Properties of Alkaline-Earth-Metal Polynitrogen Ternary Materials at High Pressure

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ABSTRACT: We report the formation of cubic and tetragonal BaSrN₃ at 100 GPa using an ab initio structure search method. Pressure ramping to 0 GPa reveals a reaction pressure threshold of 4.92 and 7.23 GPa for the cubic and tetragonal BaSrN₃, respectively. The cubic phase is stabilized by coulombic interaction between the ions. Meanwhile, tetragonal BaSrN₃ is stabilized through an expansion of the d-orbital in Ba and Sr atoms that is compensated by delocalization of π-electrons in N through reduction of π overlap. Elastic properties analysis suggests that both phases are mechanically stable. The structures also have high melting points as predicted using an empirical model, and all imaginary modes vanish at about 2000 K. These results have significant implication for the design of cleaner and environmentally friendly high energy density materials.

INTRODUCTION

Interesting chemistry and physics happen at elevated pressures, especially as it relates to the formation of novel nitrogen compounds for various applications ranging from electronics to complex integration into explosives. At ambient pressure, nitrogen adopts chemically inert van der Waals solids with N₂ molecules in which the nitrogen atoms are triple-bonded.1–4 Interestingly, at elevated pressures, studies5–9 have shown that nitrogen can exist as a single-bonded molecule, with a large amount of energy stored in the single bonds. This makes it one of the inorganic and nonradioactive elements being actively researched for high energy density (HED) applications. Following the first world appearance of the high-pressure single-bonded cubic gauge (cg) polymeric nitrogen in 2004 by Eremets et al. at a pressure of 110 GPa and temperature above 300 K,10 which by the way was the thermodynamic ground state of high-pressure nitrogen, many efforts have gone into lowering the formation pressure of single-bonded nitrogen. Although, more recently, nitrogen has also been discovered in the black phosphorous form after decades of its predicted10,11 all at relatively high pressures. It is important to reduce the formation pressure because of the experimental challenges involved in the recovery of high-pressure compounds to ambient conditions. Therefore, novel routes are being sought for the preparation of single-bonded nitrogen. Overtime, the introduction of other elements into the crystals containing polynitrogen is found to be very effective since it does promote metastability (exhibition of real vibrational frequencies) and at the same time reduces the synthesis pressure.12

Previously, materials made of alkali metals containing polynitrogen were investigated at high pressures. Much work has been done using alkali metals Li,13–15 Na,16,17 K9,21–24 and Cs.25,26 In cesium pentazolate, which was theoretically predicted27 and later synthesized experimentally,28 it was found to be made up of pentazolate N₅⁻ cation and Cs⁺ anion with characteristic electron transfer from the metal to the N₅ cluster. Furthermore, binary and ternary alkaline-earth-metal nitride compounds have been synthesized, although, with the sole aim of understanding the formation mechanism and possible application as a catalyst in nitride chemistry.29 In the same vein, a lot of work has gone into answering questions such as how many nitride phases really exist? What is responsible for the optical properties observed in some alkaline-earth-metal nitride? To further the already done work, we attempt to investigate whether Ba and Sr can form stoichiometric polynitrogen compound which is recoverable at low pressures with nonconventional N≡N molecule from elemental precursors. Several computational studies about the formation of alkaline-earth-metal polynitrogen binary systems, such as Be–N30 Mg–N31 and Ca–N32 have been done. For example, BeN₄ was predicted to form a stable structure with a three-dimensional (3D) network structure that features ten...
nitrone. In the binary system Sr–N, Sr3N was theoretically predicted31 and experimentally confirmed33 to crystallize into a CdCl2-type structure, although nitrogen-deficient. Data on nitrogen-rich alkaline-earth-metal polynitrogen structures is scarce in the literature. If formed, they have the potential of having significantly lower formation pressure while promoting metastability and forming single-bonded nitrogen molecules. The cubic and tetragonal BaSrN3 characterized by non-triple-bonded nitrogen, which are discussed in the subsequent section.

## RESULTS AND DISCUSSION

Born–Oppenheimer approximation is an encompassing theory that reflects the role that potential energy landscape plays in dynamics, structure, and thermodynamics of any functional system.48–50 Pressure, a thermodynamic variable, can give unusual structural, electronic, and mechanical properties to chemical systems, especially at extremely high regime. In addition to a change in these properties, extreme pressures can effectively lower the chemical barrier between reactants and products, thereby making such reactions that will be mere imaginations at ambient conditions possible. We have extensively studied the properties of predicted stoichiometric cubic and tetragonal BaSrN3 characterized by non-triple-bonded nitrogen, which are discussed in the subsequent section.

