I. INTRODUCTION

Poly-nitrogen materials are being actively investigated\cite{1-6} with the goal to obtain stable high-nitrogen content compounds, which are expected to outperform conventional all-organic energetic materials (EMs). The pure single-bonded cubic gauche (cg) polynitrogen crystal\cite{7} would be the leading candidate, as the decomposition of the single-bonded condensed-phase nitrogen to the gas-phase triple bonded diatomic N₂ molecules results in enormous release of energy. In 2004, Eremets et al.\cite{8} successfully synthesized the single-bonded cg phase of polymeric nitrogen, that was originally predicted to be energetically favorable over the epsilon phase of N₂ above 50 GPa. In 2014, Tomasino et al.\cite{10} discovered a new layered polymeric phase of nitrogen. Unfortunately, the synthesis of polymeric nitrogen requires excessive heating above 2000 K and enormous pressures above 100 GPa. Moreover, its recovery at ambient conditions is challenging\cite{11}. For this reason, new approaches for the synthesis of high nitrogen content materials are urgently sought\cite{1-3,6,12-14}.

Introduction of other elements into polynitrogen-containing crystals appears to be a viable route to promote metastability while reducing synthesis pressure\cite{12,13,15}. Previously, alkali polynitrogen materials including sodium\cite{13}, cesium\cite{12,16}, and lithium\cite{17} polynitrates have been investigated at high pressures. In particular, cesium pentazolate CsN₅, consisting of pentazolate N₅⁻ anions and Cs⁺ cations was predicted, and then synthesized\cite{12}. The presence of alkali metal atoms facilitates the electron transfer to nitrogen N₅ clusters, thus making cyclo-N₅⁻ aromatic. Previously studied alkali nitrides XN₃y, X = {Cs, Na, Li, K} display similarities: some of them contain N₅ pentazolates at a specific stoichiometry XN₅ or infinite nitrogen chains in XN₂ stoichiometry\cite{12,13,16-18}. First-principles calculations show that cesium pentazolate\cite{17} and lithium pentazolate\cite{17} are stable above 15 GPa whereas sodium pentazolate is predicted to be stable above 20 GPa. The cesium pentazolate material was synthesized in a diamond anvil cell by compressing and laser heating CsN₃ and N₂ to pressures near 60 GPa\cite{12}. High-nitrogen compound XN₆ containing N₆ hexazine rings is predicted to exist in the case of cesium and potassium, whereas no such structures are found in case of Li, N₃ and Na, N₃ materials\cite{12,17,18}.

Based on the similarities and differences between alkali polynitrates, the interesting question is whether rubidium pentazolate exists and whether it could be synthesized under similar conditions as CsN₅ using possible precursor mixture, RbN₃+N₂. The barrier to decomposition of cyclo-N₅⁻ into N₅⁻ + N₂ is significant, 92 kJ/mol. Therefore it is expected to be metastable at ambient conditions making it a promising candidate for high nitrogen content EMs\cite{19,20}. The relative stability of cyclo-N₅⁻ allowed the synthesis of cyclo-N₅⁻ compounds at ambient conditions\cite{21-24}.

In this work, rubidium polynitrogens are investigated with the goal to explore novel polynitrogen EMs. Being similar to cesium, rubidium polynitrogens are interesting as for both elements, d electrons of the core begin to play a prominent role at high pressures. An indirect indication of the expected diversity in rubidium polynitrogen compounds is the complex phase diagram of pure Rb, which possesses six phases between 0 and 48 GPa\cite{25,26}. This is in contrast to Na that has only two stable phases between 0 GPa and 100 GPa with the phase transition from bcc to fcc occurring at sufficiently high pressure 60 GPa\cite{27}. It is suggested that the presence of occupied 3d orbital results in destabilization of the bcc and fcc structures at high pressures\cite{25}. The goal of this work is to predict and characterize new rubidium polynitrogen materials, including but not limited to RbN₅ and RbN₂, as well as to discuss future experimental realization of our predictions by suggesting possible precursors and corresponding pressures to initiate the high pressure chemistry.
II. COMPUTATIONAL METHODS

