

## Progress in the chemistry of ternary and quaternary nitrides

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# Progress in the chemistry of ternary and quaternary nitrides

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**Abstract:** A review is given of recent developments in the chemistry of nitrides and oxynitrides of multi-component systems. In the first part recent work in the Si-Al-O-N-Mg system is described. In the second part attention is paid to lithium ion conductors, new earth alkaline compounds, zirconium oxynitrides and B-C-N compounds.

## 1 Introduction

Nitride chemistry comprises a very extensive field. The crystal chemistry of nitrides and oxynitrides has been reviewed recently (1) and in this paper the attention will be focussed mainly on properties of nonmetallic, multi-component nitrides. Si- and Al-based nitrides have since long attracted attention because of their good thermomechanical properties. Ceramists became interested in  $\text{Si}_3\text{N}_4$  as soon as it became possible to densify the material. This was achieved by means of liquid phase sintering with the aid of oxidic sintering additives. Oxides such as MgO,  $\text{Al}_2\text{O}_3$  or rare earth oxides form eutectics with the silica on the surface of the nitride. This has led to further investigations of phase relations and properties of oxynitrides in the system Si-Al-O-N-Me. Although many interesting materials are found in this system, only a limited number has been investigated in detail. In part 1 some new results will be discussed which may lead to new applications for materials which are known already. In part 2 a brief survey will be given of recently prepared new compounds.

## 2 Compounds in the system Me-Si-Al-O-N

As an example of such a quinary diagram Fig. 1 shows the well known Jänecke representation of Me-Si-Al-O-N (Me=metal such as Y, Ca, Mg) and we will use this to discuss some new results on subsystems hereof.

The ternary system Al-N-O has been investigated several times. During a study of optical translucent materials we became interested in  $\gamma$ -Alon as a possible lamp envelope material for high pressure Na-lamps. However, there was uncertainty about the phase diagram and we decided to study this in more detail (2,3). The compound has a spinel-type structure and McCauley has proposed two possible models; the so-called constant anion model  $\text{Al}_{(64+x)}\text{V}_{\text{Al}(8-x)}\text{O}_{32-x}\text{N}_x$ , with vacancies on octahedral sites, or the constant cation model  $\text{Al}_{24}\text{O}_{(72-3x)}\text{N}_x(\text{O,N})_{i(4-x)}$ , with interstitial anions (4). Recent neutron diffraction results indicate the first model i.e. the predominant defects are Al vacancies on octahedral sites (5). Results of a study of the phase diagram are shown in Fig. 2 (6). The stability range lies between  $x=2.3$  and  $x=4.7$ . From this figure it is clear that  $\gamma$ -Alon is not stable at temperatures below  $1640^\circ\text{C}$ . We have also performed thermodynamic calculations showing the stability conditions at

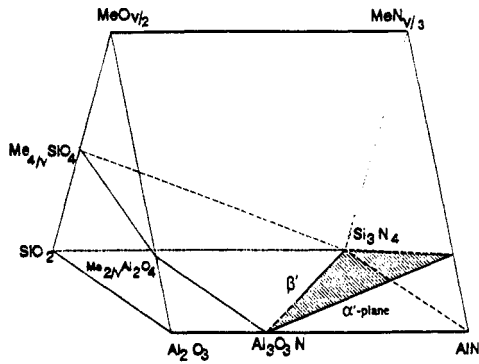


Fig.1 Jänecke representation of the Me-sialon system (Me=metal ion with valency v), showing the plane where  $\alpha'$ -sialon occurs and the plane with cation/anion ratio 3/4.

