The New High-Pressure Phases of Nitrogen-Rich Ag–N Compounds

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Abstract: The high-pressure phase diagram of Ag–N compounds is enriched by proposing three stable high-pressure phases (P4/mmm-AgN4, P1-AgN6 and P-1-AgN7) and two metastable high-pressure phases (P-1-AgN4 and P-1-AgN8). The novel N2 rings and N20 rings are firstly found in the folded layer structure of P-1-AgN7. The electronic structure properties of predicted five structures are studied by the calculations of the band structure and DOS. The analyses of ELF and Bader charge show that the strong N–N covalent bond interaction and the weak Ag–N ionic bond interaction constitute the stable mechanism of Ag–N compounds. The charge transfer between the Ag and N atoms plays an important role for the structural stability. Moreover, the P-1-AgN7 and P-1-AgN8 with the high-energy density and excellent detonation properties are potential candidates for new high-energy density species.

Keywords: polymeric nitrogen; high-energy density; high-pressure

1. Introduction

Due to the significant energy differences between the N–N bond, N=N bond and N≡N bond, polymeric nitrogen with the single/double bond structure is the potential high-energy-density materials (HEDMs). Moreover, the decomposition product of polymeric nitrogen is the clean diatomic nitrogen gas (N2). Thus, the polymeric nitrogen can be used as the environmentally friendly HEDM. Many efforts have been performed for exploring the novel polymeric nitrogen structures, such as the chain-shaped structures (ch, Cmcm, PP) [1,2], the layered structures (A7, BP-N, LP-N, LB-N) [1,3–5], the caged structures (N30) [6], the networked structures (cg-N, rcg-N, P-42m, P212121, P211/m, C2/c, P212121-500, Pnmn, P21, CW) [1,7–9] and the molecular crystal structures (N2-N6, N5, N9, 2N3) [10–13]. Up to now, the cg-N, BP-N, LP-N and HLP-N have been successfully synthesized at (110 GPa, 2000 K), (146 GPa, 2200 K), (150 GPa, 3000 K) and (244 GPa, 3300 K), respectively. The study of decomposition shows that the cg-N, BP-N, LP-N and HLP-N can be quenched down to 42 GPa, 48 GPa, 52 GPa and 66 GPa, respectively [14–18]. Clearly, the harsh synthesis conditions (P > 100 GPa, T > 2000 K) and the low stability of polymeric nitrogen limit its application.