A search for new compounds of varying RbₓNᵧ stoichiometry is performed using the first-principles evolutionary structure prediction method USPEX²⁸⁻³⁰ at four pressures, 0, 30, 60 and 100 GPa. For each pressure the search begins by generating crystal structures containing variable amounts of elemental rubidium and nitrogen with 8 - 16 atoms in the unit cell. The crystals in the first generation are built with a random composition and lattice parameters. Density functional theory (DFT) is then used to minimize the total energy at fixed hydrostatic pressure by relaxing the atomic coordinates and the unit cell parameters of each structure of the entire population. The structures are then ranked by their formation enthalpy, those with the lowest formation enthalpy being the most favorable. A new generation of crystals is then produced with a combination of the lowest enthalpy structures from the previous generation, new random structures, and by applying variation operators, such as atom mutations and lattice permutations, to the lowest enthalpy structures to make a set of new crystals. This cyclic process of creating and optimizing new generations repeats until the best structures do not change for the last ten generations.

If applied properly, the USPEX method is very robust. In particular, we search for 99 compositions of RbₓNᵧ over a wide range of pressure. Taking into account such an exhaustive set of stoichiometries and the relative simplicity of the chemistry of the binary compounds, it is very likely the method found all the important compounds consisting of a reasonable number of atoms per unit cell. In two cases, a molecular search was also conducted in addition to the standard USPEX variable composition search to determine if larger crystals would lower the enthalpy compared to the smaller molecular crystals that were found during the variable composition search.

The convex hull, a formation enthalpy versus composition plot, is generated to determine which compounds are thermodynamically stable. The convex hull is constructed with the lowest formation enthalpy phases of each compound. If the compound lies on the convex hull, it is considered thermodynamically stable³¹ and will not decompose into the constituent pure elements or other RbₓNᵧ compounds. The formation enthalpy is defined as the difference in enthalpy of a given compound and the sum of the enthalpies of the pure referenced structures, Rb and N, in their aggregate state at a given pressure and temperature. The reference structures of elemental N and Rb used to calculate the enthalpy of formation are α-N₂ and bcc Rb at 0 GPa, ε-N₂ and I₄/m amd Rb at 30 GPa, and c₅-N and Conca Rb at 60 GPa and 100 GPa. As the reference structures are not the focus of this paper and their phase diagrams are well known, pure Rb and N were not included in this USPEX search. The correct phases of rubidium have been predicted at high pressures using the USPEX algorithm²⁶ while a similar method was used by C.J. Pickard and R. J. Needs³² to discover both experimentally known phases of nitrogen as well as new phases.

First-principles calculations are performed using DFT code VASP³³ and employing Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) to DFT³⁴, projected augmented wave (PAW) pseudopotentials, plane wave basis set with 350 eV energy cutoff, and k-point sampling with density 0.07 Å⁻¹. For each pressure, the lowest enthalpy structures and those close to the convex hull are then calculated at higher accuracy to compute the true convex hulls. As triply-bonded nitrogen has extremely small bond lengths, the hard nitrogen PAW pseudopotential with the core radius 0.582 Å is used. Correspondingly, the energy cutoff for the high accuracy calculations is raised to 1000 eV, while the k-point density is increased to 0.04 Å⁻¹. The chemical bonding (atomic charges and the bond orders) in novel rubidium polynitrogen compounds is analyzed using local combination of atomic orbitals (LCAO) code DMol³⁵,³⁶. The off-resonant Raman frequencies are obtained within frozen phonon approximation by calculating phonons at the gamma point, and their intensities – by calculating the derivatives of macroscopic dielectric polarizability tensor along the normal mode eigenvectors³⁷,³⁸.

III. RESULTS AND DISCUSSION

Our first-principles structure search of RbₓNᵧ compounds of varying stoichiometry produced several new rubidium polynitrogen structures at various pressures. The thermodynamically stable structures discovered in the search are displayed in the convex hulls (Fig. 1a) which are then used to produce the corresponding phase diagram (Fig. 1b). The crystal structures of several newly predicted RbₓNᵧ compounds are shown in Fig. 2.