### Structure Search and Thermodynamic Stability of BaSrN3

It has been reported that Ba, Sr, and N crystallize into hexagonal Ba–V (P63/mmc) at pressures above 30 GPa,51 an orthorhombic body-centered lattice Sr-III (Imma) at pressures above 31.3 GPa,12 and cg-N at pressures > 50 GPa,12 respectively. The potential energy surface of BaSrN3 was searched at 100 GPa, and their enthalpies were compared with the enthalpy of elemental composition 1/2[2Ba+2Sr+3N2], as shown in Figure 1. The crystal structures for elemental composition were chosen as those stable in the pressure range explored. The cubic and tetragonal BaSrN3 were formed at 100 GPa. The structure search with 4 BaSrN3 f.u. converged to the cubic structure, while the 2 BaSrN3 f.u. converged to the tetragonal structure, both possessing similar enthalpy of formation at 100 GPa. Meanwhile, pressure ramping to 0 GPa reveals a reaction pressure threshold of 4.92 and 7.23 GPa for the cubic and tetragonal BaSrN3, respectively. As far as we know, this is the lowest formation pressure for a ternary alkaline-earth-metal polynitrogen system to be reported. Between 4.92 and 60 GPa, the cubic BaSrN3 is the thermodynamic ground state, while the tetragonal BaSrN3 becomes preferable at high pressures above 120 GPa up to 160 GPa that was considered in this study. Therefore, we refer to the cubic phase as the low-pressure phase and the tetragonal phase as the high-pressure phase of the ternary BaSrN3 system. Between 60 and 120 GPa, both the cubic and tetragonal BaSrN3 become similar in enthalpy, and as such, one cannot discriminate between the two structures solely based on their energetics.

Furthermore, we investigated the energy-storage capacities of the predicted structures and compare them with other known nitrogen-containing HED materials. We calculated the energy density of both cubic and tetragonal BaSrN3. The BaSrN3 structures can decompose into Ba, Sr, and N2 at 0 GPa as follows

\[ 4\text{BaSrN}_3 \rightarrow 4\text{Ba} + 4\text{Sr} + 6\text{N}_2 \] (1)

\[ 2\text{BaSrN}_3 \rightarrow 2\text{Ba} + 2\text{Sr} + 3\text{N}_2 \] (2)

for the cubic (eq 1) and tetragonal (eq 2) BaSrN3 structures, respectively. In this process, 1.23 eV of energy is released per f.u., corresponding to ~8.38 kJ·g⁻¹ of energy density for the tetragonal structure, and 1.20 eV of energy is released per f.u., corresponding to ~8.18 kJ·g⁻¹ of energy density for the cubic structure. In general, the value of energy density for the BaSrN3 systems is higher than those of TNT at 0 GPa,53 N3H at 30 GPa,54 and CNO at 50 GPa,55 but less than those of cg-N at 110 GPa,12 HMX at 0 GPa,53 and some recently proposed heterostructures and 2D materials containing single-bonded nitrogen.56,57 The cubic and tetragonal BaSrN3 structures, unlike the heterostructures and 2D materials reported in,56,57 are thermally stable up to at least 2000 K without decomposition.

### Structural Properties

Before discussing the high-pressure electronic, mechanical and dynamic properties of the Ba−Sr–N system, it is necessary to assess and have a clear understanding of the structure they adopt. This helps establish the connection between the geometry and various properties of the material exhibits.

#### Cubic BaSrN3

BaSrN3 at high pressure is predicted to crystallize into a cubic cell with space group P43m. The structural parameters of the P43m structure at 100 GPa (shown in Figure 2a) are \(a = 5.87 \text{ Å}\) with Ba atoms located at 1a: 0.00, 0.00, and 0.00; 3d: 0.50, 0.00, and 0.00; Sr atoms located at 4e: 0.34, 0.34, and 0.34; and N atoms located at 12i: 0.38, 0.38, and 0.95. This structure at 100 GPa is characterized by six \(N_4\) units with a bond length of 1.50 Å as shown in Figure 2a, which is close to the experimental single-bond N–N (1.35 Å) at 115 GPa. The most intriguing feature of the crystal structure is displayed by nitrogen atom-forming \(N_4\) molecules (four membered rings). Each \(N_4\) unit occupies a face-centered position, thereby stabilizing the Sr atoms entrapped in the enclosed space (detail shown in Figure 2a). The system is stabilized by coulombic interaction between all ions in the crystal. The formation of the P43m structure at 100 GPa

