The First Nitride Spinels—New Synthetic Approaches to Binary Group 14 Nitrides**

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The discovery of novel element allotropes[1] as well as the synthesis and structure elucidation of new binary compounds are usually recognized as important landmarks in chemistry. In the case of binary compounds the structural-chemical properties of the constituent elements and especially their mutual behavior is clearly revealed.

Owing to their limited number, only rarely have novel representatives of basic solid-state compounds like binary oxides or nitrides been discovered or their hitherto unknown structures elucidated.[2] For these reasons it is remarkable that very recently binary tin(IV) nitride, Sn_3N_4,[3] as well as the high-pressure polymorphs γ-Si_3N_4[4] and γ-Ge_3N_4[5] have been synthesized and structurally investigated. All three compounds are isotypic and crystallize in a spinel structure type that previously has not been found for nitrides (Figure 1). Though Si, Ge, and Sn are three homologous elements and the three nitrides are isotypic, the motivation of these research projects and the synthetic procedures used differ substantially. With respect to its chemical, thermal, and mechanical properties, silicon nitride is remarkably resistant. Therefore this compound gained significance as the most important non-oxidic ceramic material.[6] In contrast the homologous tin(IV) nitride was expected to show a much lower stability, and until recently no proof for the existence of Sn_3N_4 had been obtained.[7]

Under ambient conditions the binary oxides SiO_2 and GeO_2 are made up of MO_4 tetrahedra (M = Si, Ge). Their high-pressure chemistry has been studied in detail, and both finally crystallize in the rutile structure type. An essential feature of this transformation is the increase in coordination number and the formation of MO_6 octahedra. Recently, spectacular materials properties have been observed for stishovite, a high-pressure polymorph of SiO_2 that also occurs as a mineral: Microhardness investigations have proved that this material is the hardest oxidic material known so far, and together with diamond and cubic boron nitride it is among the three hardest materials.[8] Thus the oxides MO_2 (T = Si, Ge, Sn, Pb) follow the pressure–homologues rule,[9] because under high-pressure conditions the lighter homologues (SiO_2, GeO_2) adopt exactly the structure type (rutile) that is observed for the heavier homologues (SnO_2, PbO_2) under ambient conditions.

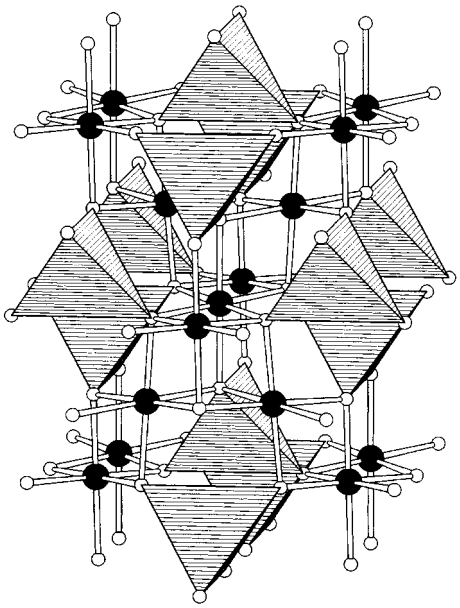

Figure 1. Tin(IV) nitride, Sn_3N_4, as well as the high-pressure polymorphs γ-Si_3N_4 and γ-Ge_3N_4 crystallize in the spinel structure type, which until now has predominantly been observed for oxides like $MgAl_2O_4$ or Fe_3O_4. Here the anions (white circles) form a cubic closest sphere packing, whereas the metal cations (black spheres and centers of the closed polyhedra) occupy one-half of the octahedral and one-eighth of the tetrahedral voids in an ordered manner. According to Pauling's rules the remaining empty voids of the spinel type, in the case of ionic compounds, may not be occupied due to an electrostatic blockade.

The recent high-pressure investigations on Si_3N_4[4] have been targeting fields of application as well. The sintered silicon nitride ceramics are usually manufactured under the influence of high temperatures and pressures. In this context numerous investigations have been published in the material scientific literature. However investigations above a pressure of 9 GPa have not been reported so far. Already the normal-pressure polymorphs α-Si_3N_4 and β-Si_3N_4 are desired materials owing to their mechanical hardness and stability. For the high-pressure polymorph of silicon nitride even more advanced materials properties and a mechanical hardness comparable to that of stishovite are expected.[4]