At 0 GPa, there are two stable compounds: RbN₂-P-1 consisting of N₂ molecules (Fig. 2a) and Rb atoms, as well as experimentally known rubidium azide (RbN₃) polymorph with I₄/mcm symmetry (Fig. 2b)³⁹. These two compounds, RbN₂ and RbN₃, remain stable at 15 GPa, RbN₃ transforming to the C2/m phase and eventually becoming metastable at pressures above 30 GPa. This study correctly predicts the RbN₃-I₄/mcm phase to be the most energetically favorable at ambient conditions³⁹, as well as the pressure-induced phase transition of this phase to that of C2/m symmetry⁴⁰ in agreement with experiment. The validation of the USPEX method in the scope of this work is demonstrated by the correct prediction the RbN₃ phases listed above.

Wang et al.⁴¹ found that RbN₃ undergoes the following phase transitions: to a P-1 phase containing infinite chains of nitrogen at 30 GPa, and to P6/mmm phase containing N₆ hexazine rings at 50 GPa. This is not what we found in this work. At 30 GPa, the lowest enthalpy structure is still the C2/m phase. The P6/mmm phase is not on the convex hull at 60 GPa, see corresponding open
violet circle in Figure 1a). Eventually, upon increasing pressure to 100 GPa, the $P6/mmm$ phase of RbN$_3$ with 6-membered hexazine rings becomes stable.

Several other structures appear above 15 GPa. One of them, Rb$_3$N$_4$-P-1 crystal with 1:1 stoichiometry, consisting of bent N$_3$ chains and three Rb atoms per each N$_3$ molecule (Fig. 2c), remains the lowest formation enthalpy compound at pressures up to 38.4 GPa where it transforms to Rb$_3$N$_4$-P-1 crystal with the same 1:1 stoichiometry containing one-dimensional four-atom nitrogen chains (N$_4$) and isolated Rb atoms, see Fig. 2d).

A phase diagram for the phases with 1:1 stoichiometry is constructed to predict the interval of pressures where the novel Rb$_x$N$_y$ compounds are thermodynamically stable at pressures greater than 30 GPa and K$_5$N$_6$ becomes thermodynamically stable at pressures greater than 60 GPa, above this pressure it transforms to RbN$_5$-Pnma.

To understand the structure and bonding in the novel Rb$_x$N$_y$ compounds, their charges and bond orders are calculated. b) Composition versus pressure phase diagram of Rb$_x$N$_y$ crystals.

**FIG. 1.** a) Convex hulls at pressures 0, 15, 30, 60, and 100 GPa. Thermodynamically stable structures are marked by filled circles; metastable structures are marked with open circles. b) Composition versus pressure phase diagram of Rb$_x$N$_y$ crystals.
FIG. 2. Crystal structures of select rubidium polynitrides: a) RbN$_2$-P-1 (stable at 0-30 GPa); b) RbN$_3$-I4/mcm (stable at 0-15 GPa); c) RbN-P-1 (stable at 30-60 GPa); d) RbN-P-1 (stable above 60 GPa); e) RbN$_2$-C2/m (stable at 15-30 GPa); f) RbN$_3$-Pc (stable at 30-60 GPa); g) RbN$_2$-Pbcn (stable above 60 GPa); h) Rb$_4$N$_6$-P-1 (stable above 60 GPa)

calculated at 0 GPa and shown in Fig. 4. The N$_2$ molecules in RbN$_2$-P-1 crystal carry a net charge of $-0.248\text{e}$ and have the N-N bond order of 2.05, which indicates a double bond. At ambient conditions the bond order for the azide in rubidium azide (RbN$_3$) is 1.97 while the charge on both outer N atoms of the azide is $-0.508\text{e}$ and the charge on the center atom is $+0.397\text{e}$. The average bond order of the N-N bond in bent N$_3$ azides in Rb$_3$N$_3$-P-1 crystal (which is stable above 60 GPa) is 1.32, see Fig. 3. The smaller bond order compared to the double N-N bonds (bond order 2) of N$_3$ azide in RbN$_3$-I4/mcm is due to the filling of the anti-bonding orbitals by extra negative charge (the charge on the azide N$_3$ chain in RbN$_3$-I4/mcm is -0.619 compared to -1.305 in Rb$_3$N$_3$-P-1). The lowest enthalpy phase of RbN between 60 and 100 GPa, Rb$_4$N$_4$-P-1, consists of bent N$_4$ molecules. The bond order of the N-N bonds in Rb$_4$N$_4$-P-1 crystal involving the outer N atom, carrying $-0.621\text{e}$, and the inner nitrogen atom, carrying the charge $-0.253\text{e}$, is 1.17 and the bond order of the bond between the two inner nitrogen atoms is 1.04. The charges on the nitrogen atoms in the cyclo-N$_5$ ring of the RbN$_5$-Pc compound are $-0.171\text{e}$, $-0.121\text{e}$, $-0.182\text{e}$, $-0.167\text{e}$, and $-0.156\text{e}$ and the corresponding N-N bond orders range from 1.39 to 1.43, which demonstrates the aromatic nature of the pentazo- late N$_5$ anion.