![Figure 1](https://dx.doi.org/10.1021/acsomega.0c03880)
therefore can be described as pressure-driven with some contribution from electronic topology, which will be discussed later. The Sr (atomic radius = 2.55 Å) atoms in P43m can be thought of as a low pressure isoatomic substitution for the Ba (atomic radius = 2.68 Å) atoms while maintaining the 2+ charge state. This substitution favors the enclosure of all Sr atoms within the network of the N4 unit. As shown in Figure 2c, the N4 molecule adopts the 3D tetrahedral geometrical structure motif like the P4 but in an isolated form. The geometry of the polymeric nitrogen rings gives a very rich insight into the electron localization within this chemical system, which is further discussed in the subsequent section.

**Tetragonal BaSrN3.** BaSrN3 at high pressure, on the other hand, is predicted to crystallize into a tetragonal cell with space group P4/nmm. The structural parameters of the P4/nmm structure at 100 GPa (shown in Figure 2d) are a = 3.62 Å and c = 7.57 Å with Ba atoms located at 2c: 0.00, 0.50, and 0.60; Sr atoms located at 2c: 0.00, 0.50, and 0.98; and N atoms located at 2c: 0.00, 0.50, and 0.28; 4f: 0.50, 0.50, and 0.79. This structure at 100 GPa is characterized by a novel N8 puckered ring like the S8 ring (analogue of cubane) with a bond length of 1.87 Å. Unlike the N4 unit in the cubic BaSrN3, the N8 ring in the tetragonal BaSrN3 includes two different types of nitrogen (N1, N2). The N8 ring forms an infinitely long network [N8]∞ as shown in Figure 2e. The tetragonal BaSrN3 has an ABC′B′ stacking in which A, B, and C correspond to Sr, N, and Ba atoms, respectively, with interplanar distance ranging between 4.28 and 4.36 Å. The B′ is a conformation of B as shown in Figure 2f. The tetragonal BaSrN3 is stabilized through an expansion of the d-orbital in Ba and Sr atoms (Figure S1) that is compensated by delocalization of π-electrons in N through a reduction of π overlap. The geometric N8 ring of the polymeric nitrogen gives a very rich insight into the electron localization within this compound and explains why nitrogen could accommodate more electrons than in the cubic BaSrN3 (see later). Ideally, one would expect the N=N=N bond angle in the N8 ring to range between 60 and 120°, however, the angle is 150.26°, although one can argue that the wide nitrogen angle accompanies a depopulation of the lone pair orbital when nitrogen is placed in the electron-donating chemical environment. However, this is likely not what happened in the tetragonal phase as we could not find any evidence of the formation of lone pair, even though both Ba and Sr act as electron donors. A plausible reason for the large N=N=N angle exhibited by the N8 network could be the ring size. This is a consequence of the high angular flexibility of the N=N single bond, which is an indication of ease of rehybridizations to the sp2 structure (~120°) if pressure is further increased. Apparently, the wider angle permits more π bonding, making more electrons available around the N8 ring and its planes during delocalization of π-electron, leading to stronger metallic properties in the tetragonal BaSrN3, should the pressure be further increased.

The general motif is that alkaline-earth-metals (Ba, Sr, Ca) that are incapable of oxidation states greater than 2+ should form diazenides featuring N≡N with bond distances in the range 1.20–1.24 Å leading to a very low bulk moduli ranging from 45 to 70 GPa as observed in SrN2.61 The structures reported in this study, however, are characterized with properties that counter this motif: both the cubic and tetragonal BaSrN3 structures exhibit single-bonded nitrogen network with a very high bulk modulus, which is further discussed in the subsequent section. A possible explanation for this behavior is that at high pressure, Ba and Sr atoms undergo an s → d transition which causes them to chemically behave like the transition metals Os, Ru, Ir, Ti, and Pt. These transition metals (M) are known to have stable oxidation states of +4 and form pernitrides M4+[N−N]4− with an N=N bond distance of ~1.40 Å and a very high bulk modulus in the order of 362 GPa and above.61 Therefore, BaSrN3 system forms pernitride Ba3Sr[N−N]4− with N=N bond distance in the range of ~1.50 to ~1.87 Å with a very high bulk modulus in a similar order as that formed by transition metals.61

**Electronic Properties.** The bonding properties are not evident at ambient condition but can be inferred at high pressure. The cubic (P43m) and tetragonal (P4/nmm) BaSrN3 structures are therefore studied at 100 GPa. For a long time, understanding the chemical bonding in metal nitrides such as BaSrN3 has posed a challenge to theorists.62 Jacobs et al.62 identified some unusual chemical bonding in some nitrides of barium and strontium. The valence electron concentration (VEC) of BaSrN3 is less than 8. It has been found that
nmm structure (Ba = green, Sr = brown, and N = silver). The Ba and Sr atoms also have the electron clouds localized around them, which shows they do not covalently bond with the N atoms.

