nitrogen atoms, and the lithium atoms between the layers have a linear environment of two nitrogen atoms.

$\text{Li}_{10}\text{N}_3\text{Br}$ ²⁰⁹ ($x = 1/4$ in $\text{Li}_{3-2x}\text{N}_{1-x}\text{X}_x$) contains nitrogen in a pentagonal bipyramidal coordination by lithium atoms. These NLi_7 units share common edges and vertices forming the three-dimensional framework ${}^3[\text{Li}_{10}\text{N}_3^+]$. The bromine atoms occupy large trigonal prismatic voids formed by lithium in this network. Figure 16 shows layers of NLi_7 pentagonal bipyramids, which are linked at the apexes to form the three-dimensional network.

The structure of Li_4NCl ($x = 1/2$)²¹⁰ is best described as an ordered cubic close packing of the nitrogen and chlorine atoms. The lithium atoms are located in all trigonal holes formed only by nitrogen in the layer and in all tetrahedral voids formed by one nitrogen and three chlorine atoms between the layers. In this way, nitrogen is coordinated hexagonally bipyramidally by eight lithium atoms as in $\alpha\text{-Li}_3\text{N}$, whereas the chlorine ions are located in trigonal antiprisms that are capped at both trigonal faces.

In Li_5NBr_2 ($x = 2/3$)²¹¹ NLi_6 octahedra occur. These octahedra share opposite vertices to form linear chains.

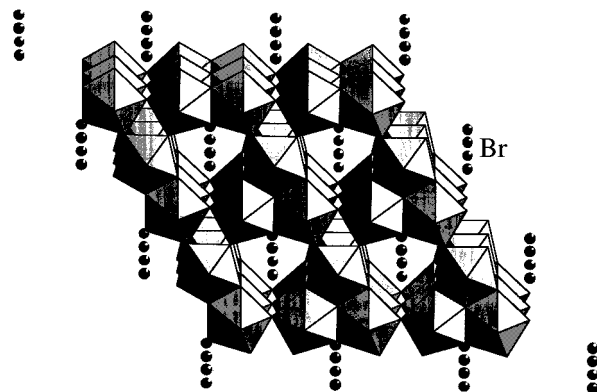


Figure 16. A section of the structure of $\text{Li}_{10}\text{N}_3\text{Br}$. NLi_7 pentagonal bipyramids are connected at corners and edges to form layers. These layers are additionally linked at the apexes to form a three-dimensional network.

The shared lithium atoms are linearly coordinated by two nitrogen atoms, and the remainder are tetrahedrally coordinated by one nitrogen and three bromine atoms. For Li_5NCl_2 ($x = 2/3$)²¹² high- and low-temperature modifications have been characterized. The low temperature form is built from alternating layers of $[\text{Li}_4\text{N}^+]$ and $[\text{LiCl}_2^-]$. The high-temperature modification, in contrast, exhibits a Li_2O type structure with the nitrogen and chlorine atoms essentially disordered over the face center sites. However, the investigations also indicate nitrogen-chlorine short-range order. Lithium atoms are distributed over the tetrahedral voids, so that each site is occupied to 5/6.

Li_6NBr_3 ²¹³ was found to possess a complex temperature behavior of four closely related phases. $\text{Li}_6\text{NBr}_3(\text{I})$ and Li_6NI_3 ($x = 3/4$) crystallize isotypic with each other²¹⁴ in a cubic body-centered arrangement of nitrogen and halogen atoms, arranged in an ordered fashion. In the idealized structure, lithium ions occupy octahedral holes formed by one nitrogen and five halogen atoms. In the real structure, however, the lithium is displaced from this ideal position in the direction of an edge of this octahedra formed by two halogen atoms. This displacement leads to a 4-fold split position, the coordination of which is closer to a tetrahedron of one nitrogen and three halogen atoms. On cooling, $\text{Li}_6\text{NBr}_3(\text{I})$ undergoes a phase transition to its (I') phase, crystallizing in an antitype of cryolite Na_3AlF_6 . The phase transition involves a distortion from the cubic symmetry to monoclinic, due to a small shift of bromine ions. In this way, ordering of the disordered lithium atoms in the higher temperatures phase (I) can occur through tilting of the NLi_6 octahedra.

Zirconium Nitride Chlorides, $\text{CN}(\text{N}) = 6$. New superconducting phases A_xZrNCl ($\text{A} = \text{Li}, \text{Na}, \text{K}$) were obtained by intercalation of lithium in $\beta\text{-ZrNCl}$ by using n -butyllithium or alkali metal naphthalenes of sodium or potassium, respectively.^{215,216} $\beta\text{-ZrNCl}$ has a layered structure with ZrN double layers between chlorine layers. These sandwich units are stacked together according to $\text{Cl-ZrN-ZrN-Cl-Cl-ZrN-ZrN-Cl}$ so that two adjacent chlorine layers are held together only by van der Waals interactions²¹⁷ (Figure 17). The alkali metal atoms intercalate in these van der Waals gaps. Whereas the yellowish-green $\beta\text{-ZrNCl}$ is a semiconductor with an optical gap of ~ 3 eV, the introduction of

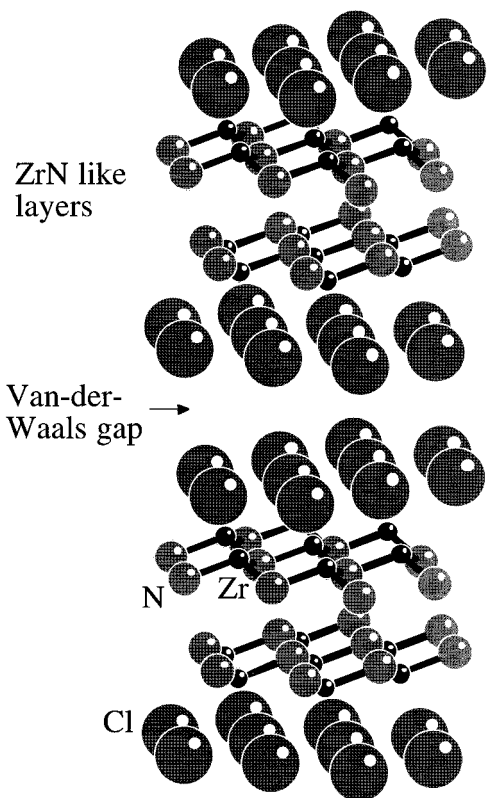


Figure 17. Structure of β -ZrNCl with ZrN like layers isolated from each other by chlorine ions. Intercalated alkali metal atoms are found in the van der Waals gap between chlorine layers for the compounds $A_x\text{ZrNCl}$ ($A = \text{Li}, \text{Na}, \text{K}$).

additional carriers in Li_xZrNCl with $x = 0.16$ results in a change of color to black and the appearance of a superconducting transition at ~ 12 K.²¹⁵ A similar T_c was found for all $A_x\text{ZrNCl}$ samples with $x \leq 0.5$, whereas the transition temperature starts to decrease with higher alkali metal content. In this region of composition ($x \geq 0.5$), the superconducting transition temperature seems to depend only on the doping level, not on the kind of alkali metal intercalated. No additional effect of intercalated hydrogen or solvent molecules on the superconducting transition temperature was detected.

