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Nitrides and Oxynitrides: Preparation, Crystal Chemistry and Properties

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Abstract

As compared to oxides, nitride-type compounds can have specific properties and applications. The outline of this review focuses on the crystal chemistry of nitrides and oxynitrides. Given the nitride–oxynitride association, this article mainly deals with compounds which are predominantly covalent in character and does not include compounds which are metallic in character and in which nitrogen can be considered as an interstitial element. The classification which is used thus highlights the two main coordination polyhedra: nitrided or oxynitrided tetrahedra or octahedra.

Nitride besitzen im Vergleich zu Oxiden spezielle Eigenschaften, die sie für bestimmte Anwendungen besonders geeignet erscheinen lassen. Dieser Artikel gibt einen Überblick über die Kristallchemie von Nitriden und Oxinitriden. Legt man die gesamte Bandbreite der Nitride–Oxinitride zu Grunde, so beschränkt sich diese Arbeit auf vorwiegend kovalent gebundene Verbindungen. Metallische Verbindungen, und solche die Stickstoff als Zwischengitteratome enthalten, werden nicht berücksichtigt. Die hier benüzte Einteilung basiert also auf den beiden hauptsächlich auftretenden Koordinationspolyedern: stickstoffhaltige oder stickstoff- und sauerstoffhaltige Tetraeder oder Oktaeder.

Les composés de type nitrure, comparativement aux oxydes, peuvent présenter des propriétés et des applications spécifiques. Cet article général a pour thème principal l'étude cristallochimique des nitrures et oxynitrures. Etant donné l'association nitrures–oxynitrures, le développement porte essentiellement sur les composés dans lesquels le caractère covalent est prédominant, excluant les composés à caractère métallique dans lesquels l'azote peut être considéré comme élément interstitiel. La classification adoptée met ainsi en évidence les deux principaux polyèdres de coordination rencontrés: tétraèdres et octaèdres azotés et oxyazotés.

1 Introduction

Nitrides are compounds which are formed by nitrogen with elements which are less electronegative than nitrogen itself. Nitride chemistry is extremely rich since nitrogen can be combined with most elements to give stable compounds. Although etymologically the French word 'azote' means 'without life' in Greek, nitrogen cannot be considered as chemically inert.

However, the great stability of the N_2 molecule should be mentioned, as compared, for example, to oxygen or to halogens, which are much more reactive. The enthalpy of dissociation, which is 226 kcal mol^{-1}, is about two times larger than that of the O_2 molecule; direct reaction with nitrogen is therefore sometimes difficult. This also implies that nitriding reactions are generally high-temperature reactions and that they often involve nitrogen-containing species, such as ammonia, which are more reactive than molecular nitrogen.

The nature of the obtained phases shows the specific location of nitrogen in the periodic table, where it acts as an intermediate element which can have similarities with such or such a neighboring element. On the one hand, nitrogen belongs to group V; but it is often clearly different from the other elements located in the subsequent periods, i.e. phosphorus and arsenic, because of its higher electronegativity and of its lack of *d* orbitals. On the other hand, nitrogen occurs after carbon and before

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oxygen in the second period. Thus, it will sometimes form compounds which are similar in their structure and physical or chemical properties to carbides. This can be observed mainly with the transition element nitrides, which show metallic behavior and in which the nitrogen atoms are located interstitially in the metal structure. At other times, nitrides show similarities with oxides: this is illustrated by the fact that oxynitrides can be obtained. Such nitrides and oxynitrides have an ionocovalent character, the ionic character being all the more significant, since the elements associated with nitrogen are more electropositive. (For covalent oxynitrides, both crystalline compounds and vitreous phases can be obtained.) This shows the diversity of nitride-type phases which exist and the richness of their physicochemistry.

Classification of nitrides as metallic, covalent or ionic compounds takes into account the dominating type of bond involved. It is found most often that more than one type of bond can exist, in particular in ternary compounds. Generally speaking, this article will not treat compounds which are metallic in character; transition metal nitrides along with the corresponding carbides have already been discussed, especially in the monograph by Toth.[1]

For the ionocovalent compounds, there are two general techniques used to maintain the electroneutrality when one considers the substitution of oxygen by nitrogen in an oxide. In the first method, the cationic network is not modified and three oxygen atoms are replaced by two nitrogen atoms:

$$2N^{3-} = 3O^{2-}$$

With the second method, each nitrogen atom which is introduced is compensated by a cation having a higher oxidation state. This cross-substitution maintains the same general stoichiometry:

$$N^{3-} + M^{(n+1)+} = O^{2-} + M^{n+}$$

Thus, after total or partial replacement of oxygen by nitrogen, the same structural type can be maintained, but the cross-substitution often yields significant modifications concerning the physical and chemical characteristics of the new compound which has been obtained.

Since their preparation requires certain precautions to be taken, the studies concerning nitrides and oxynitrides have not been as systematic as studies regarding other families, such as oxides. Thus, the development of new nitride-type materials first requires the perfecting of synthesis techniques, and chemical and structural characterizations. Such steps are indispensable before carrying out the study and the implementation of their different physical properties.

2 Preparation

In this article only two basic methods for the preparation of these compounds are described. They both resort to a gas + solid reaction.

The first method consists in synthesizing a nitride through the direct combination of elements. This method must be used with electropositive metals such as rare earth metals. The nitriding temperature is generally between 800 and 1200°C and depends on the mutual reactivity of both elements. The difficulty in preparing these nitrides lies mainly in the precautions which need to be taken, since traces of both moisture and oxygen must be avoided. At a given temperature, the reactivity of an element for oxygen is always greater than that for nitrogen. Thus, under nitriding conditions, a very low oxygen partial pressure is enough to irreversibly cause the displacement of nitrogen and the formation of an oxygenated product.

The second method concerns the reaction of ammonia with an oxide. This process can be used to prepare both nitrides and oxynitrides. Ammonia acts both as a reducing and as a nitriding agent. The reaction is carried out in flowing gas, and not under a static atmosphere as in the first method. The rate of ammonia flow depends on the temperature of the reaction: the higher the temperature, the higher the rate, because the dissociation of NH_3 into nitrogen and hydrogen must be minimized before there is any contact with the product. It has been shown that an equivalent mixture of nitrogen + hydrogen has no effect on oxides under the same conditions. The general equation is:

$$MO_x + NH_3 \rightarrow MN_y + H_2O\uparrow$$

It is clear that the reaction is not total: part of the ammonia is dissociated, and nitrogen and hydrogen coming from this dissociation help drive away the water produced by the reaction. Furthermore, with the in-situ production of water, it is not necessary to dry the ammonia. This method, which uses, from a thermodynamic point of view, an out-of-equilibrium reaction, is especially well-suited for the nitriding of refractory oxides. It was shown that, for example, from an amorphous silica having a large surface area, it is possible to prepare silicon oxynitride Si_2N_2O (at 900–1000°C) and silicon nitride Si_3N_4 (at 1200–1250°C). The latter then only crystallizes in its low-temperature modification.[2,3]

Recently, a preparation process for aluminum nitride (AlN) has been developed using this method. This process allows a highly pure nitride to be obtained by the reaction of ammonia (flow of about 15 liters h^{-1}) on alumina between 1100 and 1350°C.[4]

Comparatively, the traditional process, which involves the carbothermal reduction and nitriding of alumina, as illustrated by the following equation:

$$Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO\uparrow$$

gives, between 1600 and 1800°C only, a nitride which is nitrogen deficient. Furthermore, the product still shows traces of carbon and aluminum carbide which are detrimental to the qualities of the material, especially its thermal conductivity and its dielectric constant and losses.

Another example is the preparation of stoichiometric titanium nitride (TiN) from titanium oxide:

$$3TiO_2 + 4NH_3 \rightarrow 3TiN + 6H_2O\uparrow + \tfrac{1}{2}N_2\uparrow$$

Finally, this method also allows ternary oxynitrides to be prepared such as $BaTaO_2N$ having a perovskite structure[5] according to:

$$2BaCO_3 + Ta_2O_5 + 2NH_3 \xrightarrow{1000°C} 2BaTaO_2N + 2CO_2\uparrow + 3H_2O\uparrow$$

Thus, it is a useful method which makes synthesis of a large number of oxynitrides or nitrides from oxides possible.

3. Analysis

In association with X-ray diffraction analysis, determining nitrogen content by means of a direct analytical method is often essential in order to determine the composition of reaction products or their purity. Several factors may cause nitrogen deficiency, particularly when nitride-type compounds result from a direct solid–gas reaction. It may be seen that, for example, nitrides having an ionic character are sensitive to atmospheric moisture. It is also clear that in all cases the reactivity of nitrides and oxynitrides with oxygen generally occurs at a relatively low temperature, as was previously mentioned.