Unlike the cubic phase, no evidence of covalent interaction between the N–N bonds is observed in the tetragonal phase. There are two symmetry inequivalent nitrogen atoms occupying the C_{2v} and C_{4v} point groups, which explain the ionic nature of the N–N bond found in the tetragonal structure. The Ba and Sr atoms also have the electron clouds localized around them, which rules out the possibility of covalent interaction. The atomic Bader charges in Table 1 show the anionic nature of the N atom such that for both the cubic and tetragonal structures, each N atom gains electrons from the Ba and Sr atoms. The crystal orbital Hamiltonian population (COHP) of the N–N atoms in the cubic and tetragonal structures are shown in Figure S2, clearly indicating significant bonding interaction (positive -COHP) between the nitrogen atoms.

Recently, maximally localized Wannier functions (MLWFs) have been used to explore the bonding in periodic systems. The success of this method lies in the direct Fourier transformation of the Bloch functions into Wannier functions. In order to understand the bonding at the Fermi level, we used the Wannier projection method proposed by Abramov. The total energy density at the bond CP is obtained from the virial theorem as

$$V(f_{BCP}) = \frac{\hbar^2}{4m} \nabla^2 \rho(f_{BCP}) - 2G(\tau_{BCP})$$

where the potential energy density G was calculated from the method proposed by Abramov. The total energy density H is the algebraic sum of V and G.

$$H(r_{BCP}) = V(r_{BCP}) + G(r_{BCP})$$

Table 1. Atomic Bader Charges on Symmetry Inequivalent Atoms

| space group | atom | point group | Bader charge |
|-------------|------|-------------|--------------|
| P43m        | Ba1  | T_{d}       | +0.977       |
|             | Ba2  | D_{2d}      | +1.13        |
|             | Sr   | C_{3v}      | +1.08        |
|             | N    | C_{s}       | -0.683       |
| P4/nnm      | Ba   | C_{4v}      | +1.218       |
|             | Sr   | C_{4v}      | +1.247       |
|             | N1   | C_{4v}      | -0.534       |
|             | N2   | C_{2v}      | -0.965       |

This is not surprising as Bowen et al. and Adeleke et al. have reported that at high pressure, the low-lying Ba d orbitals may partake in the bonding. The results of electronic density of states (Figure S1, ref59) projected to atomic orbital densities. The success of this method lies in the direct Fourier transformation of the Bloch functions into Wannier functions. In order to understand the bonding at the Fermi level, we used the Wannier projection method proposed by Abramov. The total energy density at the bond CP is obtained from the virial theorem as

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Figure 3. Calculated ELFs of the (a) P43m structure and (b) P4/nnm structure (Ba = green, Sr = brown, and N = silver).

Figure 3. Calculated ELFs of the (a) P43m structure and (b) P4/nnm structure (Ba = green, Sr = brown, and N = silver).
and the bond energy dissociation can be obtained from the potential energy density as \( E_{BD} = -\frac{1}{2} V(r_{BCP}) \) \( (5) \)

The results for the cubic and tetragonal structures are summarized in Tables 2 and 3, respectively. \( M \) is the multiplicity of the interaction.

The negative Laplacian exhibited by the N–N bond in the cubic BaSrN\(_3\) agrees with the covalent bond interaction found from the ELF analysis. All other bonding interactions suggest a closed shell interaction between the bonding atoms.

