DALTON
PERSPECTIVE

Structural families in nitride chemistry

Duncan H. Gregory

Department of Chemistry, The University of Nottingham, Nottingham, UK NG7 2RD.
E-Mail: Duncan.Gregory@Nottingham.ac.uk

Received 5th October 1998, Accepted 2nd November 1998

Recent progress in the area of nitride chemistry has been rapid and increasingly diverse. Advances in ternary transition metal nitride research have been significant in the last several years to the point where the chemist can begin to correlate these compounds in terms of certain favoured structure types. It is a facet of the often intermediate bonding behaviour in these solids that the structure types so far exhibited are an intriguing mix of covalent (carbide-like), ionic (oxide-like) and unique motifs. While new motifs continue to be discovered with astonishing regularity, an attempt is made to summarise and classify just some of the major emerging ternary nitride structural families.

1 Introduction

The study of complex nitride chemistry is still very much in its infancy, with accelerated progress being made only within the last several years. This belies the fact that much of the pioneering work in nitride chemistry was first performed in the ’20s and ’30s and then over a period of several decades by Juza and coworkers,[1,2] among others. As a result, binary nitrides of numerous metals and non-metals are relatively well characterised. The properties of these compounds are often interesting and useful. Many have now found application, for example as high temperature refractory ceramics and coatings (*e.g.* BN, AlN, TaN, TiN), semiconductors (*e.g.* GaN, InN), *etc.* Progress beyond binary systems has, until recently, been hampered primarily by synthetic difficulties, but also by the previous limitations of analytical methods. Advances in the handling of air-sensitive materials together with the huge improvements in diffraction techniques (and associated structure-solution software) are major contributors to new solid state materials output, generally, and nitride output, specifically.

Oxides are by far the most numerous, most extensively studied and best characterised group of compounds known to solid state chemists. Despite the relative abundances of oxygen and nitrogen in the Earth’s atmosphere, known oxides outnumber nitrides by orders of magnitude. This contrast and irony has been highlighted in many previous publications and will not be dwelt on here, although the thermodynamic implications of making and breaking N≡N bonds in nitride synthesis are all too apparent.[3–6] Furthermore, the relatively immense energy of formation of the N^{3-} anion from atomic N (over three times that of O^{2-} from O) accounts for the reluctance of nitrogen to form predominantly ionic bonds with all but the most electropositive of elements. These thermodynamic factors, therefore, explain both the rarity of nitrides and also their tendency to form unusual and often unique structure types.

Previous reviews in the literature have covered the many different aspects of nitride chemistry. We have now reached a point where it is perhaps no longer appropriate or practical to review nitride chemistry as one specific topic. Over the last several years, nitride sub-areas have flourished in their own right, embracing non-metal and nitridosilicate chemistry,[7–9] oxynitrides and nitride halides,[4,5,10–12] sub-nitrides and nitride clusters[13] and the development of binary nitrides as industrial materials.[14,15] This is in addition to the research conducted into the ternary and higher order transition metal nitrides.[3–6,16–18] In this respect, this article will concern itself only with the nitride chemistry of the transition metals and the ternary and complex compounds formed with electropositive elements. Earlier discussions of this group of compounds have focused on a summary of crystal chemistry by element or by co-ordination environment. As the number of new nitrides grows, one can begin to delineate broad structural classes. Such classification is, of course, already well established in chalcogenide and halide chemistry[19] and many of the structure types observed in these areas are also seen in nitrides. The tendency to covalency in nitride bonding is also reflected in several carbide structural analogues, although, for example, the formation of dinitrogen bonds in ternary and higher compounds is extremely rare.[20] Perhaps most interesting is the existence of a significant number of unique structures (*i.e. without* chalcogenide, halide or carbide analogues), many of which indicate the existence of several bonding types (ionic, covalent, metallic) within one compound. The eclectic mix of bonding types frequently gives rise to rare and unexpected formal metal oxidation states, borne out by often unusual co-ordination environments to nitrogen.

This article considers the crystal chemistry of ternary and higher order transition metal nitrides in terms of the classification of key structural types. While there are still (and continue to be) many examples of nitride compounds that are unique with respect to their crystal structures (and stoichiometries), as new compositions emerge, so structural trends can begin to be established. Composition–structure–property relationships are not yet well elucidated in such a young area, but with the increased information available from synthetic chemists, theorists, physicists and materials scientists one can envisage this situation changing in the not-too-distant future. The following two sections briefly consider first the synthetic challenges facing the solid state chemist and secondly how one might approach concepts of valence and bonding in nitrides. The main section is devoted to the description of some of the major structural

Duncan H. Gregory

Duncan H. Gregory graduated in Chemistry with Physics at the University of Southampton in 1989, where he remained to obtain a PhD in solid state chemistry in 1993. He took up a position as a postdoctoral research assistant at the University of Nottingham in 1994, where he now holds an EPSRC Advanced Fellowship (since 1997). His current research interests centre around new synthetic routes to predominantly non-oxide materials (principally nitrides) and their structure–property relations.

families, known properties and the potential for exploiting structure–property relationships to develop new materials.

2 Synthetic approaches

Synthetic methodology is being designed to overcome a number of significant challenges. On the one hand, the preparation of nitrides demands high temperatures and long reactions times, as is typical with solid state ceramic materials. However, in many cases the thermodynamic restrictions brought about by the facile formation of N_2 from nominally N^{3-} dictate that reactions may need to be designed to prevent decompositions of nitride products, sometimes at relatively low temperatures. Furthermore, the often instantaneous reaction of predominantly ionic higher nitrides with water (or air) to yield hydroxides and ammonia necessitates that reactions and handling of products are performed in inert environments. Preparative techniques are further complicated by matters of stoichiometry and purity. The unusual stoichiometries of many alkaline earth and transition metal binary nitrides prevent synthesis of single phase ternary (or higher) compounds by direct solid state reaction *unless* additional nitrogen is present. There are several alternatives to using relatively unreactive (at ambient pressure) N_2 gas as a source of nitrogen. Besides increasing the nitrogen pressure, solid sources of N such as sodium azide, NaN_3, have been successfully used to produce new nitrides often in combination with a sodium flux to encourage crystallinity of nitride products.[21]

One can move further away from traditional high temperature ceramic approaches by treating molten metals with nitrogen either directly *e.g.* treating molten alkaline earth metals with transition metals under nitrogen,[22] or indirectly by forming a molten alloy of Na and alkaline earth metal.[23] This latter approach has been used extensively for producing highly pure, crystalline alkaline earth binary phases and exploits the non-reactivity of sodium with nitrogen to good effect.[24] In these instances the unchanged sodium can be removed by distillation under vacuum or by washing with liquid ammonia.

Other non-ceramic-type approaches have focused on employing "softer" conditions, often at lower temperatures, and/or on exploiting thermodynamics by the use of suitable precursors. The ammonolysis of oxide, halide or sulfide precursors has proved a fruitful route to binary and ternary compounds.[2,4,25,26] These reactions are often highly temperature-dependent; below a narrow temperature band either no reaction occurs or products are poorly crystalline, above the band ternary phase decomposition is observed. Often an added complication in these reactions is the formation of "partial nitrides" (oxynitrides, nitride halides, *etc.*) in preference to nitrides. While partial nitriding to oxynitrides *etc*. is interesting in itself, one has adequately to differentiate between N and other anionic species in ammonolysis products, in many cases. As Brese and O'Keeffe[5] point out in their earlier review, there are numerous examples of probable misinterpreted imides, amides and oxynitrides in the literature.

Solid-solid phase metathesis reactions have proved useful for synthesizing binary transition metal and lanthanide nitrides. These reactions are often rapid, highly exothermic and self-propagating.[27,28] Initiation of these reactions can be carried out by various means, including by conventional heating or by microwaves. There are also reports of nitride formation by ignition in air.[29] Reaction temperatures in excess of product decomposition temperatures exclude these metathesis routes as means to binary transition metal nitrides of elements to the right hand side of the d block. It has also yet to be used effectively for ternary nitride synthesis, although the exchange reaction at 400 °C between the existing ternary nitride $NaTaN_2$ and the binary halide CuI yielding the new ternary phase $CuTaN_2$ is an exception.[30] However, a modification to the technique, exploiting the vapour pressures of physically separated reactants, has yielded a number of nitride halide phases from the reactions of Li_3N with alkaline earth metal halides.[31]

The fleeting or non-existence of the heavier alkali metal binary nitrides (*i.e.* those besides lithium nitride) renders formation of the relevant ternary alkali metal–transition metal phases impossible by direct solid state reaction of binary nitrides. Along with ammonolysis of non-nitride precursors, perhaps the most profitable route to these compounds has been *via* reactions of transition metals with an excess of alkali metal amide melt often at high pressures in the presence of supercritical ammonia.[32] These relatively harsh reaction conditions (with pressures often ≥1 kbar) have produced a variety of compounds, predominantly nitrido-tungstates, -molybdates, -niobates and -tantalates, although other compounds of this type have been prepared under milder conditions starting with the alkali metal and the transition metal *nitride*.[33,34]

Other techniques have been employed, sometimes specific to only one or two nitride products. These include Chemical Vapour Transport (CVT) routes to Group IV nitride halides,[12,35,36] ammonolysis of molecular precursors to binary and ternary transition metal nitrides[25,37,38] and the use of transition metal melts [both in an inert (solvent) and reactive capacity] to selected ternary transition metal compounds.[39] It seems likely that new routes will continue to be developed, and indeed need to be developed, to access new and diverse materials.

3 Bonding considerations

The coexistence of different bonding types within ternary nitrides accounts for the often curious and unexpected coordination behaviour and crystal chemistry observed in these compounds. The bonding within ternary nitrides is by no means well understood. Even in ternary compositions containing high proportions of electropositive elements, such as lithium and alkaline earth metals, metal–nitrogen bonds show significant covalent character.

The tendency to covalency is exhibited in binary nitrides of the late transition metals where low valence (I) states are the norm. Even early transition metals preferentially form nitrides below their highest oxidation states. The compound Ti_2N is known in several forms and TiN is extremely stable whereas Ti_3N_4 is poorly characterised. Similarly, Group V elements form many compositions with nitrogen, yet neither V_3N_5 nor Nb_3N_5 is known. Many of the transition metal nitrides (and especially those of the early transition metals) are interstitial compounds with structures based on the eutaxy of metal atoms with varying quantities of nitrogen partially filling available sites. This accounts for the many non-stoichiometric transition metal nitride phases in existence and for the essentially metallic properties that are often observed (*e.g.* hardness, lustre, conductivity, *etc.*).