The novel high-pressure polymorph γ-Si_3N_4 was synthesized from the elements or from N_2 and Si_3N_4 at 2000 K and 15 GPa using a laser-heated diamond anvil cell.[4] The amount of sample obtained by this procedure was extremely small, and thus only sufficient for vibration spectroscopy and electron microscopy investigations. The spinel structure for γ-Si_3N_4 was derived from the cubic metric determined by electron diffraction and the observed extinction conditions.[4] In retrospect the increase in coordination number for Si in γ-Si_3N_4 caused by high pressure sounds plausible, because recently $Ce_{15}Si_{16}O_6N_{32}$ was discovered as the first compound

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to contain SiN_6 octahedra.[10] SiN_6 octahedra have also been found in spinel-type γ-Si_3N_4. According to $(Si^{[6]})_2[Si^{[4]}N_4]$ one third of the Si atoms are still tetrahedrally coordinated, forming SiN_4 units. The latter coordination solely occurs in α-Si_3N_4 and β-Si_3N_4.[7] According to Liebau[11] γ-Si_3N_4 thus might be classified as disilicon nitridosilicate.

Homologous γ-Ge_3N_4 was obtained under similar conditions (14 GPa),[5a] but in the meantime larger amounts of this polymorph (ca. 100 mg) were synthesized at 1000 – 1200 °C and 12 GPa utilizing a multianvil high-pressure cell.[5b] Rietveld refinement of the X-ray powder diffraction data confirmed the postulated spinel structure. Therefore γ-Si_3N_4 should also be accessible on a preparative scale by this method; then the missing X-ray diffraction investigations could be performed and the predicted materials properties[4] of this compound may be experimentally proved.

In the past the existence of Sn_3N_4 or Pb_3N_4 was extremely doubtful. Therefore a prediction of the high-pressure polymorphs γ-Si_3N_4 and γ-Ge_3N_4 using the pressure – homologues rule was not possible. However, simultaneous to the discovery of γ-Si_3N_4 and γ-Ge_3N_4, Jacobs et al. successfully synthesized and structurally characterized Sn_3N_4.[3] Although a high-pressure, high-temperature synthesis starting from the elements (analogous to the synthesis of γ-Si_3N_4 and γ-Ge_3N_4) might lead to the formation of Sn_3N_4, Jacobs et al. chose a simpler synthetic approach: Crystalline Sn_3N_4 is obtained as a by-product from the reaction of SnI_4 or $SnBr_4$ with KNH_2 in liquid NH_3 with subsequent careful thermal treatment at 573 K in vacuum. In contrast to the high-pressure procedures described above, Sn_3N_4 was obtained in preparative amounts. Consequently, X-ray and neutron powder diffraction experiments as well as ^{119}Sn MAS solid-state NMR measurements were performed, and the results unequivocally confirmed the spinel structure of Sn_3N_4.[3]

The results described so far represent an important scientific breakthrough in the investigation of main group nitrides. However, there are still open questions: The existence and the properties of carbon(IV) nitride, C_3N_4, are still under controversial discussion, though a huge number of investigations have been published focusing on these topics. According to theoretical considerations C_3N_4 was expected to exhibit a spectacular mechanical hardness exceeding that of diamond.[12] In the absence of reliable data the structure of C_3N_4 was assumed to be isotypic with β-Si_3N_4 or with willemite II (Zn_2SiO_4). The spinel structure, which according to the results discussed above may also be appropriate, has not been considered for C_3N_4 so far.[4]

Furthermore, the question arises if at higher pressure the nitrides M_3N_4 (M = Si, Ge, Sn) show a phase transformation to a polymorph with an even higher density. Such an ultra-high-pressure polymorph may solely contain M atoms with a higher coordination number (>4), like Zr_3N_4,[13] which crystallizes in a distorted Eu_3O_4 structure type. Another candidate with an octahedral coordination of the M atoms is represented by the Mg_3NF_3 structure type,[14] which is a defect variant of NaCl. For tungsten nitride, W_3N_4,[15] which has only been poorly characterized so far, the latter structure has been postulated.

At first glance the different coordination numbers of Si in γ-Si_3N_4 (octahedrally and tetrahedrally coordinated $Si^{[6]}$ and $Si^{[4]}$ with a molar ratio of 2:1) seem to be unusual. However, in $La_2(O^{[4]})_2O^{[6]}$ a similar situation occurs: One third of the O atoms are tetrahedrally and the others are octahedrally coordinated by La.[16] Therefore in solid γ-Si_3N_4 and La_2O_3 the possibility of ternary substitution variants is apparent, and this has already been found for La_2O_3 (e.g. La_2O_2S[17] or the anti-type $CaMg_2N_2$[18]). Consequently ternary nitride spinels may be possible.

The question concerning the existence of lead(IV) nitride remains unanswered. With respect to the observation that Sn_3N_4 is much less stable than Ge_3N_4, the synthetic limits have probably been reached in the case of Pb_3N_4. Accordingly its existence remains unclear.

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