A First Foray into High-Pressure Carbon Nitride Wonderland

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Abstract

The recently discovered C_3N_4 polymorphs, consisting exclusively of corner-sharing CN_4 tetrahedra, were synthesized after more than three decades of effort.[1,2] These materials exhibit exceptional physical properties, including superhardness, ultraincompressibility, piezoelectricity, and photoluminescence, while being recoverable to ambient conditions. However, aside from chemical doping, the three known polymeric C_3N_4 polymorphs offer limited opportunities for tuning their physical and chemical properties.

A natural route toward expanding the chemistry of such CN_4-based carbon nitrides is to draw inspiration from silicon nitrides, which originally motivated the prediction of these C_3N_4 structures.[3] In particular, nitridosilicates constitute a large family of silicon nitride materials built from corner-sharing SiN_4 tetrahedra that form extended, often porous, anionic frameworks hosting metal cations. The incorporation of these cations not only enables remarkable structural diversity but also strongly influences the physical properties of the resulting materials, underpinning applications ranging from solid-state lighting to other advanced technologies. Given carbon's propensity to behave like silicon at high pressures, carbon-based analogues of nitridosilicates, termed nitridocarbonates, are expected to exist.

In this talk, we explore whether nitridocarbonates can be realized in ternary C–N systems using high pressures and high temperatures. To achieve this, carbon, nitrogen and various transition metals were compressed in diamond anvil cells and subsequently laser heated. The resulting compounds were characterized by synchrotron single-crystal X-ray diffraction and density functional theory (DFT) calculations.

Remarkably, several synthesized ternary phases contain extended anionic frameworks of corner-sharing CN_4 tetrahedra and are direct structural analogues of known nitridosilicates. Other novel compounds display a far richer structural chemistry, incorporating not only CN_4 tetrahedra but also $C(CN_3)$ and $C(C_2N_2)$ tetrahedral units, as well as N–N bonds. Their physical properties, including stability ranges, compressibility, and electronic band gaps, will also be presented.

Together, these findings establish nitridocarbonates as a new class of pressure-stabilized materials. Compared with their nitridosilicate counterparts, they offer enhanced chemical flexibility while retaining attractive physical properties, opening new opportunities for the design of functional materials and future technological applications.

References:

1. Laniel *et al*. Advanced Materials **36**, 2308030 (2024)
2. Laniel *et al*. Advanced Functional Materials **35**, 2416892 (2025)
3. Liu *et al*. Science **245**, 841-842 (1989)