High-pressure BaCN$_2$ phases explored by genetic algorithm

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Polymers containing nitrogen have attracted much attention in connection with their application to high energy density materials (HEDMs), in which energy is inherent in the triple bond. It is an interesting question whether such polymerized phases appear in the high-pressure phase of metal carbodiimide MCN$_2$, of which synthesis have been reported in recent years, but few studies have investigated the crystal structure at high pressure. We have adopted a structure search based on the genetic algorithm coupled with ab initio electronic structure calculations to investigate possible crystal structures that may appear in the high-pressure phase of BaCN$_2$. The structure search successfully reproduced the previously reported crystal structures in the lower pressure range. With confirmed reliability of its predictive ability, the genetic search further predicts a polymerized phase with Imma appearing at higher pressure above 42 GPa. The polymerized phase takes the structure of a linear network of CN$_2$ planar triangular units. It is understood that the anion site units CN$_2$, which are close to each other under high pressure, form covalent bonds directly with each other and stabilize the phase.

I. INTRODUCTION

Polymetric nitrogen appeared in high pressure range is expected for the application to the high energy density materials (HEDMs) storing energy in the triple bond. N$_2$ molecules in the high pressure phase has hence been studied theoretically [1-5] and experimentally [6, 7], but found to be not suitable for the practical application because the triple bond gets disappeared during the decompression process. As such, metal nitrides in high pressure range, instead, have attracted interests for this purpose. For instance, an azide ion compound LiN$_3$ with N=N=N$^-$ chain is predicted to undergo the phase transition to N-zigzag-chain-structure as the pressure gets increased [8]. It is reported for the metallic nitrides that they undergo the polymerization at relatively lower pressure, and the polymerized structure is kept even during the decompression [9, 10]. The phase is actually interesting because the structure is stabilized by the network formed only by the anion, being a rare case among inorganic compounds. Metal nitrides with polyatomic anion-sites have also been studied, such as those with carbodiimide ions (N=CN=N$^-$) [11-27] or cyanamide ions (N=C=N$^-$) [28, 31]. Their structure are originally stabilized by the 3-dimensional network formed the metal cation bonding. It is then interesting to see whether these compounds undergo the transition to the polymerized phase where the structure is kept instead by the anion only to form a network, but this point is not well investigated so far. Since in these compounds, the anion sites are replaced from 'dots' into the 'extended arms' of the polyatomic unit, it is expected to realize more easier condition to form the anion network leading to the polymerized phase. The 'arms' also provides more internal degrees of freedom such as the orientation and the bending, giving more complicated competition between enthalpy and entropy. It is hence expected to get rich variety of phases and corresponding responses for functional materials.

Only a few studies have examined the crystal structure of $M$-NCN (MCN$_2$) at high pressure, including the examples of cyanamide compounds, HgCN$_2$ and PbCN$_2$. HgCN$_2$ starts to decompose at 1.9 GPa. A theoretical prediction based on the density functional theory (DFT) reports that the lattice parameter of PbCN$_2$ changes nonlinearly at 5 GPa [22, 33]. For the alkali metal carbodiimides, SrCN$_2$ and BaCN$_2$, their synthesis has been reported. [14, 27, 34] The tetragonal structure phase of BaCN$_2$ is particularly interesting as a phosphor, BaCN$_2$:Eu, showing red luminescence up to 5.34 GPa. This tetragonal structure is retained even after depressurization and does not decompose in this pressure range. [35] The tetragonal BaCN$_2$ is found to be stable than the rhombohedral BaCN$_2$ over the entire temperature range up to the pyrolysis. It has also been reported to be applied as a flux for oxynitrides because it melts at temperatures lower than those at which the structure pyrolyzes. [36, 37] The solid solution based on BaCN$_2$ with Ba partially replaced by Sr, Ba$_{0.9}$Sr$_{0.1}$CN$_2$, was synthesized and reported as a orthorhombic crystal structure. [38] In these compounds, we expect a variety of phase transitions originating from the complexity of the internal degrees of freedom of the anion units, as described above. Investigating struc-
tural transitions of these materials as the dependence on the pressure is an important issue to be clarified. In particular, if polymerized phases emerge in the high-pressure region, as mentioned at the beginning of this section, we might see potential applications in HEDMs. However, the search for new structure of carbodiimide compounds is still unexplored, and in particular, there are still no reports of high-pressure polymorphs.