The infinite N-N chains in RbN$_2$-Pbcn crystal (the lowest enthalpy phase above 60 GPa), have varying N-N bond orders from 0.99 to 1.35. The charges on N atoms follow a cyclic pattern with two N atoms having charge of $-0.156\text{e}$ while the next two nitrogen atoms $-0.335\text{e}$ followed by two more nitrogen atoms of charge $-0.156\text{e}$ and so on. The irregular geometry of the nitrogen chains and the proximity of the nitrogen atoms to the rubidium atoms results in such irregular charge distribution.

The Rb$_4$N$_6$-P-1 phase, which is thermodynamically stable at pressures exceeding 60 GPa, contains N$_6$ hexazine rings. These rings are made of symmetric groups of three nitrogen atoms with bond orders of 1.03, 1.05,

FIG. 3. Enthalpy difference between Rb$_3$N$_3$-P-1 phase and other phases of crystals with RbN stoichiometry (Rb$_2$N$_2$-P-1-a from the 0 GPa search, Rb$_2$N$_2$-P-1-b phase transition found during the compression study, and Rb$_4$N$_2$-P-1 from the 60 GPa search) showing where each phase is thermodynamically favorable.
FIG. 4. Charges on the nitrogen atoms and the N-N bond orders for several Rb$_x$N$_y$ crystals calculated at 0 GPa.

The most nitrogen-rich compound, RbN$_5$, consisting of cyclo-N$_5$ pentazolates, can in principle be synthesized at high pressures by compressing rubidium azide (RbN$_3$) and nitrogen (N$_2$) mixture in a diamond anvil cell. Rubidium azide is well studied with several known phase transitions$^{40-42}$. To investigate whether synthesis can be achieved at modest pressures, the enthalpy difference between the phases of RbN$_5$ and precursors RbN$_3$-C2/m + N$_2$-R-3c is calculated as a function of pressure and shown in Fig. 5. As RbN$_5$-Pc is thermodynamically stabilized with respect to the precursors at 9.42 GPa, it can be synthesized upon compression above this pressure. Also seen from Fig. 5, RbN$_5$-Pc phase undergoes a phase transition to RbN$_5$-Pnma phase at 37.9 GPa, the latter being found in molecular search at 60 GPa.

As our work indicates a possibility of synthesis of RbN$_5$ upon compression of the mixture of rubidium azide RbN$_3$ and nitrogen (N$_2$) precursors upon compression above 9.42 GPa, we calculated the pressure-dependent Raman spectra of RbN$_5$-Pnma from 30.6 GPa up to 57.7 GPa to assist in experimental identification of pentazolates, see Fig. 6. CsN$_5$ was successfully synthesized upon compressing and laser heating the precursors to pressures near 60 GPa$^{12}$. Due to the chemical similarities of Cs
and Rb, it is likely that synthesis of RbN$_5$ might occur under similar conditions of pressures high enough to provide additional $PV$ enthalpy contribution to stimulate the chemical transformation. Due to this reason, the Raman spectrum of RbN$_5$-$Pnma$ phase, the lowest formation enthalpy pentazolate phase at higher pressures, is calculated and shown in Fig. 4. The low frequency region in the Raman spectrum at 30.6 GPa from 85 to 401 cm$^{-1}$ contains the lattice and N$_2^-$ librational modes (L + T). Although there are several other librational modes in this region, three of them stand out due to their strong intensity at 166 cm$^{-1}$, 253 cm$^{-1}$, and 322 cm$^{-1}$, see Fig. 6. In addition, there are several N$_2^-$ bending Raman modes with weak intensity at 781 cm$^{-1}$ at 30.6 GPa. However, these modes split at higher pressures into two clearly visible bands at 778 cm$^{-1}$ and 795 cm$^{-1}$ at 57.7 GPa. Another mode splitting is found at higher pressures for the N$_5$ deformational (def.) band at 1125 cm$^{-1}$ at 30.6 GPa, which splits into two clearly visible bands at 1151 cm$^{-1}$ and 1189 cm$^{-1}$ at 57.7 GPa. The two highest frequency bands are made of symmetry (sym.) and anti-symmetric breathing or stretching (str.) modes as seen in Fig. 6. All the calculated modes show normal pressure behavior with increasing pressure: the mode frequencies blue shift and their character does not change upon compression.