The metallic nature of bonding in binary nitrides is not restricted to transition metals. Only the most electropositive metals form nitrides which one might regard as classically ionic. The heavier, less electropositive alkaline earth metals preferentially form sub-nitrides. The existence of the expected stoichiometric compounds such as Ba_3N_2 and Sr_3N_2 is doubtful whereas "reduced" compositions such as Sr_2N[40] and Ba_3N[41] are well characterised. Calcium forms stoichiometric Ca_3N_2[42] *and* the sub-nitride Ca_2N.[43] Only Mg and Be show no evidence for low oxidation state compounds. One can interpret the bonding in the Group II binary nitrides in several ways: first as in sub-oxide and -nitride metal clusters where the normal formal charges are assigned to cations and anions and the excess of charge is attributed to metal valence electrons contributing to metallic bonding, *e.g.* $Ba_3N \equiv Ba^{2+}{}_3N^{3-}\cdot(3e^-)$.[41] Alternatively, one can assign low formal oxidation states to alkaline earth metals and N. Bond valence and Madelung potential calculations tend to favour this latter representation as do density functional theory (DFT) calculations performed on related

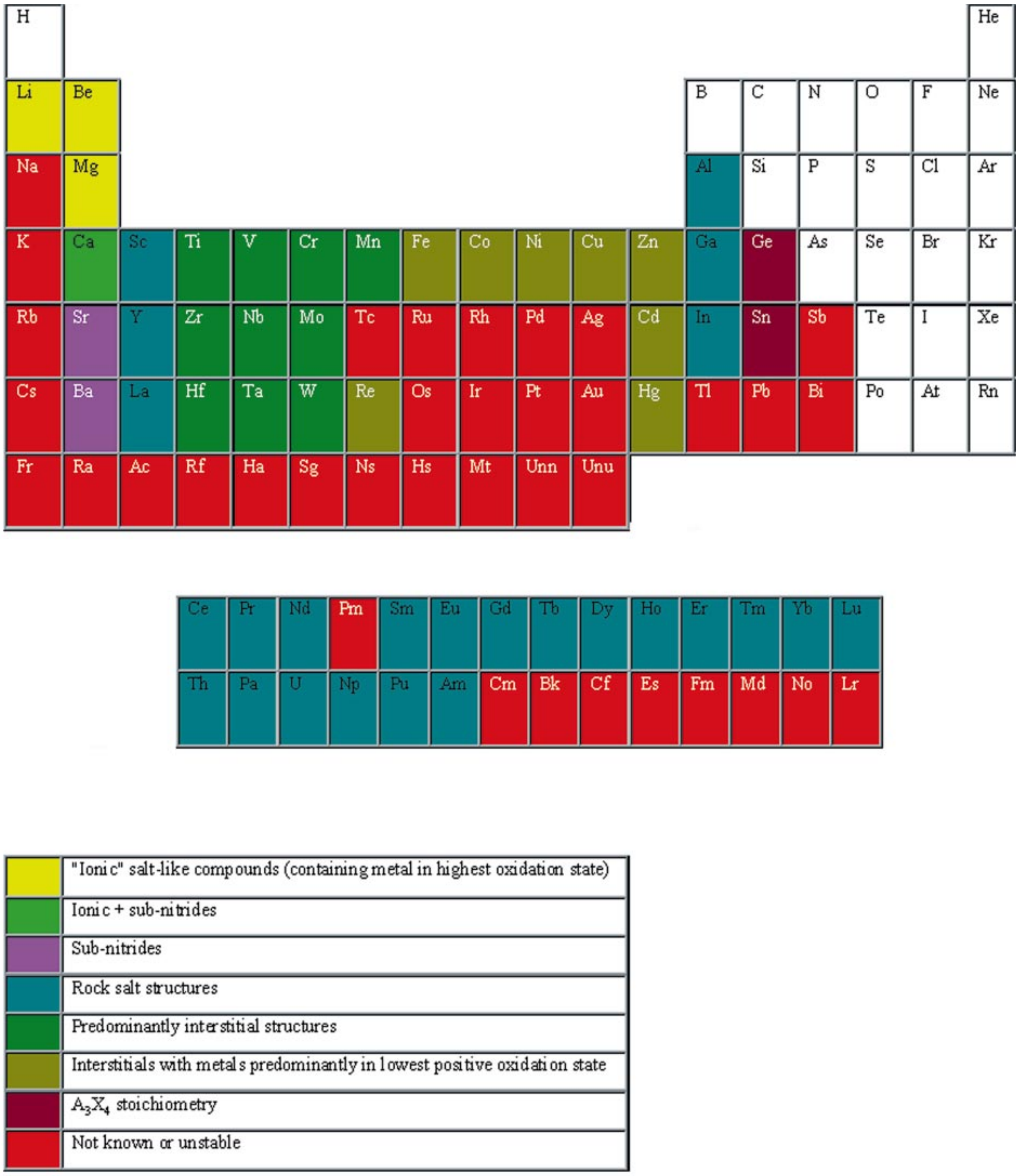

Fig. 1 The broad structure types adopted by binary metal nitrides by element.

nitride hydrides (*e.g.* Sr_2NH, Ba_2NH).[44] These calculations imply that while the charge on the hydride anions in these materials is very close to -1, significant covalent interactions between metal and nitrogen lead to charges of $\approx +1.3$ and ≈ -1.7 for cation and anion respectively. The classification of binary metal nitrides is depicted in Fig. 1.

Theoretical studies of bonding in ternary and higher nitrides have focused so far on several of the more well characterised groups of compounds.[45,46] What is already apparent from calculations performed on these systems and from experimentally observed structures and bond lengths is that covalent bonding contributions, and π interactions especially, are significant in the majority of transition metal compounds. This is often manifested in low co-ordination numbers for transition metals and unexpectedly short bonds to nitrogen. It has been noted previously that cation co-ordination numbers are almost routinely low in metal-rich compositions but become higher as the metal : N ratio decreases.[5] One alternative representation of ternary nitride bonding is to consider bonds as σ–π hybrid "banana" bonds incorporating $d_\pi \longrightarrow p_\pi$ bonding from filled transition metal d orbitals to empty nitrogen p orbitals.[47] This scheme provides for what can essentially be regarded as double and triple metal–nitrogen bonds.

Various methods have been employed to model nitride bonding and to test the validity of nitride structures. These include, among others, Madelung potential and bond valence calculations[5] in addition to extended Hückel-type calculations[45] and various aspects of density functional theory [*e.g.* local density approximation (LDA)[48] and generalized gradient approximation (GGA)[44]]. The strong covalent character of metal–nitrogen bonds in ternary and higher nitrides often apparently devalues the use of bond valence calculations in validating structural models. While quantitatively bond valence sums are often high for transition metals and low for Group I and II metals, this indirectly points to deviations from ionic bonding and becomes a useful qualitative tool. Just as with oxides and fluorides some years ago, as more nitrides continue to be discovered one can envisage the progressive refinement of the relevant bond valence parameters.

4 Structural families

Common structural aspects

As has been highlighted in previous reviews of this area, the crystal chemistry of the ternary and higher nitrides is often dominated by the low co-ordination environments of nitrogen around transition metals. Ternary transition metal nitrides commonly form low dimensional structures containing isolated complex anions or one-dimensional chains of anionic groups. While the number of examples of layered extended structures in nitrides is steadily increasing, three-dimensional frameworks are largely restricted to non-metal compounds such as nitridosilicates and nitridophosphates. These latter materials will not be covered here, but are evolving a rich and unique crystal chemistry on a par with their oxygen-containing counterparts.[7,8] Transition metal compounds are typically, but not exclusively, metal-rich and with nitrogen frequently co-ordinated to 5 or 6 metal atoms. Metal co-ordination numbers rarely exceed 6, even in compounds containing large alkaline earth or lanthanide ions.

Unusually low metal co-ordination numbers, coupled with the stoichiometric restrictions imposed by the nominal 3− charge of the nitride ion, limit to a certain extent structural analogues based on ternary chalcogenides and halides. Nonetheless, many of these are already known. Furthermore, since nitride anion co-ordination numbers are often higher than those of the cations, *anti* structures are commonplace in binary and ternary nitride systems alike (*e.g.* Ca_2N[43] and Sr_2N[40] with the *anti*-$CdCl_2$ structure, $CaMg_2N_2$[49] with the *anti*-La_2O_3 structure and LiMgN and LiZnN with the *anti*-fluorite structure[50]). Compounds of this nature emphasise the usefulness of the anion-centred polyhedral approach in the structural description of nitrides described by Brese and O'Keeffe.[5]

Given the above features of metal–nitrogen co-ordination in nitrides, it is not surprising that a significant number of structures are unique to nitrides. There are some examples of carbide and pnictide (*e.g.* phosphide) isotypes but these are, if anything, less common than chalcogenide and halide analogues. This suggests that, despite the significance of covalency in nitride bonding, the relative electronegativity of N^{3-} (and the lack of available d orbitals for bonding) plays a significant part in determining crystal structure.

"Well established" nitride structural groups

While, the definition of "well established" is perhaps rather loose in connection to ternary nitride crystal chemistry, there exist several well characterised structural groups which have been known for some years and discussed previously. These will be mentioned briefly here but in most cases no major developments in these areas have occurred recently and the reader will be directed to the appropriate existing reviews of the relevant literature.

Much of the fundamental research into the ternary transition metal nitrides of lithium was conducted by Juza and co-workers over several decades. Two significant structural families emerged from this research and broadly these divide the left and right of the top row transition metals. Metals from Ti to Mn (and additionally Nb, Ta, Al, Ga, Mg and Zn) form ordered variants or superstructures of the *anti*-fluorite structure whereas Co, Ni and Cu form substituted Li_3N-type structures (Fig. 2) as solid solutions ($Li_{3-x}M_xN$; $x \le 0.6$).[1] Interestingly, the former group of compounds all contain transition metals in high oxidation states (in most cases, the highest possible) while the latter contains metals in the univalent state. These two sets of compounds typify the oxidation state behaviour of the first row transition metals in ternary nitrides. Intriguingly, iron does not fit conveniently into either one of these two structural groups, forming an *anti*-fluorite superstructure (Li_3FeN_2; Fe^{III})[51] *and* a defect variant of the Li_3N-type structure (Li_4FeN_2; Fe^{II}) (Fig. 3).[52] More recent studies have shown other structures to exist for ternary nitride compounds of lithium with first row transition metals and some of these are discussed in more detail in later sections.

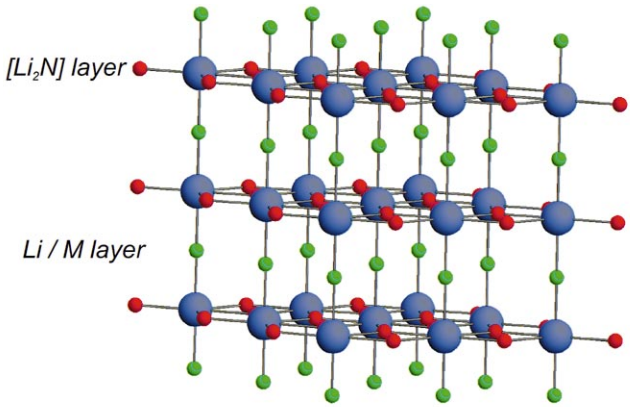

Fig. 2 Structure of $Li_{3-x}M_xN$ (M = Co, Ni or Cu): Li, small red spheres; Ni, small green spheres; N, large blue spheres.

A third class of lithium ternary compounds was first established approximately 25 years ago, crystallising with the *anti*-La_2O_3 structure. These Li_2MN_2 compositions exist for transition metals, M = Zr or Hf (in addition to Ce, Th or U).[53] Lithium and M are tetrahedrally and octahedrally co-ordinated to nitrogen respectively. The only ternary alkaline earth metal-containing example of this structure contains no transition metal, Mg_2CaN_2.[49] Alkaline earth–transition metal ternary phases of this stoichiometry form very different structures, typically with later transition metals in low co-ordination environments. These are covered in more detail in later sections.

