Calculation of XRD spectra of N-H Extended Solids under High Pressure.

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A method for calculating x-ray diffraction spectra based on LAMMPS (Large-scale Atomic Molecular Massively Parallel Simulator) toolkit was developed and applied for the search of the optimum crystalline structure of N-H gas mixtures under high pressure. The structure of N-H under high pressure was modelled using the evolutionary program USPEX based on plane wave density functional theory (DFT) calculations using VASP. The set of the LAMMPS tools, shell scripts, and matlab subroutines was used for an automatic generation of XRD spectra which are in excellent agreement with that generated by crystal structure analyzer Mercury (The Cambridge Structure Database). Our script was used for search of the best fit structure over 3000 evolutionary simulated structures for each concentration of N and H. The concentration ratio of N\textsubscript{2} to H\textsubscript{2} gas used in this work was 3:1, 4:1, and 9:1. The range of the studied pressures was 10 – 50 GPa on compression, and 50-10 GPa on isotropic decompression of the extended network. The formation of an extended network with covalent bonds occurs at 30-50 GPa. Higher concentrations of N require higher pressures to form a covalent bond network. New structures of NH extended solids with covalent bonds are predicted: with P-1(C1-1) symmetry group for the 9:1 ratio, with PBAM (D2H+9) symmetry group for the 4:1 ratio, and with P-1(C1-1) symmetry for 3:1 ratio of N\textsubscript{2} to H\textsubscript{2} gas. Calculations of the mixtures of N\textsubscript{2} and H\textsubscript{2} gases at pressures in the range 10-20 GPa resulted in a variety of structures without covalent network formation, consisting instead of nitrogen moieties such as tetrazene and N\textsubscript{2}. At 10 GPa the lowest energy structures for 3:1 and 4:1 N-H ratio are combination of protonated ammonia, nitrogen pentagons and N\textsubscript{2} molecules. Raman spectra were calculated and vibration modes were identified for the final structure at each concentration to complement the XRD calculations.