High-pressure synthesis of a hafnium carbonitride hosting a hexazine ring

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Abstract

The formation of polymeric nitrogen and carbon-nitrogen configurations remains a long-standing challenge in chemistry. High pressure synthesis has emerged as an effective strategy, enabling the preparation of a range of polymeric nitrogen species and carbonitride anionic species in metal-C-N ternary systems (e.g., [1-10]). The *cyclo*-N_6 ring, one of the most sought-after yet elusive polymeric nitrogen species, has hitherto been identified only in metal-N binary systems and exhibits poor stability upon decompression, with no reports of recovery to ambient conditions.[8-10]

In this study, we report a novel hafnium carbonitride, synthesized using a laser-heated diamond anvil cell under near-megabar pressures and temperatures reaching several thousand kelvin. Solved by multigrain X-ray crystallography (**Figure 1**), its crystal structure features a 3D C-N anionic framework consisting of [CN_4] tetrahedral units interconnected by polymeric nitrogen chains. Remarkably, within this framework, a fully single-bonded armchair-shaped *cyclo*-N_6 anion is trapped. The hafnium carbonitride structure remained intact upon decompression down to below 10 GPa and is predicted to be dynamically stable at 0 GPa by DFT calculations.

Our results demonstrate that embedding a *cyclo*-N_6 ring within a carbonitride framework provides an effective route to enhance the stability of this otherwise highly labile species. This strategy open a new pathway for the synthesis of *cyclo*-N_6 rings and other novel nitrogen-based species that are typically accessible only under extreme conditions, potentially enabling their stabilization at ambient conditions.

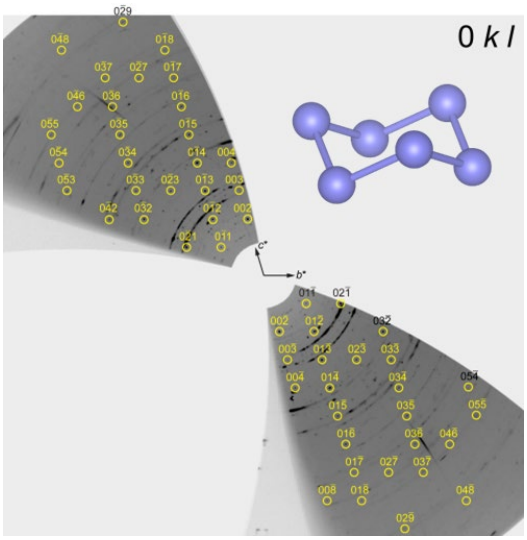

Figure 1. Reconstructed reciprocal lattice section 0*kl* based on the single-crystal X-ray diffraction data of a hafnium carbonitride crystallite collected at the synthesis pressure.

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