



	Experiment title: Bonding in nitrido- and carbidonitridosilicates	Experiment number: HS-2146
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Shifts: 9	Local contact(s): Dr. Michael HANFLAND	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Karsten Knorr*, Stephanie Rath*: Institut für Geowissenschaften, Universität Kiel, Olshausenstrasse 40, D-24098 Kiel, Germany Alexandra Friedrich*, Björn Winkler: Institut für Mineralogie, Universität Frankfurt, Senckenberganlage 30, D-60325 Frankfurt am Main, Germany Alexandra Lieb*, Wolfgang Schnick: Department Chemie, Universität München (LMU), Butenandtstr. 5-13 (D), D-81377 München, Germany		

Report:

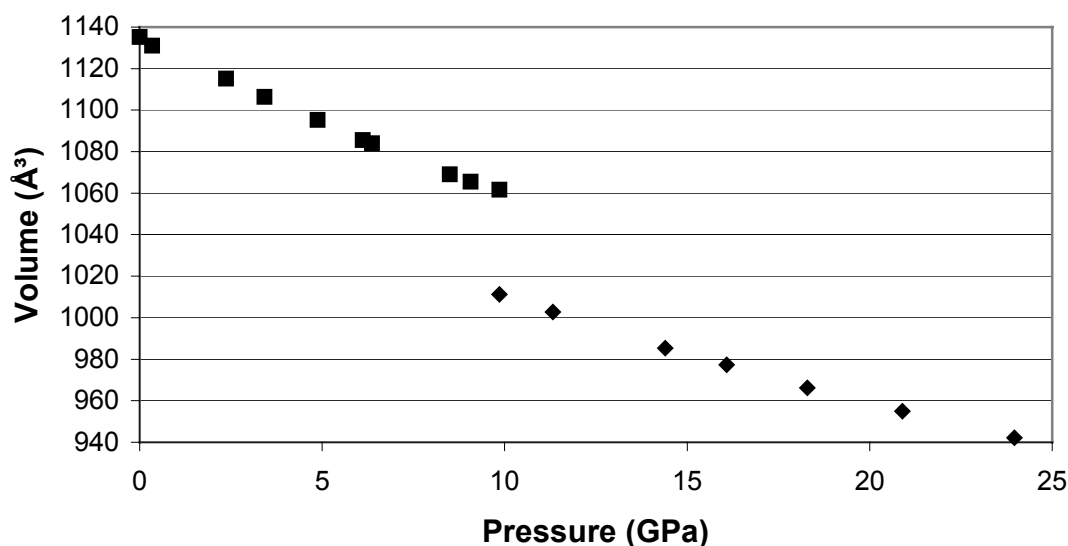
The systematic investigation of nitridosilicates [1-3] opened a new exciting field in material science, due to the exceptional thermal, chemical, and mechanical stability of these compounds. Nitridosilicates and oxonitridosilicates can be formally derived from oxosilicates by a total or partial exchange of oxygen by nitrogen. This replacement extends the structural possibilities significantly. 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]. The central nitrogen of this unit can be formally exchanged by carbon, hence, forming carbidonitridosilicates [5]. A long range of cation- and anion-substitution mechanisms within nitridosilicates leads to a variation of their physical properties.

We performed *in situ* high-pressure powder diffraction experiments up to pressures of 36 GPa using synchrotron X-ray radiation at a wavelength of 0.4138 Å and a MAR345 image plate system. The samples were loaded into LeToulllec diamond anvil cells using liquid neon as a pressure-transmitting medium. The images were processed and integrated with *FIT2D* [6]. *LeBail* refinements were carried out with *GSAS* [7].

We investigated the high-pressure behavior of the carbidonitridosilicates $\text{Ho}_2[\text{Si}_4\text{N}_6\text{C}]$ [$P2_1/c$, $a = 5.931(1)$, $b = 9.900(1)$, $c = 11.877(3)$ Å, $\beta = 119.69(1)^\circ$, $V = 605.74(5)$ Å³] and isotypic $\text{Er}_2[\text{Si}_4\text{N}_6\text{C}]$ [$V = 602.70(5)$ Å³] up to 36 and 21 GPa, respectively. Both compounds show a similar compressional behavior. Hence, the substitution of Ho and Er seems to have no significant influence on the high-pressure properties. Third-order Birch-Murnaghan equations of state were fitted to the P - V data and values for the isothermal bulk modulus and its pressure derivative of $B_0 = 160(4)$ GPa and $B' = 5.5(3)$ for $\text{Ho}_2[\text{Si}_4\text{N}_6\text{C}]$ and of $B_0 = 165(6)$

GPa and $B' = 4.7(7)$ for $\text{Er}_2[\text{Si}_4\text{N}_6\text{C}]$ were obtained. The bulk modulus is higher if compared to the DFT-computed bulk moduli of other nitridosilicates, such as $\text{SrSiAl}_2\text{O}_3\text{N}_2$ [$B_0 = 131.9(3)$ GPa] and $\text{Ce}_4[\text{Si}_4\text{O}_4\text{N}_6]\text{O}$ [$B_0 = 131(2)$ GPa, $B' = 5.0(2)$] [8]. 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.

We preliminary investigated the high-pressure behavior of the oxonitridosilicate $\text{Ce}_4[\text{Si}_4\text{O}_3\text{N}_7]\text{Cl}$ (space group $P2_13$, $a = 10.43$ Å). This compound is isotypic to $\text{Ce}_4[\text{Si}_4\text{O}_4\text{N}_6]\text{O}$ which crystallizes in a novel layer-type structure [9]. The topology of the layer is hyperbolically corrugated. Quantum-mechanical DFT-based computations on $\text{Ce}_4[\text{Si}_4\text{O}_4\text{N}_6]\text{O}$ at high pressures indicated structural instabilities and a possible phase transition at high pressures up to 18 GPa [8]. 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 (see Figure). This phase transition is reversible and shows a hysteresis. The space group symmetry is reduced to $P2_12_12_1$ ($a = 8.957$, $b = 10.458$, $c = 10.747$ Å at 10.22 GPa) following a group-subgroup relationship, which indicates a displacive structural mechanism. Fitting the p - V data with a third-order Birch-Murnaghan equation of state results in an isothermal bulk modulus $B_0 = 123(1)$ GPa ($B' = 5$) for the low-pressure phase, and $B_0 = 121(1)$ GPa ($B' = 5$) for the high-pressure phase. Further experiments on $\text{Ce}_4[\text{Si}_4\text{O}_4\text{N}_6]\text{O}$, which shows differently occupied Ce atom positions, could give an insight into the effects of O-Cl anion substitution on the high-pressure properties.



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