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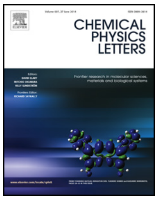

Sodium pentazolate: A nitrogen rich high energy density material

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ABSTRACT

Sodium pentazolates NaN_5 and Na_2N_5, new high energy density materials, are discovered during first principles crystal structure search for the compounds of varying amounts of elemental sodium and nitrogen. The pentazole anion (N_5^-) is stabilized in the condensed phase by sodium Na^+ cations at pressures exceeding 20 GPa, and becomes metastable upon release of pressure. The sodium azide (NaN_3) precursor is predicted to undergo a chemical transformation above 50 GPa into sodium pentazolates NaN_5 and Na_2N_5. The calculated Raman spectrum of NaN_5 is in agreement with the experimental Raman spectrum of a previously unidentified substance appearing upon compression and heating of NaN_3.

1. Introduction

Nitrogen-rich high energy density materials (HEDMs) [1–4] are being explored as new propellants and explosives. Their high energy content is due to the large amount of energy released upon decomposition of single- and/or double-bonded nitrogen in the condensed phase into triple-bonded gas-phase diatomic N_2 molecules. Solid phases of nitrogen at low pressure and temperature are composed of weakly interacting N_2 molecules, leading to a plethora of stable molecular crystal phases [5,6]. It was predicted in 1992 that at 50 GPa the ϵ-N_2 molecular crystal transforms into the single-bonded cubic-gauche (cg) polymeric phase of nitrogen [7], which was eventually synthesized by Eremets et al. [8]. Most recently, a layered polymeric nitrogen crystal has also been discovered [9]. However, the synthesis of these materials occurs at very high pressures ($\sim$100 GPa) and temperatures ($\sim$2000 K) and the recovery at ambient conditions was found to be problematic [8–10]. To be useful in real-world applications, HEDMs must at least be metastable at ambient conditions. Therefore new high-nitrogen content materials are actively being searched [1–4].

One promising idea is to achieve metastability of nitrogen-rich HEDMs by introducing foreign atomic impurities into the nitrogen system to facilitate their synthesis, as well as to enhance stability at ambient conditions. For example, the addition of metallic elements to the pure nitrogen system causes electron transfer from metallic to nitrogen atoms. The competition between ionic and covalent bonding might promote new nitrogen phases other than triply bonded N_2. The appreciable degree of ionicity might also help to stabilize the new nitrogen condensed phases at ambient conditions.

The high-pressure synthesis of novel high-nitrogen HEDMs can be facilitated by compressing group-I metallic azide precursors, such as sodium azide (NaN_3) [11,12]. An azide is a double bonded linear anion consisting of three nitrogen atoms. The presence of double bonds is believed to assist in either the conversion of azides into extended single-bonded nitrogen structures, or the formation of multi-atom nitrogen clusters. An indirect sign of such processes was seen previously in Raman measurements performed on sodium azide compressed to above 50 GPa [11]. The new peaks in the 700–800 cm^{-1} and 1000–1300 cm^{-1} range appearing upon compression and laser heating, cannot be attributed to molecular vibrations of the initial azide precursor [13]. The authors assumed that these new peaks originate from either polymeric nitrogen or a compound containing nitrogen molecular clusters [11]. However the exact crystal structure was never determined.

Recent advances in structure prediction methods [14–17] make it possible to screen compounds of all possible stoichiometries and find the most stable structures using first-principles density functional theory. Being motivated by the goal of discovery of high-nitrogen content HEDM's stabilized by metallic cations, we undertook a systematic search of Na_xN_y materials containing variable number of elemental sodium and nitrogen atoms in the crystal lattice. The calculated enthalpies of the predicted structures are used to determine the most stable compounds at a given pressure, allowing us to construct the phase diagram of the materials of varying stoichiometry. Although the structure search has not been specifically biased towards systems containing N_5^-, new compounds, sodium pentazolates NaN_5 and Na_2N_5, metastable at ambient conditions, are discovered. The detailed characterization of these materials is performed by comparing the calculated Raman

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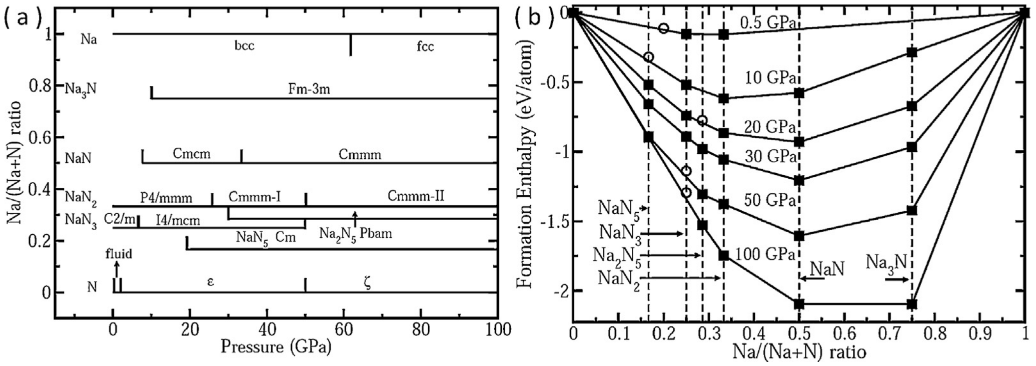

Figure 1. (a) Pressure-composition phase diagram of new Na–N crystal phases discovered in simulations. (b) Convex hull diagram at pressures 0.5, 10, 20, 30, 50 and 100 GPa. Solid squares represent thermodynamically stable phases, open circles – metastable phases.

spectra with those obtained in experiment [11], to answer the important question whether the sodium pentazolates appear upon compression and heating of sodium azide precursor.