Rare Earth Nitride Halides, CN(N) = 4. Also some new developments were published for rare earth nitride halides. $\text{Ce}_3\text{Br}_6\text{N}^{218}$ crystallizes isotypic with $\text{Ce}_3\text{Cl}_6\text{N}^{219}$ and similar to $\text{Gd}_3\text{Cl}_6\text{N}^{220}$ (distorted to a triclinic unit cell). These crystals are built from isolated units $[(\text{NLn}_2\text{Ln}_{2/2})_2]^{12+}$ of two edge-connected tetrahedra. The structures of $\text{Ce}_2\text{Br}_3\text{N}^{221}$, $\text{Gd}_2\text{Br}_3\text{N}^{222}$ and $\text{Gd}_2\text{Cl}_3\text{N}^{223}$ are formed from NLn_4 tetrahedra that are connected via opposite edges to infinite chains ${}^\infty[\text{NLn}_{4/2}^{3+}]$. These chains are nearly linear in the earlier reported $\text{Gd}_2\text{Cl}_3\text{N}$, but more and more bent in $\text{Ce}_2\text{Br}_3\text{N}$ and $\text{Gd}_2\text{Br}_3\text{N}$. Similar infinite chains of edge linked NCE_4 tetrahedra ${}^\infty[\text{NCE}_{4/2}^{3+}]$ occur in $\text{Ce}_{15}\text{N}_7\text{I}_{24}$, but accompanied by isolated trigonal planar $[\text{NCE}_3]^{6+}$ units.²²⁴ Hence, the composition can be written as $[\text{Ce}_3\text{N}]^{6+} {}^\infty[\text{Ce}_{4/2}\text{N}^{3+}]_6\text{I}_{24}$.

A number of interesting compounds were discovered in the rare earth nitride systems containing chlorine and sulfur in the last couple of years. A very comprehensive review focusing on these compounds just re-

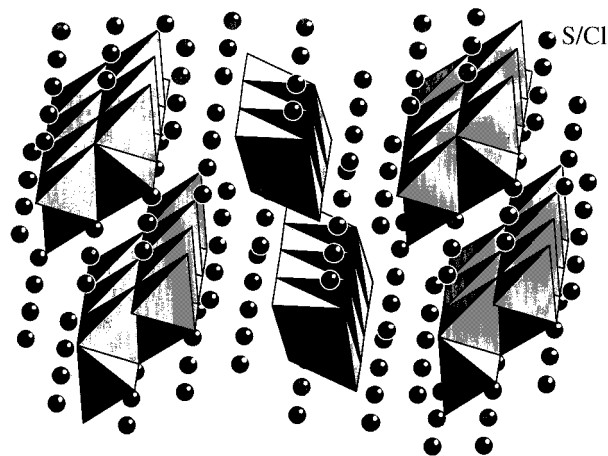


Figure 18. Structure of $\text{Pr}_5\text{N}_3\text{S}_2\text{Cl}_6$ showing two different types of chains running parallel to each other. One chain consists of two chains of cis-edge-connected tetrahedra NPr_4 , linked at an additional edge, leading to ${}^\infty[(\text{NPrPr}_{1/3}\text{Pr}_{2/4})-(\text{NPr}_{2/3}\text{Pr}_{2/4})^{3+}]$. The other chain is built from two chains of vertex-sharing tetrahedra, again connected at an additional edge to form the double chain ${}^\infty[\text{NPrPr}_{4/2}^{3+}]$. The chains are isolated from each other by anions S^{2-} and Cl^- , which could not be distinguished and might be randomly distributed over the sites.

cently appeared,⁸ therefore we will only briefly describe the structures of the newest members of this group of compounds. Isolated $[\text{NPr}_4]^{9+}$ tetrahedra were found in $\text{Pr}_4\text{NS}_3\text{Cl}_3$ ²²⁵ (isotypic with $\text{Ln}_4\text{NS}_3\text{Cl}_3$ compounds with $\text{Ln} = \text{La}-\text{Nd}, \text{Gd}^{226}$). These tetrahedra are three-dimensional, connected by chlorine and sulfur atoms according to $[\text{NPr}_4]\text{S}_{9/3}\text{Cl}_{9/3}$. The compounds of the formula $\text{Ln}_6\text{N}_3\text{S}_4\text{Cl}$ ($\text{M} = \text{La}-\text{Nd}$)²²⁷ also contain NLn_4 tetrahedra, but now connected to two different types of infinite chains. In one type, the tetrahedra are cis-edge-connected to ${}^\infty[\text{NLnLn}_{3/3}^{3+}]$. The other type is best described as built from double tetrahedra units with a common edge. These units are further connected via four outer corners to ${}^\infty[\text{N}_2\text{Ln}_2\text{Ln}_{4/2}^{6+}]$ double chains. $\text{Pr}_5\text{N}_3\text{S}_2\text{Cl}_2$ also contains two different types of double chains of condensed NPr_4 tetrahedra.²²⁸ One double chain consists of two chains of cis-edge-connected tetrahedra, linked at an additional edge leading to ${}^\infty[(\text{NPrPr}_{1/3}\text{Pr}_{2/4})(\text{NPr}_{2/3}\text{Pr}_{2/4})^{3+}]$. The other double chain is built from two chains of vertex sharing tetrahedra, again connected at an additional edge to form the double chain ${}^\infty[\text{N}_2\text{Pr}_2\text{Pr}_{4/2}^{6+}]$. Figure 18 depicts these two types of chains running parallel to each other through the structure of $\text{Pr}_5\text{N}_3\text{S}_2\text{Cl}_2$. For the latter two compounds, the sulfur and chlorine atom sites were indistinguishable by the applied X-ray diffraction method.

Similar chains ${}^\infty[\text{NLn}_{4/2}^{3+}]$ of trans-edge-connected tetrahedra were found in $\text{Cs}_x\text{Na}_{1-x}\text{La}_9\text{I}_{16}\text{N}_4$ ($x = 0.64$)²²⁹ that crystallizes isotypic with the compounds $\text{ALa}_9\text{I}_{16}\text{N}_4$ ($A = \text{Na}, \text{Rb}, \text{Cs}$)²²⁹ according to X-ray Guinier patterns. These chains are coordinated by the iodide ions. Additionally, one lanthanum site is only coordinated by iodine in a square antiprismatic arrangement, whereas the alkali metal atoms partially occupy another site (to 1/2) where they are surrounded by six iodine atoms in a trigonal prism.

For $\text{Na}_2\text{Pr}_4\text{Br}_9\text{NO}$ (isotypic with $\text{Na}_2\text{Pr}_4\text{Cl}_9\text{O}_2$)²³⁰ and $\text{Pr}_8\text{Br}_{13}\text{N}_3\text{O}$,²³¹ the authors were not able to distinguish between nitrogen and oxygen atoms in tetrahedral

coordination by praseodymium. These tetrahedra are again linked over common edges to infinite zigzag chains ${}^1_{\infty}[\text{XPr}_{4/2}]$ ($X = \text{N}, \text{O}$).