The perovskite (ABX_3) structure and its distorted variants are a common feature in ternary oxide chemistry. Examples of nitride perovskites are rare (although the structure and various distortions are observed in transition metal oxynitrides of the lanthanides or alkaline earth metals). A larger structural group is that of compounds crystallising in the *anti*-perovskite structure, Ca_3XN. To date, however, this class of compounds has been mostly restricted to main group elements,[54] with Ca_3AuN[22a] being the sole transition metal-containing example. Unlike the main group *anti*-perovskites, however, whose bonding can be represented ionically as $Ca^{2+}{}_3X^{3-}N^{3-}$ (where X here is P, As, Sb, Bi, Ge, Sn or Pb), the gold compound can be considered as a sub-nitride ($Ca^{2+}{}_3Au^-N^{3-}\cdot 2e^-$). In bonding terms, the auride nitride has more in common with the sub-nitrides of Group I/Group II elements (*e.g.* $NaBa_3N \equiv Na^+Ba^{2+}{}_3N^{3-}\cdot 4e^-$)[23a] than with the main group *anti*-perovskite nitrides. There are also earlier reported examples of *anti*-perovskites Mn_3MN (M = Ni, Cu, Zn, Ga, Rh, Ag, Sn, Sb or Pt) (and associated $Mn_3M_{1-x}M'_xN$ phases) based on Mn_4N.[55] Many of these compounds are either ferrimagnetic or antiferromagnetic with significant hybridisation of the manganese d orbitals and nitrogen p orbitals proposed.

Emerging structural families in nitrides

The stoichiometry AMN. This stoichiometry exists for combinations of lithium or alkaline earth metals (A) with transition metals (M) but embraces several different structure types, some unique to nitrides. The compound LiZnN forms an ordered *anti*-fluorite structure, as mentioned above, with Li and Zn distributed over the available tetrahedral sites (LiMgN forms a

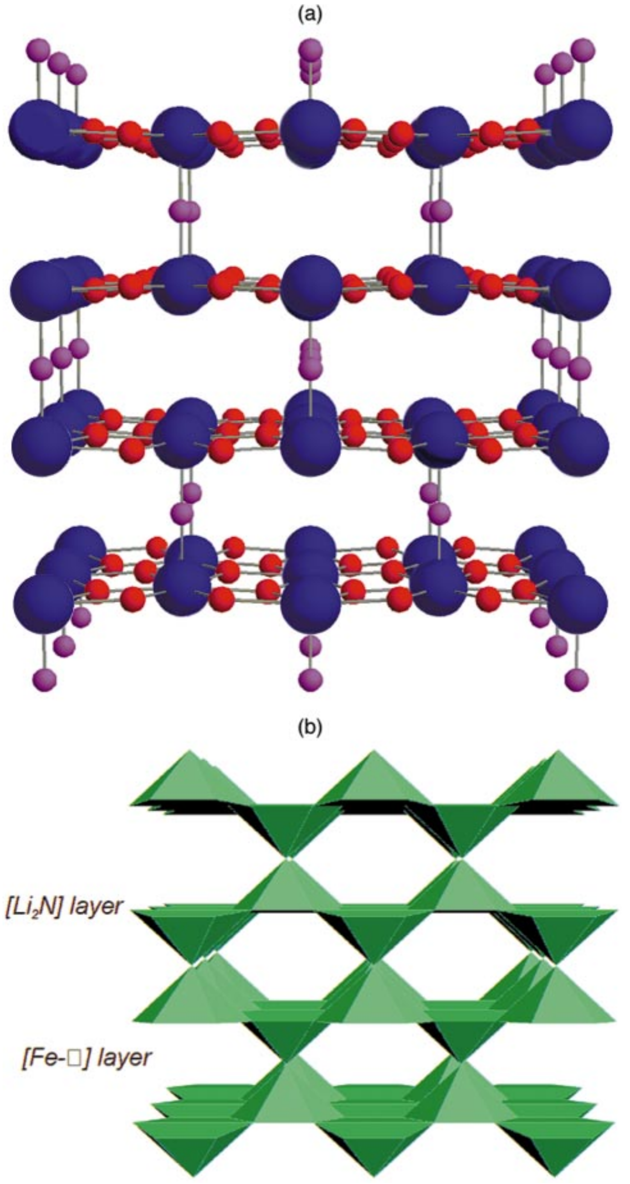

Fig. 3 The defect variant of the Li_3N-type structure formed by Li_4FeN_2; (a) ball and stick representation with Li as small red spheres, Fe as small purple spheres and N as large blue spheres, (b) perspective plot showing the linking of seven-co-ordinate N-centred polyhedra and [Li_2N] and [Fe/□] layers (□ = vacancy).

similar cubic cell but with an alternative, disordered, cation distribution).[50]

Among more recently reported compounds is $(Li,Mn)_2N$ which crystallises not in the *anti*-fluorite structure but in the disordered *anti*-rutile structure.[56] While this is not an uncommon structure type for binary transition metal nitrides, M_2N (*e.g.* ε-Ti_2N),[57] this is the first example of a ternary compound adopting this structure. There is evidence of a range of Li/Mn compositions in this system and as with the earlier reported $Li_{3-x}M_xN$ compounds this displays the ease with which Li can (partially) replace transition metal ions and form solid solutions. The metals are co-ordinated to nitrogen in distorted triangular planes, a motif seen surprisingly widely in ternary nitrides (as described later). The compound appears to be semiconducting with a possible antiferromagnetic transition at 115 K.

The compound LiNiN is stoichiometric and forms a structure related to Li_3N.[58] In contrast to earlier reported Li–Ni–N compositions, however, the structure is not a simple substituted derivative of lithium nitride, $Li_{3-x}Ni_xN$, but a new lithium vacancy-ordered structure closer in nature to Li_4FeN_2[52] than Li_3N. Unlike the iron nitride, however, metal vacancies lie *within* Li_2N planes rather than between them, reducing the co-ordination of nitrogen from hexagonal bipyramidal to trigonal bipyramidal. This would appear to have implications with respect to the Li^+ ionic conductivity of the nitride. There is also evidence of other vacancy-ordered compounds in the Li–Ni–N system ($Li_{3-x-y}Ni_x\square_yN$; □ = vacancy) which show an evolution of nitrogen co-ordination with vacancy concentration.

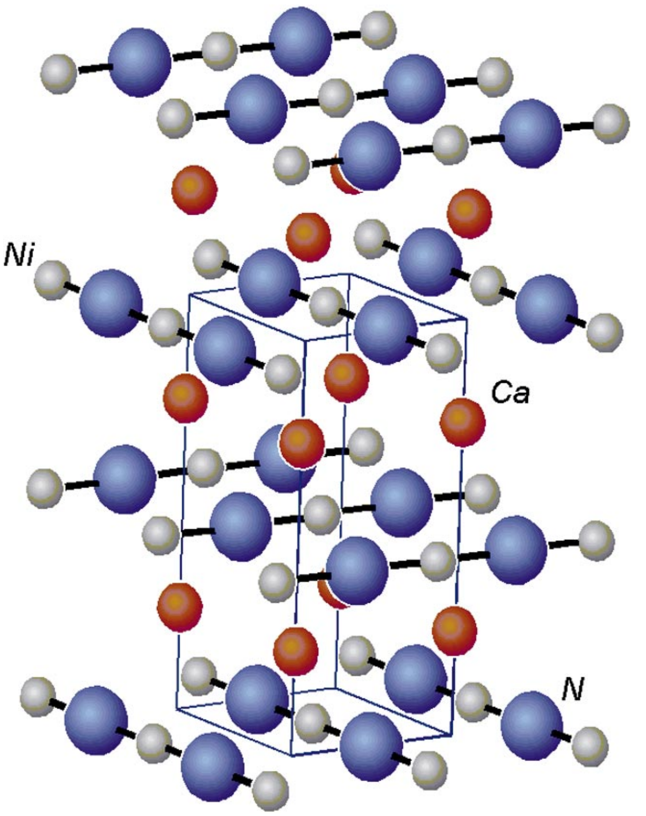

Fig. 4 Crystal structure of CaNiN. (The unit cell is delineated by the solid line.)

Alkaline earth metal compositions exist for transition metals in Groups IX, X and XI in a univalent state. The structures appear to show a significant dependence on the size of the alkaline earth metal cation. A common structural motif throughout is the extended –N–M–N– chain. These $^1_\infty[MN_{2/2}{}^{2-}]$ infinite chains tend to be straight when the alkaline earth metal cation is small (Ca) and bent as the ionic radius increases (Sr, Ba). The compound CaNiN[59] [and also LiSrN[60] and the Li-substituted compounds, Ca(Ni,Li)N[61]] crystallises with the YCoC structure. In this relatively simple, tetragonal structure, layers of straight –N–Ni–N– chains are sandwiched between layers of Ca (Fig. 4). Alternate layers of these chains are aligned perpendicular to one another in the *ab* plane. (A similar arrangement exists in $LiSr_2[CoN_2]$, but alternate Co atoms are "replaced" by Li in –N–Li–N–Co–N–Li– chains and hence the linear $[CoN_2]^{5-}$ anions become discrete.[62]) Completely replacing Ca by Sr or Ba causes the –N–Ni–N– chains to bend into zigzag formations and also leads to distortion of the tetrahedral alkaline earth metal–nitrogen environment (Fig. 5).[63] The –N–Ni–N– chains in these orthorhombic structures are similar to –O–Cu–O– chains in CsCuO,[64] but in the nitrides the "kinks" (changes in direction) in the chains occur less frequently. The same chain conformation is observed for Cu–N in isostructural SrCuN[65] [and for Li/Cu in $Sr(Li_{1-x}Cu_x)N$; $0.33 \le x \le 0.52$].[66] *Partial* replacement of Ca by Sr is also possible, in $Ca_{1-x}Sr_xNiN$, with retention of the YCoC structure for $x \le 0.5$.[63a] The structure of BaCoN is closely related to BaNiN but here the zigzag chains are "stepped" so that the chain length on each side of a kink is not equal.[67] The chains distort further still in the related compound $Ba_8Ni_6N_7$, twisting

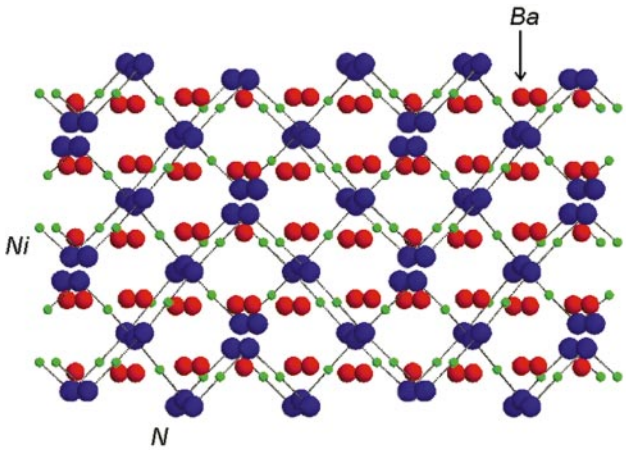

Fig. 5 Structure of Ba(Sr)NiN, illustrating the zigzag chains of –N–Ni–N– units.

in infinite helices.[68] Interestingly, the metal–metal distances are significantly shorter in the zigzag chain structures than in the YCoC-type compounds (*e.g.* Ni–Ni in CaNiN ≈ 3.5 Å, Ni–Ni in BaNiN ≈ 2.4 Å). The electrical and magnetic properties of CaNiN, SrNiN and also $Ca_{1-x}Sr_xNiN$ compositions have been studied. All show evidence of metallic conductivity and Pauli-paramagnetic behaviour.

