High-Pressure Route to Access and Recover Metastable Phases

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High-pressure and high-temperature (HPHT) is a unique technique that allows the sytem to access energy minima states which are separated from the true ground state by significant free energy and kinetic barriers.[1] These high-energy states once accessed may be recovered to ambient conditions in metastable forms. Among all the inorganic chemistries, nitrides seem to posses the highest energy scale of metastability.[2] This means many high-enthalpy phases of nitrides with exotic struture-property relation can be realized in metastable forms using HPHT technique. Here, I present two such phases in Ti-N_2 system that were accessed using laser heated diamond anvil cell technique (LHDAC) at pressures of a few tens of gigapascals (GPa) and temperatures >2300 K. [3,4] They are 1) *tetragonal*-TiN_2 (titanium pernitride) and 2) *cubic*-Ti_3N_4. The phase identification was performed using *in situ* X-ray diffraction and Raman scattering supported by *first principles* theoretical calculations. Both the compounds exhibit distinct electronic and mechanical properties as compared to corresponding mononitride, TiN. The first non-noble metal pernitride,TiN_2 exhibits crystal structure that consists of single-bonded nitrogen dimers (N–N dumbbells) that results in its ultraincompressible nature (bulk modulus 385 GPa). TiN_2 is metallic and fully recoverable to ambient conditions and is stable in air. On the other hand *cubic*-Ti_3N_4 is dynamically unstable below 5 GPa but it is the first known semiconducting nitride phase (bandgap ~ 0.9 eV) of titanium and exhibits a crystal structure with coordination numbers of Ti and N that are much higher than that of transition metal mononitrides with rocksalt structure.

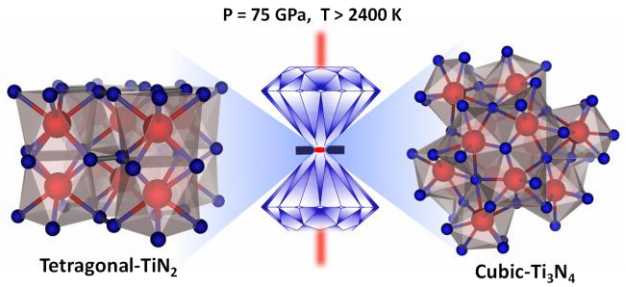

Figure 1. Schematic represention of the discovery of new nitrides of titanium using LHDAC technique.

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