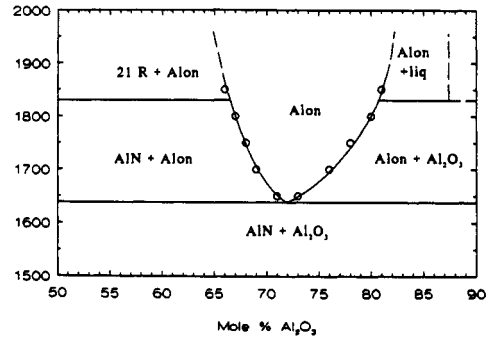


Fig.2 Stability region of  $\gamma$ -Alon

higher temperatures(7). The results of these investigations can be summarized as follows: under the appropriate conditions of gas pressure and temperature  $\gamma$ -Alon can be sintered to full density, leading to a translucent material. This material is an excellent window material (for instance for radar domes) that can be used below 800°C since the kinetics of decomposition is very slow below this temperature. We have also tried to stabilize the spinel structure by adding MgO. New results on the pseudo-ternary system Mg-Al-O-N at 1400°C and 1700°C are shown in Figs. 3 and 4 (8). Fig. 4 includes recent results of experiments in the Sialon plane by Bergman et al. (9). There are still many uncertainties about the Mg-sialon diagram. For instance the solubility of Mg in  $\beta$ -Si<sub>3</sub>N<sub>4</sub> reported by Jack (10), could not be verified in later experiments (11). Also the position of several tielines is uncertain. Part of the problems is due to the evaporation of Mg<sub>3</sub>N<sub>2</sub> and to the fact that liquid phases are formed which on cooling produce nitrogen glasses.

At T>1750°C the diagrams become more complicated because more compounds become stable in the AlON, SiAlON, MgSiON and MgSiAlON systems. For instance in the system (Si,Al)<sub>m</sub>(O,N)<sub>m+1</sub> one finds wurtzite type polytypoids with m=4,5,6,7,9,11 and Ramsdell symbols 8H, 15R, 12H, 21R, 27R, 2H (12). Physical properties of these compounds are not known in detail. For ceramic

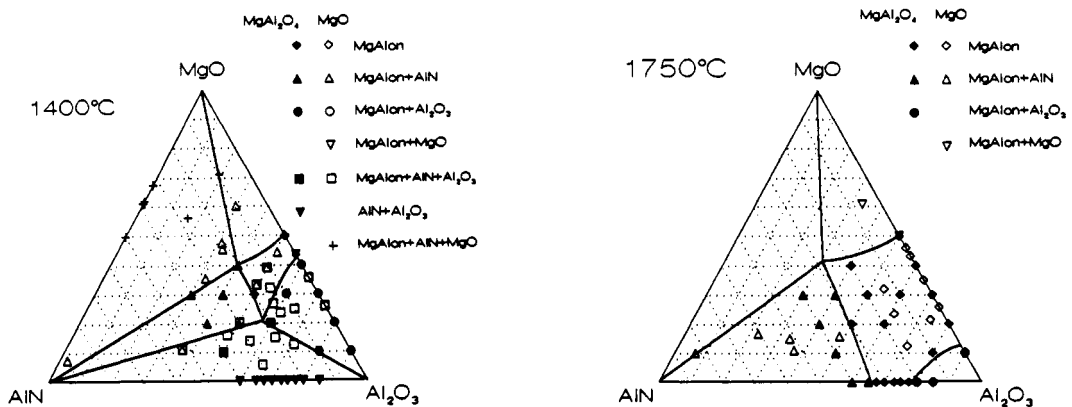


Fig. 3 Phase diagram for Mg-Alon at 1400°C (left) and 1700°C (right).

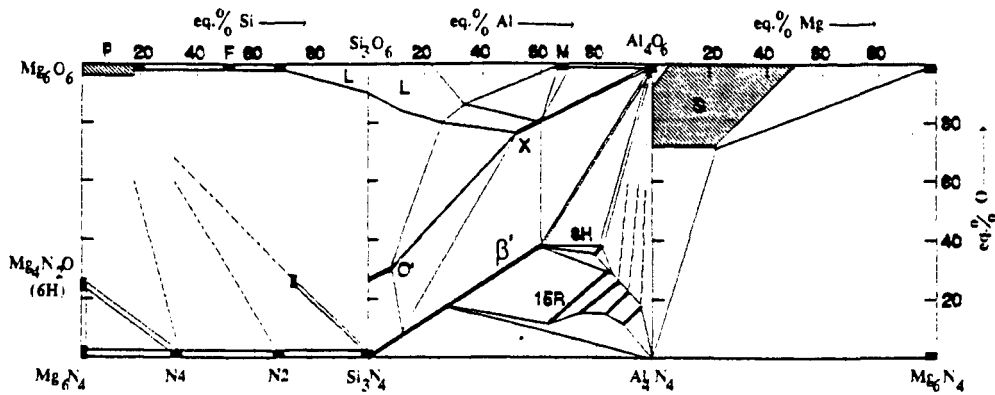


Fig. 4 Prism faces from fig. 1 for Mg-Sialon at 1700°C; position of dashed tie lines is uncertain.