The principle of the chemical analysis of nitrogen is based on the reaction of the nitride ion N^{3-} with a strong base and the formation of ammonia which is then titrated. In the traditional Kjeldahl method, the alkaline attack occurs in solution. But in some cases, with refractory nitrides such as silicon nitride or sialons, the products are not attacked under these conditions. This has been solved by using the same principle but by reacting the product at high temperature with melted potassium hydroxide.[6]

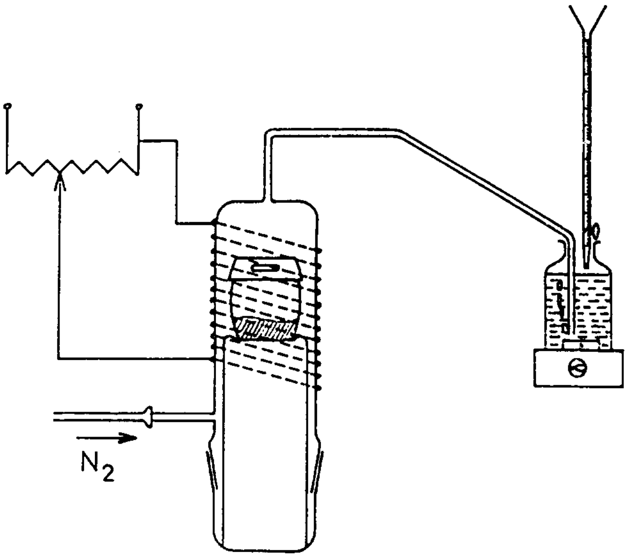

Fig. 1. Apparatus for nitrogen determination.[6]

The apparatus shown in Fig. 1 is used. The crucible containing the reaction mixture is made of alumina. The furnace is a glass tube on which a resistor is coiled. This resistor is embedded in a refractory cement which gives thermal inertia. The reaction must take place in an inert and dry atmosphere. This condition is satisfied by preheating the furnace under nitrogen flow. The reaction mixture (20–30 mg sample + several grams of potassium hydroxide) is then heated to a temperature of about 400°C. The released ammonia, which is carried away by the nitrogen flow, is neutralized by 0·02 N sulfuric acid. When it is properly conducted, the method allows the nitrogen to be determined with a 1% precision scale.

Determination of the nitrogen content may be accomplished indirectly. This determination consists in measuring the weight variation of a sample which has been transformed into oxide by heating under oxygen, while nitrogen is released in molecular form:

$$MN_x + y/2O_2 \rightarrow MO_y + x/2N_2\uparrow$$

If there is no change in the oxidation state of the element(s) which is (are) associated to nitrogen, the release of a mole of nitrogen corresponds to the fixation of 1·5 moles of oxygen. As a result, there is a weight increase of about 20 g per mole of released N_2 nitrogen. Conversely, when a nitride or an oxynitride is prepared by reacting ammonia with an oxide, the corresponding weight loss may be used to determine the nitrogen content of the product which has been obtained.

Another important point concerns the structural analysis of oxynitrides. X-ray diffraction does not allow oxygen and nitrogen to be distinguished because of the very close values of their atomic scattering factors. However, neutron diffraction is an interesting method for the study of oxynitrides because the Fermi lengths of these two elements—$b(\mathrm{O}) = 0{\cdot}58 \times 10^{-12}$ cm, $b(\mathrm{N}) = 0{\cdot}94 \times 10^{-12}$ cm—are different enough to allow detection of structural order between oxygen and nitrogen atoms.

In particular, the time-of-flight neutron diffraction method has many advantages including:

- —an excellent resolution which allows very small lattice distortions to be detected;
- —a highly reduced background thanks to the use of a statistic correlation chopper;[7]
- —the recording of a large number of diffraction lines, in particular with the small interplanar distances, since the method is not subjected to the limit condition $d = \lambda/2$;
- —the possibility to process data with a Rietveld program, which is all the simpler since neutron diffraction lines have a Gaussian profile.

4 Crystal Chemistry and Properties

There are many ways of classifying binary and ternary nitrides and oxynitrides from a crystallochemical point of view. Compounds in which there is only one element besides nitrogen and oxygen are called binary nitrides and oxynitrides. The following discussion, which is not exhaustive, describes the principal arrangements which have been observed. The compounds have been divided into two main groups: ionic nitrides, and covalent nitrides and oxynitrides. A description of the structures in terms of anion packing is better adapted to compounds having an ionic character, whereas very stable structural units made up of coordination polyhedra, such as tetrahedra and octahedra, are present in covalent compounds.

The presentation will thus necessarily be incomplete, since nitride-type compounds whose structure is unknown or is not related to a given structure type will not, for matters of simpification, be presented. In this respect, it must be added that nitrides and oxynitrides are generally compounds which cannot easily be obtained as single crystals.

4.1 Ionic nitrides

The main characteristic of ionic nitrides is their sensitivity to hydrolysis. When they are left unprotected, they quickly lose nitrogen in the form of ammonia. This sensitivity to atmospheric moisture thus imposes very strict conditions for their practical use.

Binary nitrides with an essentially ionic character involve elements such as lithium, alkaline earth elements and lanthanides.

Lithium is the only alkaline element which presents a stable binary nitride. Li_3N is a purely ionic compound containing N^{3-} ions, which are stabilized by the Li^+ ion environment.[8] It has a particular structure made up of Li_2N layers, which are perpendicular to the *c* axis of the hexagonal unit cell and which are linked to one another by lithium atoms, which occupy the sites formed by the nitrogen atoms[9,10] (see Fig. 2). The mobility of Li^+ ions gives Li_3N ionic conductor properties.[11,12]

Nitrides of group IIa elements such as Be_3N_2[13] Mg_3N_2[14] and Ca_3N_2[15] have an anti-bixbyite structure (anti-Mn_2O_3) which is derived from Na_2O. Nitrogen atoms form a cubic close-packed network and divalent ions occupy three-quarters of the tetrahedral sites of the anionic network. Be_3N_2 also exists in a high-temperature form where the beryllium coordination is also tetrahedral.[16]

Besides these nitrides, which may be described as 'normal', more particular stoichiometries are known for alkaline-earth elements. Notably, SrN[17] has a NaCl structure. The structures of Ca_2N[18] and Sr_2N[17,19] are also derived from that of NaCl, since they present the anti-$CdCl_2$-type structures, as in Cs_2O:[20]. This structure is a layer structure where half of the (111) planes containing nitrogen are empty, as compared to NaCl. Upon hydrolysis, all the nitrogen of SrN is not released as ammonia; one part of it leads to the formation of hydrazine (N_2H_4).[21] Finally, nitrides of lanthanides (LnN) have an arrangement of the NaCl type.

Ternary nitrides with an ionic character, the structures of which are known, are mainly lithium-containing nitrides. They are distributed into two structural families. The compounds of the first family are more numerous. Their general formulation is $Li_{2n-3}M_nN_{n-1}$, with the oxidation state *n* of the metal M ranging from II to VI. The structure of

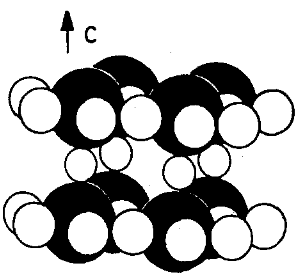

Fig. 2. A packing drawing of the structure of Li_3N. Smaller circles are the lithium atoms.[10]

these nitrides is of the Na_2O type, i.e. anti-fluorite. The tetrahedral sites of the cubic face-centered network formed by nitrogen atoms are occupied by cations, generally in an ordered way. Thus, for example, the following nitrides exist: LiMgN, LiZnN,[22] Li_3AlN_2, Li_3GaN_2,[23] Li_5SiN_3, Li_5TiN_3,[24] Li_7VN_4,[25,26] Li_7MnN_4,[26] Li_9CrN_5.[27] It should be noticed that in these ternary nitrides transition elements have a high oxidation state, in contrast to the corresponding binary nitrides. For example, chromium only forms CrN and Cr_2N combinations with nitrogen. With the anti-fluorite oxide Li_2O, several of these nitrides lead to the formation of solid solutions.

The second structural family is illustrated by nitrides such as Li_2ZrN_2[28] and Li_2CeN_2,[29] which have an anti-La_2O_3 structure, i.e. nitrogen atoms are hexagonal close-packed, with lithium atoms in tetrahedral sites and the atoms of the other metal in octahedral sites.

The new ternary nitride Ca_2ZnN_2[30] does not adopt the anti-bixbyite structure of the binary nitrides Ca_3N_2 and Zn_3N_2. It is isostructural with Na_2HgO_2[31] and Na_2PdH_2[32] and its structure is based on condensed nitrogen-centered metal octahedra with an unusual linear coordination of Zn by two nitrogen atoms.

4.2 Covalent nitrides and oxynitrides

Binary compounds: A significant covalent character may be seen in binary nitrides and oxynitrides which are formed by group III elements such as boron, aluminum or gallium, by group IV elements such as silicon or germanium, and by group V elements such as phosphorus. For group V, and above all for group VI with sulfur nitrides, molecular compounds may be found; however, this study will not discuss them.

The combination of boron and nitrogen is isoelectronic with carbon. It is thus not surprising that one of the modifications of boron nitride (BN) has a structure which is close to that of graphite. When this phase is heated under high pressure, the cubic modification of the zinc blende type may be obtained, such a form being equivalent to the diamond structure for carbon.[33]

AlN and GaN nitrides crystallize in the wurtzite-type structure. Thus, they have a 'normal' tetrahedral structure[34] in which each atom of metal is tetrahedrally coordinated by four atoms of nitrogen and vice versa.

Aluminum nitride is currently being studied in detail, since, in the field of electronics, it represents a particularly well-adapted material as a ceramic for power circuits and as a substrate for VLSI technology and for high-density circuits. The development of integrated circuits requires the perfecting of new ceramics for substrates having a high thermal conductivity λ. From this point of view, AlN is one of the ten known non-metallic materials which have a λ value more than $100\,W\,m^{-1}\,K^{-1}$. Moreover, it has a thermal expansion coefficient which is close to that of silicon within the range of 0 to 1000°C. It also has an electrical resistivity which is nearly the same as that of alumina. Table 1 shows several physical characteristics of aluminum nitride compared to those of other ceramics.