The stoichiometry AMN_2. This stoichiometry is widespread among chalcogenides and is developing rapidly now in nitride chemistry. In many cases, the observed nitride structure types are also those found in chalcogenide chemistry. This broad structural class consists mainly of 2-D layered-type compounds, although the nature of the layers and the pattern in which the layers stack vary with cation size and transition metal type. The stoichiometry already covers a wide range of nitride compositions with combinations of A = alkali metal, alkaline earth metal or transition metal with M = transition metal known. Most commonly, these layered nitrides contain six-coordinate metals in either octahedral or trigonal prismatic geometry. These structures often differ, principally, in terms of their layer stacking sequence, which leads to predominantly hexagonal unit cells with varying *c* parameters.

The α-$NaFeO_2$ type structure, favoured by many oxides of the AMX_2 stoichiometry, is also found in nitrides. This structure is adopted by predominantly 2nd and 3rd row transition metals with alkali and alkaline earth metals including $NaTaN_2$, $NaNbN_2$,[32a,33,69] $SrZrN_2$, $SrHfN_2$[70] and $CaTaN_2$.[71] The hexagonal α-$NaFeO_2$ structure is an NaCl-type superlattice and both A and M (and N) are octahedrally co-ordinated (Fig. 6). The structure can alternatively be described as an O3 type, where O represents the octahedral co-ordination of A and 3 represents the number of $[MX_2]$ layers in the unit cell. Chalcogenides with this structure type often undergo ready (de)intercalation by adding/removing A cations from between $[MX_2]$ layers. There is evidence that similar reactions can be performed in these layered nitrides (despite, in some cases, apparent stoichiometric/oxidation state restrictions). The compound $Ca_{1-x}TaN_2$ ($x \approx 0.26$) forms after prolonged heating of $CaTaN_2$ at ≈1200 °C.[71] Sodium can be removed from $NaTaN_2$ using NO_2PF_6 to produce nominal $Na_{1-x}TaN_2$ compositions with x as high as ≈0.9.[33] The stoichiometric $CaTaN_2$ compound (and, perhaps, also $Ca_{1-x}TaN_2$; $x > 0$ compositions) appears to superconduct at *ca.* 9 K. The deintercalated $Na_{1-x}TaN_2$ compounds, however, are coloured insulators. The bonding in these latter nitrides has been rationalised in terms of oxidation of N or the formation of N≡N bonds, but neither hypothesis has yet been verified.

An alternative structure type observed in AMN_2 nitrides is the P3 ($Na_{0.6}CoO_2$) structure. This differs from the α-$NaFeO_2$-type materials in the trigonal prismatic (P) (as opposed to octahedral) co-ordination of the A cations (Fig. 7). This structure is adopted by $LiMoN_2$[25] and $LiWN_2$[72] and also by the

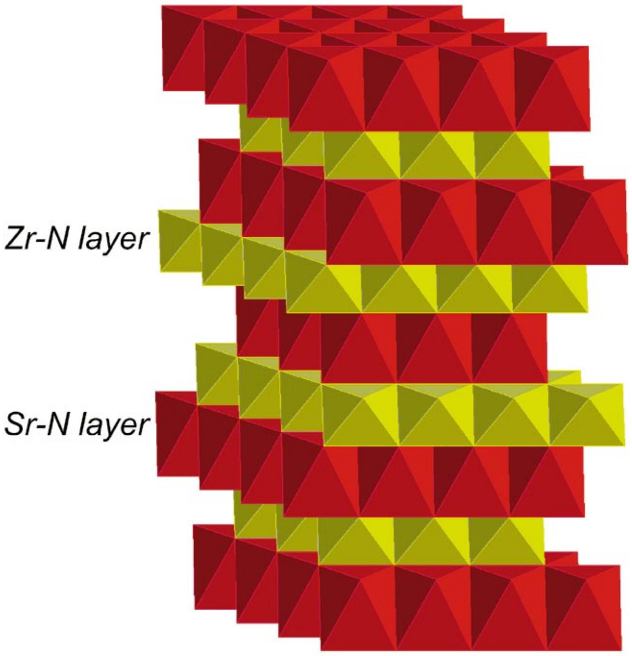

Fig. 6 The α-$NaFeO_2$ structure as adopted by $SrZrN_2$. Alternate layers of octahedrally co-ordinated Sr(A) and Zr(M) are stacked along the *c* axis.

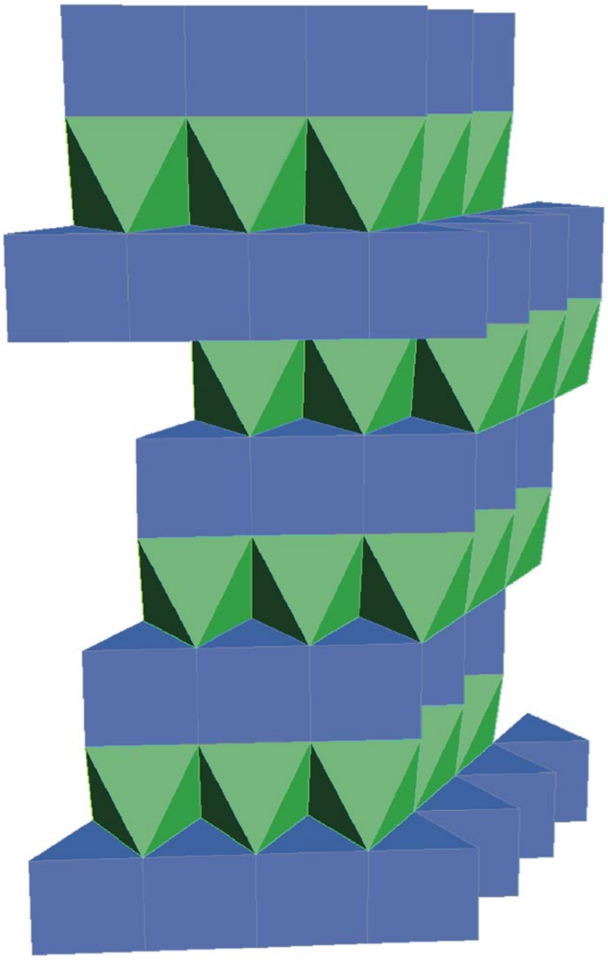

Fig. 7 Structure of $LiMoN_2$ (P3 structure) with alternating layers of metal-centred octahedra and trigonal prisms. Note the edge-sharing of polyhedra within layers but also face-sharing between layers.

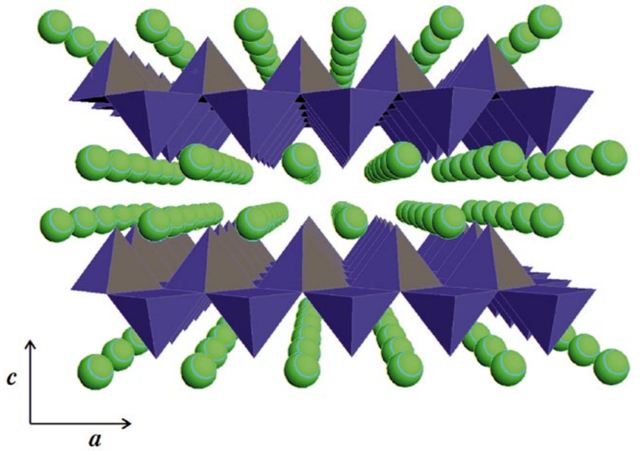

Fig. 8 Perspective polyhedral representation of the KCoO_2 structure adopted by Ba(Zr,Hf)N_2 and SrTiN_2. Layers of edge-sharing $[\text{MN}_2]^{2-}$ square pyramidal anions align perpendicular to the *c* axis. Green spheres are Ba (Sr).

mixed transition metal species CrWN_2.[38] The compounds CoWN_2 and NiWN_2 are probably isostructural with these three compounds, although their crystal structures have not been refined.[73] The compounds MnMoN_2, $\text{Li}_{0.84}\text{W}_{1.16}\text{N}_2$ (both *anti*-TiP type; P2b type), FeWN_2, $(\text{Fe}_{0.8}\text{Mo}_{0.2})\text{MoN}_2$ and $(\text{Fe}_{0.8}\text{W}_{0.2})\text{WN}_2$ (P2a) form structures closely related to the P3 structure. The structures of this latter group differ from the P3 type in (a) the number of layers within the unit cell (hence, smaller *c* parameters) and (b) the way in which octahedra are linked to trigonal prisms (face-sharing, P2a or edge-sharing, P2b).[26a,c,74,75] It is unclear whether MnWN_2 falls into the former (P3) or latter (P2) group.[73] Up to 64% lithium can be deintercalated from LiMoN_2. The fully intercalated compounds LiMoN_2 and LiWN_2 are metallic and paramagnetic. Electronic structure calculations show LiMoN_2 to be a three dimensional metal with strongly covalent $[\text{MoN}_2]$ sheets. There is also evidence of a direct *inter*-layer interaction between N atoms in $[\text{MoN}_2]$ sheets.[46a] Those of the mixed transition metal species that have been investigated are weakly metallic or semiconducting and paramagnetic.

The mixed transition metal compound CuTaN_2 is to date the only reported example of a ternary nitride with the delafossite structure.[30] This structure type is widely known for oxides $\text{A}^{\text{I}}\text{M}^{\text{III}}\text{O}_2$ (A = Cu, Ag, Pd or Pt; M = Al, Ga, In, Fe, Co, *etc.*).[76] Copper(I) is linearly co-ordinated to N and the hexagonal structure is thus made up of alternating octahedral Ta–N and linear Cu–N layers stacked in the *c* direction.

The heavier alkali metals form non-hexagonal nitride structures with transition metals. The compounds KTaN_2 and RbTaN_2 prepared at 5 kbar of NH_3 pressure form orthorhombic structures apparently isotypic to KGaO_2; CsTaN_2 prepared under similar conditions crystallises with the cubic β-crystobalite structure[32a] (a structure also adopted by LiPN_2, for example).[77] At ambient pressure, KTaN_2 and KNbN_2 are reported to form cubic structures which may be analogous to CsTaN_2.[33]

The KCoO_2 structure is not a common structure type in oxide chemistry, yet it is reported for several alkaline earth metal–Group IV metal nitrides, BaZrN_2, BaHfN_2, $\text{BaZr}_{1-x}\text{Hf}_x\text{N}_2$ and SrTiN_2.[78] These are tetragonal structures containing layers of edge-sharing $[\text{MN}_2]^{2-}$ square-based pyramids with alternate pyramids aligned "up" and "down" parallel to the *c* axis (Fig. 8). The barium compounds are reported to be paramagnetic, although this may be due to impurity phases rather than the ternary nitrides themselves (containing nominally d^0 Zr^{IV} or Hf^{IV}).