**Mechanical and Dynamic Properties.** The mechanical stability of a material can be inferred through the Born elastic stability criterion for the crystal system adopted by the material. A mathematical description of the elastic behaviors of a crystal lattice is characterized by its second-order elastic

### Table 2. Structural Topological Properties at the Bond CPs for the Cubic (\( P\bar{4}3m \)) Structure of BaSrN\(_3\)

| bond type | \( d \) (Å) | \( M \) | \( \rho(r_{BCP}) \) (eÅ\(^{-3}\)) | \( \nabla^2 \rho \) (eÅ\(^{-5}\)) | \( G \) (kJ/mol) | \( V \) (kJ/mol) | \( H \) (kJ/mol) | \( E_{BD} \) (kJ/mol) |
|-----------|------|------|-----------------|-----------------|----------|----------|----------|-------------|
| N–N       | 1.50 | 12   | 1.77            | -6.68           | 690.68   | -1563.28 | -872.60  | 781.64      |
| N–Sr      | 2.30 | 12   | 0.44            | 5.49            | 180.42   | -211.37  | -30.96   | 105.69      |
| Ba–N      | 2.25 | 24   | 0.43            | 5.30            | 172.86   | -201.52  | -28.67   | 100.76      |
| Sr–N      | 2.42 | 24   | 0.35            | 4.73            | 140.87   | -152.97  | -12.10   | 76.48       |
| Ba–Ba     | 2.71 | 6    | 0.30            | 2.36            | 83.79    | -103.27  | -19.48   | 51.64       |
| Sr–Sr     | 2.72 | 6    | 0.27            | 3.27            | 94.79    | -100.81  | -5.88    | 50.41       |
| Sr–Ba     | 2.88 | 12   | 0.20            | 2.72            | 69.90    | -65.76   | 4.14     | 32.88       |
| Ba–N      | 3.09 | 12   | 0.14            | 1.04            | 30.75    | -33.05   | -2.30    | 16.52       |
| Sr–Ba     | 3.28 | 4    | 0.13            | 0.74            | 23.82    | -27.43   | -3.62    | 13.72       |

The bond energy dissociation can be obtained from the potential energy density as \( E_{BD} = -\frac{1}{2} V(r_{BCP}) \) \( (5) \)
constant matrix. The crystal class of a material is a dominant source of symmetry constraints on these elastic constants.\textsuperscript{73} In addition to dynamical stability which requires (within harmonic approximation) that, in the absence of external load, all phonon modes have positive frequencies, the elastic energy is given by eq 6

$$E = E_0 + \frac{1}{2} V_0 \sum_{i,j=1}^{6} C_{ij} \epsilon_i \epsilon_j + O(\epsilon^3)$$  

(6)

where $C_{ij} = \left( \frac{\partial^2 E}{\partial \epsilon_i \partial \epsilon_j} \right)$ is the second-order elastic constant matrix, $V_0$ is the equilibrium volume, and $\epsilon$ is the strain and is always positive. The general formulations of the Born elastic stability criteria for a relaxed crystal are necessary and sufficient for inferring elastic stability. These conditions require that the matrix $C$ is definite positive and that all eigenvalues of $C$ are positive.

Cubic BaSrN$_3$. The $C$ matrix (in the unit of GPa) for the $P4m$-BaSrN$_3$ system obtained from our calculations are as shown in eq 1 of ref 59. The eigenvalues of eq 1 of ref 59 were calculated through numerical diagonalization and were found to be all positive, and $C_{ij}$ is symmetric, suggesting that the $P4m$-BaSrN$_3$ system is elastically stable. The elastic constant matrix is presented in eq 1 of ref 59. The Born stability criteria for a cubic system requires that (i) $C_{11} - C_{12} > 0$, (ii) $C_{11} + 2C_{12} > 0$, and (iii) $C_{44} > 0$.\textsuperscript{73} Since the corresponding elements of eq 1 in ref 59 satisfied these conditions, mechanical stability can be inferred for the $P4/mmm$-BaSrN$_3$ system.

| bond type | $d$ (Å) | $M$ | $\rho(\text{atC})$ (eÅ$^{-3}$) | $V_0^2\rho$ (eÅ$^{-5}$) | $G$ (kJ/mol) | $V$ (kJ/mol) | $H$ (kJ/mol) | $F_{\text{esc}}$ (kJ/mol) |
|-----------|---------|-----|-------------------------------|--------------------------|-------------|-------------|-------------|-----------------|
| N–N       | 1.88    | 8   | 0.71                          | 3.32                     | 238.84      | -387.41     | -148.57     | 193.70          |
| N–Sr      | 2.20    | 8   | 0.54                          | 3.86                     | 182.42      | -259.78     | -77.36      | 129.89          |
| Ba–N      | 1.80    | 2   | 0.47                          | 7.01                     | 214.89      | -238.97     | -24.08      | 119.49          |
| Sr–N      | 2.28    | 8   | 0.46                          | 4.79                     | 172.10      | -213.75     | -81.65      | 106.87          |
| Ba–Ba     | 1.20    | 2   | 0.38                          | 4.15                     | 138.39      | -163.76     | -25.37      | 81.88           |
| Sr–Sr     | 2.30    | 4   | 0.29                          | 5.54                     | 138.70      | -128.49     | 11.21       | 64.24           |
| Sr–Ba     | 2.38    | 8   | 0.20                          | 3.36                     | 99.05       | -106.74     | -7.69       | 53.37           |
| Ba–N      | 2.75    | 4   | 0.14                          | 2.76                     | 85.36       | -95.56      | -10.20      | 47.78           |
| Sr–Ba     | 2.40    | 2   | 0.13                          | 0.21                     | 24.33       | -42.91      | -18.58      | 21.45           |

