Crystal Structure of Silver Pentazolates AgN$_5$ and AgN$_6$

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Abstract

Silver pentazolate, a high energy density compound containing cyclo-N$_5^-$ anion, has recently been synthesized at ambient conditions. However, due to high sensitivity to irradiation, its crystal structure has not been determined. In this work, silver-nitrogen crystalline compounds at ambient conditions and high pressures, up to 100 GPa, are predicted and characterized by performing first-principles evolutionary crystal structure searching with variable stoichiometry. It is found that newly discovered AgN$_5$ and AgN$_6$ are the only thermodynamically stable silver-nitrogen compounds at pressures between 42 and 80 GPa. In contrast to AgN$_5$, pentazolate AgN$_6$ compound contains N$_2$ diatomic molecules in addition to cyclo-N$_5^-$. These AgN$_5$ and AgN$_6$ crystals are metastable at ambient conditions with positive formation enthalpies of 54.95 kJ/mol and 46.24 kJ/mol, respectively. The underlying cause of the stability of cyclo-N$_5^-$ silver pentazolates is the enhanced aromaticity enabled by the charge transfer from silver atoms to nitrogen rings. To aid in experimental identification of these materials, calculated Raman spectra are reported at ambient pressure: the frequencies of N$_5^-$ vibrational modes of AgN$_5$ are in good agreement with those measured in experiment.
Introduction

Polynitrogen high energy density materials are in the focus of intense experimental and theoretical investigations\textsuperscript{1,2} due to their promise of delivering high explosive power upon decomposition of single and double bonded nitrogen atoms to triply bonded \(N_2\)\textsuperscript{3,4}. Although pure nitrogen extended solids such as cubic gauche (cg) and layered polymeric nitrogen have been predicted\textsuperscript{5} and subsequently synthesized at high pressures\textsuperscript{6,7}, their recovery at ambient conditions is challenging\textsuperscript{8}.

Another possibility to achieve high energy density is to realize compounds containing single and double bonded nitrogen molecular species, such as cyclo-\(N_5^-\) anion.\textsuperscript{9–18} The negative charge on pentazoles requires an electron donating component, therefore, a family of alkali pentazolate crystals have been predicted\textsuperscript{10–13,19–23} and then synthesized\textsuperscript{9,12,14–18,24,25} at high pressures. Success has recently been achieved in synthesizing cyclo-\(N_5^-\) pentazolates at ambient conditions using traditional methods of synthetic chemistry\textsuperscript{9,14–17}. However, the challenge of recovering simpler cyclo-\(N_5^-\) pentazolate compounds at ambient conditions still remains.

Most of metal pentazolates discovered so far are the crystals with alkali cations Li\textsuperscript{+}\textsuperscript{18,21,23,24}, Na\textsuperscript{+}\textsuperscript{20}, K\textsuperscript{+}\textsuperscript{19}, and Rb\textsuperscript{+}\textsuperscript{13} with 1:5 metal/nitrogen stoichiometry. They are just the one of several \(M_xN_y\) materials featuring isolated nitrogen atoms/ions, finite and infinite chains, 2D layers and other polynitrogen complexes. Such rich chemistry is due to the ease of alkali atoms to donate electrons to nitrogen species, resulting in plethora of \(M_xN_y\) chemical compositions.

Silver, being one of the coinage elements (Cu, Ag, and Au), is “noble”, i.e. almost unreactive, compared to reactive alkali metals. This is because the outer valence electrons are more tightly bound than those of alkali atoms due to poor screening of the nuclear charge by the d- sub-shells compared to much stronger screening by filled s/p shells of alkali atoms. Therefore, less variety is expected among stoichiometries of Ag\textsubscript{x}N\textsubscript{y} compounds; it is highly probable that 1:5 stoichiometry would be the only one that displays negative formation
enthalpies at high pressures. In fact, even the existence of AgN₅ was questioned more than a century ago when it was purportedly synthesized by Lifschitz and then refuted by Curtius et al. Only two silver nitrogen crystalline compounds are known to exist at ambient conditions: silver nitride Ag₃N₂₈ and silver azide AgN₃, both of them being extremely sensitive explosive materials. Sun et al. reported the synthesis of a solvent-free pentazolate complex AgN₅ in a compound which does not contain counter ions such as Cl⁻, NH₄⁺ and H₃O⁺. The authors failed to obtain single crystal AgN₅ suitable to XRD characterization as this compound is highly unstable upon irradiation or heating. Instead, they converted AgN₅ complex to a 3D framework [Ag(NH₃)₂][Ag₃(N₅)₄]⁻ in order to characterize its crystal structure. Therefore, the important question is whether AgN₅ exists and if it does, what is its crystal structure. The light and heat instability of AgN₅ indicates a high degree of its metastability, similar to known silver azide AgN₃ crystal which possesses a very high positive enthalpy of formation 310.3 kJ/mol. It is known that application of pressure imparts a substantial thermomechanical energy of compression to precursor materials, which may promote unusual chemistry of resulting compounds. Therefore, the investigation of AgN₅ as well as other Ag-N materials with different stoichiometries (if they exist) at high pressures is of great importance for elucidating bonding and structure of silver-nitrogen compounds.