S=spinel,  $\beta'$ = $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ , L=liquid, M=mullite( $2\text{SiO}_2 \cdot 3\text{Al}_2\text{O}_3$ ),  $\text{O}'=\text{Si}_{2-z}\text{Al}_z\text{N}_{2-z}\text{O}_{1+z}$ ,  $\text{X}=\text{Si}_{12}\text{Al}_{18}\text{O}_{36}\text{N}_{10}$ , F=forsterite( $\text{Mg}_2\text{SiO}_4$ ), P=periclasite, N2 =  $\text{MgSiN}_2$ , N4 =  $\text{Mg}_4\text{SiN}_4$ .

applications the most interesting and most extensively studied compounds are  $\beta'$ - and  $\alpha'$ -sialons.

The  $\beta'$  material has the same structure as  $\beta\text{-Si}_3\text{N}_4$  and has the general formula  $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ ,  $0 \leq z \leq 4.2$  (Fig. 4). It is an oxynitride with  $[\text{SiO}_{4-x}\text{N}_x]$  tetrahedra. In  $\text{Si}_3\text{N}_4$  nitrogen occupies 6h and 2c sites (Fig. 5a), in  $\text{Si}_2\text{N}_2\text{O}$  oxygen occupies the 2c sites (Fig. 5b) (13,14). From neutron diffraction studies it was found that oxygen in  $\beta$ -sialon with  $z=3$  has a preference for 2c sites (15,16). If we compare the parts within the rectangles in Fig. 5 it is clear that sialon can be considered as intermediate between  $\text{Si}_3\text{N}_4$  and  $\text{Si}_2\text{N}_2\text{O}$ . In  $\alpha\text{-Si}_3\text{N}_4$  the lower half of the unit cell is the same as in  $\beta\text{-Si}_3\text{N}_4$ , but the upper part is related to the lower half by a c-glide plane. In this way the large channel visible at the left hand side of Fig. 5a in  $\beta\text{-Si}_3\text{N}_4$  is interrupted and a large interstitial site is formed. The  $\alpha'$ -sialons have the structure of  $\alpha\text{-Si}_3\text{N}_4$  with a metal ion Me at the interstitial site. The general formula is  $\text{Me}_x\text{Si}_{12-(m+n)}\text{Al}_{m+n}\text{O}_n\text{N}_{16-n}$ , with  $x < 2$ ; Me can be Li, Ca, Y or a rare earth ion. If  $v$  is the valency of the metal Me,  $x=m/v$ . We have recently shown for an Yttrium  $\alpha'$ -sialon with  $m=1.5$ ,  $n=0.75$  that, in contrast with results for  $\beta'$ -sialon, Al and Si are ordered over the 6c sites (17).

From a ceramic point of view  $\alpha\text{-}\beta$  composite materials are of great interest. The  $\beta$ -phase forms elongated grains in an isomorphous  $\alpha$ -matrix and because of the analogy to whisker toughened materials they are called self-reinforced  $\text{Si}_3\text{N}_4$ . Such materials show high fracture toughness,  $K_{Ic} > 8 \text{ MPa}\cdot\text{m}^{1/2}$  and high flexure strengths  $> 1000 \text{ MPa}$  (18).