In this study, we performed a structure search of the polymorphs of BaCN$_2$ over the high-pressure range using the genetic algorithm to evolve crystal structures. [39–44] The structure search is confirmed to reproduce the previously reported crystal structures such as the orthorhombic Ba$_{0.9}$Sr$_{0.1}$CN$_2$, tetragonal BaCN$_2$, rhombohedral BaCN$_2$, and the structure of SrCN$_2$ reported at low temperature. Getting confirmed the predictive reliability, the search predicts new polymerized structure appearing at high pressures above 42 GPa, where the planar triangular units of CN$_3$ are polymerized to form linear chains. Compared with the monocationic azide ion compounds [9, 45], the present compound with polyatomic anion indicates that higher pressures are required to obtain the polymerized phase. It implies that the useful properties found in the phases with lower pressure, such as pressure-dependent fluorescence, are kept up to higher pressure. The properties of the compound MCN$_2$ has been reported up to 10 GPa in experiments and 15 GPa in calculations. The present work is the first to predict what kind of structural phases may appear in the high-pressure range.

II. METHOD

The evolutionary algorithm (EA) implemented in Universal structure predictor: evolutionary Xtallography software (USPEX) was used to predict the ternary nitride BaCN$_2$ at the pressures of 5, 10, 25, 30, 40, 50 and 100 GPa. [46] The first generation is generated at random from 500 structures, with each subsequent generation generating 50 structures with 30% heredity, 50% random, 10% mutation, and 10% soft mutation. Each structure undergoes 4 steps of relaxation to minimize stress and force.

Energies in USPEX were evaluated using the ‘Vienna Ab Initio Simulation Package’ (VASP) code [47–50] at the level of density functional theory (DFT). Our DFT simulations adopted the Perdew-Burke-Ernzerh (PBE) [51] functional within the generalized gradient approximation (GGA). For predicted structures, structural relaxations and electronic structures were also performed at the same level of theory as the structural explanation. For Ba element, 5$s$ and 5$p$ states are treated as valence state. A plane wave basis with cutoff energy of 600 eV and Monkhorst-Pack k-meshes of $8 \times 8 \times 8$ were sufficient for getting the total energies converged within an accuracy of 1 meV/atom. [52] Fitting the Birch-Murnaghan EOS and calculating the bulk modulus were done with the open source program pymatgen. [53, 54] The phonon properties are calculated using the finite displacement method used implemented in Phonopy with a supercell of $2 \times 2 \times 2$ dimension.

FIG. 1. BaCN$_2$ polymorphs predicted by our genetic algorithm at 0 GPa for BaCN$_2$, giving (a) $I4/mcm$ (140), (b) $Pnnm$ (58), (c) $R3c$ (167), (d) $R3m$ (166), (e) $C2/c$ (15), and (f) $Ima2$ (46) space groups.

III. RESULTS AND DISCUSSION

A. Predicted low-pressure phases

We begin with the lower pressure range where several known structures are known to be compared with our predicted structures as shown in Fig. 1. The figure shows a total of six polymorphs obtained by the genetic algorithm at 0 GPa for BaCN$_2$. Experimentally, tetragonal $I4/mcm$ (140) has been reported in the pressure region of $0 \sim 6$ GPa [56], which surely appears in the figure showing the consistency. The coordination number of Ba is eight, and it has a tetragonal inverted prismatic structural unit. Fig. 1(b) is a rectangular $Pnnm$ (58) structure, which is found in Ba$_{0.9}$Sr$_{0.1}$CN$_2$ experimentally. In (c) and (d), rhombohedral $R3m$ and $R3c$ are found, which would correspond to the structure found in MgCN$_2$ ($R3m$), CaCN$_2$ ($R3m$), and BaCN$_2$ ($R3c$), experimentally. [14]

The structure, $C2/c$ shown as (e) has the same structural
units as the tetragonal 14/mcm, but with a distorted structure with reduced symmetry. An interesting new structure is found as shown in Fig. [1(f)], which is tetragonal Ima2. The structure has nine-coordinated Ba connected with N, forming linear chains of anions [CN]n-.