The compounds $\text{ATh}_{12}\text{N}_6\text{X}_{29}$ ($A = \text{Li}, \text{Na}, \text{Rb}; X = \text{Cl}, \text{Br}$)^{232,233} contain clusters with the cluster core Th_{12}N_6 formed from six cyclic cis-edge-sharing NTh_4 tetrahedra $[(\text{NTh}_{3/3})_6]$. These are surrounded by 41 halogen ligands to form the $\text{Th}_{12}\text{N}_6\text{X}_{41}$ cluster. Nineteen of the 41 ligands belong to only one cluster, 16 ligands link two clusters, and the remaining six link three clusters. The connection scheme can be written as $[\text{Th}_{12}\text{N}_6\text{X}_{19}^i\text{X}_{4/2}^{i-a}\text{X}_{8/2}^{a-a}\text{X}_{6/3}^{a-a}\text{X}_{4/2}^{a-i}]^-$ ($i =$ inner ligand, $a =$ outer ligand; the first superscript applies to the central cluster; the second superscript to other clusters linked by this ligand). As might be expected from the small fraction of alkali metal, in the lithium bromide compound the alkali metal positions could not be determined by single-crystal X-ray diffraction nor by neutron diffraction. However, it was possible to refine the crystallographic site of rubidium ions in the chlorine analogue, which crystallizes in a different crystal class but shows essentially the same cluster and type of cluster connection.

7. Thermochemistry of Ternary Nitrides

Little is known about the thermodynamics that controls the formation of ternary nitrides. It is known that most binary nitrides have small enthalpies of formation due mainly to the stability of dinitrogen. Enthalpy data on ternary nitrides was recently obtained using high-temperature solution calorimetry, which had been shown to be very useful for understanding the energetics of ternary oxide formation.²³⁴ The first investigations²³⁵ on ternary nitrides were undertaken on LiMoN_2 , Na_3WN_3 , and $\text{Na}_3\text{WO}_3\text{N}$ (using oxidative reaction calorimetry) to help understand the formation of ternary nitrides and oxide nitrides from ternary oxides and ammonia.

More recently, a number of ternary nitrides, predominantly lithium and calcium compounds, were examined by the high-temperature solution calorimetry technique.^{236–238} Figure 19 shows the enthalpies of formation of ternary nitrides from their binary nitrides as a function of the modified ionic potential ϕ [$\phi = (Z/d)_B/(Z/d)_A$; where $Z =$ charge of metal ions A or B in a ternary nitride $\text{A}_x\text{B}_y\text{N}_z$, and $d =$ average bond length A–N and B–N in the binary nitrides). The enthalpies given are per mole of nitrogen to adjust for the different stoichiometries. Additionally, a correction factor for different metal ratios was applied. The ionic potential ϕ was chosen as a measure of the acidity of the cations. As was found for oxides, the enthalpy of formation from binary nitrides becomes more negative (exothermic) with increasing ϕ . Not surprisingly, the data in Figure 19 show considerable scatter. The applied one-parameter model does not take into account, for examples, structure, coordination number, or character of bonding orbitals. Yet the trend is clear.

It is interesting to compare the enthalpy of formation of the ternary nitrides from binary nitrides, with the standard enthalpy of formation from the elements. In oxides, this ratio, $\Delta H_{\text{bin}}/\Delta H_{\text{elem}}$, is small, rarely exceeding 15% and usually in the 5% or less range. In nitrides, this ratio is much larger, often exceeding 20%. This

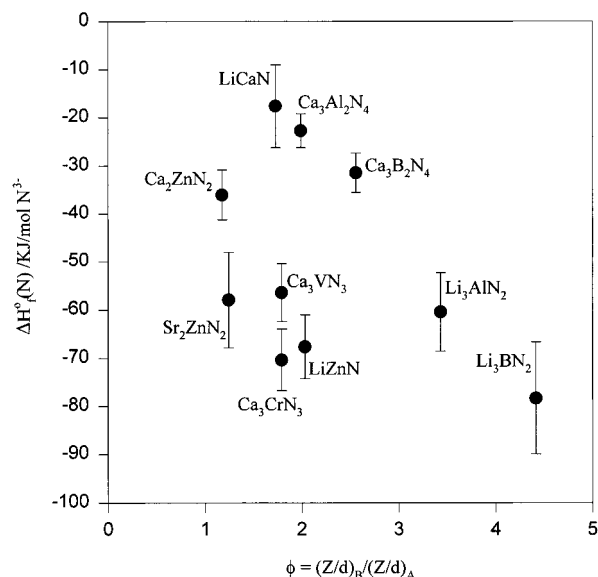


Figure 19. Enthalpies of formation from binary nitrides for ternary nitrides ΔH_f^0 as a function of the ionic potential $\phi = (Z/d)_B/(Z/d)_A$.

finding is consistent with the low formation enthalpies of most binary nitrides, which is in sharp contrast to the large formation enthalpies of most binary oxides.

8. Gallium Nitride

The group III nitrides AlN, GaN, and InN, as well as their solid solutions are attractive candidates for optoelectronic devices in the green, blue, and ultraviolet range as light emitting diodes and laser diodes. In particular, hexagonal gallium nitride, GaN, a semiconductor with a wide direct band gap of ~ 3.5 eV, has found applications for commercial blue-light-emitting diodes. The production of thin films of GaN is currently carried out by MOCVD (metal organic chemical vapor deposition) heteroepitaxy from $\text{Ga}(\text{CH}_3)_3$ or $\text{Ga}(\text{C}_2\text{H}_5)_3$ and ammonia on sapphire substrates. However, due to the large lattice mismatch and a difference of the thermal expansion coefficients between gallium nitride and the substrate material, the films have a large number of defects. Hence, the best substrate material for low defect gallium nitride films should be gallium nitride single crystals of a suitable size. These crystals cannot be prepared by standard methods of melt growth because of the high melting point of GaN that was estimated to be at ~ 2800 K²³⁹ and the high decomposition N_2 pressure. Silicon carbide (SiC) is the only other material known to have similar lattice parameters to gallium nitride, but single crystals are difficult to prepare.

Hexagonal gallium nitride plates with diameters of 5–10 mm and thicknesses of a few hundred microns have been grown at high pressure of nitrogen (up to 20 Kbar) and high temperatures (1500–1900 K).^{240,241} Gallium nitride crystals obtained by this technique were used as substrates to deposit gallium nitride films by MOCVD. Their photoluminescence spectra were investigated and their unit cell parameters compared with those of gallium nitride films grown on other substrates.²⁴² Although the high-pressure method yields high quality crystals,^{243,244} this method also requires

high temperatures. This combination of high pressure and high temperature may limit its applicability to industrial mass production.

Gallium nitride single crystals with sizes of a few hundred microns were grown at 550 °C in supercritical ammonia at pressures of 1–5 Kbars.²⁴⁵ The quality of the product depends strongly on the added ratio of lithium amide or potassium amide, which may serve as mineralizer.