Returning to the compounds in the Mg-Si-N system (Fig. 4), it was found that  $\text{MgSiN}_2$  may be of practical interest too because of its high thermal conductivity (19). As shown in Fig. 6, this compound can be seen as an orthorhombic superlattice of AlN, with  $[\text{MgN}_4]$  and  $[\text{SiN}_4]$  tetrahedra (20). The material can be sintered to full density by uniaxial hotpressing (21). Compared to BeO, which is highly toxic, and AlN which is rather expensive,  $\text{MgSiN}_2$  may become an attractive substrate material for the semiconductor industry.

In the systems Ln-Si-O-N and Ln-Si-Al-O-N many compounds are known which can be derived from silicate structure types (1). Figure 7 shows the different compounds in the system Y-Si-O-N(22). The position of the tielines is uncertain and also the solid solution region of N-apatite is not well established. This compound probably has compositions in the range between  $\text{Y}_5(\text{SiO}_3\text{N})_3$  and  $\text{Y}_5(\text{SiO}_4)_3\text{N}$ . So far these compounds have mainly attracted attention because they can occur

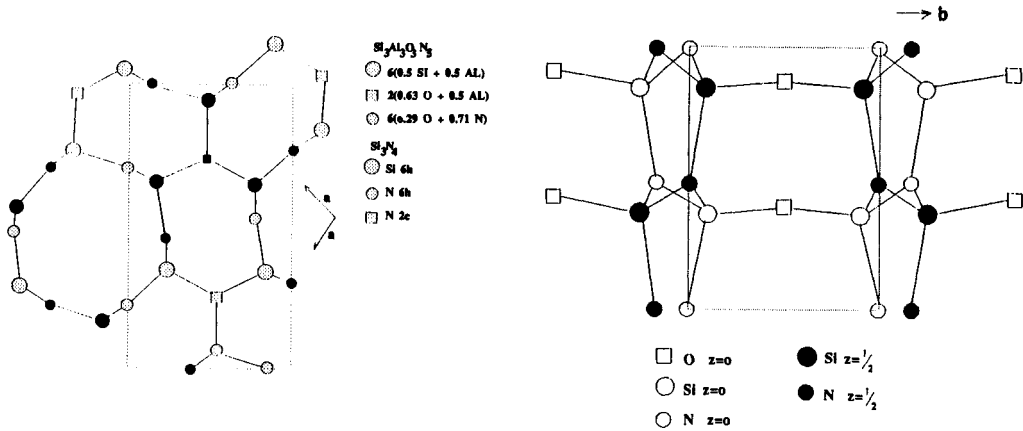


Fig. 5 Projection on (100) for (a): $\beta$ - $\text{Si}_3\text{N}_4$  or  $\beta$ - $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$  and (b): $\text{Si}_2\text{N}_2\text{O}$ . Hatched atoms at height  $z=1/2$ . Oxygen in sialon shows preference for c-sites. The rectangular parts show the similarity between the oxygen site occupancy in sialon and  $\text{Si}_2\text{N}_2\text{O}$ .

as grainboundary phases in sialon ceramics. However, recently it was found that several of these oxynitrides are excellent host lattices for luminescent rare earth ions. Examples are Tb-activated  $\text{Y}_4\text{Si}_2\text{O}_7\text{N}_2$ , a cuspidine ( $\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$ ) type structure and  $\text{Y}_2\text{Si}_3\text{O}_3\text{N}_4$ , so-called N-melilite. While the oxide melilites have  $[\text{Si}_2\text{O}_7]$  groups which consist of two corner sharing tetrahedra, N-melilite has interconnected  $[\text{Si}_2\text{O}_{7-x}\text{N}_x]$  groups which form sheets. However, also the wollastonite-type  $\text{YSiO}_2\text{N}$ , with  $[\text{Si}_3\text{O}_6\text{N}_3]$  rings of three tetrahedra and apatite-type  $\text{Y}_5(\text{SiO}_3)_3\text{N}$  can be used as host lattices. With increasing nitrogen content the absorption band shifts to lower energies due to increasing covalency. As a result all of these compounds show a high UV absorption for a low concentration of the expensive Tb and without incorporation of Ce as sensitizer as is normally the case (23). This again may lead to new applications of oxynitrides.

### 3 New compounds

Since the appearance of the review article by Marchand et al. (1) several new compounds have been synthesized and also new applications have been reported. In this section some of these will be discussed.