To predict the structural transition depending on the applied pressure, we evaluated the enthalpy for each structure to be compared for thermodynamical stability [59-61][42]. The results are shown in Fig. [2]. In the lower pressure region 0 ~ 2.8 GPa [panel (a)], Pnnm is the most stable structure, and above that, 14/mcm gets to be the most stable structure. Rhombohedral R3m and R3c structures are found not to be thermodynamically stable. The experimentally observed phases with these symmetry [14] are presumably realized as meta-stable structures. As the fact in experimental observations [59], we confirmed 14/mcm phase appears above 5 GPa with increasing pressure and kept even with decreasing pressure to 0 GPa as a hysteresis. At 0 GPa, the meta-stable 14/mcm returns back to Pnnm by re-baking at 450°C in an argon atmosphere. The hysteresis would be allowed when the enthalpy difference between the competing phases is not so large, which can be discussed using the predictions in Fig. [2] as given in the third paragraph of §III B.

In Fig. [3] we examined the lattice dynamical stability for these candidate structures by ab initio phonon calculations. Panel (a) [(b)] shows the phonon dispersion of 14/mcm [R3c] structure at 0 GPa. We confirmed no imaginary mode appeared in 14/mcm implying the dynamical stability, that is the case also for Pnnm and R3m as shown in S.I. For R3c, however, we observed some imaginary modes [panel (b)]. The imaginary modes for R3c have been confirmed to be kept even under increasing pressure. The present theoretical prediction is hence concluding that the R3c cannot exist as a stable phase. The phase is, however, observed as reported by single-crystal XRD experiments at ambient condition [14].

Fig. [4] shows the comparison of the pressure dependence of lattice constants between experiments and present calculations, evaluated for 14/mcm-BaCN2. Fairly good coincidence to experiments would ensure the reliability of the present computational conditions with GGA-PBE exchange-correlation functionals. The dependence is summarized in terms of the bulk modulus being 69 ± 2 GPa (experiments) to be compared with 71.8 GPa (calculations), being fairly good agreement as well (details are given S.I.).

B. Pressure-dependent stable phases

The main interest of this study is the high-pressure phase of BaCN2, which has not been studied experimentally. The pressure dependence of the relative enthalpies with that of 14/mcm as the reference zero is shown in Fig. [2]. Here, we exclude R3c and R3m, which are already thermodynamically unstable than 14/mcm in the low pressure region. As described in the previous subsection, Pnnm is the most stable structure ranging in the low pressure region 0 ~ 2.8 GPa, and a phase transition to the tetragonal 14/mcm is predicted at 2.8 GPa. The tetragonal 14/mcm is stable up to 25 GPa, where the phase transition to C2/c occurs. Though the C2/c has the same unit structure as 14/mcm, its symmetry drops from the four-fold (14/mcm) to two-fold (C2/c) upon pressure application. The C2/c is stable up to 42 GPa, above which the Ima2 phase appears at higher pressures.

The newly predicted high-pressure phase Ima2 is a polymerized crystal formed by a linear chain binding anionic sites CN2 only. The structure can be understood to emerged because of the high pressure making CN2 come into close proximity and it is better to stabilize them by forming covalent bonds directly. This situation is similar for the high-pressure phase of CO2, which has the same electron configuration as NCN2:-: It undergoes a phase transition from a molecular crystal to a covalent bond crystal at about 20 GPa [57] when the pressure is increased because the closer distance between the elements make it better to form covalent bonds.