Table 3. Structural Topological Properties at the Bond CPs for the Tetragonal ($P4/mnmn$) Structure of BaSrN$_3$.
CONCLUSIONS

We have reported two novel high-nitrogen content BaSrN₃ compounds predicted using first-principles particle swarm optimization search. The high pressure-temperature BaSrN₃ structures reported here are stabilized by high temperature. We have shown the BaSrN₃ compounds to exhibit structural-topological stability as the topological parameters obtained from their QTAIM analysis are consistent with the Morse sum. It is also evident from the results that the N atom plays a significant role in the formation and stability of the structure as all bonding interactions has the N atom inclusive. The ELF suggests that N–N covalent bonding in the cubic phase is absent in the tetragonal structure. The elastic constant calculation results for these structures suggest that the structures are elastically and mechanically stable. Using an empirical relationship, the predicted BaSrN₃ structures at 100 GPa have a melting temperature above 3000 K, higher than that of pure nitrogen at the same pressure. The high energy-storage capacity calculated for the BaSrN₃ systems place them in the group of competitive candidates for HED applications in clean energy, non-nuclear explosives, and propellant design.

COMPUTATIONAL DETAILS

Theoretical prediction of Ba₅Sr₅N₁₄ ternary compounds was achieved through an unbiased structure search method based on the particle swarm-intelligence optimization algorithm. The results of the search were post-processed through density functional theory calculations. The structure search was done at 100 GPa with primitive cells containing between 1 and 4 BaSrN₃ formula unit (f.u.). We then combined 60% of the offspring’s structures from one generation with the next generation that was eventually screened for a candidate structure with a global-minimum enthalpy. Full structural optimization at 100 GPa was done using force and stress minimization. The optimization and calculation of the equation of states, band structures, and lm-decomposed density of states were carried out within the generalized gradient approximation as implemented in the Vienna Ab Initio Simulation package (VASP) and the spin–orbit coupling on Ba atoms was also taken into consideration. The Wannier90 interface of VASP was used to obtain the energy-corrected band structure from a partially self-consistent GW calculation. We disentangled the various bands and generated the Wannier orbitals corresponding to the disentangled bands. Atomic Bader charges of the cubic and tetragonal BaSrN₃ structures were calculated. Their structural topological properties were also calculated from Baders QTAIM as implemented in the Critic code. The projector-augmented plane-wave potentials with a Perdew–Burke–Ernzerhof functional where 5s²5p⁶6s², 4s²4p⁶5s², and 2s²2p³ are treated as valence orbitals for Ba, Sr, and N, respectively, were used. A kinetic energy cutoff of 945 eV was used for the plane-wave basis set expansion. A k spacing of 2π × 0.02 Å⁻¹ for the Brillouin zone sampling was employed for structural optimization. Harmonic phonon calculations were performed using the linear response Hessian matrix obtained using the VASP program and postprocessed using the PHONOPY code. The obtained phonon results were cross-checked using the QUANTUM ESPRESSO package with norm-conserving pseudopotentials, along with a 6 × 6 × 6 q-point mesh and a 12 × 12 × 12 k-point mesh. The COHP analysis was performed using the LOBSTER program, considering all valence orbitals in the crystal. AIMD simulations were performed by employing an isothermal–isobaric (NpT) ensemble in a supercell with 160 atoms for P43m-BaSrN₃ and 180 atoms for P4/nmm-BaSrN₃ at 100 GPa using the VASP code. AIMD trajectories were obtained from 20 ps long MD simulations sampled with a 2 fs time step. The Langevin dynamics was used, and the system temperature was controlled using the Langevin thermostat. The high-temperature anharmonic vDOS was obtained from the VACF of the AIMD trajectories. 

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03880.

Projected electronic density of states, full list of bond CPs, elastic constant matrix, phonon dispersion, and COHP plot (PDF)

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