High-quality single crystals between 0.3 and 0.7 mm^{246–248} were grown at 600–800 °C from gallium in sodium melts and considerable lower nitrogen pressures of 50–100 bar. The nitrogen pressure was produced by thermal decomposition of sodium azide, which provides high-purity nitrogen (and sodium). The crystal morphology depends on the gallium-to-sodium ratio. The polarity of the crystals can be ascertained from surface defects.^{249,250} Perhaps this approach can be scaled up to produce a viable industrial process to prepare gallium nitride substrates. In a similar experiment, aluminum nitride was obtained from aluminum powder in sodium melts at temperatures of 600–700 °C, whereas commercial aluminum powder does not react with nitrogen at this temperature.²⁵¹

9. Conclusion

Most of the compounds discussed in the first sections contain metals in their highest oxidation state and, because of the covalent nature of the bond between nitrogen and the less electropositive element, they can be understood as nitridometalates. As for oxometalates, this leads typically to octahedral, trigonal prismatic, tetrahedral, trigonal planar, or linear coordination of the central metal atom by nitrogen ligands. The nitrogen appears to prefer 6-fold coordination by metal atoms, even when these are of a very different nature and have widely varied bond distances to nitrogen. Nevertheless, packing effects or the size of the metal atoms also result in other coordination numbers for nitrogen; for examples, four in Mg₂[PN₃] or frequently seven and up to eight with the large barium, rubidium, or cesium atoms (e.g., in Cs[TaN₂]). Lithium nitrides especially show a large variety of coordination numbers of nitrogen; eight in CaF₂ superstructure compounds such as Li₇[TaN₄], or CN(N) = 4, 6, 7, and 8 in the nitride halides discussed in Section 6.

The observed progress in the determination of the structural chemistry of ternary nitrides of the last 15 years is mainly due to new preparation techniques and the effort of what is still a relatively small number of researchers. However, the new developments arouse more and more interest in properties of nitrides such as lithium ionic conductivity, superconductivity, or structural properties, and of zeolite-type materials that also have the thermal and chemical stability of nitrides. Also, the efforts to understand the formation and reactions of ternary nitrides have just started. It is our belief and hope that within the next few years, many nitride compounds with new or even unique structures and interesting properties will be discovered.

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References

- (1) Juza, R. *Adv. Inorg. Radiochem.* **1966**, 9, 81.
- (2) Juza, R.; Langer, K.; von Benda, K. *Angew. Chem., Int. Ed. Engl.* **1968**, 7, 360.
- (3) Niewa, R.; Jacobs, H. *Chem. Rev.* **1996**, 96, 2053.
- (4) DiSalvo, F. J.; Clarke, S. J. *Curr. Opin. Solid State Mater. Sci.* **1996**, 1, 241.
- (5) Kniep, R. *Pure Appl. Chem.* **1997**, 69, 185.
- (6) zur Loye, H.-C.; Houmes, J. D.; Bem, D. S. In *The Chemistry of Transition Metal Carbides and Nitrides*, Oyama, S. T., Ed.; Blackie, A and P: Glasgow, 1996; p 154.
- (7) Röhr, C. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 1199.
- (8) Schleid, T. *Eur. J. Solid State Inorg. Chem.* **1996**, 33, 227.
- (9) Simon, A. *Coord. Chem. Rev.* **1997**, 163, 253.
- (10) Schnick, W.; Huppertz, H. *Chem. Eur. J.* **1997**, 3, 679.
- (11) Houmes, J. D.; zur Loye, H.-C. *J. Solid State Chem.* **1997**, 130, 266.
- (12) Houmes, J. D.; zur Loye, H.-C. *Chem. Mater.* **1996**, 8, 2551.
- (13) Vaidhyanathan, B.; Rao, K. J. *Chem. Mater.* **1997**, 9, 1196.
- (14) Gregory, D. H.; Barker, M. G.; Edwards, P. P.; Siddons, D. J. *Inorg. Chem.* **1996**, 35, 7608.
- (15) Goldsztaub, S. *Bull. Soc. Fr. Minér.* **1935**, 58, 6.
- (16) Jacobs, H.; von Pinkowski, E. *J. Less-Common Met.* **1989**, 146, 147.
- (17) Rauch, P. E.; DiSalvo, F. J. *J. Solid State Chem.* **1992**, 100, 160.
- (18) Jacobs, H.; Hellmann, B. *J. Alloys Compd.* **1993**, 191, 51.
- (19) Brokamp, Th. Ph.D. Thesis, Universität Dortmund, Dortmund, Germany, 1991.
- (20) Balbarin, V.; Van Dover, R. B.; DiSalvo, F. J. *J. Phys. Chem. Solids* **1996**, 57, 1919.
- (21) Seeger, O.; Hofmann, M.; Strähle, J.; Laval, J. P.; Frit, B. *Z. Anorg. Allg. Chem.* **1994**, 620, 2008.
- (22) Gregory, D. H.; Barker, M. G.; Edwards, P. P.; Slaski, M.; Siddons, D. J. *J. Solid State Chem.* **1998**, 137, 62.
- (23) Jansen, M.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1975**, 417, 31.
- (24) Grey, I. E.; Steinfink, H. *J. Am. Chem. Soc.* **1970**, 92, 5093.
- (25) Gelabert, M. C.; Lachicotte, R. J.; DiSalvo, F. J. *Chem. Mater.* **1998**, 10, 613.
- (26) Gaebell, H.-C.; Meyer, G.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1983**, 498, 94.
- (27) Juza, R.; Rabenau, A.; Nitschke, I. *Z. Anorg. Allg. Chem.* **1964**, 332, 1.
- (28) Lerch, M.; Füglein, E.; Wrba, J. *Z. Anorg. Allg. Chem.* **1996**, 622, 367.
- (29) Baur, W. H.; Lerch, M. *Z. Anorg. Allg. Chem.* **1996**, 622, 1729.
- (30) Füglein, E.; Hock, R.; Lerch, M. *Z. Anorg. Allg. Chem.* **1997**, 623, 304 and references therein.
- (31) Balbarin, V.; Yamane, H.; DiSalvo, F. J.; Parise, J. B., manuscript in preparation.
- (32) Hardy, A. *Acta Crystallogr.* **1962**, 15, 179.
- (33) Clarke, S. J.; DiSalvo, F. J. *J. Solid State Chem.* **1997**, 132, 394.
- (34) Assabaa-Boultif, R.; Marchand, R.; Laurent, Y. *Eur. J. Solid State Chem.* **1995**, 32, 1101.
- (35) Tessier, F.; Assabaa, R.; Marchand, R. *J. Alloys Compd.* **1997**, 262, 512.
- (36) Brokamp, Th.; Jacobs, H. *J. Alloys Compd.* **1992**, 183, 325.
- (37) Brokamp, Th.; Jacobs, H. *J. Alloys Compd.* **1991**, 176, 47.
- (38) Tessier, F.; Marchand, R.; Laurent, Y. *J. Eur. Ceramic Soc.* **1997**, 17, 1825.
- (39) Fawcett, I. D.; Ramanujachary, K. V.; Greenblatt, M. *Mater. Res. Bull.* **1997**, 32, 1565.
- (40) Brixner, L. H. *J. Inorg. Nucl. Chem.* **1960**, 14, 225.
- (41) Brese, N. E.; DiSalvo, F. J. *J. Solid State Chem.* **1995**, 120, 378.
- (42) Brese, N. E.; DiSalvo, F. J. *J. Solid State Chem.* **1995**, 120, 372.
- (43) Chen, X. Z.; Eick, H. A. *J. Solid State Chem.* **1997**, 130, 1.
- (44) Luge, R.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1985**, 520, 39.
- (45) Köhler, J.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1982**, 495, 7.
- (46) Ostermann, D.; Zachwieja, U.; Jacobs, H. *J. Alloys Compd.* **1992**, 190, 137.
- (47) Rauch, P. E.; DiSalvo, F. J.; Brese, N. E.; Partin, D. E.; O'Keeffe, M. *J. Solid State Chem.* **1994**, 110, 162.
- (48) Jacobs, H.; Niewa, R. *Eur. J. Solid State Chem.* **1994**, 31, 105.
- (49) Niewa, R.; Jacobs, H. *J. Alloys Compd.* **1996**, 233, 61.
- (50) Niewa, R.; Jacobs, H. *J. Alloys Compd.* **1996**, 234, 171.
- (51) Liebau, F. *Structural Chemistry of Silicates*; Springer-Verlag: Berlin, Heidelberg, 1985.
- (52) Niewa, R.; Jacobs, H. *J. Alloys Compd.* **1996**, 236, 13.
- (53) Ostermann, D.; Jacobs, H. *J. Alloys Compd.* **1994**, 106, 15.
- (54) Niewa, R.; Jacobs, H. *Z. Anorg. Allg. Chem.* **1996**, 622, 881.
- (55) Jacobs, H.; von Pinkowski, E. *J. Less-Common Met.* **1989**, 146, 147.
- (56) Jacobs, H.; Hellmann, B. *J. Alloys Compd.* **1993**, 191, 277.