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REFERENCES

1P. R. Singh, R. D. Verma, D. T. Meshri, and J. M. Shreeve, Angew. Chemie Int. Ed. 45, 3584 (2006).
2T. M. Klapötke, in High Energy Density Mater., Vol. 125 (Springer Berlin Heidelberg, Berlin, Heidelberg, 2007) pp. 85–121.
3G. Steinhauser and T. M. Klapötke, Angew. Chemie Int. Ed. 47, 3330 (2008).
4M. Talawar, R. Sivabanal, T. Mukundan, H. Muthurajan, A. Sidler, B. Gandihe, and A. S. Rao, J. Hazard. Mater. 161, 589 (2009).
5V. E. Zarko, Combust. Expls. Shock Waves 46, 121 (2010).
6T. Brinck, Green Energy. Mater., edited by T. Brinck (John Wiley & Sons, Ltd, Chichester, United Kingdom, 2014) pp. 1–290.
7M. I. Eremets, A. G. Gavriluk, I. A. Trojan, D. A. Dzivenko, and R. Boehler, Nat. Mater. 3, 558 (2004).
8M. I. Eremets, A. G. Gavriluk, N. R. Serebryanyaya, I. A. Trojan, D. A. Dzivenko, R. Boehler, H. K. Mao, and R. J. Henley, J. Chem. Phys. 121, 11296 (2004).
9C. Mailhiot, L. H. Yang, and A. K. McMahan, Phys. Rev. B 46, 14419 (1992).
10D. Tomasino, M. Kim, J. Smith, and C.-S. Yoo, Phys. Rev. Lett. 113, 205502 (2014).
11M. I. Eremets, I. A. Trojan, A. G. Gavriluk, and S. A. Medvedev, Static Compression Energy. Mater., edited by S. M. Peiris and G. J. Piermarini (Springer Berlin Heidelberg, Berlin, Heidelberg, 2008) pp. 75–97.
12B. A. Steele, E. Stavrou, J. C. Crowhurst, J. M. Zang, V. B. Prakapenka, and I. I. Olevnyk, Chem. Mater. 29, 735 (2017).
13B. A. Steele and I. I. Olevnyk, Chem. Phys. Lett. 643, 21 (2016).
14B. A. Steele and I. I. Olevnyk, J. Phys. Chem. A 121, 1808 (2017).
15G. Vaitheeswaran and K. R. Babu, J. Chem. Sci. 124, 1391 (2012).
16P. Peng, Y. Han, H. Liu, and Y. Yao, Sci. Rep. 5, 16902 (2015).
17Y. Shen, A. R. Oganov, G. Qian, J. Zhang, H. Dong, Q. Zhu, and Z. Zhou, Sci. Rep. 5, 14204 (2015).
18B. A. Steele and I. I. Olevnyk, J. Phys. Chem. A (2017), DOI: 10.1021/acs.jpca.7b08974.
19M. T. Nguyen and T.-K. Ha, Chem. Phys. Lett. 335, 311 (2001).
20A. Vij, J. G. Pavlovich, W. W. Wilson, V. Vij, and K. O. Christie, Angew. Chemie - Int. Ed. 41, 3051 (2002).
21C. Zhang, C. Yang, B. Hu, C. Yu, Z. Zheng, and C. Sun, Angew. Chemie Int. Ed. 56, 4512 (2017).
22C. Zhang, C. Sun, B. Hu, C. Yu, and M. Lu, Science (80-. ). 355, 374 (2017).
23D. Bazanov, U. Geiger, R. Carmieli, D. Grinstein, S. Welner, and Y. Haas, Angew. Chemie Int. Ed. 55, 13233 (2016).
24Y. Xu, Q. Wang, C. Shen, Q. Lin, P. Wang, and M. Lu, Nature 549, 78 (2017).
25U. Schwarz, A. Grzechnik, K. Syassen, I. Loa, and M. Hanfland, Phys. Rev. Lett. 83, 4085 (1999).
26Y. Ma, A. R. Oganov, and Y. Xie, Phys. Rev. B 78, 014102 (2008).

