A1 EHPRG Award

High-Pressure Synthesis of the First Thermodynamically Stable Silver Nitride, AgN_5

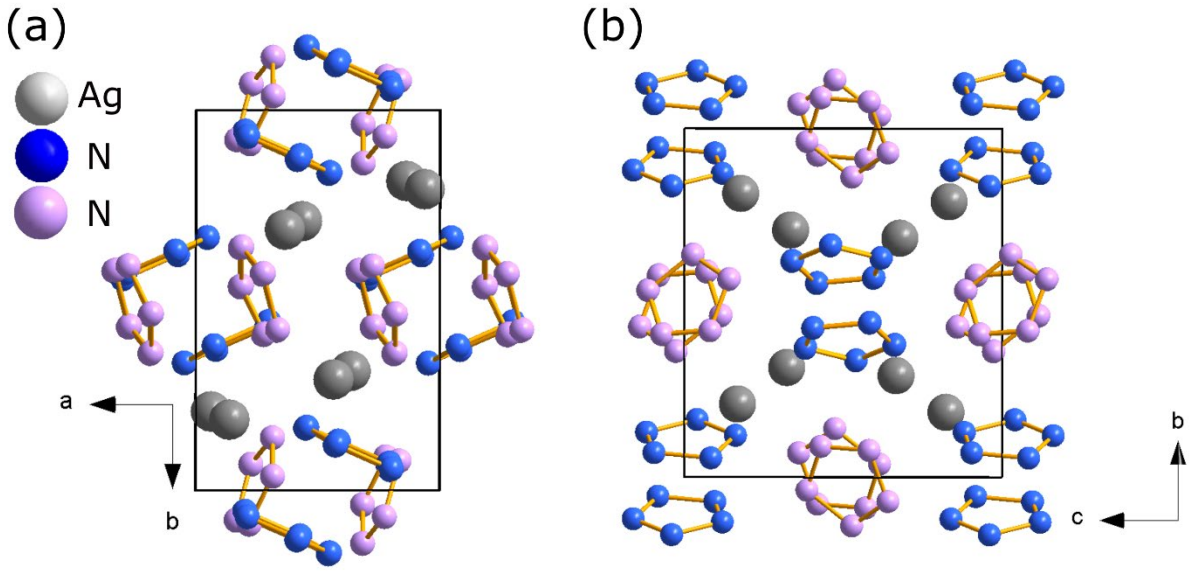
Akun LIANG (Eastern Institute of Technology, Ningbo, China),
Dominique LANIEL (University of Edinburgh, UK)

Abstract

Silver, like its group 11 counterparts copper and gold, has a valence electron configuration of $4d^{10}5s^1$. Its fully filled 4*d* subshell provides poor shielding of the 5*s* electron, and, together with relativistic effects, results in a relatively high first ionization energy (731 kJ/mol) and pronounced chemical inertness [1]. Nitrogen, owing to the strength of its triple bond, is likewise chemically inert [2]. Consequently, no direct reaction between silver and nitrogen has been observed under ambient conditions, and no thermodynamically stable Ag-N solid has been reported.

Here, we report the synthesis of the first thermodynamically stable Ag-N compound, silver pentazolate (AgN_5), obtained via the direct reaction of elemental silver with molecular nitrogen at 118(3) GPa and temperatures exceeding 2000 K. The crystal structure was solved from single-crystal X-ray diffraction (SCXRD) data, revealing two distinct types of *cyclo*-N^{5-} anions arranged in an antiparallel, offset stacking configuration. Convex-hull calculations indicate that AgN_5 lies on the thermodynamic ground state in the pressure range of 40-80 GPa. Its equation of state and stability upon decompression were investigated by in situ SCXRD measurements, showing that AgN_5 remains stable down to 55(3) GPa but cannot be recovered to ambient conditions. First-principles calculations were further performed to assess its thermodynamic stability, electronic structure, and band gap.

These results demonstrate that high-pressure and high-temperature conditions can induce unprecedented chemical reactivity between otherwise inert elements, enabling the formation of novel nitrogen-rich compounds with high energy density.



References

[1] Loock, H.-P et al, *Phys. Rev. A*. **1999**, 59, 873-875.
[2] Greenwood, N. N et al, *Chemistry of the Elements*. Elsevier Butterworth-Heinemann, **1997**.
[3] Liang A et al, *JACS Au*. **2025**, 6, 193-199.