The vast array of existing AMO_2 structures have been classified in terms of, for example, ion size, ionicity of metal–oxygen bonds and interlayer distances.[79] Similarly detailed studies of nitrides have yet to be performed, although the number of AMN_2 compounds is now relatively considerable. It is already apparent that, in many cases, MN_2 layers exhibit significant covalent character and that this is likely to have a profound effect in determining crystal structure.

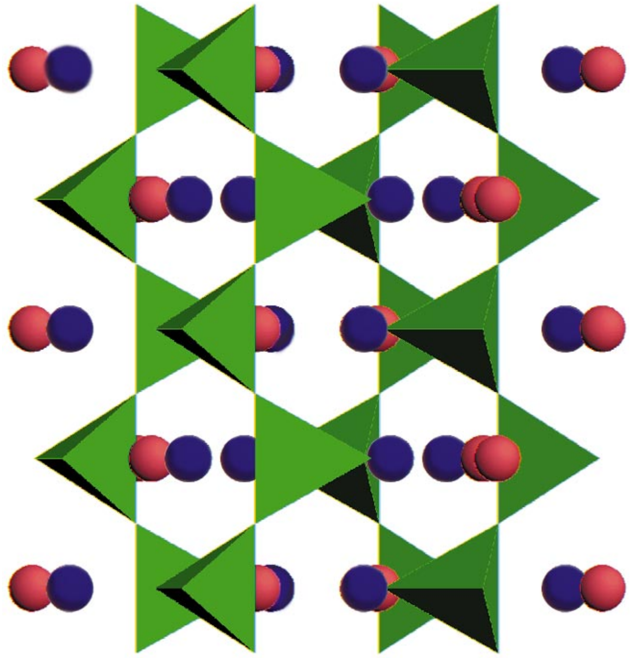

Fig. 9 Structure of Ba_2VN_3 showing chains of vertex-sharing $[\text{VN}_3]^{4-}$ tetrahedra (red and blue spheres are Ba).

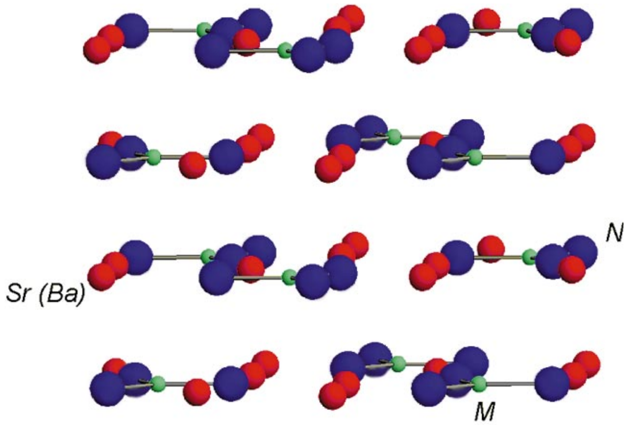

Fig. 10 Structure of $\text{Sr(Ba)}_3\text{Cr(M)N}_3$. Layers of discrete $[\text{CrN}_3]^{6-}$ triangles, alternating by 180° in direction, align perpendicular to the *c* axis.

The stoichiometry A_2MN_3. Two classes of compounds are known with this stoichiometry, one with A = Ce which will be detailed later and the other with A = alkaline earth metals. With respect to transition metals, this latter grouping consists exclusively of Group V elements in their highest oxidation state (M = V, Nb or Ta). These compounds form one of two structures which are closely related and share the common structural motif of infinite one-dimensional chains of corner-sharing $[\text{MN}_3]^{4-}$ tetrahedral anions ($^1_\infty[\text{MN}_2\text{N}_{2/2}]$). The compound Ba_2VN_3[80] (Fig. 9) adopts the orthorhombic Rb_2TiO_3 structure (also formed by Ca_2PN_3);[81] Sr_2MN_3 (M = V, Nb or Ta) and Ba_2MN_3 (M = Nb or Ta) adopt the monoclinically distorted, Ba_2ZnO_3 structure.[78a,80,82] There are no structural data reported for A = Mg, Ca nitrides although there are reports of a green, cubic Ca_2TaN_3 phase formed at high temperatures (*ca.* 1200 °C).[71] Interestingly, Mg_2PN_3 is isostructural with Li_2SiO_3,

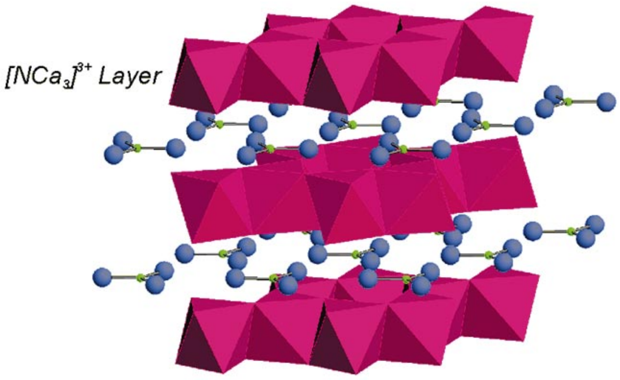

Fig. 11 Structure of $Ca_6Mn(M)N_5$. Layers of discrete $[MN_3]^{6-}$ triangles are sandwiched between $[NCa_3]^{3+}$ slabs stacked along the *c* direction.

crystallising in a smaller orthorhombic unit cell, with a different tetrahedral anion chain conformation.[83] Magnetic measurements of Ba_2VN_3 and Sr_2VN_3 indicate diamagnetic behaviour. Measurements performed on Sr_2NbN_3 and Ba_2NbN_3 show weak temperature independent paramagnetism, probably from impurities.

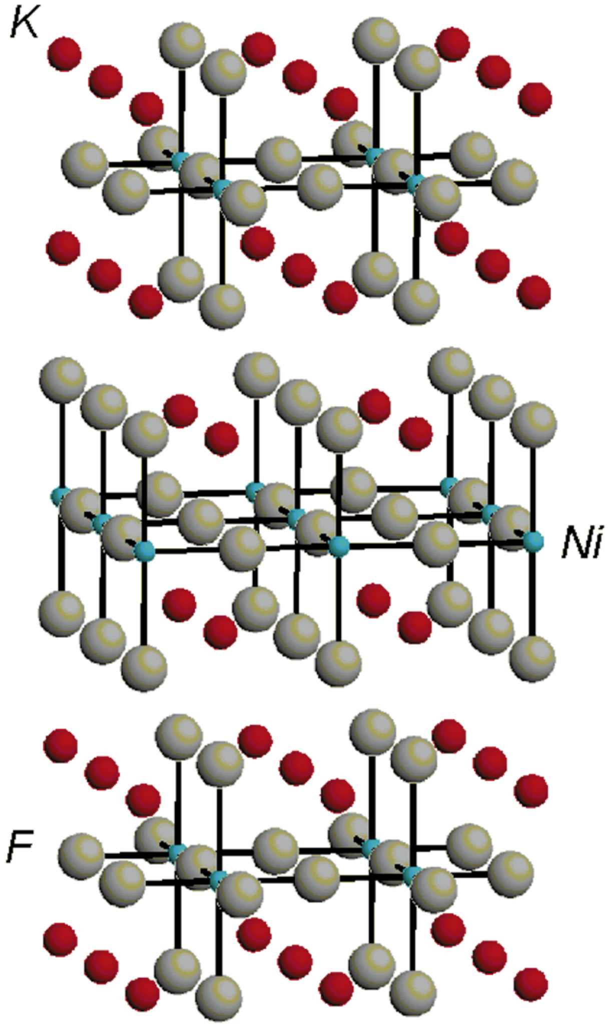

Fig. 13 Crystal structure of K_2NiF_4.

The stoichiometry A_3MN_3. There are two distinct classes of nitride with this stoichiometry (313): those with A = alkali metal and those with A = alkaline earth metal. The former class embraces compositions with the heavier Group VI metals (M = Mo or W), the latter with the first row transition metals from M = V to Fe. The nitrides A_3MN_3 (M = Mo or W) are only known for A = Na and have been successfully synthesized only by reaction of the transition metals (or their nitrides) with sodium *amide*, $NaNH_2$, and ammonia (either at ambient or high pressures).[32c,34,84] The nitridomolybdate and nitridotungstate are isostructural and contain tetrahedral ${}^{1}_{\infty}[MN_2N_{2/2}]^{3-}$ anion chains similar in nature to the ${}^{1}_{\infty}[M^{V}N_2N_{2/2}]^{4-}$ chains in the A_2MN_3 compounds described above. As in the A_2MN_3 compounds, there is evidence of significant M–N π bonding in the chains, notably to terminal (non-linking) nitrogens. Partial substitution of sodium in the 313 nitridotungstate by potassium ($Na_2K[WN_3]$) or rubidium ($Na_{11}Rb[(WN_3)_4]$) leads to new structures also containing ${}^{1}_{\infty}[WN_2N_{2/2}]^{3-}$ anion chains, although the chain conformations are subtly different.[32d] The above compounds form only a small part of a growing number of alkali metal nitridotungstates and nitridomolybdates which commonly feature anionic tetrahedral M–N units either as discrete units, oligomeric species, chains, layers or networks.

The A = alkaline earth metal 313 compounds crystallise with structures which are unique to nitrides. Two structure types are

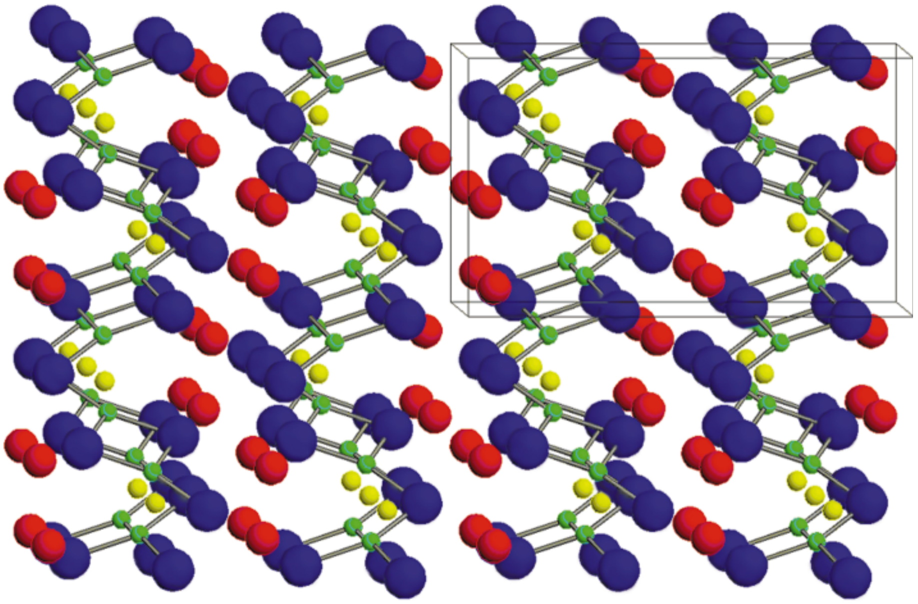

Fig. 12 Structure of $Sr_2Li[Fe_2N_3]$ containing chains of vertex-linked $[Fe_2N_3]^{5-}$ "dimeric" anions (N, large blue spheres; Sr, medium red spheres; Li, small yellow spheres; Fe, small green spheres).