Different phases known as 'alons' can be obtained by reaction between alumina and aluminum nitride.[35,36] These alons can also be prepared from precursor mixtures obtained by nitridation of alumina by ammonia.[37] The γ-aluminum oxynitride has a spinel structure and a defect cationic network as compared to the Al_3O_3N stoichiometric composition. Aluminum atoms thus occupy either tetrahedral sites, or, in a disordered way with vacancies, octahedral sites of a cubic close-packed network formed by oxygen and nitrogen atoms.[38,39]

This γ-aluminum oxynitride may be sintered in the form of ceramics which are transparent up to $5{\cdot}2\,\mu m$,[40] thus forming a very interesting new material. Thanks to its optical transparency, good

Table 1. Characteristics of aluminum nitride in comparison with other ceramic materials

Physical properties	*AlN*	*Al_2O_2*	*BeO*	*SiC*
Thermal conductivity of ceramics, $W\,m^{-1}\,K^{-1}$	100–200	20	150–200	100–200
Thermal conductivity of single crystal, $W\,m^{-1}\,K^{-1}$	320	25	370	490
Thermal expansion coefficient between 100 and 500°C, $\times 10^{-6}\,°C^{-1}$	4·5	7·3	8·0	3·7
Resistivity at 25°C, $\Omega\,cm$	$>10^{14}$	$>10^{14}$	$>10^{14}$	$>10^{13}$
Dielectric constant at 1 MHz	8·8	8·5	6·5	40
Dielectric losses at 1 MHz, $\times 10^{-4}$	5–10	3	5	50–500
Dielectric rigidity, $kV\,mm^{-1}$	14–17	10	10–14	0·07
Time constant, $\times 10^{-12}\,s\,cm^{-1}$	100	97	85	211
Density, $g\,cm^{-3}$	3·26	3·8	2·9	3·2
Sintering temperature, °C	1 800	1 500	2 000	2 000
Young's modulus, $10^{12}\,dyn\,m^{-2}$	2·81	3·7	3·2	4·0

mechanical behavior and isotropic properties due to its structure, it can thus advantageously replace alumina in many ceramic applications.[41]

Besides the wurtzite hexagonal form, GaN may also be obtained in the zinc blende cubic form.[42] More particularly, by the action of ammonia on various gallates of transition elements and then by purification by means of a suitable chemical treatment, an oxynitride phase $Ga_{1-x/3}N_{1-x}O_x$ ($x \sim 0{\cdot}1$) is prepared. Its structure is that of a polytype with mixed hexagonal and cubic close-packing.[43]

Silicon gives the α- and β-modifications of Si_3N_4 and the Si_2N_2O. Equivalent compounds of germanium are isotypical. For the α- and β-forms of the nitride, silicon is tetrahedrally surrounded by nitrogen, whereas the latter has a planar triangular coordination. The α-form[44] (see Fig. 3) has a lower symmetry than the β-form,[45] which is isostructural with phenacite (Be_2SiO_4).

Si_2N_2O has a defect tetrahedral structure which is derived from that of the wurtzite type and in this review is denoted □ Si_2N_2O. Around the silicon there is a formation of mixed $[SiON_3]$ tedrahedra.[46]

It is a well-known fact that, as a result of its refractory properties, Si_3N_4 is the basic material of thermomechanical nitrogen ceramics. In 'sialons', some of the silicon atoms are replaced by aluminum atoms, with an equivalent oxygen/nitrogen exchange. Their structure is thus built up from tetrahedral $[(Si, Al)(O, N)_4]$ structural units.[47]

Whereas phosphorus nitride (P_3N_5) is not well known from a structural point of view, the oxynitride (PON) which is isoelectronic with SiO_2 has a three-dimensional structure of the β-cristobalite type.[48,49] Phosphorus atoms are located at the center of mixed $[PO_2N_2]$ tetrahedra, as shown in Fig. 4.

An α-quartz-type modification has also been obtained under high pressure (45 kbar, 700°C).[50,51]

The possibility of preparing thin insulating layers of phosphorus oxynitride for the surface passivation of group III–V semiconductors—in particular indium phosphide (InP)—has also been studied.[52]

Ternary compounds: In this class of compounds it is easier to draw a parallel with oxides. The substitution of oxygen by nitrogen can be carried out if a cationic element having a given oxidation

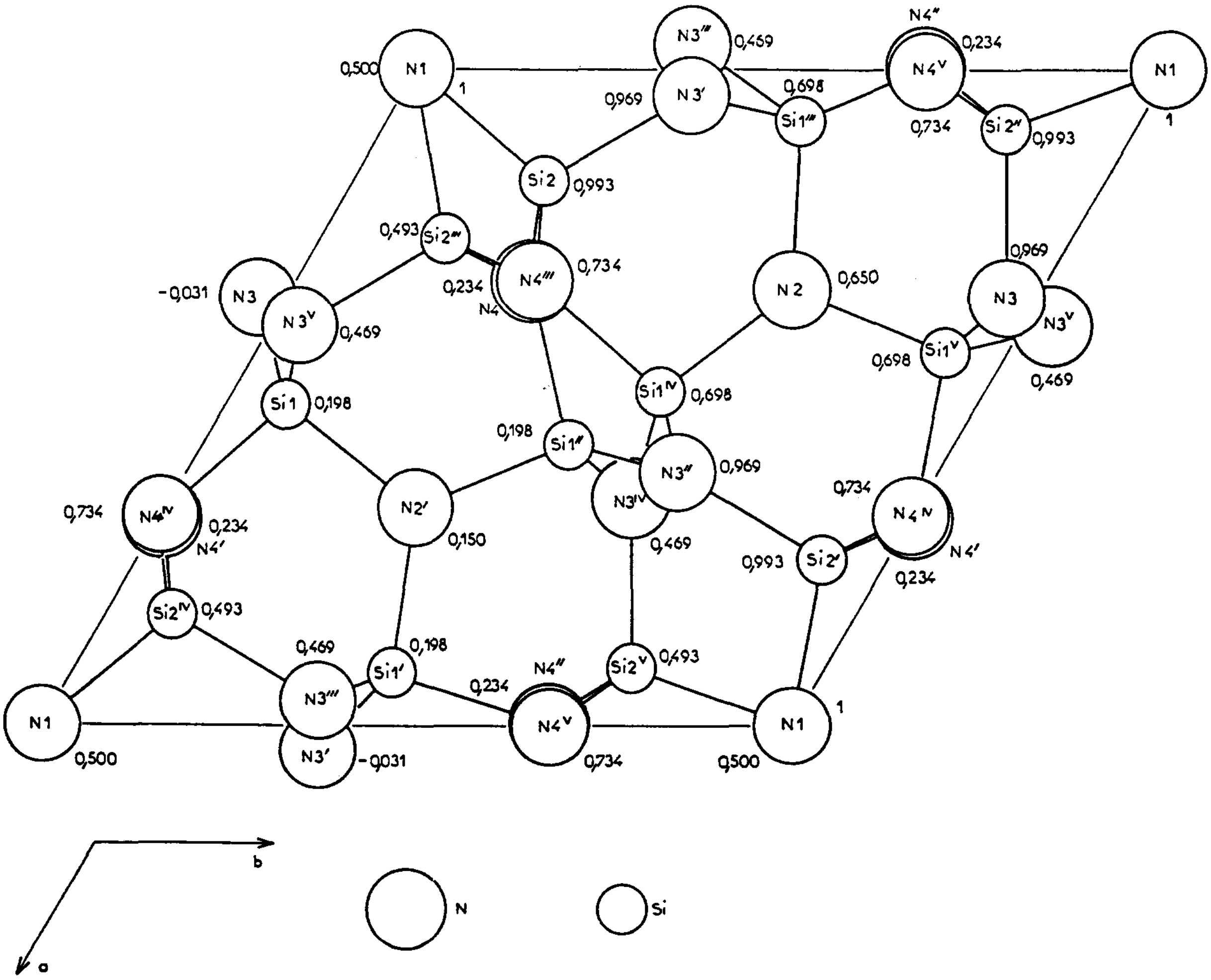

Fig. 3. Projection of the hexagonal structure of α-Si_3N_4 along the c axis.[44]