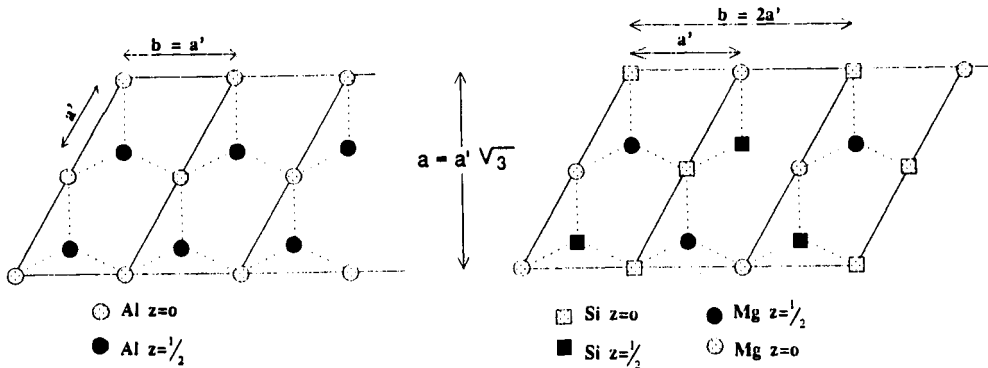


Fig.6 (001) projection of  $\text{AlN}$  and  $\text{MgSiN}_2$  wurtzite type structures. N-atoms at  $z=1/4$  and  $3/4$  project on the cations.

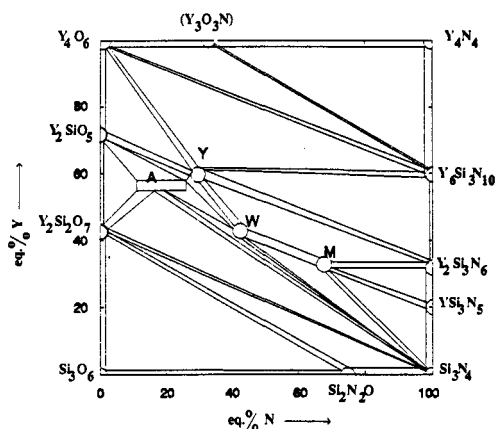


Fig.7 Crystalline phases in the Y-Si-O-N system at 1450°C.

### 3.1 Lithium ion conductors

Lithium compounds have always attracted attention of solid state chemists because of their potential use as ionic conductors. Lithium nitrides also have ionic character. Of all the lithium containing nitrides the binary compound  $\text{Li}_3\text{N}$  was most promising as ionic conductor with a conductivity at 300K of  $10^{-5}$  S/cm. This compound consists of  $\text{Li}_2\text{N}$  layers connected by Li layers (24,25). The  $\text{Li}^+$ -ions in the  $\text{Li}_2\text{N}$  layers have a high mobility, which may be related to a 1-2% Li deficiency (26). However, detailed research showed that it decomposes already at 0.44 V, which is too low for battery applications. Many of the ternary Li-nitrides have the general formula  $\text{Li}_{2n-3}\text{M}^{\text{II}}\text{N}_{n-1}$ , with anti-fluorite type structure. M is an n-valent metal like Mg, Zn, Al, B, Ga, Si, Ti, V, Ta, Mn, Cr i.e.  $2 \leq n \leq 6$  (1,27). Also  $\text{Li}_6\text{CrN}_4$ ,  $\text{Li}_{15}\text{Cr}_2\text{N}_9$ ,  $\text{Li}_8\text{SiN}_4$ ,  $\text{Li}_{18}\text{Si}_3\text{N}_{10}$ ,  $\text{Li}_{21}\text{Si}_3\text{N}_{11}$  and the oxynitrides  $\text{Li}_3\text{SiN}_3 \cdot 2\text{Li}_2\text{O}$ ,  $\text{Li}_{16}\text{Ta}_2\text{N}_8\text{O}$  and  $\text{Li}_{14}\text{Cr}_2\text{N}_8(\text{O},\text{NH})$  have this structure type (28-31).

