

Synthesis of novel polynitrogen anions in magnesium-nitrogen salts

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Polynitrogen compounds have been actively pursued driven by their potential as ultrahigh-performing propellants and explosives. Despite remarkable breakthroughs in the past two decades, conventional chemistry methods have fallen short of fully exploiting the potential of polynitrogen compounds. The pressure parameter, however, has recently been demonstrated to allow the synthesis of exotic and highly energetic novel polynitrogen (poly-N) entities with relevance as high energy density materials (HEDM).

In particular, the synthesis of the pentazolite entity in the $(\text{Li})^+(\text{N}_5)^-$ salt at only 45 GPa showcased the proclivity of highly reducing elements to rupture the N_2 triple bond at moderate pressure and to increase the crystal's cohesive energy through strongly ionic bonds, ultimately allowing the compound's retrieval at ambient conditions [1]. With a formal charge of 2+, alkaline earth elements are the next logical step to obtain poly-N species as they are expected to favor the low pressure formation of salts with an even greater energy density and an enhanced stability. Indeed, at only 15 GPa, the MgN_4 and MgN_{10} compounds, both composed of energetic polynitrogen anions, were calculated to be stable [2–4]. Despite their obvious appeal, until now nitrogen-rich alkaline earth materials have never been obtained.

Here, molecular nitrogen was compressed along with pure magnesium up to 60 GPa and laser-heated to 3000 K. Under these conditions, two new Mg-N solids were produced and characterized by X-ray diffraction as well as Raman spectroscopy measurements. Their crystalline structure was solved by single crystal X-ray diffraction experiments (see Fig. 1) and they were shown to possess the Mg_2N_4 and MgN_4 chemical compositions. The $(\text{Mg})^{2+}(\text{N}_4)^{2-}$ salt is composed of 8-fold (cubic) N coordinated Mg^{2+} atoms while nitrogen forms exotic infinite anionic polythiazyl-like 1D N-N chains. These energetic nitrogen chains, with a N-N bond order between one and two, are analogous to those observed in $\text{ReN}_8 \cdot x\text{N}_2$ and FeN_4 in which they form at a much higher pressure—above 1 Mbar [5, 6].

The second detected reaction product, the $(\text{Mg}_2)^{4+}(\text{N}_4)^{4-}$ salt, adopts a complex structure constituted of *cis*-tetrazene like tetranitrogen anions, synthesized for the first time. As for other energetic polynitrogen entities, the N-N covalent bonds are of low bond order, in this case also comprised between one and two. The behaviour of the

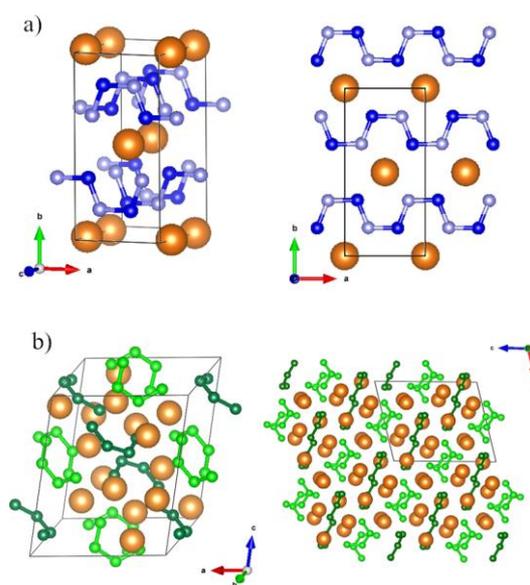


Figure 1: Crystal structure of the a) MgN_4 and b) Mg_2N_4 salts at 58.5 GPa.

Mg_2N_4 solid was followed during its decompression. Its vibrational modes and lattice parameters were found to vary smoothly with pressure down to 2.3 GPa, displaying no sign of chemical reaction, decomposition or phase transition. After the complete release of pressure however, changes in the Raman spectra and discontinuities in the diffraction lines suggest a modification of the solid's structural characteristics. Single crystal X-ray diffraction measurements at ambient conditions unveiled an isosymmetrical phase transformation in the Mg_2N_4 salt, characterized by a difference in the stacking of the N_4^{4-} units. Theoretical calculations were also performed and highlight the compound's ionicity, stability, and provide further insight into the solid's properties.

The high pressure synthesis and retrieval at ambient conditions of this new anionic polynitrogen entity opens up new research avenues. First, it further establishes high pressure as an efficient method not only to discover new forms of poly-N, but also as a tool to produce novel chemical species relevant at ambient conditions. Secondly, it provides a new building block to synthesize new high performance nitrogen-based high energy density materials.

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