2. Computational details

The search for new Na_xN_y compounds of varying stoichiometry is performed at varying pressures by using the first principles evolutionary structure prediction method USPEX [14–16]. The unit cell for the structure search contains between 6 and 16 atoms which covers a substantially large portion of the energy landscape. The prediction of new structures at a given pressure begins by generating crystal structures with randomized chemical composition, lattice parameters, and atomic coordinates, followed by energy minimization using density functional theory (DFT). The structures are ranked according to their enthalpies of formation, then variation operators are applied to the best of them having lowest enthalpies to generate structures of a new generation. The process repeats until the lowest enthalpy crystals do not change for several generations, thus indicating that no new structures with lower enthalpies will appear. For a given pressure, the convex hull, a formation enthalpy-composition curve is constructed. It consists of points that correspond to the structure with the lowest formation enthalpy at a given composition with respect to the lowest enthalpy structures of the base elements. The reference structures are α-N_2, ϵ-N_2, and cg-N for nitrogen and bcc-Na and fcc-Na for sodium each taken at corresponding pressure.

First-principles calculations are performed using the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) functional [18] within density functional theory (DFT) implemented in VASP [19] and DMol [20]. The PBE functional has been previously shown to give reliable results for sodium azide [13,21]. In VASP calculations, ultrasoft pseudopotentials [22] with inner core radii of 1.757 Å for Na and 0.873 Å for N and plane wave basis sets are used with an energy cutoff of 600 eV and a 0.05 $Å^{-1}$ k-point sampling. Charges on atoms and bond orders are calculated with DMol, the latter is also used to perform molecular dynamics simulations at high temperatures to establish dynamical stability of new compounds. Vibrational properties including phonon dispersion curves are calculated – using the PHONOPY code [23], which interfaces with VASP.

In addition, the adequate accuracy in predicting the small enthalpy differences is established by comparing the formation enthalpies calculated by the PBE GGA and HSE06 hybrid functionals. The formation enthalpy for each crystal include zero-point energy contributions that are calculated using the vibrational spectra. The calculations using the HSE06 functional use projector augmented wave (PAW) pseudopotentials [24] with inner core radii of 1.757 Å for Na and 0.582 Å for N. A large energy cutoff of 1000 eV is used to accurately describe the wavefunction near the nitrogen core. Convergence studies show that only a 0.10 $Å^{-1}$ k-point sampling is adequate. Dmol all-electron calculations of charges and bond order are performed using DND local combination of atomic orbitals (LCAO) basis sets.

3. Results and discussion

The robustness of the algorithm for discovering new crystal phases of materials with varying stoichiometries is demonstrated by predicting known phases of sodium azide (NaN_3) without any prior input. The structure search correctly finds the α-phase of NaN_3 with the symmetry C2/m at 0.5 GPa in agreement with experiment, while at 30 GPa it correctly produces the I4/mcm polymorph of NaN_3 [21,25]. At 60 GPa, the P6/m-Na_2N_6 structure featuring N_6 rings is found to be the lowest enthalpy phase with a 1:3 sodium to nitrogen ratio, consistent with previous calculations [21].

In addition to known phases of NaN_3, several new crystals with novel stoichiometries are discovered, their crystal structure information being provided in Supplementary Table S1. In Figure 1(a) and (b), the predicted phase diagram, as well as the calculated convex hull, at several pressures are shown. The crystal structures of materials with variable composition are labeled by the symmetry followed by the chemical formula. Figure 2 displays the crystal structures of several newly discovered materials.

In order to further justify the adequate performance of PBE functional in predicting accurate formation enthalpies, the convex hull at 50 GPa has been calculated using both PBE functional and the hybrid HSE06 functional [26], see comparison in Figure 3. The HSE06 formation enthalpies for most of the compounds are slightly higher than those calculated using PBE functional, with exception of Na_3N which has lower HSE06 formation enthalpy. Overall, both HSE06 and PBE convex hulls are very similar. The HSE06 functional is considered to be state-of-the-art and gives formation enthalpies and atomization energies close to experiment across a wide range of molecules and crystals [27]. Therefore, the similarity of the two curves demonstrates a good accuracy of the PBE calculations of the systems under study.

It is found that NaN_3 no longer resides on the convex hull above 50 GPa, thus implying that it is thermodynamically unstable beyond this pressure. This results is also reproduced with the HSE06 functional, see Figure 3. Therefore, upon compression in a diamond anvil cell (DAC) above 50 GPa, NaN_3 will transform into a combination of Na_xN_y phases.

The crystal phases P2/c-NaN_5, Cm-NaN_5, and Pbam-Na_2N_5, shown in Figure 2(a)–(c), are the most interesting of all the newly discovered materials since they contain pentazole molecules that can be potential sources of unidentified Raman peaks in experiments on compression of NaN_3 at high pressures [11]. Our