

**BULK MODULI AND PHASE TRANSITIONS OF CARBIDONITRIDOSILICATES
AND OXONITRIDOSILICATES AT HIGH PRESSURES UP TO 36 GPa**

**A. Friedrich¹, K. Knorr², A. Lieb³, St. Rath², H. A. Höppe³, B. Winkler¹,
W. Schnick³ & M. Hanfland⁴**

¹Institut für Mineralogie, Abteilung Kristallographie
Johann Wolfgang Goethe-Univ., Senckenberganlage 30, D-60054 Frankfurt a. M., Germany

²Institut für Geowissenschaften

Christian-Albrechts-Universität, Olsenhausenstrasse 40, D-24098 Kiel, Germany

³Department Chemie

Ludwig-Maximilians-Universität, Butenandtstrasse 5-13/D, D-81377 München, Germany

⁴European Synchrotron Radiation Facility (ESRF)

B.P. 220, F-38043 Grenoble, France

A new exciting field in material science was opened by the systematic investigation of nitridosilicates [1-3]. Nitridosilicates and oxonitridosilicates can be formally derived from oxosilicates by a total or partial exchange of nitrogen for oxygen. All of them are synthesised by high-temperature reactions and mainly form condensed three-dimensional networks. The exceptional thermal and chemical stability combined with high performance mechanical properties (hardness and strength) make these compounds very interesting for the materials science community. The replacement of oxygen by the more covalently behaving nitrogen extends the structural possibilities significantly. New structural features appear which are not known in oxosilicate chemistry. For example, nitridosilicates with star-like units $[\text{N}^{(4)}(\text{SiN}_3^{(2)})_4]$ of four SiN_4 -tetrahedra, which share a common corner, were recently found for the first time [4-6]. A further extension of the nitridosilicates can be found by a formal exchange of the central nitrogen of the $[\text{N}^{(4)}(\text{SiN}_3^{(2)})_4]$ unit by carbon in carbidonitridosilicates [7]. Nitridosilicates allow a long range of cation- and anion-substitution mechanisms leading to a variation of their physical properties. We have begun to study the influence of substitution effects on the properties of these materials by in situ high-pressure X-ray diffraction as well as ab initio computations.

In situ high-pressure powder diffraction experiments up to pressures of 36 GPa were performed at beamline ID09 of the ESRF. The samples were loaded into diamond anvil cells using liquid neon as a pressure-transmitting medium. Pressures were determined by means of the laser-induced ruby fluorescence method. Full powder diffraction rings were recorded on a MAR345 image plate system using a wavelength of 0.4138 Å. The images were processed and integrated with FIT2D [8]. LeBail refinements were carried out with GSAS [9].

Carbidonitridosilicates: $Ln^{III}_2[Si_4N_6C]$ ($Ln = Ho, Er$)

In the $Ln_2[Si_4N_6C]$ compounds [7], the carbon atom is negatively polarised. It connects four Si tetrahedra-centres to form a star-like unit $[C^{4-}(SiN_3^{2+})_4]$. $Ho_2[Si_4N_6C]$ [$P2_1/c$, $a = 5.931(1)$, $b = 9.900(1)$, $c = 11.877(3)$ Å, $\beta = 119.69(1)^\circ$, $V = 605.74(5)$ Å³] and isotypic $Er_2[Si_4N_6C]$ [$V = 602.70(5)$ Å³] were both investigated up to pressures of 36 and 21 GPa, respectively.

Both compounds show a similar compressional behaviour. Hence, the substitution of lanthanides, such as Ho and Er, seems to have no significant influence on the high-pressure properties. A third-order Birch-Murnaghan equation of state was fitted to the P-V data of $Ho_2[Si_4N_6C]$ between 0.0001 and 36 GPa. The values obtained for the isothermal bulk modulus and its pressure derivative are $B_0 = 159(3)$ GPa and $B' = 5.6(2)$. The bulk modulus is higher if compared to the computed bulk moduli of other nitridosilicates, such as $SrSiAl_2O_3N_2$ with $B_0 = 131.9(3)$ GPa, and $Ce_4[Si_4O_4N_6]O$ with $B_0 = 131(2)$ GPa and $B' = 5.0(2)$ [10]. The more covalent character of the Si-C bond compared with the Si-N bond might have an influence on the improved hardness and structural high-pressure stability of these compounds. The axial compressibilities show anisotropic behaviour with the b axis being most compressible. Quantum-mechanical DFT-based computations of the high-pressure properties of $Y_2[Si_4N_6C]$ are on-going and will be compared to the experimental results, allowing a further evaluation of the influence of lanthanide substitution.

