High-pressure synthesis of alkali metal carbodiimides

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Abstract

Metal carbodiimides, comprised of the $[N=C=N]^{2-}$ anion, constitute a structurally versatile class of inorganic compounds. In many of these compounds,[1–6] metal cations and $[N=C=N]^{2-}$ anions are typically arranged in alternating layers, with the $[N=C=N]^{2-}$ units being perpendicular to the cation layers, producing structure types derived from metal oxides/chalcogenides (Figure 1a–d).[2,6] A particularly interesting subgroup of this class of materials are alkali metal carbodiimides (A_2CN_2, A = Li/Na/K). While Li_2CN_2[7] remains structurally related to oxide-derived archetypes (Figure 1e and 1f), Na_2CN_2[8] and K_2CN_2[9] display markedly tilted $[N=C=N]^{2-}$ units with respect to the layers of cations (Figure 1g and 1h), resulting in these structures having thus far no clear counterparts. Understanding the unique nature of these alkali carbodiimide compounds can presumably be understood through crystal chemical principles and high-pressure investigations; with alkali carbodiimide being fully *terra incognita* at extreme densities.

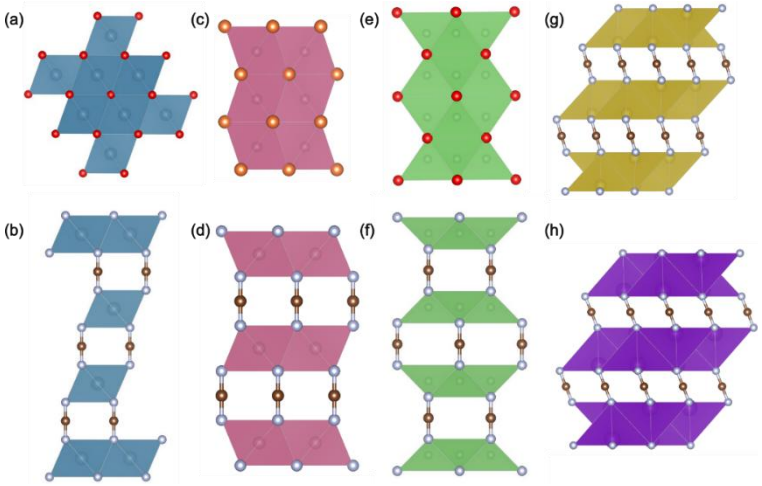

Figure 1. Analogies between the crystal structures of metal oxides/chalcogenides (O, S) and carbodiimides. Red, orange, grey, brown, blue, pink, green, yellow and purple spheres represent oxygen, sulfur, nitrogen, carbon, calcium, iron, lithium, sodium and potassium atoms, respectively, drawn using the atomic radii for O/S/N/C and the ionic radii for Ca/Fe/Li/Na/K. (a) CaO and (b) $CaCN_2$[2]. Ca-centered octahedra are shown in blue; (c) FeS[6] and (d) $FeCN_2$[6]. Fe-centered octahedra are shown in pink; (e) Li_2O[8] and (f) *I*4/*mmm* Li_2CN_2[7]. Li-centered tetrahedra are shown in green. The *C*2/*m* (g) Na_2CN_2[8] and (h) K_2CN_2[8]. Na/K-centered square pyramids are shown in yellow/purple. The latter two have no such direct counterparts.

In this talk, the unique nature of the Na_2CN_2[8] and K_2CN_2[9] compounds will first be rationalized based on i) the cation to anion ratio and ii) chemical precompression of the metal cation. Then, the investigation of the Li-, Na- and K-C-N systems up to 50 GPa using laser-heated diamond anvil cells (LHDACs) will be presented, demonstrating the synthesis of four novel carbodiimide polymorphs through synchrotron single-crystal X-ray diffraction (SCXRD). These novel compounds not only shed light on the interplay between cation size, pressure, and the orientation of the $[N=C=N]^{2-}$ units, but also demonstrate important trends across alkali metal carbodiimide compounds. These results will serve as a template for future investigations of metal carbodiimide studies, as well as provide knowledge on the thermodynamically stable A-C-N compounds up to 50 GPa.

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