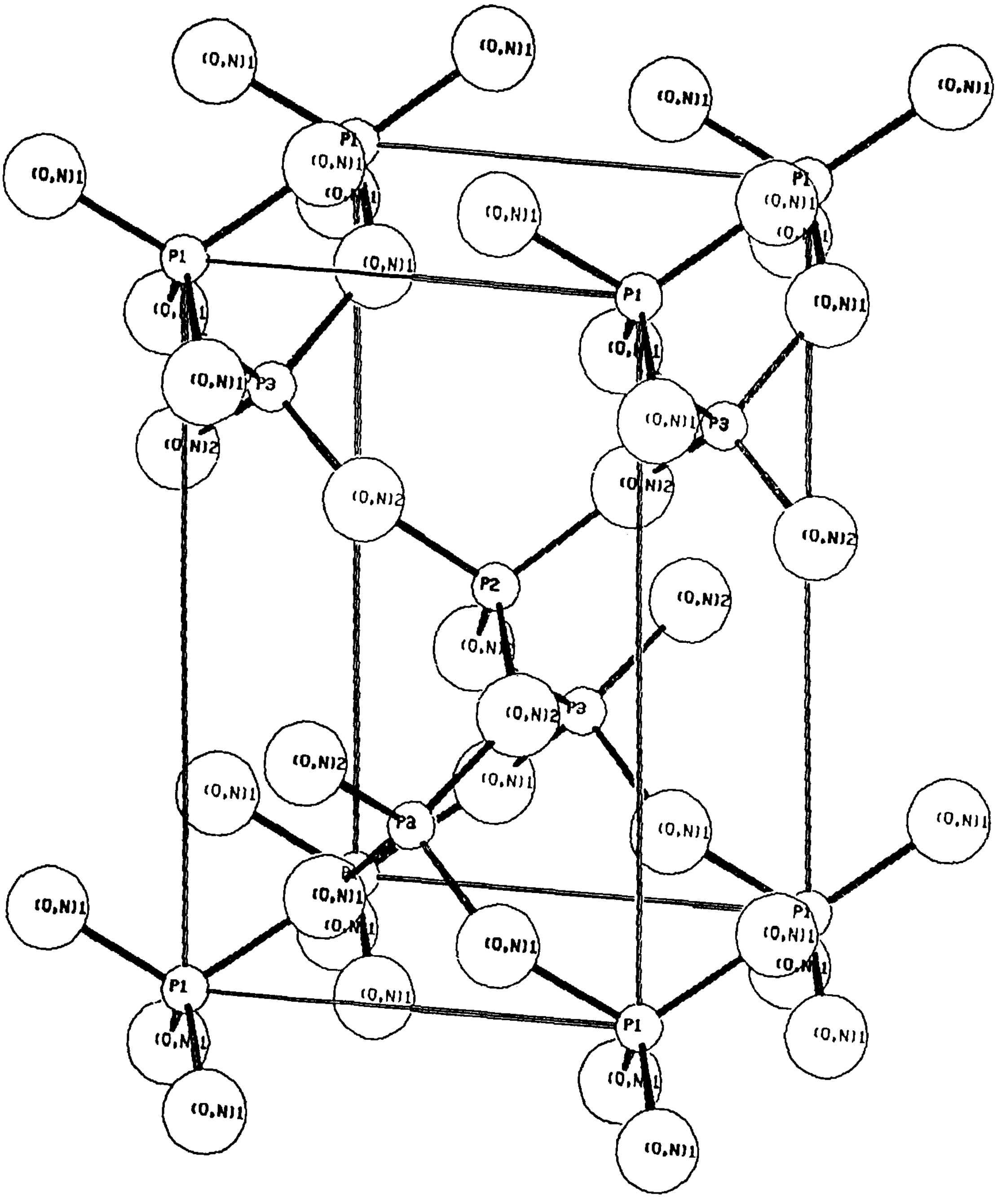

Fig. 4. Perspective view of the PON structure.[49]

state is replaced by another element having a higher oxidation state. If the same structural type is to be kept, the size of the different elements must be taken into account. A typical example is the substitution of calcium by a lanthanide atom, which allows one oxygen atom to be replaced by one nitrogen atom. This can be summarized by the following equation:

$$Ln^{3+} + N^{3-} = Ca^{2+} + O^{2-}$$

It may also be noted that, whereas the partial substitution of oxygen by nitrogen can be seen in a great number of structure examples, total substitution is not as frequent. The only known cases concern the wurtzite structure, and the cristobalite structure, and recently the sodium chloride structure with the new nitride $NaTaN_2$.[53] This may be explained by the high value of reticular energy, which compensates for the energy difference which exists between the Me–N bond and the Me–O bond, because electronegativity is lower for nitrogen than for oxygen.

The high value of the structure's reticular energy also explains the existence of stable compounds having sodium–nitrogen bonds such as NaSiON, NaGeON, $NaGe_2N_3$, $NaPN_2$ and even potassium–nitrogen bonds such as KGeON, whereas these bonds are very unstable or do not exist in corresponding alkaline binary nitrides.

4.2.1 Tetrahedral environment

4.2.1.1 Wurtzite-type structure (with Si, Ge or P as coordinating element). As already seen, aluminum nitride is an example of a binary nitride having a wurtzite-type structure. The structure of AlN is made up of the hexagonal close-packing of nitrogen atoms, aluminum atoms regularly occupying half of the tetrahedral sites. Within this arrangement, nitrogen atoms are also tetrahedrally surrounded by four aluminum atoms. The valence electron concentration must be equal to 4 so that the normal tetrahedral structure can exist.[34] The valence electron concentration (VEC) is defined as the ratio between the sum of valence electrons of the different atoms and the sum of atoms.

The VEC = 3 rule also holds when cross-substitutions are carried out. For example, the cationic network for aluminum atoms may be substituted, i.e. two atoms of group III may be replaced by one atom of group II and by one atom of group IV. This filiation can be symbolized by:

$$3\,5 \rightarrow 2\,4\,5_2$$
$$\mathrm{AlN} \rightarrow \mathrm{MgSiN_2}$$

Concerning the ternary nitride $MgSiN_2$, magnesium and silicon atoms are at the center of the nitrogen tetrahedra, whereas nitrogen atoms are tetrahedrally coordinated by two magnesium and two silicon atoms.

The following examples make up the family of known 245_2 nitrides: $BeSiN_2$,[54] $MgSiN_2$,[55,56] $MnSiN_2$,[57,58] $MgGeN_2$,[55] $MnGeN_2$,[57,59] $ZnGeN_2$.[60-62] In these compounds cations are ordered so that the crystalline symmetry is no longer hexagonal, as in the wurtzite, but orthorhombic, as shown in Fig. 5.

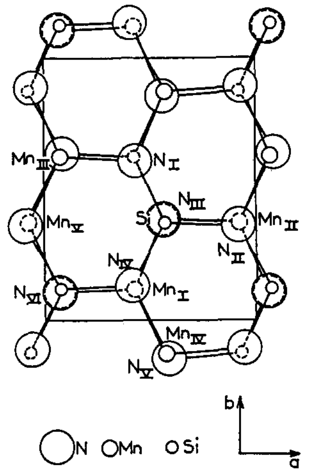

Fig. 5. The structure of orthorhombic $MnSiN_2$ projected along the c axis.[57]

The VEC = 4 rule is also obtained with the following simple formulations:

—14_25_3 examples: $LiSi_2N_3$ and $LiGe_2N_3$,[63] $NaGe_2N_3$.[64]

Tetrahedral environment of the atoms (for $LiSi_2N_3$):

Li: 4N — N_1: 2Li + 2Si
Si: 4N — N_2: 1Li + 3Si

—2_255_3 examples: Mg_2PN_3,[65(a)] Mn_2PN_3[65(b)] and Zn_2PN_3 (Jullien, H. & Marchand, R., pers. comm.) 1983.

Tetrahedral environment of the atoms (for Mg_2PN_3):

Mg: 4N — N_1: 2Mg + 2P
P: 4N — N_2: 3Mg + 1P

2_255_3 nitrides are isostructural with 14_25_3 nitrides, with lithium in $LiSi_2N_3$ being the equivalent of phosphorus in Mg_2PN_3. Figure 6 displays the ordered arrangement and the orthorhombic unit cell of Mg_2PN_3.

—1465 examples: LiSiON,[66,67] NaSiON and NaGeON,[68] KGeON.[69] In this case, the anionic sub-network contains both nitrogen and oxygen.

Tetrahedral environment of the atoms (for LiSiON):

Li: 3O + 1N — O: 3Li + 1Si
Si: 2N + 1O — N: 1Li + 3Si

With the KGeON oxynitride, and given the size of potassium, the tetrahedral environment becomes distorted and a coordination number of 5 is found. The tetrahedron thus becomes a triangular pyramid made up of 1N and 4O. Figure 7 compares the environments in LiSiON and KGeON, showing the deformation of the ideal structure.

In the case of the Li–Ge–O–N system,[70] a solid solution has been obtained, the formulation of which is $Li_{1+x}Ge_{2-x}O_{3x}N_{3-3x}$. This solid solution

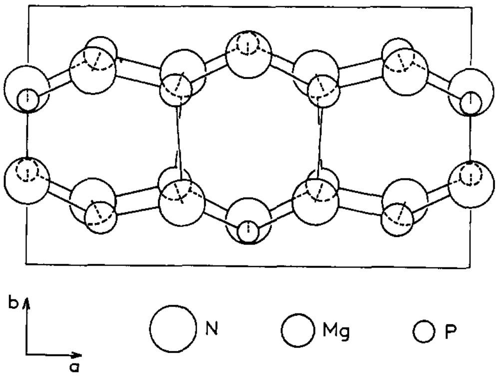

Fig. 6. Projection along the c axis of the orthorhombic Mg_2PN_3 structure.[65(a)]