Recent studies show that introducing an impurity element (M) into the pure nitrogen structure can induce the novel polynitrogen structures, which may exhibit the excellent properties, such as the mild synthesis conditions, high stability, etc. A series of polynitrogen structures has been reported in theoretical studies. Typically, the novel N4 ring is reported for P4/mmm-MnN4, Cm-Al2N7, P-1-Na2N8, P21/c-Li2N4, C2/m-MgN4 and Immm-AlN4 compounds [19–22]. Especially, the regular N4 rings results in a superhard property of P4/mmm-MnN4 and Cm-Al2N7. The N5 ring structures are found in the M2N5 (M = Na) and MN5 (M = Li, Na, Rb, Cs, Ca, Sr, Ba, Cu) compounds [23–29]. More interestingly, the double-, triple- and quadruple-N5 ring structures are found in Mn10 (M = Be, Mg, Ba), Mn15 (M = Al, Ga, Sc, Y) and HfN20 compounds, respectively [30–33]. Among these
reported structures, the P2_1-LiN_5, Cm-NaN_5, P3c-RbN_5 and P-1-BaN_10 are stable with the pressure larger than 9.9 GPa, 20 GPa, 30 GPa and 12 GPa, respectively. The Fdd2-BeN_10 and Fdd2-MgN_10 compounds are possibly synthesized at relatively low pressures (around 28 GPa for BeN_10 and 12 GPa for MgN_10) and can be preserved under ambient pressure. The good gravimetric energy density of Fdd2-BeN_10 (5.39 kJ/g), Fdd2-MgN_10 (3.48 kJ/g) and Sc-AlN_15 (5.31 kJ/g) makes them the potential (HEDMs). The novel N_6 ring structures are found in MN_3 (M = Cs, Ca, Sr, K, Mg) [26–28, 34–38] and MN_6 (M = W) compounds [39, 40]. Among them, the P-1-MgN_3 phase with the N_6 ring structure is recoverable at ambient pressure [36]. The superhard R-3m-WN_6 remains dynamically stable at ambient conditions [40]. The N-chain structures are found in MN_4 (M = Be, Cd, Fe, Gd, Re, Os, W, Ru, Zn) [41–48], GdN_6 [45], ReN_6 [49] and HfN_10 compounds [50]. Among them, P-1-BeN_4, γ-P-1-BeN_4 and δ-P-1-BeN_4 with the N-chain structures can be synthesized under pressures of 25.4, 20.8 and 27.4 GPa, respectively, which is greatly lower than 110 GPa for synthesizing the cg-N. The analysis of dynamical and thermal stability shows that the P-1-GdN_4 can be recovered to ambient conditions upon synthesis under compression. The Immm-HfN_10 is discovered to be stable at moderate pressure above 23 GPa and can be preserved as a metastable phase at ambient pressure. The novel N_18-ring, N_6 + N_10-ring, N_10-ring and N_18-ring layered structures are found in P6/mcc-KN_16, C2/m-BaN_6, P2_1/c-BeN_4 and P-31c-CoN_6 compounds, respectively [31, 51–53]. Moreover, the N_14-ring band-shape structure is the first reported for P-1-CoN_10 [53]. The P-31c-CoN_6 (6.14 kJ/g) and P-1-CoN_10 (5.18 kJ/g) with high-energy density can be quenched down to ambient conditions. The three-dimensional network structures are found in the C2/m-CdN_6, I4_1/a-HeN_6, R-3m-HeN_6, P63/m-HeN_10 and C2/m-HeN_22 [43, 54, 55]. The C2/m-CdN_6 and C2/m-HeN_22 with respectively high-energy-density values of 3.82 kJ/g and 10.44 kJ/g may be quenchable to ambient pressure. In the experiment, the cyclo-N_5 ring in LiN_5, NaN_5 and CsN_5 compounds are synthesized at 45, 52 and 65 GPa, respectively [56–58]. The CsN_5 and LiN_5 can be quenched down to 18 GPa and ambient pressure, respectively. The armchair-like hexazene N_6 ring in R-3m-WN_6 is synthesized with pressure larger than 126 GPa [59]. The N-chain structure in Ib4-m-MgN_6 and FeN_4 are synthesized at 50 and 180 GPa, respectively [60, 61]. As the review above, we know that the introduced impurity element can induce the novel polymeric nitrogen structures, which may exhibit more prominent properties than the pure polymeric nitrogen structures, such as the milder synthesis pressure and the higher stability.

Silver nitrides have received much attention for their outstanding chemical and physical properties, such as the energetic explosive, propulsion application, gas generators, photographic materials, etc. [62–64]. Recently, the armchair-antiarmchair N-chain and N_5 ring structures are severally reported for AgN_3 and AgN_5/AgN_6 compounds [65, 66]. Beyond that, no other new silver nitrides with the high-pressure polymeric structures have been reported. Thus, a detailed high-pressure study that considers the different stoichiometry in silver nitrides is necessary for exploring new polynitrogen polymeric structures.