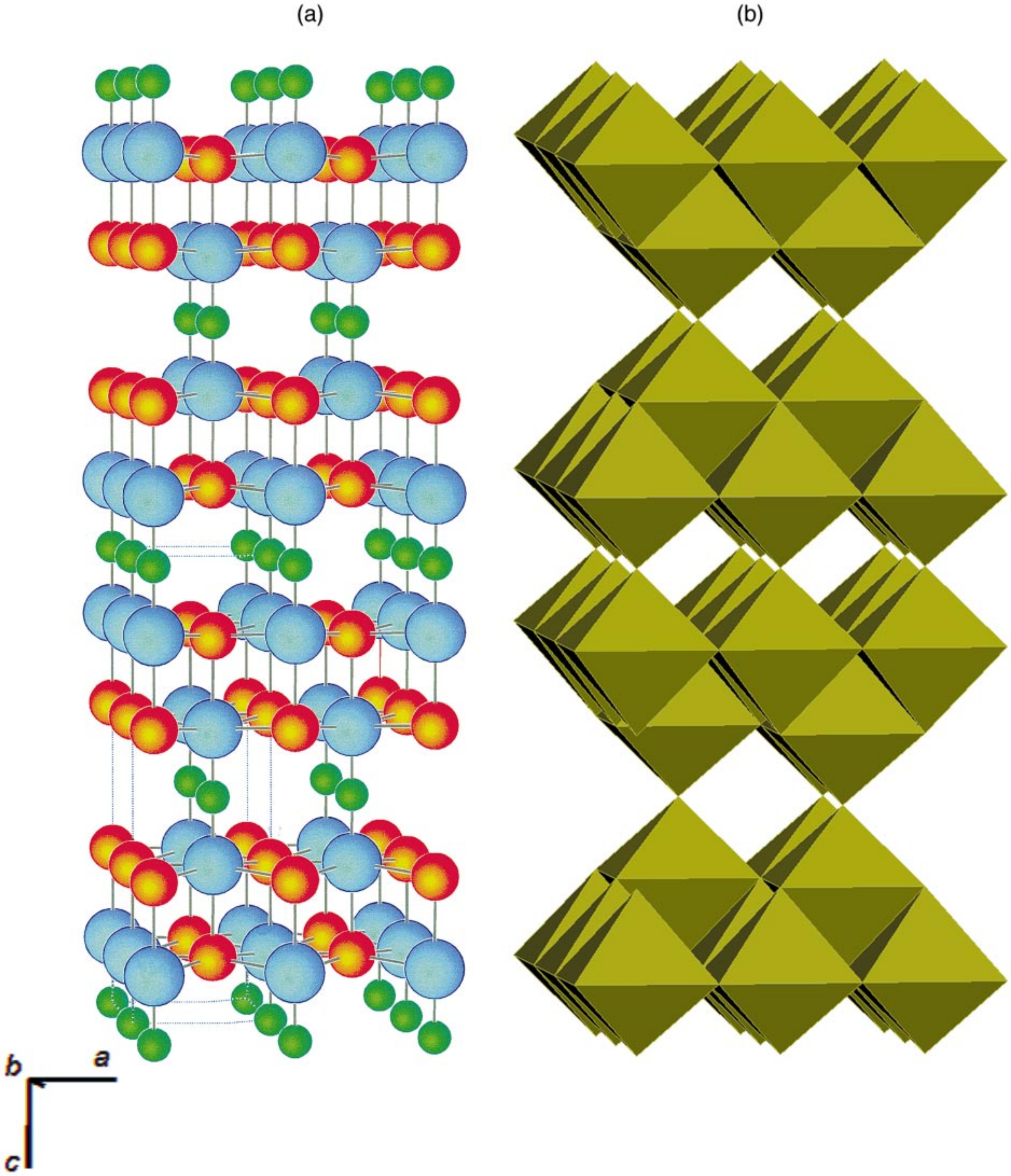

Fig. 14 Crystal structure of $Sr(Ba)_2ZnN_2$: (a) ball and stick representation (N, large blue spheres; Sr, medium orange spheres; Zn, small green spheres); (b) polyhedral representation showing edge and vertex linking of N-centred octahedra.

known and these are commonly linked by the trigonal planar $[MN_3]^{6-}$ anion. The anion is isoelectronic with carbonate $[CO_3]^{2-}$, but analogous *metal* species are very rare in other areas of solid state chemistry ($RbNa_7[CoO_3]_2$ is an example).[85] The calcium ternary compounds Ca_3MN_3 (M = V, Cr or Mn) have orthorhombic structures containing isolated $[MN_3]^{6-}$ anions with C_{2v} symmetry.[86] The strontium and barium compounds $Sr(Ba)_3MN_3$ (M = Cr, Mn or Fe) have hexagonal structures (Fig. 10) with $[MN_3]^{6-}$ anions with D_{3h} symmetry.[22b,87] The change in anion symmetry and crystal structure was originally postulated to be a consequence of Jahn–Teller distortion in the low spin $[MN_3]^{6-}$ anion. However, recent experimental evidence suggests the changes in symmetry are more a consequence of the size of the counter cation, A^{2+}. While the nitridovanadate Ca_3VN_3 appears to be essentially intrinsically diamagnetic and insulating, measurements conducted on Ca_3CrN_3 suggest a paramagnetic, insulating material with an antiferromagnetic transition at 240 K. The exchange energy in Ca_3CrN_3 is surprisingly large (185 K) given the distance between Cr atoms (*ca.* 5 Å) and this was attributed to large covalent bonding contributions. Although theoretical investigations tend to confirm the unusual, low spin state of these anions,[45a] measurements of the magnetic properties of these materials are not extensive. New detailed structural and magnetic studies of some of these materials validate earlier spin state arguments, but the evidence for co-operative magnetic interactions is less certain.[88]

It is valuable at this point to mention a number of compounds related to these $A^{II}{}_3MN_3$ compounds, that are more usefully described in this context than as stoichiometric groups in their own right. These include Ca_6MN_5 [M = Mn or Fe (and Ga)] (615),[89] A_2FeN_2 (A = Ca or Sr)[90] and $A_2LiFe_2N_3$ (A = Sr or Ba).[91] The Ca_6MN_5 compounds have structures in which layers of isolated trigonal planar $[MN_3]^{6-}$ anions are stacked alternately along the *c* axis between $[NCa_3]^{3+}$ layers (Fig. 11). These N–Ca layers resemble the edge-sharing octahedral N-Ca layers ("$[NCa_2]^+$") in Ca_2N. The three 615 compounds are isostructural, with $[MN_3]^{6-}$ anions of D_{3h} symmetry. No detailed magnetic measurements have yet been performed on these materials. The compounds Ca_2FeN_2 and Sr_2FeN_2 both contain "dimeric" $[Fe_2N_3]^{8-}$ units constructed from two distorted trigonal planar units sharing one triangular edge. These units are isosteric with the $[In_2P_4]^{6-}$ anion. The compound Sr_2FeN_2 also contains discrete linear $[Fe^{II}N_2]^{4-}$ anions which are isoelectronic with CO_2. (Similar, but not isoelectronic, discrete $[Cu^{I}N_2]^{5-}$ units are observed in $Sr_6Cu_3N_5$ which additionally contains $[Cu_2N_3]^{7-}$ V-shaped anions.)[65] In the lithium compounds $A_2LiFe_2N_3$ (A = Sr or Ba) Fe is also co-ordinated to N in a trigonal planar geometry, here interlinking to form infinite ${}^{1}_{\infty}[(FeN_{3/2})_2]^{5-}$ chains. These staggered chains are essentially made up of dimeric $[M_2N_4]$-like links joined by the "free" (non-bridging) vertices (Fig. 12). The Fe···Fe distances in the A_2MN_2 and $A_2LiFe_2N_3$ compounds are both short across "dimers" (*ca.* 2.4 Å). The physical properties of both groups of materials have yet to be investigated.

The recently reported nitridomanganate $Li_6Ca_2[Mn_2N_6]$[48] is also related to the above compounds in that Mn is, again, trigonally co-ordinated to N [as in A_3MnN_3 (A = Ca, Sr or Ba) and Ca_6MnN_5]. Importantly, however, the co-ordination sphere of Mn is completed with an unbridged Mn–Mn bond [2.358(1) Å] linking two triangular MnN_3 units to form $[Mn^{IV}{}_2N_6]^{10-}$ anions.

Stoichiometries A_2MN_2 and A_2MN_3; relations of the K_2NiF_4 structure. Whereas compounds of both these stoichiometries have been covered separately above, a convergent structural class "A_2MN_{4-y} ($y = 1$ or 2)" exists containing both these stoichiometries and based on the K_2NiF_4 structure. Compounds with $y = 2$ exist for A = Ca, Sr or Ba and M = Zn.[92] Compounds for $y = 1$ exist for A = Th, U or Ce and M = Cr or Mn.[93] The K_2NiF_4 structure (Fig. 13) is well known in oxides and halides, with a perovskite-like "core" (interposed with rock-salt type layers) and structural flexibility in terms of possible combinations of substituent cations (or anions).

The zinc nitrides A_2ZnN_2 (A = Ca, Sr or Ba) contain divalent zinc co-ordinated to 2 nitrogen atoms to form isolated, dumbbell $[ZnN_2]^{2-}$ anions. In terms of the K_2NiF_4 structure, Zn is bound to the axial N (F) equivalents of the NiF_6 octahedron with all equatorial N (F) positions vacant (Fig. 14). These nitrides are isostructural with Na_2HgO_2 (a structure also adopted by the non-oxides Na_2PdH_2 and U_2IrC_2). The compound Ca_2ZnN_2 is a diamagnetic insulator. The properties of the strontium and barium compounds have not been studied. Interestingly, BaO rock-salt layers can be inserted into Ba_2ZnN_2 to create Ba_3ZnN_2O by treating Ba metal with ZnO, Na and NaN_3 at 750 °C.[94] This is the first sign that the "building block" methodology used in oxide perovskite chemistry (*e.g.* in the superconducting cuprates) can be similarly pursued in (oxy)-nitride chemistry.

The A_2MN_3 nitrides contain Mn or Cr co-ordinated to N in an unusual square planar arrangement. Referring to the K_2NiF_4 "parent" structure, now the axial and two of the four equatorial anion positions of the NiF_6 octahedron are occupied and the structure distorts from tetragonal (*I*4/*mmm*) to orthorhombic (*Immm*) (Fig. 15). The squares are vertex linked to form infinite, straight $-N-MN_2-N-MN_2-$ (${}^{1}_{\infty}[MN_2N_{2/2}]$) chains parallel to the *a* axis. Recent studies of the A = Ce compounds suggest that the nitrides are best expressed as M^{I} species, $(Ce^{4+})_2M^{+}(N^{3-})_3$, and therefore contain $[MN_3]^{8-}$ anions.[93b,c] Extended Hückel calculations performed on Ce_2MnN_3 illustrate that the bridging Mn–N bonds in the ${}^{1}_{\infty}[MnN_2N_{2/2}]$ chains are strongly covalent π interactions whereas terminal Mn–N bonds are essentially single bonds.[93c] The apparent difficulty in synthesizing equivalent Ln^{3+}-containing nitrides would also suggest these materials are highly unusual manganese(I) and chromium(I) compounds. The compound Ce_2MnN_3 is metallic but the properties of the other A_2MN_3 compounds have not been investigated.