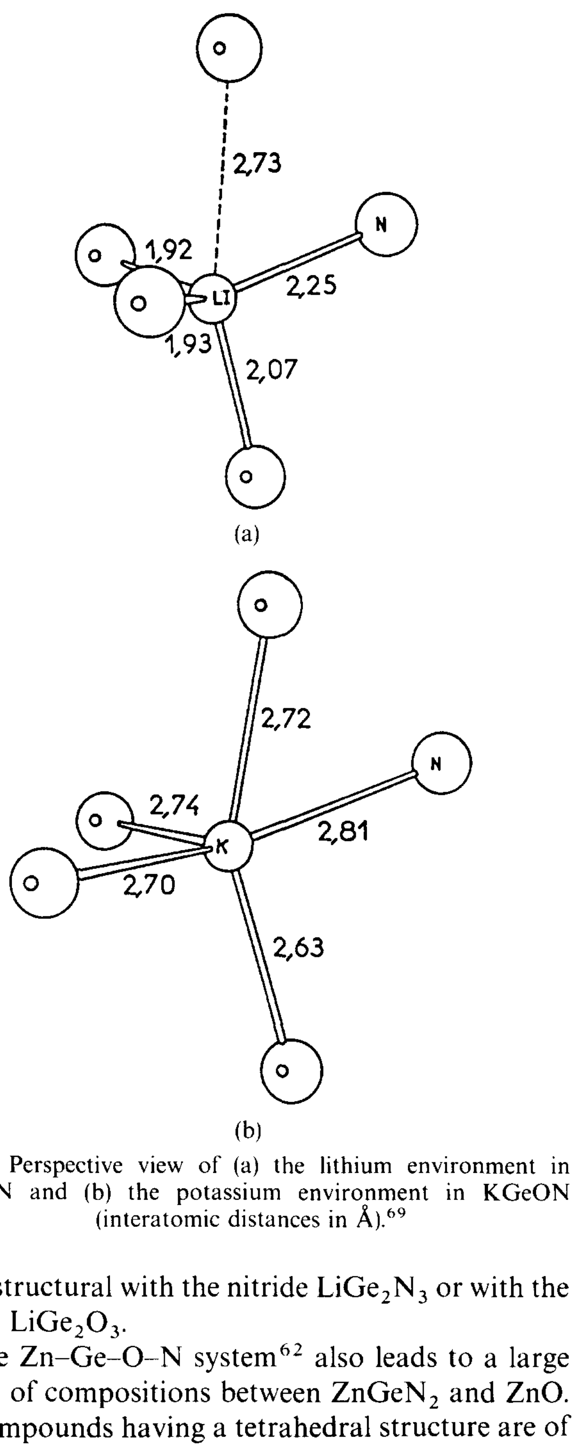

Fig. 7. Perspective view of (a) the lithium environment in LiSiON and (b) the potassium environment in KGeON (interatomic distances in Å).[69]

is isostructural with the nitride $LiGe_2N_3$ or with the oxide $LiGe_2O_3$.

The Zn–Ge–O–N system[62] also leads to a large range of compositions between $ZnGeN_2$ and ZnO.

Compounds having a tetrahedral structure are of interest because some of them have semi-conducting properties. The semi-conducting properties of the phases of the Zn–Ge–O–N system (n-type, gap ~2·7 eV) have thus been used in gas absorption studies. These oxynitrides strongly chemisorb oxygen, which acts as an electron acceptor trap and which modifies the electrical resistance of the samples. More specific tests have been carried out, aiming at an application in the field of gas sensors. These oxynitrides prove to be selective detectors for ammonia.[71] Gallium oxynitrides, which have already been mentioned, could also be interesting in this field.[72] It should be noted that, like GaN and Zn–Ge–O–N oxynitrides, the bianionic compound Zn_2NF[73] is also isoelectronic with ZnO.

4.2.1.2 Cristobalite-type structure (with Ge or P as coordinating element). The cristobalite structure is made up of a three-dimensional network of $[SiO_4]$ tetrahedra which share their four corners. Silicon atoms occupy the position of carbon atoms in the diamond structure. Within this arrangement, some holes exist, which can be occupied by a second cation. This second cation ensures the electrical neutrality when oxygen is replaced by nitrogen in the anionic network. The compound $CaGeN_2$ thus shows a 'filled' cristobalite structure. Similarly, in $LiPN_2$[75,76] and $NaPN_2$ (Marchand, R., unpublished), M^+ ions compensate the charge of the $[PN_2]^-$ skeleton, whereas for the PON oxynitride, the PO_2N_2 tetrahedra are neutral *per se*. The charge transfer between lithium and the network has been characterized for $LiPN_2$.[77,78] Figure 8 shows the location of Li^+ ions within the $[PN_4]$ tetrahedra network.

4.2.1.3 Scheelite-type structure (with Os or W as coordinating element). It is a well-known fact that the O^{2-} ligand can stabilize high oxidation states of transition elements for tetrahedral oxygenated anions. This is the case for V^V in the $[VO_4]^{3-}$ vanadate ion, of Cr^{VI} or W^{VI} in $[CrO_4]^{2-}$ chromate or $[WO_4]^{2-}$ tungstate ions, and this is also the case with Mn^{VII} in the $[MnO_4]^-$ permanganate ion.

With Os^{VIII} and the $[OsO_4]^0$ tetrahedra, the maximum oxidation state exists in a stable molecular compound.

The aqueous solution of OsO_4 reacts with ammoniacal silver chloride and, after replacement of

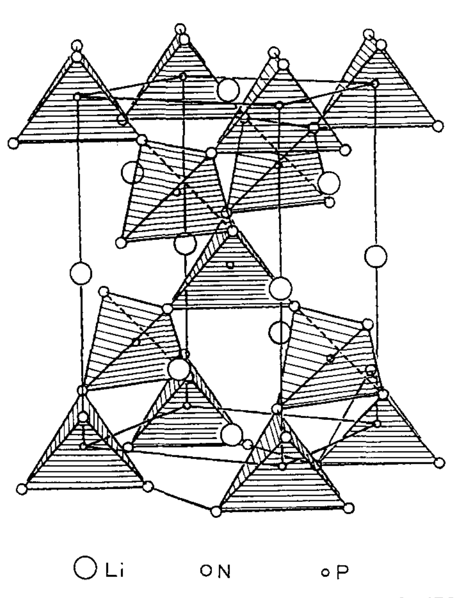

Fig. 8. Perspective view of the structure of $LiPN_2$.[75]

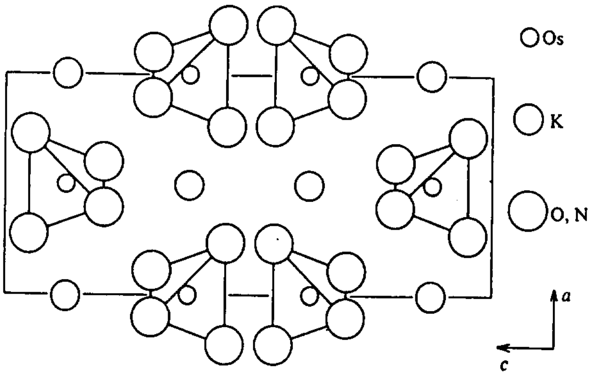

Fig. 9. The tetragonal structure of $KOsO_3N$ projected along its *b* axis.[79]

Ag^+ by K^+, it is possible to obtain the nitrido-osmate $KOsO_3N$. The structure of the latter is a $CaWO_4$ scheelite-type structure, which is made up of $[OsO_3N]$ isolated tetrahedra which are linked to each other by the K^+ cations, the coordination number of which is equal to 8 (Fig. 9). The structural study of this compound has shown that an oxygen–nitrogen order does not exist in the $[OsO_3N]$ tetrahedron.[79]

When potassium is replaced by rubidium, the $RbOsO_3N$ metallate is obtained, the structure of which is a $CsReO_4$-type structure which is very similar to the scheelite type. The oxygen–nitrogen arrangement is also disordered in $RbOsO_3N$.[80]

Now, if calcium in $CaWO_4$ scheelite is replaced by a lanthanide atom, taking into consideration the cross-substitution:

$$Ln^{+III} + N^{-III} = Ca^{+II} + O^{-II}$$

the oxynitride family having the formulation $LnWO_3N$ (Ln = Nd, Sm, Gd, Dy) is obtained, which also has the scheelite structure.[81] They are not prepared in an aqueous solution, like osmium compounds, but rather by heating the corresponding tungstates having the $Ln_2W_2O_9$ composition in an ammonia atmosphere at 700–750°C. The behavior of these oxynitrides is perfectly consistent with the presence of tungsten in oxidation state VI, which is thus stabilized in a tetrahedral site. Yet the two facts were *a priori* unfavourable for the conservation of the oxidation state VI of tungsten: the ammonia environment during the preparation which presents a rather reducing character, and the fact that W is surrounded by nitrogen atoms. As a matter of fact, there is no corresponding nitride in the tungsten–nitrogen binary system, where only WN and W_2N are known.

4.2.1.4 Barytine-type structure (with Os as coordinating element). An example of oxynitride having a structure of the $BaSO_4$ type is given by the $CsOsO_3N$ compound. Cs^+ ions have a coordination number equal to 10. Unlike the preceding nitrido-osmates, the oxygen–nitrogen arrangement is ordered in the $[OsO_3N]$ tetrahedra with a shorter and thus stronger bond between osmium and nitrogen than between osmium and oxygen.[82]

4.2.1.5 Silicate derived structures (with Si as coordinating element). The structural unit of silicates is made up of the $[SiO_4]$ tetrahedron. Tetrahedra can be either isolated or associated in a more or less complex way. The cohesion between these tetrahedra is ensured by cations. The configuration is identical with phosphates and alumino-silicates. In this latter case, aluminum partly replaces silicon in the tetrahedral sites.

From a crystallochemical point of view, silicates present a rather large field of investigation concerning the nitrogen/oxygen substitution. The replacement of oxygen by nitrogen in an $[SiO_4]$ tetrahedron increases the negative formal charge of the tetrahedron. Neutrality is obtained by increasing the cationic charge, and in many examples a lanthanide element is used to replace an alkaline earth element. The size of lanthanide ions is similar to that of alkaline earth ions, and with nitrogen they yield strong bonds.

Apatite type: Apatites, the representative material of which is the fluorapatite $Ca_{10}(PO_4)_6F_2$, constitute a large family of compounds which correspond to various cationic and anionic substitutions. The introduction of nitrogen into the anionic sub-network increases the substitution possibilities even more.