2. Computation Details

The structural research has been performed by the particle swarm optimization methodology implemented in the CALYPSO structure prediction method [67]. The structure optimizations and property calculations have been carried out by the Vienna ab initio simulation package (VASP) code [68]. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange–correlation function has been employed for the first-principles calculations [69–71]. The 4d^{10}5s^{1} and 2s^{2}2p^{3} are treated as the valence electrons of Ag and N atoms, respectively. In order to ensure that the enthalpy is converged to less than 1 meV/atom, the cutoff energy of Projector Augmented Wave (PAW) pseudopotential and the Monkhorst–Pack k-mesh density are severally set to 520 eV and $2\pi \times 0.03 \text{ Å}^{-1}$ in the calculation. The $\Delta H^{f}$ of each Ag–N structure is calculated by using the following equation: $\Delta H^{f}(\text{AgN}_x) = [H(\text{AgN}_x) - H(\text{Ag}) - (x - 1) H(N)]/(1 + x)$. The most stable structures of AgN (Abma-phase) and N (P2/c- and cg-phases) are chosen as the reference structures in their corresponding stable pressure range. The phonon frequencies
have been calculated by using the finite displacement approach through the PHONOPY code [72]. The $2 \times 2 \times 2$ supercell with the lattice size of about 10 Å is constructed in the calculation of phonon. The dissociation energies are calculated by considering the following decomposition paths: $\text{AgN}_x \rightarrow \text{Ag} + x/2\text{N}_2$. The $\text{P6}_3/mmc$ phase of Ag and Pa 3 phase are the decomposition productions, respectively. The detonation velocity and detonation pressure have been calculated by using the Kamlet–Jacobs semi-empirical equation: $V_d = 1.01(NM^{0.5}E_d^{0.5})(1 + 1.30\rho)$ and $P_d = 15.58\rho^2NM^{0.5}E_d^{0.5}$. $N$ represents the moles of gas per gram of AgNx, $M$ represents the average molar mass of gas products, $E_d$ is the detonation chemical energy, and $\rho$ is the mass density.

3. Results and Discussion

Eight stoichiometries of Ag$_x$N$_y$ (x = 2, 3, 4, 5, 6, 7, 8, 10) are considered in the structural research with the simulation cells containing 1, 2 and 4 formula units (f.u.). The prediction for each stoichiometry is carried out at three pressures (50, 100 and 150 GPa). As shown in Figure 1a–c, the formation enthalpies ($\Delta H_f$) of Ag–N compounds are presented in the thermodynamic convex hull. The solid squares on the convex hull are the thermodynamically stable phases, while the ones that deviate from the convex hull are the metastable/unstable phases. For the AgN$_2$ stoichiometry, we found the thermodynamically stable P4/mmm phase at 100 and 150 GPa. At 50 and 100 GPa, the reported P-1-AgN$_2$ is the detonation chemical energy, and $\rho$ is the mass density.

The mechanical stability criteria of monoclinic structure are shown as follows [73]:

$$C_{11} > 0, C_{22} > 0, C_{33} > 0, C_{44} > 0, C_{55} > 0, C_{66} > 0, [C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0,$$

$$C_{33}C_{55} - C_{35}^2 > 0, C_{44}C_{66} - C_{46}^2 > 0, C_{22} + C_{33} - 2C_{23} > 0,$$

$$C_{22}(C_{33}C_{55} - C_{35}^2) + 2C_{23}C_{25}C_{35} - (C_{23}^2)C_{33} > 0,$$

$$2[C_{15}C_{25}((C_{33}C_{12} - C_{13}C_{23}) + C_{15}C_{35}(C_{22}C_{13} - C_{12}C_{23}) + C_{25}C_{35}(C_{11}C_{23} - C_{12}C_{13})] -$$

$$C_{15}^2(C_{22}C_{33} - C_{23}^2) + C_{25}C_{25}(C_{11}C_{33} - C_{13}^2) + C_{35}C_{35}(C_{11}C_{22} - C_{12}^2)] - C_{55}g > 0.$$
Figure 1. The formation enthalpies of Ag-N phases with respect to the Abma-AgN phase and nitrogen solids at different pressures (a–c). (d) shows the phase diagram of AgN$_2$ and AgN$_7$.

Figure 2. The phonon dispersion of P4/mmm-AgN$_2$ at 100 GPa (a), the P1-AgN$_7$ at 50 GPa (b) and P-1-AgN$_7$ at 150 GPa (c).

