Crystal chemical design and high-pressure synthesis of non-dense polynitrides

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High-pressure chemistry is known to inspire the creation of unexpected new classes of compounds with exceptional properties. Despite general trends that pressure leads to the formation of dense compounds with highly coordinated elements, sometimes high-pressure synthesis may counterintuitively lead to the formation of porous or even van der Waals (vdW) bonded layered compounds. Since vdW compounds could potentially be used as precursors to 2D materials, the structural diversity of the accessible high-pressure phases may be used for the design of novel single-layer materials.

Here, we employ the laser-heated diamond anvil cell technique for synthesis of a Dirac material BeN_4 and pentagonal NiN_2. A triclinic phase of beryllium tetranitride *tr*-BeN_4 was synthesized from elements at ~85 GPa. Upon decompression to ambient conditions, it transforms into a compound with atomic-thick BeN_4 layers interconnected via weak van der Waals bonds and consisting of polyacetylene-like nitrogen chains with conjugated π systems and Be atoms in square-planar coordination. Theoretical calculations for a single BeN_4 layer show that its electronic lattice is described by a slightly distorted honeycomb structure reminiscent of the graphene lattice and the presence of Dirac points in the electronic band structure at the Fermi level. The BeN_4 layer, *i.e.*, beryllonitrene, represents a qualitatively new class of 2D materials that can be built of a metal atom and polymeric nitrogen chains and host anisotropic Dirac fermions.

High-pressure synthesis from elements leads to a novel nickel diazenide NiN_2 which possesses atomic-thick layers comprised of Ni_2N_3 pentagons forming Cairo-type tessellation. The layers of NiN_2 are weakly bonded with the calculated exfoliation energy of 0.72 J/m^2, which is just slightly larger than that of graphene. The compound crystallizes in the space group of the ideal Cairo tiling (*P*4/*mbm*) and possesses significant anisotropy of elastic properties. The single-layer NiN_2 is a direct-band-gap semiconductor, while the bulk material is metallic. This indicates the promise of NiN_2 to be a precursor of a pentagonal 2D material with a tunable direct band gap.

References:

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