- (57) Subramanya Herle, P.; Hegde, M. S.; Subbanna, G. N. *J. Mater. Chem.* **1997**, *7*, 2121.
- (58) Süsse, P.; Bueger, M. J. *Z. Kristallogr.* **1970**, *131*, 161.
- (59) Elder, S. H.; DiSalvo, F. J.; Parise, J. B.; Hriljac, J. A.; Richardson, J. W., Jr. *J. Solid State Chem.* **1994**, *108*, 73.
- (60) Ostermann, D.; Jacobs, H.; Harbrecht, B. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1277.
- (61) Monz, M.; Ostermann, D.; Jacobs, H. *J. Alloys Compd.* **1993**, *200*, 211.
- (62) Niewa, R.; Jacobs, H. *J. Alloys Compd.* **1995**, *217*, 38.
- (63) Niewa, R.; Jacobs, H. *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 463.
- (64) Wachsmann, Ch.; Jacobs, H. *Z. Kristallogr.* **1996**, *211*, 477.
- (65) Chen, X. Z.; Eick, H. A. *J. Solid State Chem.* **1996**, *127*, 19.
- (66) Wachsmann, Ch.; Höhn, P.; Kniep, R.; Jacobs, H. *J. Alloys Compd.* **1997**, *248*, 1.
- (67) Yamane, H.; DiSalvo, F. J. *J. Alloys Compd.* **1996**, *234*, 203.
- (68) Wachsmann, Ch.; Brokamp, Th.; Jacobs, H. *J. Alloys Compd.* **1992**, *185*, 109.
- (69) Tennstedt, A.; Kniep, R.; Hüber, M.; Haase, W. *Z. Anorg. Allg. Chem.* **1995**, *621*, 511.
- (70) Cordier, G.; Höhn, P.; Kniep, R.; Rabenau, A. *Z. Anorg. Allg. Chem.* **1990**, *591*, 58.
- (71) Gregory, D. H.; Barker, M. G.; Edwards, P. P.; Siddons, D. J. *Inorg. Chem.* **1995**, *34*, 5195.
- (72) Clarke, S. J.; DiSalvo, F. J. *Z. Kristallogr.* **1997**, *212*, 309.
- (73) Höhn, P.; Kniep, R.; Maier, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1350.
- (74) Karam, R.; Ward, R. *Inorg. Chem.* **1970**, *9*, 1849.
- (75) Höhn, P.; Ludwig, M.; Kniep, R. *Z. Naturforsch.* **1997**, *52b*, 1349.
- (76) Patterson, F. K.; Ward, R. *Inorg. Chem.* **1966**, *5*, 1312.
- (77) Wachsmann, Ch.; Jacobs, H. *Z. Anorg. Allg. Chem.* **1996**, *622*, 885.
- (78) Niewa, R.; Vajenine, G. V.; DiSalvo, F. J.; Luo, H.; Yelon, W. B. *Z. Naturforsch.* **1998**, *53b*, 63.
- (79) Broll, S.; Jeitschko, W. *Z. Naturforsch.* **1995**, *50b*, 905.
- (80) Benz, R.; Zachariasen, W. H. *J. Nucl. Mater.* **1970**, *37*, 109.
- (81) Teske, Chr. L.; Müller-Buschbaum, Hk. *Z. Anorg. Allg. Chem.* **1970**, *379*, 234.
- (82) Teske, Chr. L.; Müller-Buschbaum, Hk. *Z. Anorg. Allg. Chem.* **1969**, *371*, 235.
- (83) Pouchard, M.; Shin, Y. J.; Doumerc, J. P.; Hagenmuller, P. *Eur. J. Solid State Chem.* **1991**, *28*, 461.
- (84) Anselin, F.; Lorenzelli, N.; Lallement, R.; Veyssie, J. J. *Phys. Lett.* **1965**, *19*, 174.
- (85) Barker, M. G.; Begley, M. J.; Edwards, P. P.; Gregory, D. H.; Smith, S. E. *J. Chem. Soc., Dalton Trans.* **1996**, *1*.
- (86) Vennos, D. A.; DiSalvo, F. J. *J. Solid State Chem.* **1992**, *98*, 318.
- (87) Höhn, P.; Kniep, R.; Rabenau, A. *Z. Kristallogr.* **1991**, *196*, 153.
- (88) Vennos, D. A.; Badding, M. E.; DiSalvo, F. J. *Inorg. Chem.* **1990**, *29*, 4059.
- (89) Tennstedt, A.; Röhr, C.; Kniep, R. *Z. Naturforsch.* **1993**, *48b*, 1831.
- (90) Tennstedt, A.; Röhr, C.; Kniep, R. *Z. Naturforsch.* **1993**, *48b*, 794.
- (91) Yamamoto, T.; Kikkawa, S.; Kanamaru, F. *J. Solid State Chem.* **1995**, *119*, 161.
- (92) Vennos, D. A.; Badding, M. E.; DiSalvo, F. J. *Inorg. Chem.* **1990**, *29*, 4059.
- (93) Yee, K. A.; Hughbanks, T. *Inorg. Chem.* **1992**, *31*, 1921.
- (94) Niewa, R.; DiSalvo, F. J.; Yang, D.-K.; Zax, D. B.; Luo, H.; Yelon, W. B. *J. Alloys Compd.* **1998**, *266*, 32.
- (95) Rabenau, A.; Schulz, H. *J. Less-Common Met.* **1976**, *50*, 155.
- (96) Cordier, G.; Gudat, A.; Kniep, R.; Rabenau, A. *Angew. Chem.* **1989**, *101*, 1689.
- (97) Sabrowsky, H.; Mertens, P.; Thimm, A. *Z. Kristallogr.* **1985**, *171*, 1.
- (98) Jäger, J. Ph.D. Thesis, Technische Hochschule Darmstadt, Darmstadt, Germany, 1995.
- (99) DiSalvo, F. J.; Traill, S. S.; Yamane, H.; Brese, N. E. *J. Alloys Compd.* **1997**, *255*, 122.
- (100) Gudat, A.; Haag, S.; Kniep, R.; Rabenau, A. *J. Less-Common Met.* **1990**, *159*, L29.
- (101) Niewa, R.; DiSalvo, F. J. *J. Alloys Compd.*, in press.
- (102) Kowach, G. R.; Lin, H. Y.; DiSalvo, F. J. *J. Solid State Chem.*, in press.
- (103) Kowach, G. R. Ph.D. Thesis, Cornell University, Ithaca, New York, 1997.
- (104) Hannebauer, B.; Schmidt, P. C., unpublished results.
- (105) Bem, D. S.; zur Loye, H.-C. *J. Solid State Chem.* **1993**, *104*, 467.
- (106) Bem, D. S.; Lampe-Önnerud, C. M.; Olsen, H. P.; zur Loye, H.-C. *Inorg. Chem.* **1996**, *35*, 581.
- (107) Subramanya Herle, P.; Vasanthacharya, N. Y.; Hegde, M. S.; Gopalakrishnan, J. *J. Alloys Compd.* **1995**, *217*, 22.
- (108) Grins, J.; Käll, P.-O.; Svensson, G. *J. Mater. Chem.* **1995**, *5*, 571.
- (109) Houmes, J. D.; Deo, S.; zur Loye, H.-C. *J. Solid State Chem.* **1997**, *131*, 374.
- (110) Bem, D. S.; Olsen, H. P.; zur Loye, H.-C. *Chem. Mater.* **1995**, *7*, 1824.
- (111) Panda, R. N.; Gajbhiye, N. S. *J. Alloys Compd.* **1997**, *256*, 102.
- (112) Bem, D. S.; Gibson, C. P.; zur Loye, H.-C. *Chem. Mater.* **1993**, *5*, 397.