Figure 3. The phonon dispersion of P-1-AgN$_4$ at 150 GPa (a) and P-1-AgN$_8$ at 150 GPa (b).
The crystal structures of P4/mmm-AgN₂, P1-AgN₇, P-1-AgN₇, P-1-AgN₄ and P-1-AgN₈ are presented in Figure 4. In P4/mmm-AgN₂, the polymeric N-structure unit is the dumbbell-shaped N₂ structure, which is composed of two equivalent nitrogen atoms. At 100 GPa, the bond length of N₁-N₁ is 1.165 Å. For the P-1-AgN₇ presented in Figure 4b, one unit cell contains one dumbbell-shaped N₂ structure and one N₅ ring structure. The N₅ ring structure is composed of five inequivalent nitrogen atoms (N₁->N₅), while the dumbbell-shaped N₂ structure is composed of two inequivalent nitrogen atoms (N₆-N₇). At 50 GPa, the bond lengths of N₁-N₅, N₂-N₃, N₃-N₄, N₄-N₅, N₅-N₁ and N₆-N₇ are 1.296 Å, 1.309 Å, 1.296 Å, 1.307 Å and 1.114 Å, respectively. The P-1-AgN₇ is the folded layer structure, which is constituted by the N₂₀ ring and two fused N₇ rings. At 150 GPa, the bond lengths of ten N–N bonds (N₁-N₄, N₄-N₃, N₃-N₂, N₂-N₅, N₅-N₆, N₆-N₁, N₆-N₄, N₄-N₇ and N₇-N₇) that are constructed by seven inequivalent nitrogen atoms (N₁->N₇) are 1.286 Å, 1.315 Å, 1.270 Å, 1.286 Å, 1.274 Å, 1.282 Å, 1.254 Å, 1.318 Å, 1.277 Å and 1.261 Å, respectively. Up to now, the reported N-rings in the polynitrogen structures are the N₅, N₆, N₁₀, N₁₂, N₁₄ and N₁₈ rings [51–54]. As the construction unit of the layer structure, the novel N₇ rings and N₂₀ rings are firstly reported for this work. The P-1-AgN₄ is the 1-D chain structure, which is constructed by the alternate N₂ and N₆ ring. At 150 GPa, the bond lengths of five N–N bonds (N₁-N₁, N₁-N₂, N₂-N₃, N₃-N₄ and N₄-N₂) that are constructed by four inequivalent nitrogen atoms (N₁->N₄) are 1.266 Å, 1.282 Å, 1.300 Å, 1.281 Å and 1.306 Å, respectively. The P-1-AgN₈ is the layer structure, which is constructed by the fused N₁₈ ring structure. At 150 GPa, the bond lengths of five N–N bonds (N₁-N₄, N₄-N₃, N₃-N₂, N₂-N₅ and N₅-N₆) that are constructed by four inequivalent nitrogen atoms (N₁->N₄) are 1.271 Å, 1.257 Å, 1.272 Å, 1.269 Å and 1.280 Å, respectively.

The electronic structural properties including the band structure, the density of states (DOS), the electronic local function (ELF) and the Bader charge transfer are calculated for analyzing the electronic structure property and stable mechanism of structures. As shown in Figure 5, the P4/mmm-AgN₂ at 100 GPa and P1-AgN₇ at 50 GPa are the semiconductor phases with the band gaps of 1.0 eV and 2.4 eV, respectively. For the P4/mmm-AgN₂, the electronic states of valence bands near the Fermi level are mainly contributed by the Ag_d and N_p orbitals, while the conduction bands near the Fermi level are mainly contributed by the Ag_s and N_p orbitals. For the P-1-AgN₇, the electronic states of valence bands near the Fermi level are mainly contributed by the Ag_d and N_p orbitals, while the conduction bands near the Fermi level are mainly contributed by the Ag_d and N_p orbitals.