Although their formulation is comparable to that of fluorapatite, the oxynitrides $Ln_{10}Si_6O_{24}N_2$ (Ln = La, Ce, Nd, Sm, Gd and Y)[83–85] and $Ln_8Cr_2Si_6O_{24}N_2$ (Ln = La–Dy)[83] are different because nitrogen atoms are not located in the same crystallographical position as fluorine atoms, which are placed in a so-called 'tunnel' position. On the contrary, nitrogen atoms are part of the silicon environment, thus forming $[SiO_{4-x}N_x]$ mixed tetrahedra.[86,87] Figure 10 shows the $Sm_{10}Si_6N_2O_{24}$ structure. More than two nitrogen atoms per unit cell can thus be introduced. This has been shown with, for instance, $Ln_8M_2^{IV}Si_6N_4O_{22}$ (M^{IV} = Ti or Ge) nitrided apatites, the maximum enrichment being obtained by a V^V-containing composition, i.e. $Sm_{8\cdot65}V_{1\cdot35}Si_6N_{4\cdot7}O_{21\cdot3}$.[88]

β-K_2SO_4 type: $LnEu^{II}SiO_3N$ oxynitrides (Ln = La, Nd, Sm)[89] have the β-K_2SO_4 structure which is close to the olivine structure. Isolated

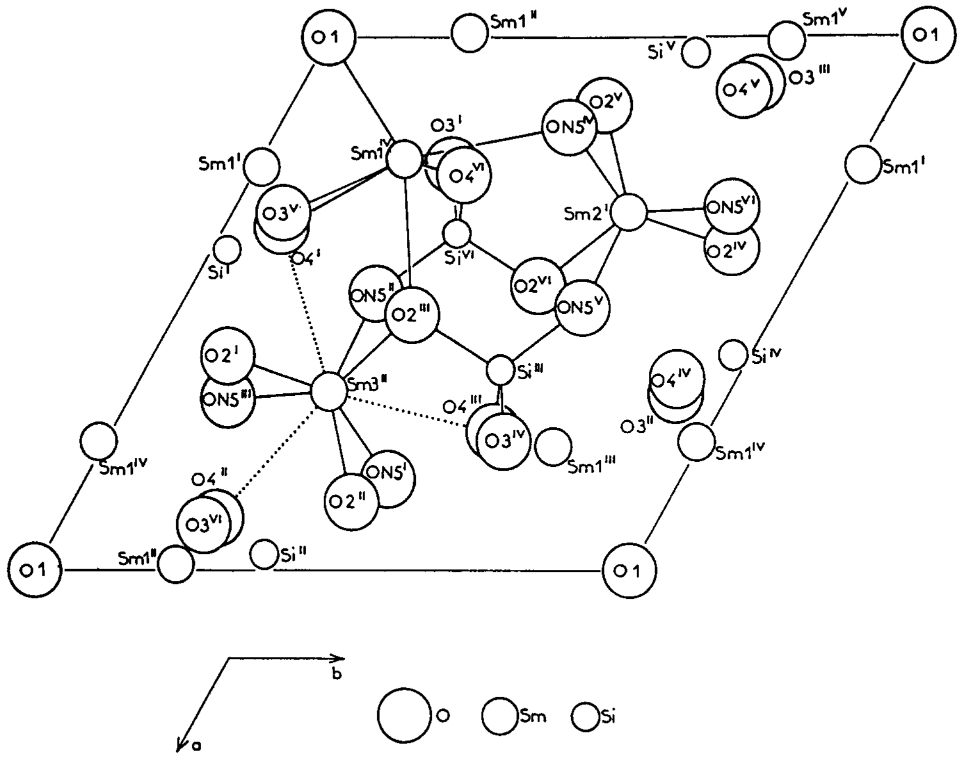

Fig. 10. Projection of the hexagonal apatite structure of $Sm_{10}Si_6N_2O_{24}$ along the *c* axis.[86]

tetrahedra can be found which are linked by the large lanthanide ions. The method used for the preparation of these divalent europium compounds is quite original. The oxidoreduction reaction:

$$3Eu^{3+} + N^{3-} \rightarrow 3Eu^{2+} + \tfrac{1}{2}N_2\uparrow$$

is carried out *in situ*; this enables the use of the Eu_2O_3 oxide rather than the EuO oxide. To achieve that, an excess of silicon nitride is introduced in the reaction mixture, so as to obtain the following reaction:

$$3Eu_2O_3 + 3Ln_2O_3 + 2Si_3N_4 \rightarrow 6LnEuSiO_3N + N_2\uparrow$$

Melilite type: Melilites are natural alumino silicates having the general formula $(Ca,Na)_2(Mg,Al)(Si,Al)_2O_7$ and in whose structure there are $[Si_2O_7]$ pyrosilicate-type groupings which are made up of two tetrahedra sharing one corner.

An example is the akermanite $Ca_2MgSi_2O_7$. The coordination number of calcium is 7, whereas magnesium occupies a tetrahedral site. By simultaneously replacing calcium by lanthanide and magnesium by silicon, a maximum nitrogen enrichment is obtained in the $Ln_2Si_3O_3N_4$ oxynitride series (Ln = La–Yb and Y),[90–92] along with the formation of $[SiO_2N_2]$ tetrahedra.

Cuspidine type: The $Ca_4Si_2O_7F_2$ cuspidine structure is also made up of $[Si_2O_7]$ groupings.[93] This structure is also that of the lanthanide aluminates $Ln_4Al_2O_9$.[94] Concerning these aluminates, the cross-substitution:

$$Si^{+IV} + N^{-III} = Al^{+III} + O^{-II}$$

leads to $Ln_4Si_2N_2O_7$ oxynitrides (Ln = Nd–Yb and Y)[84,90,91] with $[SiO_3N]$ tetrahedra. Neutron diffraction shows that oxygen and nitrogen atoms are crystallographically ordered, as in melilite-type oxynitrides.[95]

Wollastonite type: In the structure of the α-$CaSiO_3$ pseudo-wollastonite, $[Si_3O_9]$ rings of three tetrahedra can be found.[96] Isostructural $LnSiO_2N$ oxynitrides (Ln = La, Ce, Y)[97,98] result from the lanthanide/calcium–nitrogen/oxygen substitution with $[SiO_2N_2]$ tetrahedra forming $[Si_3O_6N_3]$ rings.

The nitrogen/oxygen substitution in the $[SiO_4]$ tetrahedra is such that $[SiO_{4-x}N_x]$ tetrahedra are now known for all the integer values of x. Besides $[SiO_3N]$ and $[SiO_2N_2]$, which have already been mentioned, the $[SiN_3O]$ tetrahedron is known in Si_2N_2O and in LiSiON-related oxynitrides as well as the $[SiN_4]$ tetrahedron in Si_3N_4 and in $BeSiN_2$- and $LiSi_2N_3$-type nitrides, and also in $LaSi_3N_5$.

The structure of the ternary nitride $LaSi_3N_5$ is built up from $[SiN_4]$ tetrahedra which are linked by sharing corners to form rings of five tetrahedra. They determine pentagonal spaces at the center of which are located the large lanthanum ions (Fig. 11). Some of the features of the Si_3N_4 structure can be found in the $LaSi_3N_5$ structure.[99]

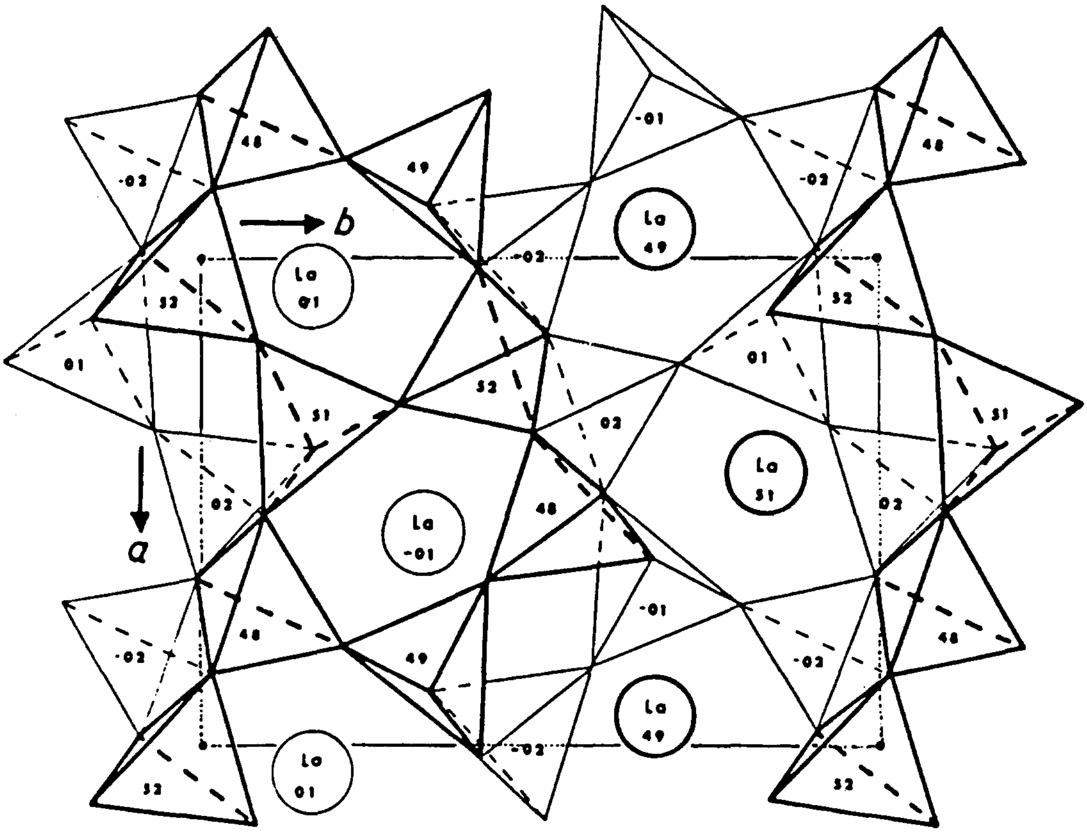

Fig. 11. The orthorhombic structure of $LaSi_3N_5$ projected along its *c* axis.[99]

The different crystalline phases of the Ln–Si–O–N system are interesting because such phases form during the densification of sialon-(Si–Al–O–N) type thermomechanical ceramics. The densification of sialons is actually made much easier when oxides are added, and more particularly Y_2O_3. From this point of view, the Ln–Si–Al–O–N quinary system, which can be represented by a triangular prism, whose apexes are the three SiO_2–Al_2O_3–Ln_2O_3 oxides and the three corresponding nitrides Si_3N_4–AlN–LnN, represents a major field of investigation (Fig. 12). In particular, the study has enabled the presence of Ln–Si–Al–O–N vitreous phases to be shown, which make the densification of sialon ceramics easier.