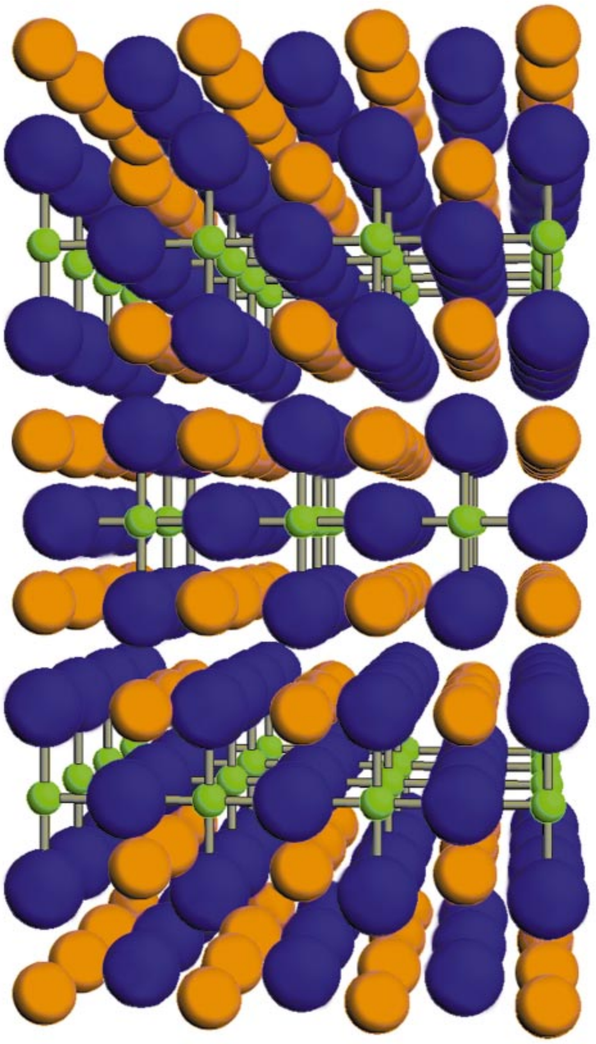

Fig. 15 Perspective representation of $Ce_2Mn(M)N_3$ containing chains of unusual vertex-linked square planar $[MN_3]^{8-}$ anions (Ce, medium orange spheres; N, large blue spheres; Mn, small green spheres).

5 Concluding remarks

Despite its youth, it is clear that the swelling contemporary momentum in nitride chemistry is driving the subject rapidly into new areas. The unique characteristics of "N^{3-}" and the nature of its bonding to metals continue to deliver surprising new compounds with unusual crystal structures and unexpected valence and co-ordination behaviour. As our feeling for nitride crystal chemistry develops, so we can establish the structure–property relationships that are the mainstay of solid state chemistry. Exciting times lie ahead as ternary nitrides begin to show evidence of intriguing and useful physical properties. Control of anion type and stoichiometry may well be crucial in this respect. Perovskite-related oxynitrides already show some of the flexibility that enables structural fine tuning to potentially useful properties. Interstitial nitrides exhibit ferromagnetic behaviour that can be modified *via* nitrogen stoichiometry. Superconducting lithium-doped, Group IV nitride fluorides demonstrate maximum critical temperatures (T_c) approaching high T_c superconductors.

This article has highlighted some of the developing relationships in nitride crystal chemistry. The solid state chemist can usefully apply knowledge of existing structural relationships, for example in chalcogenide and halide chemistry, in his or her quest to establish an understanding of nitrides. What is also obvious, however, is that only by continuing to explore the unknown reaches of nitride chemistry itself will we ultimately gain a sufficient grasp of structure and bonding in these materials. It is both exciting and encouraging that completely new nitride structures and motifs continue to be unearthed with such regularity. Many of these structures have no analogues in solid state chemistry and cannot yet be placed into any kind of structure-type classification. Despite the growing number of such examples, one suspects we have merely scratched the surface of what may yet exist.

6 Acknowledgements

The author would like warmly to acknowledge his colleagues of the last several years, Professor Peter P. Edwards and Dr Marten G. Barker for many useful discussions which have contributed to the views expressed herein. He would also like to extend thanks to the numerous other postgraduate and postdoctoral workers involved in various aspects of our work. Finally, the author would like to thank the EPSRC for the award of an Advanced Fellowship and for funding associated research projects.

7 References

1 R. Juza, K. Langer and K. Von Benda, *Angew. Chem.*, *Int. Ed. Engl.*, 1968, **7**, 360.

2 See for example: R Juza and H. Hahn, *Z. Anorg. Allg. Chem.*, 1938, **239**, 282; R. Juza and W. Sachsze, *Z. Anorg. Allg. Chem.*, 1945, **253**, 95; R. Juza, A. Gabel, H. Rabenau and W. Klose, *Z. Anorg. Allg. Chem.*, 1964, **329**, 136.

3 F. J. DiSalvo, *Science*, 1990, **247**, 649.

4 R. Marchand, Y. Laurent, J. Guyader, P. L'Haridon and P. Verdier, *J. Eur. Ceram. Soc.*, 1991, **8**, 197.

5 N. E. Brese and M. O'Keeffe, *Struct. Bonding* (*Berlin*), 1992, **79**, 307.

6 F. J. DiSalvo and S. J. Clarke, *Curr. Opin. Solid State Mater. Sci.*, 1996, **1**, 241.

7 W. Schnick, *Angew. Chem.*, *Int. Ed. Engl.*, 1993, **32**, 806.

8 W. Schnick and H. Huppertz, *Chem. Eur. J.*, 1997, **3**, 679.

9 J. V. Badding, *Adv. Mater.*, 1997, **9**, 877.

10 See for example, Ch. Wachsmann and H. Jacobs, *Z. Anorg. Allg. Chem.*, 1996, **622**, 885.

11 See for example, R. Marx, *J. Solid State Chem.*, 1997, **128**, 241.

12 See for example, S. Yamanaka, K. Hotehama and H. Kawaji, *Nature* (*London*), 1998, **392**, 580.

13 See for example, A. Simon, *J. Alloys Comp.*, 1995, **229**, 158.

14 L. E. Toth, *Transition Metal Carbides and Nitrides*, Academic Press, New York, 1971.

15 See for example, C. C. Wang, S. A. Akbar, W. Chen and V. D. Patton, *J. Mater. Sci.*, 1995, **30**, 1627.

16 R. Metselaar, *Pure Appl. Chem.*, 1994, **66**, 1815.

17 R. Kniep, *Pure Appl. Chem.*, 1997, **69**, 185.

18 H. Jacobs, R. Niewa, T. Sichla, A. Tenten and U. Zachwieja, *J. Alloys Comp.*, 1997, **246**, 91.

19 A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, Oxford, 5th edn., 1984.

20 L. LeGendre, R. Marchand and B. Piriou, *Eur. J. Inorg. Solid State Chem.*, 1997, **34**, 973.

21 See for example: R. Karam and R. Ward, *Inorg. Chem.*, 1970, **9**, 1849; U. Steinbrenner and A. Simon, *Angew. Chem.*, *Int. Ed. Engl.*, 1996, **35**, 552; S. J. Clarke, G. R. Kowach and F. J. DiSalvo, *Inorg. Chem.*, 1996, **35**, 7009; S. J. Clarke and F. J. DiSalvo, *Inorg. Chem.*, 1997, **36**, 1143.

22 See for example: (*a*) J. Jäger, D. Stahl, P. C. Schmidt and R. Kniep, *Angew. Chem.*, *Int. Ed. Engl.*, 1993, **32**, 709; (*b*) A. Tennstedt, C. Röhr and R. Kniep, *Z. Naturforsch.*, *Teil B*, 1993, **48**, 794.

23 See for example: (*a*) P. E. Rauch and A. Simon, *Angew. Chem.*, *Int. Ed. Engl.*, 1992, **31**, 1519; (*b*) G. J. Snyder and A. Simon, *J. Am. Chem. Soc.*, 1995, **117**, 1996; (*c*) H. Yamane and F. J. DiSalvo, *J. Alloys Comp.*, 1996, **240**, 33; (*d*) S. J. Clarke and F. J. DiSalvo, *J. Alloys Comp.*, 1997, **259**, 158.

24 See for example, C. C. Addison, R. J. Pulham and E. A. Trevellion, *J. Chem. Soc.*, *Dalton Trans.*, 1975, 2080.

25 S. H. Elder, L. H. Doerrer, F. J. DiSalvo, J. B. Parise, D. Guyomard and J. M. Tarascon, *Chem. Mater.*, 1992, **4**, 928.

26 See for example: (*a*) D. S. Bem and H.-C. zur Loye, *J. Solid State Chem.*, 1993, **104**, 467; (*b*) J. Grins, P.-O. Käll and G. Svensson, *J. Mater. Chem.*, 1995, **5**(4), 571; (*c*) D. S. Bem, C. M. Lampe-Önnerud, H. P. Olsen and H.-C. zur Loye, *Inorg. Chem.*, 1996, **35**, 581; (*d*) P. S. Herle, M. S. Hegde, N. Y. Vasathacharya, S. Philip, M. V. R. Rao and T. Sripathi, *J. Solid State Chem.*, 1997, **134**, 120.

27 E. G. Gillan and R. B. Kaner, *Inorg. Chem.*, 1994, **33**, 5693; R. E. Treece, E. G. Gillan and R. B. Kaner, *Comments Inorg. Chem.*, 1995, **16**, 313; E. G. Gillan and R. B. Kaner, *Chem. Mater.*, 1996, **8**, 333.

28 See for example: J. C. Fitzmaurice, A. L. Hector and I. P. Parkin, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 2435; J. C. Fitzmaurice, A. Hector, A. T. Rowley and I. P. Parkin, *Polyhedron*, 1994, **13**, 235; A. L. Hector and I. P. Parkin, *Chem. Mater.*, 1995, **7**, 1728; S. Ali, M. D. Aguas, A. L. Hector, G. Henshaw and I. P. Parkin, *Polyhedron*, 1997, **16**, 3635.

29 P. E. Bacon, J. G. Hou, A. W. Sleight and R. L. Nielsen, *J. Solid State Chem.*, 1995, **119**, 207.

30 U. Zachwieja and H. Jacobs, *Eur. J. Solid State Inorg. Chem.*, 1991, **28**, 1055.

31 P. M. O'Meara, M. G. Barker, D. A. Rees and D. H. Gregory, in preparation.

32 See for example: (*a*) H. Jacobs and E. von Pinkowski, *J. Less-Common Met.*, 1989, **146**, 147; (*b*) Th. Brokamp and H. Jacobs, *J. Alloys Comp.*, 1991, **176**, 47; (*c*) D. Ostermann, U. Zachwieja and H. Jacobs, *J. Alloys Comp.*, 1992, **190**, 137; (*d*) R. Niewa and H. Jacobs, *J. Alloys Comp.*, 1996, **233**, 61; (*e*) R. Niewa and H. Jacobs, *Z. Anorg. Allg. Chem.*, 1996, **622**, 881.