### Table 1. The elastic constants Cij (GPa) of the Ag–N compounds at high pressure.

| AgNₓ   | (GPa) | C₁₁ | C₂₂ | C₃₃ | C₄₄ | C₅₅ | C₆₆ | C₁₂ | C₁₃ | C₁₅ | C₂₃ | C₂₅ | C₃₅ | C₄₆ |
|--------|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| P4/mmm-AgN₂ | 100   | 563 | -   | 648 | 85  | -   | 22  | 313 | 310 | -   | -   | -   | -   | -   |
| P1-AgN₇  | 50    | 215 | 294 | 231 | 70  | 68  | 42  | 160 | 154 | -3  | 173 | -5  | 8   | 24  |
| P-1-AgN₇ | 150   | 943 | 942 | 800 | 221 | 207 | 279 | 513 | 396 | -85 | 377 | -113| -19 | -85 |
| P-1-AgN₄ | 150   | 910 | 912 | 710 | 127 | 148 | 270 | 593 | 354 | -42 | 338 | -39 | 49  | 27  |
| P-1-AgN₈ | 150   | 1163| 1114| 861 | 193 | 56  | 250 | 604 | 152 | -17 | 228 | -24 | 12  | 0.24|
Table 1. The elastic constants $C_{ij}$ (GPa) of the Ag–N compounds at 150 GPa.

| Compound   | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{22}$ | $C_{23}$ | $C_{33}$ | $C_{44}$ | $C_{55}$ | $C_{66}$ | $C_{12}$ | $C_{13}$ | $C_{23}$ |
|------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| P4/mmm-AgN$_2$ | 115 | 95 | 81 | 218 | 177 | 174 | 38 | 338 | 313 | 113 | 173 | 338 |
| P1-AgN$_7$ | 150 | 943 | 942 | 800 | 221 | 207 | 279 | 513 | 396 | 2022 | 2005 | 1598 |
| P1-AgN$_7$ | 50 | 215 | 294 | 231 | 70 | 68 | 42 | 160 | 154 | 2022 | 2005 | 1598 |

In Figure 4, as the fixed value of isovalue (0.8) in ELF, the high localization electronic states between the nitrogen atoms indicate the strong N–N covalent bond interaction. The lone electron pairs distribute at the outside corner of N atoms for reducing the repulsive interaction. In combination with the analysis of Figure 4, we know that the N atom in the dumbbell-shaped N$_2$ structure of P4/mmm-AgN$_2$ and P1-AgN$_7$ hybridizes in the sp state, which is formed by one N–N $\sigma$ bond and one lone pair electron. The N atom in the N$_5$ ring hybridizes in the sp$^2$ state, which is formed by two N–N $\sigma$ bonds and one lone electron pair. In the P1-AgN$_7$, the N$_5$, N$_3$, N$_5$ and N$_7$ atoms hybridize in sp$^2$ states, which are formed by two N–N $\sigma$ bonds and one lone electron pair, while the N$_2$, N$_4$, and N$_6$ atoms hybridize in sp$^3$ states, which are formed by three N–N $\sigma$ bonds and one lone electron.
pair. In the P ̅ T-AgN₄, the N₁, N₃, and N₄ atoms hybridize in sp² states, which are formed by two N–N σ bonds and one lone electron pair, while the N₂ atom hybridizes in the sp³ state, which is formed by three N–N σ bonds and one lone electron pair. In the P ̅ T-AgN₈, the N₂, N₃, and N₄ atoms hybridize in sp² states, which are formed by two N–N σ bonds and one lone electron pair, while the N₁ atom hybridizes in the sp³ state, which is formed by three N–N σ bonds and one lone electron pair. No localization electron is distributed around the Ag atom and between the Ag and N atoms due to the weak Ag–N electronic overlap interaction. As the presented charge transfer in Table 2, we can see that the Ag and N atoms are severally the electron donor and receptor, which means the weak Ag–N ionic bond interaction. Clearly, this charge transfer enhances the N–N covalent bond and Ag–N ionic bond interaction, which improves the structural stability. According to the above discussion, we know that the stable mechanism of our predicted Ag–N compounds originates from the strong N–N covalent bond interaction and the weak Ag–N ionic bond interaction. Moreover, the charge transfer between the Ag and N atoms plays an important part in their structural stability.