Another group has the anti- $\text{La}_2\text{O}_3$  structure type e.g.  $\text{Li}_2\text{MN}_2$  with  $\text{M}=\text{Si}, \text{Zr}, \text{Ce}$ , while  $\text{LiSi}_2\text{N}_3$  crystallizes with wurtzite type structure. Although all these compounds are lithium ion conductors none of them could satisfy the requirements for battery applications. Yet, new interest has been raised after the discovery of B-C-N materials with graphite-like structure. Kaner et al. (32) produced a material with approximate composition  $\text{B}_{0.35}\text{C}_{0.30}\text{N}_{0.35}$ , Morita et al. (33) prepared films of  $\text{BC}_2\text{N}$ . These materials can be made by a gas phase reaction of  $\text{BCl}_3$  with acetylene and ammonia or with acetonitrile. The structure is not accurately known, but for  $\text{BC}_2\text{N}$  a possible arrangement is shown in Fig.8 (33). The material itself is a semiconductor, but the most interesting aspect is that it can be intercalated by both reducing and oxidizing agents. Experiments by Morita et al. (33) show that it can be used as a negative intercalation electrode for rechargeable Li-batteries with an open-cell voltage of 0.47 V; the maximum doping corresponded to a composition  $\text{Li}_{0.58}(\text{BC}_2\text{N})$ . Recently Kawaguchi and Kawashima also reported the preparation of a graphite-like material with composition  $\text{BC}_3\text{N}$  (34). This material is a p-type semiconductor with a very high basal plane conductivity of 88.5 S/cm, which is about  $10^5$  higher than for the material produced by Kaner et. al (33) and an activation energy of only 6.29 meV. No intercalation properties were reported yet for  $\text{BC}_3\text{N}$ , but the interlayer spacing of 0.35 nm is approximately the same for all materials and equal to that for graphite.

### 3.2 Earth alkaline compounds

Nitrides with perovskite type structure  $MT_3N$  form a large group. Here M denotes a non-transition metal, T a transition metal. These compounds are of interest because of the electric and dielectric properties. Recently several ternary calcium nitrides were prepared with anti-perovskite structure,  $Ca_3MN$ , with  $M=P, As, Sb, Bi, Ge, Sn, Pb$  (35). It is interesting to note that both the group V elements P, As, Sb, Bi and the group IV elements Ge, Sn, P have a formal oxidation state 3-. As a result the electrical properties change from insulating for P and As, via semiconducting for Bi and Sb, to metallic conductivity for Pb, Sn and Ge (Fig. 9).

Other new Ca nitrides prepared by the same group are  $Ca_3CrN_3$ ,  $Ca_3VN_3$ ,  $Ca_2ZnN_2$  and  $CaNiN$ . (36-39). The first two compounds contain  $Cr^{3+}$  and  $V^{3+}$  in the unusual low-spin state. Like the  $CaNiN$  also the solid solutions  $Ca_{1-x}Sr_xNiN$ ,  $0 \leq x \leq 0.75$ , show metallic conductivity, while  $Ca_3CoN_3$  is semiconducting (40).  $CaNiN$  is peculiar because of the unusual oxidation state  $Ni^{1+}$ . The compound is also of interest because, unlike most ternary calcium nitrides which have nitrogen octahedrally coordinated by metal atoms, one here finds infinite Ni-N chains. In  $SrNiN$  and  $BaNiN$  there are also infinite Ni-N chains, but these are zigzag instead of straight, while  $Ba_8Ni_6N_7$  has helical chains (41,42). Other recently prepared alkaline earth-transition metal nitrides are  $Ca_6FeN_5$  and  $Ba_3FeN_3$  and  $Sr_3FeN_3$ , with trigonal-planar  $[FeN_3]^{6-}$  ions (43,44). Similar planes of  $[MN_3]^{6-}$  anions, separated by cations are found in the above mentioned  $Ca_3CrN_3$  and in  $Ca_6FeN_5$  and  $Ca_6GaN_5$ .