Oxonitridosilicates (Sions):

With $Ce_4[Si_4O_4N_6]O$ (space group $P2_13$) a novel layer structure type was found [11]. The topology of the layer is hyperbolically corrugated, which can explain the unprecedented cubic symmetry for a layer silicate. The layer is built up by three-membered rings of corner-sharing $SiON_3$ tetrahedra, cross-linked through additional $SiON_3$ tetrahedra. While such small rings are not favoured in oxosilicates due to the electrostatic repulsion of SiO_4 tetrahedra, they are frequently found in less ionic nitridosilicates. Quantum-mechanical DFT-based computations at high pressures revealed a bulk modulus of $B_0 = 131(2)$ GPa for $Ce_4[Si_4O_4N_6]O$ [10]. However, when calculating the elastic constants of $Ce_4[Si_4O_4N_6]O$ by imposing finite strains, very large errors for the bulk modulus [$B_0 = 155(23)$ GPa] indicated structural instabilities and a possible phase transition at high pressures up to 18 GPa. Our experiments up to 28 GPa confirmed the proposed instability of this structure type. We detected a first-order phase transition occurring in a range between 8 and 10 GPa. This phase transition is reversible and shows a slight hysteresis. The space group symmetry is reduced to $P2_12_12_1$ following a group-subgroup relationship, which indicates a displacive structural mechanism.

The authors gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (DFG) through a Research Fellowship (WI 1232/17-1) within the project SPP-1136. Thanks are due to the ESRF for synchrotron beam time.

Literature

- [1] SCHNICK, W. & HUPPERTZ, H. (1997): Nitridosilicates - a Significant Extension of Silicate Chemistry. - Chem. Eur. J., 3, 679-683.

- [2] SCHNICK, W., HUPPERTZ, H. & LAUTERBACH, R. (1999): High-Temperature Syntheses of Novel Nitrido- and Oxonitridosilicates and Sialons Using RF Furnaces. - *J. Mater. Chem.*, 9, 289-296.
- [3] SCHNICK, W. (2001): Nitridosilicates, Oxonitridosilicates (Sions), and Oxonitridoaluminosilicates (Sialons) – New Materials with Promising Properties. - *Int. J. Inorg. Mater.*, 3, 1267.
- [4] HUPPERTZ, H. & SCHNICK, W. (1996): BaYbSi₄N₇ - überraschende strukturelle Möglichkeiten in Nitridosilicaten. - *Angew. Chem.*, 108, 2115; *Angew. Chem. Int. Ed. Engl.*, 35, 1983.
- [5] HUPPERTZ, H. & SCHNICK, W. (1997): Synthese, Kristallstruktur und Eigenschaften der Nitridosilicate SrYbSi₄N₇ und BaYbSi₄N₇. - *Z. Anorg. Allg. Chem.*, 623, 212.
- [6] HUPPERTZ, H. & SCHNICK, W. (1997): Eu₂Si₅N₈ and EuYbSi₄N₇ - The First Nitridosilicates with a divalent Rare Earth. - *Acta Crystallogr. Sect. C*, 53, 1751.
- [7] HÖPPE, H. A., KOTZYBA, G., PÖTTGEN, R. & SCHNICK, W. (2001): High-temperature synthesis, crystal structure, optical properties, and magnetism of the carbidonitridosilicates Ho₂[Si₄N₆C] and Tb₂[Si₄N₆C]. - *J. Mater. Chem.*, 11, 3300-3306.
- [8] HAMMERSLEY, A. (1998): FIT2D, Version 10.27, Reference Manual, ESRF, Grenoble, France.
- [9] LARSON, A. C. & VON DREELE, R. B. (1994): Los Alamos National Laboratory Report LAUR, 86-748.
- [10] WINKLER, B., HYTHA, M., HANTSCH, U. & MILMAN, V. (2001): Theoretical study of the structures and properties of SrSiAl₂O₃N₂ and Ce₄[Si₄O₄N₆]O. - *Chemical Physics Letters*, 343, 622-626.
- [11] IRRAN, E., KÖLLISCH, K., LEONI, S., NESPER, R., HENRY, P. F., WELLER, M. T. & SCHNICK, W. (2000): Ce₄[Si₄O₄N₆]O – a Hyperbolically Layered Oxonitridosilicate Oxide with an Ordered Distribution of Oxygen and Nitrogen. - *Chem. Eur. J.*, 6, 2714-2720.