Figure 7. The ELFs of P4/mmm-AgN₂ (a), P1-AgN₇ (b), P-1-AgN₇ (c), P-1-AgN₄ (d) and P-1-AgN₈ (e) (isovalue = 0.8).

Table 2. The Bader charge analysis of P4/mmm-AgN₂, P1-AgN₇, P-1-AgN₇, P-1-AgN₄ and P-1-AgN₈ at different pressures. The negative and positive values mean the donor and the receptor of charge, respectively.

| Structures     | Pressure | Element | σ(e)/Atom |
|----------------|----------|---------|-----------|
| P4/mmm-AgN₂    | 100      | Ag      | −0.70     |
|                |          | N       | +0.35     |
| P1-AgN₇        | 50       | Ag      | −0.82     |
|                |          | N       | +0.117    |
| P-1-AgN₇       | 150      | Ag      | −0.623    |
|                |          | N       | +0.089    |
| P-1-AgN₄       | 150      | Ag      | −0.64     |
|                |          | N       | +0.16     |
| P-1-AgN₈       | 150      | Ag      | −0.76     |
|                |          | N       | 0.095     |

The energy densities and detonation properties of P-1-AgN₇ and P-1-AgN₈ are presented in Table 3. It can be seen that the energy density of P-1-AgN₇ and P-1-AgN₈ is
3.9 kJ/g, which is close to that of the TNT (4.3 kJ/g). The detonation velocities of P-1-AgN\(_7\) (13.58 km/s) and P-1-AgN\(_8\) (17.59 km/s) are 2.0 and 2.5 times the value (6.90 km/s) of TNT, respectively. The detonation pressures of P-1-AgN\(_7\) (115.5 GPa) and P-1-AgN\(_8\) (210.7 GPa) are 6 and 11 times the value (19.00 GPa) of TNT. Thus, the P-1-AgN\(_7\) and P-1-AgN\(_8\) are potential candidates for new high-energy density species.

Table 3. The energy density and detonation properties of P-1-AgN\(_7\) and P-1-AgN\(_8\) compounds in comparison to TNT.

| Compounds   | Energy Densities (kJ/g) | Detonation Velocity (km/s) | Detonation Pressure (GPa) |
|-------------|-------------------------|----------------------------|---------------------------|
| P-1-AgN\(_7\) | 3.90                    | 13.58                      | 115.5                     |
| P-1-AgN\(_8\) | 3.90                    | 17.59                      | 210.7                     |
| TNT         | 4.30                    | 6.90                       | 19.00                     |

4. Conclusions

The crystal structure, electronic structure and energy property of silver nitrides in nitrogen-rich aspects are studied by using the first-principles calculations combining the particle-swarm structural searching. In addition to the reported P-1-AgN\(_3\), three stable high-pressure phases (P4/mmm-AgN\(_2\), P1-AgN\(_7\) and P-1-AgN\(_7\)) and two metastable high-pressure phases (P-1-AgN\(_4\) and P-1-AgN\(_8\)) are proposed by the structural prediction method. The stable pressure range of P4/mmm-AgN\(_2\), P1-AgN\(_7\) and P-1-AgN\(_7\) are proposed by the enthalpy difference analysis. Interestingly, the novel N\(_7\) rings and N\(_20\) rings are firstly found in the folded layer structure of P-1-AgN\(_7\). In electronic structure analysis, the P4/mmm-AgN\(_2\) and P1-AgN\(_7\) are the semiconductor phases, while the P-1-AgN\(_7\), P-1-AgN\(_4\) and P-1-AgN\(_8\) are the metal phases. The analysis of ELF and Bader charge shows that the stable mechanism of predicted Ag–N compounds originates from the strong N–N covalent bond interaction and the weak Ag–N ionic bond interaction. Moreover, the charge transfer between the Ag and N atoms plays an important role for their structural stability. The P-1-AgN\(_7\) and P-1-AgN\(_8\) with the high energy densities and excellent detonation properties are potential candidates for new high-energy density species. This work not only enriched the high-pressure phase diagram of Ag–N compounds but also proposed two new high-energy density structures.

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