- (113) Chen, F.; Aitken, J.; Parasher, S. In *Solid-State Chemistry of Inorganic Materials*, Materials Research Society Symposium Proceedings, Davies, P. K.; Jacobson, A. J.; Torardi, C. C.; Vanderah, T. H., Eds.; Boston, MA, 1996; Vol. 453.
- (114) Houmes, J. D.; zur Loye, H.-C. *J. Solid State Chem.* **1997**, *127*, 267.
- (115) Weil, K. S.; Kumta, P. N. *Mater. Sci. Eng.* **1996**, *B38*, 109.
- (116) Weil, K. S.; Kumta, P. N. *Acta Crystallogr.* **1997**, *C53*, 1745.
- (117) Sriram, M. A.; Weil, K. S.; Kumta, P. N. *Appl. Organomet. Chem.* **1996**, *11*, 163.
- (118) Weil, K. S.; Kumta, P. N. *J. Alloys Compd.* **1998**, *265*, 96.
- (119) Bem, D. S.; Houmes, J. D.; zur Loye, H.-C. In *Covalent Ceramics II: Non-Oxides*, Materials Research Society Symposium Proceedings, Barron, A. R.; Fischman, G. S.; Fury, M. A.; Hepp, A. F., Eds.; Boston, MA, 1993; Vol. 327.
- (120) Weil, K. S.; Kumta, P. N. *J. Solid State Chem.* **1997**, *128*, 185.
- (121) Chen, X. Z.; Dye, J. L.; Eick, H. A.; Elder, S. H.; Tsai, K.-L. *Chem. Mater.* **1997**, *9*, 1172.
- (122) Clarke, S. J.; DiSalvo, F. J. *J. Solid State Chem.* **1997**, *129*, 144.
- (123) Yamane, H.; DiSalvo, F. J. *J. Alloys Compd.* **1996**, *240*, 33.
- (124) Schlieper, T.; Schnick, W. *Z. Kristallogr.* **1996**, *211*, 254.
- (125) Woike, M.; Jeitschko, W. *Inorg. Chem.* **1995**, *34*, 5105.
- (126) Schlieper, T.; Schnick, W. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1535.
- (127) Woike, M.; Jeitschko, W. *Z. Kristallogr.* **1996**, *211*, 813.
- (128) Inoue, Z.; Mitomo, M.; Ii, N. *J. Mater. Sci.* **1980**, *15*, 2915.
- (129) Ekström, T. C.; MacKenzie, K. J. D.; Ryan, M. J.; Brown, I. W. M.; White, G. V. *J. Mater. Chem.* **1997**, *7*, 505.
- (130) Koroglu, A.; Apperley, D. C.; Harris, R. K.; Thompson, D. P. *J. Mater. Chem.* **1996**, *6*, 1031.
- (131) Wang, P.-L.; Werner, P.-E.; Gao, L.; Harris, R. K.; Thompson, D. P. *J. Mater. Chem.* **1997**, *7*, 2127.
- (132) Huppertz, H.; Schnick, W. *Chem. Eur. J.* **1997**, *3*, 249.
- (133) Huppertz, H.; Schnick, W. *Z. Anorg. Allg. Chem.* **1997**, *623*, 212.
- (134) Huppertz, H.; Schnick, W. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1983.
- (135) Huppertz, H.; Schnick, W. *Acta Crystallogr.* **1997**, *C53*, 1751.
- (136) Schlieper, T.; Milius, W.; Schnick, W. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1380.
- (137) Huppertz, H.; Schnick, W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2651.
- (138) Woike, M.; Jeitschko, W. *J. Solid State Chem.* **1997**, *129*, 312.
- (139) Huppertz, H.; Stock, N.; Schnick, W. *Adv. Mater.* **1996**, *8*, 844.
- (140) Riedle, R.; Greiner, A.; Mieke, G.; Dressler, W.; Fuess, H.; Bill, J.; Aldinger, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 603.
- (141) Clarke, S. J.; DiSalvo, F. J., manuscript in preparation.
- (142) Clarke, S. J.; Einstein, F.; DiSalvo, F. J., manuscript in preparation.
- (143) Morimoto, N.; Koto, K. *Z. Kristallogr.* **1969**, *129*, 65.
- (144) Morimoto, N.; Appleman, D. E.; Evans, H. T., Jr. *Z. Kristallogr.* **1960**, *114*, 120.
- (145) Clarke, S. J.; Kowach, G. R.; DiSalvo, F. J. *Inorg. Chem.* **1996**, *35*, 7009.
- (146) Malik, A.-S., unpublished results.
- (147) Yamane, H.; DiSalvo, F. J. *J. Alloys Compd.* **1996**, *241*, 69.
- (148) Clarke, S. J.; DiSalvo, F. J. *J. Alloys Compd.*, in press.
- (149) Verdier, P.; L'Haridon, P.; Maunay, M.; Marchand, R. *Acta Crystallogr.* **1974**, *B30*, 226.
- (150) Cordier, G. *Z. Naturforsch.* **1988**, *43b*, 1253.
- (151) Cordier, G.; Ludwig, M.; Stahl, D.; Schmidt, P. C.; Kniep, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1761.
- (152) Cordier, G.; Rönninger, S. *Z. Naturforsch.* **1987**, *42b*, 825.
- (153) Yamane, H.; DiSalvo, F. J. *Acta Crystallogr.* **1996**, *C52*, 760.
- (154) Clarke, S. J.; DiSalvo, F. J. *Inorg. Chem.* **1997**, *36*, 1143.
- (155) Blase, W.; Cordier, G.; Ludwig, M.; Kniep, R. *Z. Naturforsch.* **1994**, *49b*, 501.
- (156) Gudat, A.; Kniep, R.; Rabenau, A. *J. Less-Common Met.* **1990**, *161*, 31.
- (157) Leineweber, A. Diploma Thesis, Universität Dortmund, Dortmund, Germany, 1996.
- (158) Gregory, D. H.; Barker, M. G.; Edwards, P. P.; Siddons, D. J. *Inorg. Chem.* **1995**, *34*, 3912.
- (159) Schultz-Coulon, V.; Schnick, W. *Z. Anorg. Allg. Chem.* **1997**, *623*, 69.
- (160) Schnick, W.; Schultz-Coulon, V. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 280.
- (161) Völlenkne, H. *Z. Kristallogr.* **1981**, *154*, 77.
- (162) Jacobs, H.; Nymwegen, R. *Z. Anorg. Allg. Chem.* **1997**, *623*, 429.
- (163) Peters, D.; Paulus, E. F.; Jacobs, H. *Z. Anorg. Allg. Chem.* **1990**, *584*, 129.
- (164) Ronis, J.; Bondars, B.; Vitola, A.; Millers, T. *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.* **1990**, *90*, 35.
- (165) Jacobs, H.; Nymwegen, R.; Doyle, S.; Wroblewski, T.; Kockelmann, W. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1467.
- (166) Horstmann, S.; Irran, E.; Schnick, W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1992.