33 P. E. Rauch and F. J. DiSalvo, *J. Solid State Chem.*, 1992, **100**, 160.

34 P. E. Rauch, F. J. DiSalvo, N. E. Brese, D. E. Partin and M. O'Keeffe, *J. Solid State Chem.*, 1994, **110**, 162.

35 M. Ohashi, S. Yamanaka, M. Sumihara and M. Hattori, *J. Solid State Chem.*, 1988, **75**, 99; M. Ohashi, S. Yamanaka and M. Hattori, *J. Solid State Chem.*, 1988, **77**, 342.

36 S. Yamanaka, H. Kawaji, K. Hotehama and M. Ohashi, *Adv. Mater.*, 1996, **8**, 771; H. Kawaji, K. Hotehama and S. Yamanaka, *Chem. Mater.*, 1997, **9**, 2127.

37 See for example: D. V. Baxter, M. H. Chisholm, G. J. Gama, V. F. DiStasi, A. L. Hector and I. P. Parkin, *Chem. Mater.*, 1996, **8**, 1222; N. A. K. Hansen and W. A. Herrmann, *Chem. Mater.*, 1998, **10**, 1677.

38 K. S. Weil and P. N. Kumta, *J. Solid State Chem.*, 1997, **128**, 185.

39 D. J. Siddons, P. M. O'Meara, M. G. Barker and D. H. Gregory, in preparation.

40 N. E. Brese and M. O'Keeffe, *J. Solid State Chem.*, 1990, **87**, 134.

41 U. Steinbrenner and A. Simon, *Z. Anorg. Allg. Chem.*, 1998, **624**, 228.

42 Y. Laurent, Y. Lang and M. T. LeBihan, *Acta Crystallogr.*, *Sect. B*, 1968, **24**, 494.

43 E. T. Keve and A. C. Skapski, *Inorg. Chem.*, 1968, **7**, 1757.

44 H. Smolinski and W. Weber, *J. Phys. Chem. Solids*, 1998, **59**, 915.

45 (*a*) K. A. Yee and T. Hughbanks, *Inorg. Chem.*, 1992, **31**, 1921; (*b*) M. T. Green and T. Hughbanks, *Inorg. Chem.*, 1993, **32**, 5611.

46 See for example: (*a*) D J Singh, *Phys. Rev. B*, 1992, **46**, 9332; (*b*) L. F. Mattheis, *Phys. Rev. B*, 1993, **47**, 8224.

47 R. B. King, *Can. J. Chem.*, 1995, **73**, 963.

48 O. Hochrein, Y. Grin and R. Kniep, *Angew. Chem.*, *Int. Ed. Engl.*, 1998, **37**, 1582.

49 V. Schultz-Coulon and W. Schnick, *Z. Naturforsch.*, *Teil B*, 1995, **50**, 619.

50 R. Juza and F. Hund, *Z. Anorg. Allg. Chem.*, 1948, **257**, 1.

51 A. Gudat, R. Kniep, A. Rabenau, W. Bronger and U. Reschewitz, *J. Less-Common Met.*, 1990, **161**, 31.

52 A. Gudat, R. Kniep and A. Rabenau, *Angew. Chem.*, *Int. Ed. Engl.*, 1991, **30**, 199.

53 A.-P. Palisaar and R. Juza, *Z. Anorg. Allg. Chem.*, 1971, **384**, 1; M. G. Barker and I. C. Alexander, *J. Chem. Soc.*, *Dalton Trans.*, 1974, 2166; R. Niewa, H. Jacobs and H. M. Mayer, *Z. Kristallogr.*, 1995, **210**, 513.

54 M. Y. Chern, D. A. Vennos and F. J. DiSalvo, *J. Solid State Chem.*, 1992, **96**, 415.

55 D. Fruchart, E. F. Bertaut, R. Madar, G. Lorthioir and R. Fruchart, *Solid State Commun.*, 1971, **9**, 1793; D. Fruchart and E. F. Bertaut, *Physica*, 1977, **86–88B**, 423; *J. Phys. Soc. Jpn.*, 1978, **44**, 781.

56 R. Niewa, F. J. DiSalvo, D.-K. Yang, D. B. Zax, H. Luo and W. B. Yelon, *J. Alloys Comp.*, 1998, **266**, 32.

57 B. Holmberg, *Acta Chem. Scand.*, 1962, **16**, 255.

58 D. J. Siddons, S. E. Smith, M. G. Barker, A. J. Blake, P. P. Edwards, D. H. Gregory and T. A. Hamor, in preparation.

59 M. Y. Chern and F. J. DiSalvo, *J. Solid State Chem.*, 1990, **88**, 459.

60 G. Cordier, A. Gudat, R. Kniep and A. Rabenau, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 201.

61 A. Gudat, R. Kniep and J. Maier, *J. Alloys Comp.*, 1992, **186**, 339.

62 P. Höhn and R. Kniep, *Z. Naturforsch., Teil B*, 1992, **47**, 434.

63 (*a*) T. Yamamoto, S. Kikkawa and F. Kanamaru, *J. Solid State Chem.*, 1995, **115**, 353; (*b*) A. Gudat, S. Haag, R. Kniep and A. Rabenau, *J. Less-Common Met.*, 1990, **159**, L29.

64 H. Klassen and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1983, **497**, 70.

65 F. J. DiSalvo, S. S. Trail, H. Yamane and N. E. Brese, *J. Alloys Comp.*, 1997, **255**, 122.

66 J. Jäger and R. Kniep, *Z. Naturforsch., Teil B*, 1992, **47**, 1290.

67 A. Tennstedt and R. Kniep, *Z. Anorg. Allg. Chem.*, 1994, **620**, 1781.

68 A. Gudat, W. Milius, S. Haag, R. Kniep and A. Rabenau, *J. Less-Common Met.*, 1991, **168**, 305.

69 H. Jacobs and B. Hellmann, *J. Alloys Comp.*, 1993, **191**, 51.

70 D. H. Gregory, M. G. Barker, P. P. Edwards and D. J. Siddons, *Inorg. Chem.*, 1996, **35**, 7608.

71 V. Balbarin, R. B. Van Dover and F. J. DiSalvo, *J. Phys. Chem. Solids*, 1996, **57**, 1919.

72 P. S. Herle, M. S. Hegde, N. Y. Vasanthacharya, J. Gopalakrishnan and G. N. Subbanna, *J. Solid State Chem.*, 1994, **112**, 208.

73 P. S. Herle, N. Y. Vasanthacharya, M. S. Hegde and J. Gopalakrishnan, *J. Alloys Comp.*, 1995, **217**, 22.

74 D. S. Bem, H. P. Olsen and H.-C. zur Loye, *Chem. Mater.*, 1995, **7**, 1824; J. D. Houmes, S. Deo and H.-C. zur Loye, *J. Solid State Chem.*, 1997, **131**, 374.

75 S. Kaskel, D. Hohlwein and J. Strähle, *J. Solid State Chem.*, 1998, **138**, 154.

76 J.-P. Doumerc, A. Ammar, A. Wichainchai, M. Pouchard and P. Hagenmuller, *J. Phys. Chem. Solids*, 1987, **48**, 37.

77 W. Schnick and J. Lücke, *Z. Anorg. Allg. Chem.*, 1990, **588**, 19.

78 (*a*) O. Seeger, M. Hofmann, J. Strähle, J. P. Laval and B. Frit, *Z. Anorg. Allg. Chem.*, 1994, **620**, 2008; (*b*) D. H. Gregory, M. G. Barker, P. P. Edwards, M. Slaski and D. J. Siddons, *J. Solid State Chem.*, 1998, **137**, 62; (*c*) D. H. Gregory, M. G. Barker, P. P. Edwards and D. J. Siddons, *Inorg. Chem.*, 1998, **37**, 3775.

79 See for example: C. Delmas, C. Fouassier and P. Hagenmuller, *Mater. Res. Bull.*, 1976, **11**, 1483; C. Delmas, J.-J. Braconnier, C. Fouassier and P. Hagenmuller, *Z. Naturforsch., Teil B*, 1981, **36**, 1368.

80 D. H. Gregory, M. G. Barker, P. P. Edwards and D. J. Siddons, *Inorg. Chem.*, 1995, **34**, 3912.

81 W. Schnick and V. Schultz-Coulon, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 280.

82 F. K.-J. Helmlinger, P. Höhn and R. Kniep, *Z. Naturforsch., Teil B*, 1993, **48**, 1015; X. Z. Chen, H. A. Eick and W. Lasocha, *J. Solid State Chem.*, 1998, **138**, 297.

83 V. Schultz-Coulon and W. Schnick, *Z. Anorg. Allg. Chem.*, 1997, **623**, 69.

84 H. Jacobs and R. Niewa, *Eur. J. Solid State Inorg. Chem.*, 1994, **31**, 105.

85 J. Birx and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1990, **588**, 7.

86 D. A. Vennos, M. E. Badding and F. J. DiSalvo, *Inorg. Chem.*, 1990, **29**, 4059; D. A. Vennos and F. J. DiSalvo, *J. Solid State Chem.*, 1992, **98**, 318; A. Tennstadt, C. Röhr and R. Kniep, *Z. Naturforsch., Teil B*, 1993, **48**, 1831.

87 P. Höhn, R. Kniep and A. Rabenau, *Z. Kristallogr.*, 1991, **196**, 153; M. G. Barker, M. J. Begley, P. P. Edwards, D. H. Gregory and S. E. Smith, *J. Chem. Soc., Dalton Trans.*, 1996, 1.

88 D. H. Gregory, R. W. Strange and M. Slaski, in preparation.

89 G. Cordier, P. Höhn, R. Kniep and A. Rabenau, *Z. Anorg. Allg. Chem.*, 1990, **591**, 58; D. H. Gregory, M. G. Barker, P. P. Edwards and D. J. Siddons, *Inorg. Chem.*, 1995, **34**, 5195.

90 P. Höhn and R. Kniep, *Z. Naturforsch., Teil B*, 1992, **47**, 477.

91 P. Höhn, S. Haag, W. Milius and R. Kniep, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 831.

92 M. Y. Chern and F. J. DiSalvo, *J. Solid State Chem.*, 1990, **88**, 528; H. Yamane and F. J. DiSalvo, *J. Solid State Chem.*, 1995, **119**, 375.

93 (*a*) R. Benz and W. H. Zachariasen, *J. Nucl. Mater.*, 1970, **37**, 109; (*b*) S. Broll and W. Jeitschko, *Z. Naturforsch., Teil B*, 1995, **50**, 905; (*c*) R. Niewa, F. J. DiSalvo, H. Luo and W. B. Yelon, *Z. Naturforsch., Teil B*, 1998, **53**, 63.

94 H. Yamane and F. J. DiSalvo, *J. Alloys Comp.*, 1996, **234**, 203.

Paper 8/07732K