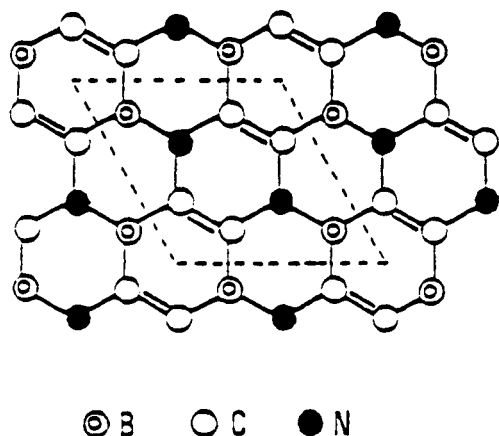


Fig. 8 Possible atom arrangement in the basal plane of  $BC_2N$ . Graphite type structure, layer spacing  $c/2=0.354$  nm (after 34).

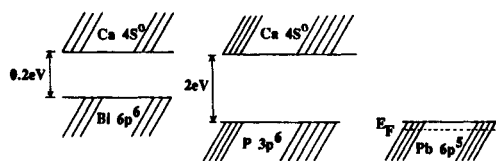


Fig. 9 Band structure of  $Ca_3MN$ . For  $M=Bi$  or  $P$  the empty Ca 4s levels form the conduction band, the filled p levels of Bi and P the valence band. With Pb the Fermi level lies in the  $p^5$  band.

### 3.3 Zirconium oxynitrides

Zr oxynitrides are known for a long time. Gilles prepared three phases,  $\gamma$ ,  $\beta$ , and  $\beta'$  from mixtures of  $ZrO_2$  and  $ZrN$  in  $NH_3$  at  $1000-2000^\circ C$  (45). These phases have the fluorite type structure with vacancies in the anion lattice:  $ZrO_{2-2x}N_{4x/3}V_{O,2x/3}$ . The  $\gamma$ -phase is a solid solution with  $0.5 \leq x \leq 0.8$ ,  $\beta$  and  $\beta'$  have formulas  $Zr_7N_4O_8$  and  $Zr_7N_2O_{11}$ , respectively. Recently it was shown that these compounds can be prepared also using  $\beta$ - $ZrNCl$  as a nitrogen source (46). These authors showed that in spite of the presence of oxygen vacancies  $\gamma$  and  $\beta$  do not show ionic conductivity. Instead, both are semiconductors

with band gap energies 2.5 and 3.2 eV, respectively. Earlier Claussen et. al showed that the cubic zirconia structure can be stabilized by introduction of nitrogen (47). At the ZrN side of the phase diagram a new phase was found with the NaCl-type structure of ZrN. It is supposed to be ZrN(O) with oxygen atoms in the ZrN host lattice in an ordered way (48).

### 3.4 $C_3N_4$

Above we discussed  $BC_2N$  as a material that may become important in battery applications. A material that is even more intriguing is the compound  $\beta-C_3N_4$ , with  $\beta-Si_3N_4$  structure type. Calculations by Liu and Cohen (49) showed that this compound should have a hardness comparable to diamond or cubic BN. Recently three groups reported to have grown carbon nitride films with  $\beta-Si_3N_4$  type structure (50-52). So far, however, these films which are made by reactive sputtering or laser ablation, have poor crystallinity and contain only about 40-45 at% N instead of 57%. Yet, electron microscopy showed diffraction patterns which correspond with a  $\beta-Si_3N_4$  type structure (cf. Fig. 5a) and with the theoretically expected lattice constants for  $\beta-C_3N_4$ . Moreover, a strong IR absorption band at  $1297\text{ cm}^{-1}$  may be assigned to the  $\beta-Si_3N_4$  type network.

This review of compounds prepared in the last few years cannot be complete. For instance we have left out both metallic systems and nitrogen glasses. However, it is clear that the chemistry of nitrides and oxynitrides is continually expanding and that many new compounds can still be discovered. Also most of these compounds hardly have been characterized and interesting physical properties can be expected. Such information is essential for applications. In conclusion I strongly believe that nitride chemistry offers exciting prospects for future research.

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