- (167) Kingma, K. J.; Gerald Pacalo, R. E.; McMillan, P. F. *Eur. J. Solid State Inorg. Chem.* **1997**, *34*, 679.
- (168) Léger, J. M.; Haines, J.; de Oliveira, L. S.; Chateau, C.; Le Sauze, A.; Marchand, R. *J. Phys.: Condens. Matter* **1996**, *8*, L773.
- (169) Horstmann, S.; Schnick, W. *Z. Naturforsch.* **1997**, *52b*, 490.
- (170) Horstmann, S.; Irran, E.; Schnick, W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1873.
- (171) Schnick, W.; Lücke, J.; Krumeich, F. *Chem. Mater.* **1996**, *8*, 281.
- (172) Schnick, W.; Horstmann, S.; Häser, M. *Phosphorus Sulfur* **1996**, *109/110*, 93.
- (173) Schnick, W.; Lücke, J. *Z. Anorg. Allg. Chem.* **1994**, *620*, 2014.
- (174) Schnick, W.; Stock, N.; Lücke, J.; Volkmann, M.; Jansen, M. *Z. Anorg. Allg. Chem.* **1995**, *621*, 987.
- (175) Schnick, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 806.
- (176) Wester, F.; Schnick, W. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1281.
- (177) Weitkamp, J.; Ernst, S.; Cubero, F.; Wester, F.; Schnick, W. *Adv. Mater.* **1997**, *9*, 247.
- (178) Conanec, R.; Feldmann, W.; Marchand, R.; Laurent, Y. *J. Solid State Chem.* **1996**, *121*, 418.
- (179) Somer, M.; Carrillo-Cabrera, W.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Z. Kristallogr.* **1996**, *211*, 635.
- (180) Berger, U.; Schnick, W. *J. Alloys Compd.* **1994**, *206*, 179.
- (181) Vannenberg, N.-G. *Acta Chem. Scand.* **1962**, *16*, 2263.
- (182) Schnick, W.; Huppertz, H. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1703.
- (183) Becker, M.; Jansen, M.; Lieb, A.; Milius, W.; Schnick, W. *Z. Anorg. Allg. Chem.* **1998**, *624*, 113.
- (184) Barker, M. G.; Harper, A.; Hubberstey, P. *J. Chem. Res., Synop.* **1978**, 432.
- (185) Berger, U.; Milius, W.; Schnick, W. *Z. Anorg. Allg. Chem.* **1995**, *621*, 2075.
- (186) DeVries, R. C.; Fleischer, J. F. *Mater. Res. Bull.* **1969**, *4*, 433.
- (187) Yamane, H.; Kikkawa, S.; Horiuchi, H.; Koizumi, M. *J. Solid State Chem.* **1986**, *65*, 6.
- (188) Somer, M.; Herterich, U.; Curda, J.; Peters, K.; von Schnering, H. G. *Z. Kristallogr.* **1996**, *211*, 54.
- (189) Somer, M.; Herterich, U.; Curda, J.; Peters, K.; von Schnering, H. G. *Z. Kristallogr.* **1994**, *209*, 182.
- (190) Curda, J.; Herterich, U.; Peters, K.; Somer, M.; von Schnering, H. G. *Z. Kristallogr.* **1994**, *209*, 618.
- (191) Herterich, U.; Curda, J.; Peters, K.; Somer, M.; von Schnering, H. G. *Z. Kristallogr.* **1994**, *209*, 617.
- (192) Somer, M.; Herterich, U.; Curda, J.; Carrillo-Cabrera, W.; Peters, K.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1997**, *623*, 18.
- (193) Down, M. G.; Haley, M. J.; Hubberstey, P.; Pulham, R. J.; Thunder, A. E. *J. Chem. Soc., Dalton Trans.* **1978**, 1407.
- (194) Curda, J.; Herterich, U.; Peters, K.; Somer, M.; von Schnering, H. G. *Z. Kristallogr.* **1994**, *209*, 181.
- (195) Reckeweg, O.; Meyer, H.-J. *Z. Naturforsch.* **1997**, *52b*, 340.
- (196) Wörle, M.; Muhr, H.-J.; Meyer zu Altenschildesche, H.; Nesper, R. *J. Alloys Compd.* **1997**, *260*, 80.
- (197) Wörle, M.; Meyer zu Altenschildesche, H. M.; Nesper, R. *J. Alloys Compd.* **1998**, *264*, 107.
- (198) Cava, R. J.; Zandbergen, H. W.; Batlogg, B.; Eisaki, H.; Takagi, H.; Krajewski, J. J.; Peck, W. F., Jr.; Gyorgy, E. M.; Uchida, S. *Nature* **1994**, *372*, 245.
- (199) Zandbergen, H. W.; Jansen, J.; Cava, R. J.; Krajewski, J. J.; Peck, W. F., Jr. *Nature* **1994**, *372*, 759.
- (200) Siegrist, T.; Zandbergen, H. W.; Cava, R. J.; Krajewski, J. J.; Peck, W. F., Jr. *Nature* **1994**, *367*, 259.
- (201) Wideman, T.; Cava, R. J.; Sneddon, L. G. *Chem. Mater.* **1996**, *8*, 2215.
- (202) King, R. B. *J. Solid State Chem.* **1996**, *124*, 329.
- (203) Rauch, P. E.; Simon, A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1519.
- (204) Snyder, G. J.; Simon, A. *J. Am. Chem. Soc.* **1995**, *117*, 1996.
- (205) Snyder, G. J.; Simon, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 689.
- (206) Steinbrenner, U.; Simon, A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 552.
- (207) Simon, A.; Steinbrenner, U. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2117.