IV. CONCLUSION

Three novel high-nitrogen content Rb$_3$N$_{y}$ compounds are discovered using first principles evolutionary structure search. The first, rubidium pentazolate RbN$_5$-$Pc$ consisting of cyclo-N$_5^-$ anions is predicted to be thermodynamically stable at pressures exceeding 15 GPa. Heating and compressing the mixture of rubidium azide RbN$_3$ and N$_2$gas is expected to produce RbN$_5$ as our calculations demonstrate that RbN$_5$-$Pc$ becomes thermodynamically preferred compared to the stoichiometric mixture of the precursors at pressures above 9.42 GPa. Raman spectrum of rubidium pentazolate RbN$_5$-$Pnma$ is calculated to assist in experimental identification of N$_5$ modes, which should be observed in experiment if such compound appears upon its synthesis. The second high-nitrogen content compound, RbN$_2$-$Phcn$, consisting of single bonded infinite nitrogen chains becomes thermodynamically stable at 60 GPa. The third newly discovered compound, Rb$_3$N$_6$-$P-I$, consists of N$_6$ hexazine rings is thermodynamically stable at 60 GPa. In addition, a compound Rb$_3$N$_3$-$P-I$ consisting of bent N$_3$ molecules, is predicted to be stable between 30 and 60 GPa. Although there are some similarities in structures of Rb polynitrogens with those found for other alkali polynitrates, the N$_3$ anions in Rb$_3$N$_3$-$P-I$ phase have not been seen before.
27M. Hanfland, I. Loa, and K. Syassen, Phys. Rev. B 65, 184109 (2002).
28C. W. Glass, A. R. Oganov, and N. Hansen, Comput. Phys. Commun. 175, 713 (2006).
29A. R. Oganov and C. W. Glass, J. Chem. Phys. 124, 244704 (2006).
30A. O. Lyakhov, A. R. Oganov, and M. Valle, Comput. Phys. Commun. 181, 1623 (2010).
31A. Hermann (John Wiley & Sons, Inc., 2017) pp. 1–41.
32C. J. Pickard and R. J. Needs, Phys. Rev. Lett. 102, 125702 (2009).
33G. Kresse and J. Furthmüller, Comput. Mater. Sci. 6, 15 (1996).
34J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
35B. Delley, J. Chem. Phys. 92, 508 (1990).
36B. Delley, J. Chem. Phys. 113, 7756 (2000).
37M. Lazzeri and F. Mauri, Phys. Rev. Lett. 90, 036401 (2003).
38D. Porezag and M. R. Pederson, Phys. Rev. B 54, 7830 (1996).
39D. Li, X. Wu, J. Jiang, X. Wang, J. Zhang, Q. Cui, and H. Zhu, Appl. Phys. Lett. 105, 071903 (2014).
40D. Li, F. Li, Y. Li, X. Wu, G. Fu, Z. Liu, X. Wang, Q. Cui, and H. Zhu, J. Phys. Chem. C 119, 16870 (2015).
41X. Wang, J. Li, N. Xu, H. Zhu, Z. Hu, and L. Chen, Sci. Rep. 5, 16677 (2015).
42W. Zhu, J. Xiao, and H. Xiao, J. Phys. Chem. B 110, 9856 (2006).