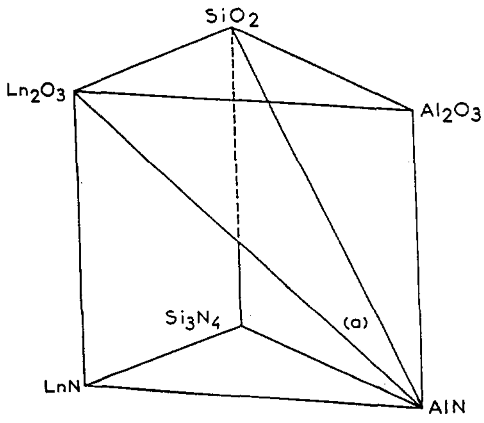

Fig. 12. Perspective view of the Ln–Si–Al–O–N system.

4.2.2 Octahedral environment

The number of examples in which nitrogen replaces oxygen in the octahedral environment of an atom is more restricted than in the case of the tetrahedral environment. Some oxynitrides are known which belong to the perovskite and K_2NiF_4 structure types, which are closely related.

4.2.2.1 Perovskite-type structure (with Ta, Nb, W, Mo or V as coordinating element). In the perovskite structure having the ABX_3 stoichiometry, $[BX_6]$ octahedra form a three-dimensional arrangement by sharing corners. These octahedra delimit sites having a coordination number of 12, and being occupied by atom A.

Concerning oxygenated perovskites, respecting the valence conditions implies one of the possibilities for the A–B couple given in Table 2.

Table 2. Various possibilities of oxygenated perovskites

A–B couple	*Example of A element in site 12*	*Example of B element in site 6*	*Example*
3–3	Ln	Al	$LnAlO_3$
2–4	Ba	Ti	$BaTiO_3$
1–5	Li	Nb	$LiNbO_3$
0–6	□	Re	□ReO_3

The formation of oxynitrides $ABO_{3-x}N_x$ requires an atom with a higher valence for A or for B, or for A and B simultaneously, so as to comply with the relation $a+b=6+x$, where a and b are the respective 'charges' of atoms A and B. It can be seen that the $a+b$ sum, which can range in a continuous way between 6 and 9, allows various possibilities concerning A–B couples. Such oxynitrides differ from the nitrides having the general formulation MT_3N, where T is a transition metal or a lanthanide, and M is another metal. These nitrides are anti-perovskites, since it is nitrogen, which, by replacing the cation B, is situated at the center of T atom octahedra. They belong to the category of nitrided alloys.[100,101]

Among the above-mentioned examples of perovskites, barium titanate ($BaTiO_3$) is a thoroughly studied material as it is one of the basic components of ceramic capacitors with high dielectric constant values. Barium can be partly or totally replaced by strontium or lead, for instance, and titanium can be replaced by zirconium; in particular this has an influence on the ferroelectric transition temperature. In the field of ceramic capacitors, the miniaturization of the components has been achieved by using the multilayer technique, which implies a co-sintering of the electrode and dielectric material. The sintering is carried out in an oxidizing atmosphere so as to prevent the ceramic from suffering stoichiometry defects which are detrimental to the dielectric qualities. This operation requires the use of metals or alloys which do not become oxidized at elevated temperature as the electrode material; this can be platinum, platinum–palladium alloys or, more recently, palladium–silver alloys.

Apart from the fundamental aspect, and from an application point of view, perovskite-type oxynitrides thus appear to be new materials which can be sintered in a non-oxidizing atmosphere, which would allow electrodes made with less noble, and thus less expensive, metals to be used.

Dielectric perovskites: The first examples of oxynitride perovskites have been obtained by replacing titanium in $BaTiO_3$ by an element with an oxidation state V, such as tantalum or niobium. Thus, one can obtain Ba (or Sr or Ca) TaO_2N and Ba (or Sr) NbO_2N,[5] which are oxynitrides with dielectric features.[102]

$BaTaO_2N$ and $BaNbO_2N$ have a cubic symmetry and no crystallographic transition could be seen even at the temperature of liquid helium.[103] The $SrTaO_2N$ oxynitride shows a unit cell having a tetragonal symmetry (Fig. 13) and, even in that case, oxygen and nitrogen are still randomly distributed, as shown by neutron diffraction studies.[104]

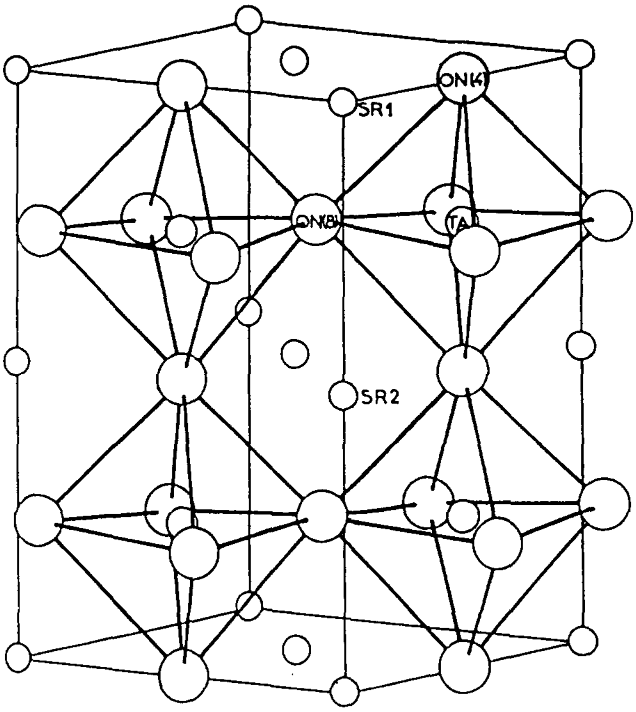

Fig. 13. Perspective view of the unit cell of $SrTaO_2N$.[104]

The substitution of barium by a lanthanide leads to $LnTiO_2N$ oxynitrides (Ln = La, Nd),[105] in which the oxidation state IV of titanium is thus stabilized. These compounds have almost the same crystalline unit cell as the $LnTiO_3$ perovskites which formally correspond to Ti^{III}. But $LaTiO_2N$ and $NdTiO_2N$ have an insulating feature, whereas $LaTiO_3$ has a metallic behavior above −170°C and whereas $NdTiO_3$ is a semi-conductor at room temperature.[106,107]

Finally, the simultaneous substitution of barium and titanium allows a new family of oxynitrides $LnTaON_2$ (Ln = La → Dy) and $LaNbON_2$ to be obtained.[105]

$LnTiO_2N$ and LnTa(or Nb)ON_2 oxynitrides are orthorhombic perovskites of the $GdFeO_3$ type; the slight deformation,which provokes the loss of the cubic symmetry, gives an 8(+4) coordination for atom A, instead of 12.

A certain degree of empiricism exists when the densification of these oxynitrides is studied. The densification study is carried out mainly with the $BaTaO_2N$ and $SrTaO_2N$ compounds. Various reactive sintering possibilities are studied by using different types of additives which could aid densification, such as additives commonly used for the sintering of $BaTiO_3$ (LiF, $BaLiF_3$), different oxygenated or nitrided silicate glasses, non-oxygenated products (fluorides and nitrides), barium and strontium borates which yield a liquid phase at a low temperautre.[108]

Mixed-valence conducting perovskites: Concerning $BaTiO_3$, when the double substitution W^{VI}/Ti^{IV} and Ln^{III}/Ba^{II} is carried out, one could hope to obtain the ABN_3 stoichiometry for the perovskites. This ABN_3 stoichiometry corresponds to a maximum nitrogen enrichment. In fact, the phases which can be observed are still oxynitrides because, under the operational conditions which are involved, tungsten does not maintain its maximum oxidation state. Mixed-valence perovskites which are obtained thus offer conducting properties. The same phenomenon can be observed with molybdenum and vanadium. Such phases have been notably characterized by the following couples: Ca(or Sr, or Ba)–W, Sr–Mo, Ln–W (Ln = La–Eu) and La–V.[109] The oxynitride which contains the most nitrogen has the composition $LaWO_{0{\cdot}6}N_{2{\cdot}4}$, which corresponds to an average oxidation state of +5·4 for tungsten atoms.

Regarding the La–V system, the homogeneity range extends from $LaV^{III}O_3$ to $LaVO_{2{\cdot}1}N_{0{\cdot}9}$, where vanadium has the V^{III}–V^{IV} mixed valence. $LnWO_xN_{3-x}$ perovskites, which have been studied for Ln = La and Nd and $0{\cdot}6 < x < 0{\cdot}8$, are semiconductors;[110] $LaVO_{3-x}N_x$ oxynitrides also behave as semiconductors throughout the whole composition range.[111]

4.2.2.2 K_2NiF_4-type structure (with Al, Ta or Nb as coordinating element). The K_2NiF_4 structure type is closely related to perovskites. This structure consists of a two-dimensional network of NiF_6 octahedra which are linked to one another by four of their corners and which form $KNiF_3$ perovskite layers separated by KF layers according to the *c* direction of the tetragonal unit cell. This is why compounds belonging to the family are often called bidimensional perovskites.