In Sec. Introduction, we raised the interest of the application viewpoint whether the polymerized phase realized by the high pressure can be quenched stably even with decompression, as realized in LiN2. For this question, the behavior of enthalpy in Fig. [2] gives negative support: Considering two different phases involved in hysteresis, enough small difference between each enthalpy would allow the hysteresis with the compensation in entropy. As a matter of experimental fact[? ], the hysteresis exists between Pnnm and 14/mcm in the low pressure region, where the enthalpy difference is ~0.05 eV/atom. This magnitude would then be a reference to allow the hysteresis. Comparing with that, the enthalpy for the polymerized phase Ima2 increases too rapidly with decreasing pressure below below 20 GPa, giving much larger enthalpy difference, making it difficult to retain the hysteresis. Note that BaN(3) is another example of a high pressure phase showing the hysteresis to exist at ambient pressure (though it is not to be described as polymerized state but the compound of azide (NNN-) ions). In this case, the energy difference between the phases involved in hysteresis is as small as 0.033 eV/atom, and the structure of the high pressure phase is confirmed to be dynamically stable without imaginary modes in the phonon calculations, supporting the experimental fact that the high pressure phase is quenched.

From the enthalpy comparison (Fig. [2]), we have predicted the structural transitions Pnnm → 14/mcm → C2/c → Ima2 as the applied pressure gets increased. The dynamical lattice stability of these structures was then verified by phonon calculations, confirming that no imaginary modes appeared for these structures supporting the phase stability (S1). The pressure-dependent phase diagram is summarized in Fig. [2]. The coordination number increases as Pnnm (6) → 14/mcm (8), C2/c (8) → Ima2 (9), being indeed consistent with the general statement that the coordination number increases as the applied pressure gets higher. The present prediction is a new finding because for the present compound, there has been a couple of reports upto 10 GPa (experiment) and 15 GPa (computational) so far [32][33]. Compared to the azide ion compounds with single atom anions [9][45], the present result predicts that higher pressure is required to ob-
tain the polymerized phase when the anion site is replaced to the molecular unit. This can be understood as a result of increased internal degrees of freedom of the anion unit to accommodate more entropy. The structural transition requiring higher pressure implies that the pressure-dependent fluorescence properties as a useful application can robustly be maintained even under the higher pressure.
C. Electronic structures

Fig. 5 shows the bandgap values predicted for each structure depending on applied pressure. The bandgap is a key quantity in the context of the application of the compounds as a phosphor [35], where the transition of Eu$^{2+}$ ($5d \rightarrow 4f$) plays a role of its luminescence. For a phosphor, the energy change of the transition should be smaller than the bandgap of the matrix crystal, otherwise the conduction band overlaps the excited level of Eu$^{2+}$, leading to a non-radiative transition without any luminescence. It is, therefore, advantageous to have larger bandgap, and from this point of view, Pnnm seems to be more promising as a phosphor than I4/mcm.

It is worth noting that the behaviors in Fig. 5 for I4/mcm and C2/c are significantly different for these quite similar structures. The difference in the behavior would reflect how the overlap of orbitals get to be affected under the compression by the applied pressure. Compared to C2/c, I4/mcm is then implied that its orbital overlapping has more sensitive structure to be affected by the compression. Looking at the polymerized structure Ima2, the behaviors in Fig. 5 is the least sensitive, which would be a consequence of its orbital overlapping being little to be affected. That is consistent with the linear behaviors in Fig. 2 from which we can conclude that the volume is almost unchanged and the overlapping situation is also the case.

It is a general tendency for the bandgap to decrease as the applied pressure increases, being consistent with the behaviors in Fig. 5 for higher pressure range. In the lower pressure range, however, the bandgaps initially increase before decreasing in the further higher pressure range. This can be attributed to the anisotropy, without which we can simply understand that the isotropic compression leads to the monotonic reduction of the bandgap. The initial uprising behavior is especially prominent for Pnnm structure, for which the internal anisotropy in the sense of orbital overlapping at the polyatomic anion unit would be more significant than other structure.