- (208) Steinbrenner, U.; Simon, A. *Z. Kristallogr.* **1997**, *212*, 428.
- (209) Marx, R. *Z. Naturforsch.* **1995**, *50b*, 1061.
- (210) Marx, R. *J. Solid State Chem.* **1997**, *128*, 241.
- (211) Marx, R.; Mayer, H. M. *Z. Naturforsch.* **1995**, *50b*, 1353.
- (212) Marx, R.; Mayer, H. M. *J. Solid State Chem.* **1997**, *130*, 90.
- (213) Marx, R.; Ibberson, R. M. *J. Alloys Compd.* **1997**, *261*, 123.
- (214) Marx, R.; Mayer, H. M. *Z. Naturforsch.* **1996**, *51b*, 525.
- (215) Yamanaka, S.; Kawaji, H.; Hotehama, K.; Ohashi, M. *Adv. Mater.* **1996**, *8*, 771.
- (216) Kawaji, H.; Hotehama, K.; Yamanaka, S. *Chem. Mater.* **1997**, *9*, 2127.
- (217) Juza, R.; Friedrichsen, H. *Z. Anorg. Allg. Chem.* **1964**, *332*, 173.
- (218) Mattausch, H.; Simon, A. *Z. Kristallogr.* **1996**, *211*, 397.
- (219) Ehrlich, G. M.; Badding, M. E.; Brese, N. E.; Trail, S. S.; DiSalvo, F. J. *J. Alloys Compd.* **1994**, *206*, 95; **1996**, *235*, 133.
- (220) Simon, A.; Koehler, T. *J. Less-Common Met.* **1986**, *116*, 279.
- (221) Mattausch, H.; Simon, A. *Z. Kristallogr.* **1996**, *211*, 398.
- (222) Mattausch, H.; Simon, A. *Z. Kristallogr.* **1996**, *211*, 399.
- (223) Schwanitz-Schüller, U.; Simon, A. *Z. Naturforsch.* **1985**, *40b*, 705.
- (224) Mattausch, H.; Kremer, R. K.; Simon, A. *Z. Anorg. Allg. Chem.* **1996**, *622*, 649.
- (225) Schleid, Th.; Meyer, M. *Z. Kristallogr.* **1996**, *211*, 187.
- (226) Lissner, F.; Schleid, Th. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1998.
- (227) Lissner, F.; Meyer, M.; Schleid, Th. *Z. Anorg. Allg. Chem.* **1996**, *622*, 275.
- (228) Lissner, F.; Schleid, Th. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1747.
- (229) Lulei, M.; Corbett, J. D. *Eur. J. Solid State Inorg. Chem.* **1996**, *34*, 241.
- (230) Mattfeld, H.; Meyer, G. *Z. Anorg. Allg. Chem.* **1994**, *620*, 85.
- (231) Lulei, M.; Steinwand, S. J. Corbett, J. D. *Inorg. Chem.* **1995**, *34*, 2671.
- (232) Braun, T. P.; Simon, A.; Böttcher, F.; Ueno, F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 567.
- (233) Braun, T. P.; Simon, A.; Ueno, F.; Böttcher, F. *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 251.
- (234) Navrotsky, A. *Phys. Chem. Miner.* **1977**, *2*, 89.
- (235) Elder, S. H.; DiSalvo, F. J.; Topor, L.; Navrotsky, A. *Chem. Mater.* **1993**, *5*, 1545.
- (236) McHale, J. M.; Kowach, G. R.; Navrotsky, A.; DiSalvo, F. J. *J. Chem. Eur. J.* **1996**, *2*, 1514.
- (237) McHale, J. M.; Navrotsky, A.; Kowach, G. R.; Balbarin, V. E.; DiSalvo, F. J. *Chem. Mater.* **1997**, *9*, 1538.
- (238) McHale, J. M.; Navrotsky, A.; DiSalvo, F. J., manuscript in preparation.
- (239) Van Vechten, J. A. *Phys. Rev.* **1973**, *B7*, 1479.
- (240) Porowski, S. *J. Cryst. Growth* **1996**, *166*, 583.
- (241) Porowski, S. *Mater. Sci. Eng.* **1997**, *B44*, 407.
- (242) Leszczynski, M.; Teisseyre, H.; Suski, T.; Grzegory, I.; Bockowski, M.; Jun, J.; Porowski, S.; Pakula, K.; Baranowski, J. M.; Foxon, C. T.; Cheng, T. S. *Appl. Phys. Lett.* **1996**, *69*, 73.
- (243) Porowski, S.; Grzegory, I. *J. Cryst. Growth* **1997**, *178*, 174.
- (244) Monemar, B.; Bergman, J. P.; Ivanov, I. G.; Baranowski, J. M.; Pakula, K.; Grzegory, I.; Porowski, S. *Solid State Comm.* **1997**, *104*, 205.
- (245) Dwilinski, R.; Wyszomolek, A.; Baranowski, J.; Kaminska, M.; Doradzinski, R.; Garczynski, J.; Sierzputowski, L.; Jacobs, H. *Acta Phys. Pol. A* **1995**, *88*, 833.
- (246) Yamane, H.; Shimada, M.; Clarke, S. J.; DiSalvo, F. J. *Chem. Mater.* **1997**, *9*, 413.
- (247) Yamane, H.; Shimada, M.; Sekiguchi, T.; DiSalvo, F. J. *J. Cryst. Growth* **1998**, *186*, 8.
- (248) DiSalvo, F. J.; Yamane, H.; Molstad, J. C. U.S. Patent Application 60/035, 713.
- (249) Yamane, H.; Shimada, M.; Endor, T.; DiSalvo, F. J., manuscript in preparation.
- (250) Leszczynski, M.; Grzegory, I.; Teisseyre, H.; Suski, T.; Bockowski, M.; Jun, J.; Baranowski, J. M.; Porowski, S.; Domagala, J. *J. Cryst. Growth* **1996**, *169*, 235.
- (251) Yamane, H.; Shimada, M.; DiSalvo, F. J. *J. Mater. Sci. Lett.* **1998**, *17*, 399.

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