



	<b>Experiment title:</b> Bonding in nitrido- and carbidonitridosilicates	<b>Experiment number:</b> HS-2146
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## Report:

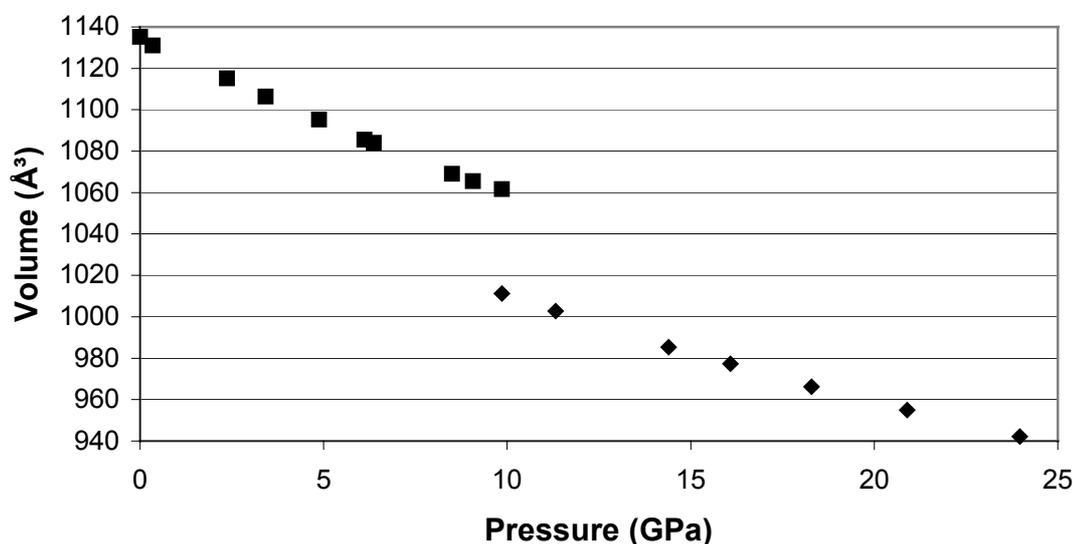
The systematic investigation of nitridosilicates [1-3] opened a new exciting field in material science, due to the exceptional thermal, chemical, and mechanical stability of these compounds. Nitridosilicates and oxonitridosilicates can be formally derived from oxosilicates by a total or partial exchange 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  $\text{SiN}_4$ -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,  $\beta = 119.69(1)^\circ$ ,  $V = 605.74(5)$  Å<sup>3</sup>] and isotypic  $\text{Er}_2[\text{Si}_4\text{N}_6\text{C}]$  [ $V = 602.70(5)$  Å<sup>3</sup>] 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.



### Literature:

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