The existence of the 'Al_3O_3N' spinel shows that aluminum may indiscriminantly occupy a tetrahedral site or an octahedral site formed by oxygen and nitrogen atoms. The octahedral environment is found in the Ln_2AlO_3N oxynitrides (Ln = La, Nd, Sm)[112] which belong to the K_2NiF_4 type and derive from the $M^{II}CaAlO_4$ isostructural aluminates (M^{II} = Ca, Sr, Eu) by the cross-substitution:

$$Ln^{+III} + N^{-III} = M^{+II} + O^{-II}$$

The comprehensive determination of the Nd_2AlO_3N structure by neutron diffraction shows the existence of an oxygen–nitrogen order. In the layer of octahedra, a nitrogen atom occupies one of the free corners of the octahedron, and the other corner along with the median plane are occupied by oxygen atoms. The coordination octahedron of aluminium thus has the formula $[AlO_5N]$; as a consequence, there are two independent neodymium atoms, having the coordination number 9[113] (see Fig. 14).

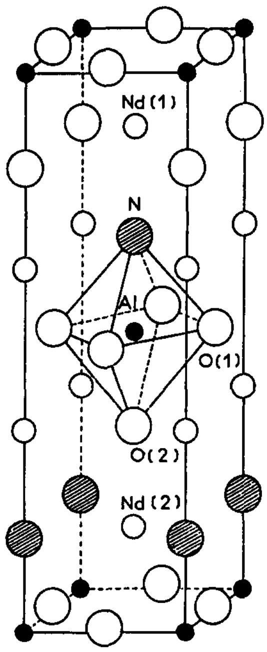

Fig. 14. Perspective view of the unit cell of Nd_2AlO_3N.[113]

The same proportion of nitrogen in the anionic network exists in oxynitrides having the formulation $A_2^{II}B^VO_3N$ (A^{II} = Ca, Sr, Ba; B^V = Ta, Nb), notably Sr_2TaO_3N and Ba_2TaO_3N, which have been well characterized.[114] it should be noted that oxyfluorides Sr_2FeO_3F[115] and K_2NbO_3F[116] were the only mixed anion compounds belonging to this structural type until now.

4.2.2.3 'Spinel-type' structure (with Al as coordinating element). It has previously been seen that in the AlN–Al_2O_3 system, γ-aluminum oxynitride had the spinel structure with the ideal formulation Al_3O_3N. Yet no ternary nitride or oxynitride of the spinel type, i.e having a formulation $MM'_2(O, N)_4$, has been described until now. The oxynitrides presented here have a structure in which only spinel blocks may be found: these are the magnetoplumbite structure and the β-alumina structure.

Lanthanide and aluminum oxynitrides, which have a composition close to $LaAl_{12}O_{18}N$ (Ln = La–Gd),[117] have an hexagonal structure which is similar to that of magnetoplumbite $PbFe_{12}O_{19}$. It is made up of spinel blocks which are separated by mirror planes containing the lanthanide atoms. It is assumed that, as compared to defect lanthanide hexaluminates $LnAl_{11}\square O_{18}$ (Ln = La–Sm),[118,119] nitrogen has a role in the stabilization of the magnetoplumbite structure, which is probably due to the presence of Al_3O_3N units in the spinel blocks.[120] An oxynitride phase has been shown in the Na_2O–Al_2O_3–AlN system;[121] it belongs to the β-alumina type and its structure is very similar to that of magnetoplumbite.

4.2.3 'Cubic' environment

Recently, oxynitrides have been prepared which belong to the fluorite and pyrochlore structure and which the authors have chosen to classify in this category. Yet, the environment of the coordinating element is in fact defect and distorted as compared to the cubic environment.

4.2.3.1 Fluorite-type structure (with W as coordinating element). The structure of the fluorite CaF_2 is made up of cubes of F^- with the Ca^{2+} cations occupying one cube out of two (Fig. 15(a)) in an ordered way, and the symmetry of their arrangement is of cubic face-centered type.

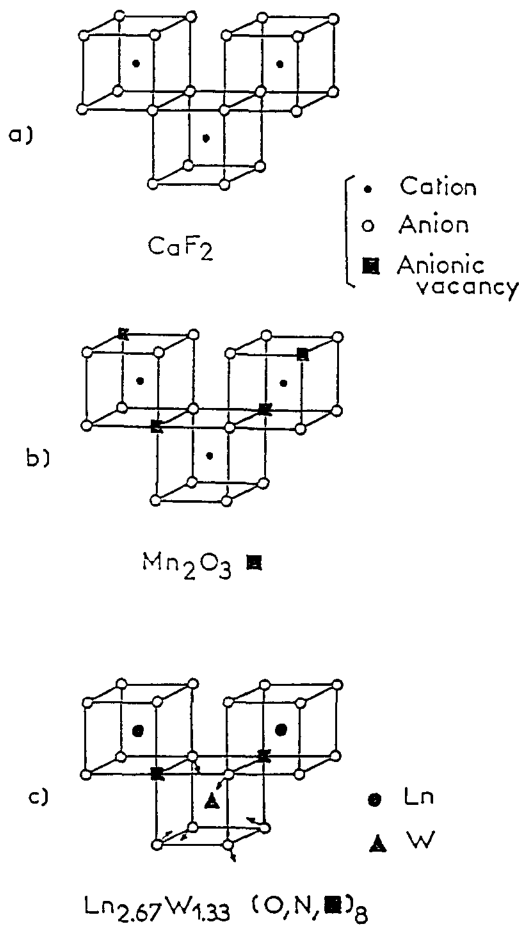

Fig. 15. Drawings illustrating the structural filiation between (a) fluorite (CaF_2), (b) bixbyite (Mn_2O_3) and (c) $Ln_{2\cdot67}W_{1\cdot33}(O, N, \square)_8$ oxynitrides.[122] (a) and (b) ●, Cation; ○, anion; ■, anionic vacancy; (c) ●, Ln; ▲, W.

It has previously been seen that a certain number of ternary nitrides containing lithium, such as Li_3AlN_2, have an anti-fluorite-type structure. In the case of the phases $Ln_{2\cdot67}W_{1\cdot33}(O, N, \square)_8$ (Ln = Nd–Yb and Y),[122] the oxygen and nitrogen anions occupy the corners of the cube, with lanthanide and tungsten forming a cubic face-centered arrangement such as the calcium atoms in CaF_2.

The observed cation/anion stoichiometry, which is always close to $A_4X_{6\cdot6}$ whatever the lanthanide, is halfway between that of fluorite (A_4X_8) and that of Mn_2O_3 bixbyite (A_4X_6).

In Mn_2O_3, only six out of the eight corners of the anionic cubes are occupied, and the vacancies are regularly distributed either according to the diagonal of a face, or according to the main diagonal of the cube (Fig. 15(b)).

Concerning these defect fluorides $Ln_{2\cdot67}W_{1\cdot33}(O, N, \square)_8$, Fig. 15(c) shows that when the cationic arrangement is kept, a displacement of certain anions from their ideal position, added to the presence of vacancies, allows a high coordination environment for lanthanide atoms to be maintained and to obtain a tetrahedral coordination for tungsten which is in these oxynitrides at the oxidation state VI.

4.2.3.2 Pyrochlore-type structure (with Ta as coordinating element). Oxynitrides $Ln_2Ta_2O_5N_2$ (Ln = Nd–Yb and Y)[123] have enriched the family of pyrochlores $A_2B_2X_7$, which already accepts numerous substitutions in the different cationic and anionic sites of the structure, not to mention the possibility of vacancies on the A and X sites. From a crystallographic point of view, the general formula may be written $A_2B_2X_6X'$; the variable value of the coordinate n of anions X being responsible for the more or less distorted environment of cations A (6X + 2X′) and B (6X). In the studied oxynitrides, this distortion is expected to be maximum for the largest lanthanides; the trigonal antiprism around the tantalum thus becomes octahedral, whereas lanthanides having a smaller ionic radius would tend towards a defect fluorite structure. Furthermore $Ln_2Ta_2O_5N_2$ stoichiometry, which has already been seen with oxyfluorides such as $Cd_2Ti_2O_5F_2$,[124] needs a partial disorder for at least one of the two anionic positions.

5 Conclusion

This study was dedicated to nitrides and oxynitrides, and was deliberately limited to ionocovalent compounds. This study enables one to see that the compounds for which the covalent feature is predominant are those which have been studied most thoroughly. On the one hand, there is a possibility to discover new nitrided compositions in the field, and, if the structural types which are known for oxides are taken into account, it can be clearly seen that, from a fundamental point of view, all the nitrogen/oxygen substitution alternatives have not yet been envisaged. On the other hand, the study of these compounds enables interesting properties of these new materials to be pointed out and exploited.

Finally, apart from crystalline nitrides and oxynitrides, oxynitride vitreous phases exist for which the presence of nitrogen in the anionic network dramatically modifies the physicochemical characteristics of the glasses, as compared to the corresponding purely oxygenated compositions. The structural unit of these nitrided glasses, whether they are of the aluminosilicate or of the phosphate type, is the mixed nitrogen/oxygen tetrahedron, which is quite widespread, as previously seen, in the crystalline phases.

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