IV. CONCLUSION

We investigated the high-pressure phase of metal carbodiimide ceBaCN2 using genetic algorithm coupled with ab initio electronic structure calculations, with particular interest in whether the polymerized phase appears at high pressures. The structure search properly reproduced the previously reported crystal structures appearing in the lower pressure range, ensuring its reliability to some extent. The genetic structure search further predicts a polymerized phase with Ima2 appearing at higher pressure above 42 GPa. The polymerized phase takes the structure of a linear network of CN$_2$ planar triangular units. It is understood that the anion site units CN$_2$, which are close to each other under high pressure, form covalent bonds directly with each other and stabilize the phase. The comparison of the behaviors of enthalpy as the pressure dependence for each structure phase implies that the polymerized phase is expected not to be kept upon pressure reduction. Bandgaps were evaluated for each structure phase, showing that the phase realized in the lower pressure range has the largest bandgap, being advantageous for phosphor applications.

V. ACKNOWLEDGMENTS

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VI. SUPPLEMENTAL INFORMATION

A. Equation of states and bulk modulus
TABLE I. Crystal structures of BaCN$_2$ predicted at each pressure ($P$). Lattice parameters ($a$, $b$ and $c$) are given in unit of Å.

|                  | $P$ (GPa) | Lattice parameters | Atomic coordinates (fractional) |
|------------------|-----------|--------------------|---------------------------------|
|                  |           |                    | Atoms                           |
|                  |           | $a = b = 6.07585$  | $x$ $y$ $z$                     |
|                  |           | $c = 7.30079$     |                                 |
| BaCN$_2$         | 0         | $\alpha = \beta = \gamma = 90^\circ$ | Ba(4a) 0.00000 0.00000 0.25000 |
|                  |           |                    | C(4d) 0.00000 0.50000 0.00000  |
|                  |           |                    | N(8h) 0.14452 0.35548 0.50000  |
|                  | 1         | $a = b = 5.58515$ |                                 |
|                  |           | $c = 4.31738$     |                                 |
|                  |           | $\alpha = \beta = \gamma = 90^\circ$ | Ba(2a) 0.00000 0.00000 0.00000 |
|                  |           |                    | C(2c) 0.00000 0.50000 0.00000  |
|                  |           |                    | N(4g) 0.18844 0.59941 0.00000  |
|                  | 2         | $a = b = 15.16878$|                                 |
|                  |           | $c = 7.53574$     |                                 |
|                  |           | $\alpha = \beta = 90^\circ$ | Ba(18e) 0.00000 0.20987 0.25000 |
|                  |           | $\gamma = 120^\circ$ | C(18e) 0.00000 0.21645 0.75000 |
|                  |           |                    | N(36f) 0.04871 0.24013 0.89123  |
|                  | 3         | $a = b = 4.33547$ |                                 |
|                  |           | $c = 15.47892$    |                                 |
|                  |           | $\alpha = \beta = 90^\circ$ | Ba(3a) 0.00000 0.00000 0.00000 |
|                  |           | $\gamma = 120^\circ$ | C(3b) 0.00000 0.00000 0.50000  |
|                  |           |                    | N(6c) 0.00000 0.00000 0.41979  |
|                  | C2/c     | $a = b = 8.50422$ |                                 |
|                  |           | $c = 5.28698$     |                                 |
|                  |           | $\alpha = \gamma = 90^\circ$ | Ba(4e) 0.00000 0.29276 0.75000 |
|                  |           | $\beta = 128.438^\circ$ | C(4d) 0.25000 0.25000 0.50000  |
|                  |           |                    | N(8f) 0.20203 0.11282 0.29637  |
|                  | Ima2     | $a = 4.39979$     |                                 |
|                  |           | $b = 6.79556$     |                                 |
|                  |           | $c = 5.54136$     |                                 |
|                  |           | $\alpha = \gamma = \beta = 90^\circ$ | Ba(4b) 0.25000 0.15835 0.50064 |
|                  |           |                    | C(4b) 0.25000 0.55642 0.48557  |
|                  |           |                    | N(4a) 0.00000 0.00000 0.11315  |
|                  |           |                    | N(4b) 0.25000 0.65223 0.28574  |

FIG. 6. EOS of BaCN$_2$ (a) GGA (b) LDA.