The goal of this research is to answer these outstanding questions by performing crystal structure searching of new silver-nitrogen crystalline compounds, including AgN₅, at ambient conditions and high pressures up to 100 GPa using variable composition first-principles evolutionary crystal structure prediction method. Once the new compounds are uncovered their stability, bonding and structure as well as electronic and vibrational properties are analyzed. Chemical pathways for synthesis of discovered thermodynamically stable compounds are proposed and Raman spectra of the resultant compounds are calculated to aid in experimental detection of these materials at ambient pressure.
Computational Details

The silver-nitrogen compounds $\text{Ag}_x\text{N}_y$ of variable stoichiometry are searched using first-principles evolutionary structure prediction method implemented in Universal Structure Predictor: Evolutionary Xtallography code (USPEX)\textsuperscript{35–37}. The variable composition searches are performed at several pressures using unit cells containing varying amounts of silver and nitrogen atoms between 8 to 16 atoms in the cell. In total, about 100 different $\text{Ag}_x\text{N}_y$ stoichiometries are sampled. Once the variable composition search at a given pressure is complete, fixed composition or molecular searches using larger unit cell sizes up to 48 atoms are performed at stoichiometries corresponding to the thermodynamically stable compounds at the vertices of the convex hull and the metastable compounds up to 20 meV above the convex hull.

The process of structure prediction begins by generating structures based on all space groups and random lattice parameters in the first generation. The obtained structures are then optimized to a target pressure. Their normalized formation enthalpy is determined as follows:

$$\Delta H_{\text{Ag}_x\text{N}_y} = (H_{\text{Ag}_x\text{N}_y} - xH_{\text{Ag}} - yH_{\text{N}})/(x + y),$$

where $H_{\text{Ag}_x\text{N}_y}$, $H_{\text{Ag}}$ and $H_{\text{N}}$ are enthalpy of the compounds and best structures of pure elements, respectively. Based on the normalized formation enthalpy, the convex hull at each pressure is constructed using the lowest formation enthalpy structures. For each subsequent generation, a small subset of the lowest enthalpy structures is kept while a new generation is built by adding more random crystals and by applying variation operators to the best “parent” structures. The process is repeated until the best kept structures do not change for ten consecutive generations.

Once combined variable and fixed stoichiometry searches are completed at several pressures, all the resulting crystal structures are combined in one single database, which is then
used for high precision geometry optimization and construction of the final convex hull at every pressure of our interest, from 0 to 100 GPa. Such combined method was shown to be successful in overcoming computational limitations of the variable composition search. For example, during variable composition search at 50 GPa only one thermodynamically stable stoichiometry, AgN\textsubscript{5}, was found. However, a second thermodynamically stable stoichiometry AgN\textsubscript{6} was uncovered in subsequent fixed stoichiometry molecular search using twice larger unit cell containing four silver atoms and twenty-four nitrogen atoms.

The USPEX method and similar structure search methods\textsuperscript{38,39} have already been successful in prediction of experimentally known crystal structures of pure elements. To speed up the search, the known lowest enthalpy reference structures of pure elements were taken: fcc Ag-\textit{Fm-\textit{3m}} for Ag across the entire pressure range, and \textalpha-N\textsubscript{2} at 0 GPa, \textepsilon-N\textsubscript{2} at 50 GPa, and cg-N above 50 GPa for reference structures of nitrogen. If a compound lies on the convex hull it is considered thermodynamically stable meaning it will not decompose into either the pure elements or into a mixture of other Ag\textsubscript{x}N\textsubscript{y} compounds. Compounds that lie above the convex hull must be dynamically stable, i.e. no negative phonon frequencies, to be considered metastable.

Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) to DFT\textsuperscript{41} implemented in Vienna ab initio simulation package VASP\textsuperscript{42} is used to perform the first-principles calculations. The projector augmented wave (PAW) pseudopotentials are employed. During the USPEX search, each crystal is optimized using a plane wave basis set with 500 eV energy cutoff and k-point sampling density of 0.07 Å\textsuperscript{-1}. At the completion of a search, the structures that are on the convex hull as well as a subset of possible metastable structures with higher formation energy, up to 100 meV above the convex hull, are optimized using high accuracy setting to generate the accurate convex hull. During the high accuracy calculations, the hard nitrogen PAW pseudopotential is used to address a possibility of overlapping cores of N atoms in triple bonded N\textsubscript{2}. In addition, the energy cutoff and k-point density are increased to 1000 eV and 0.03 Å\textsuperscript{-1} respectively. Frozen phonon approximation is
used to calculate the phonons at the gamma point as well as off-resonant Raman frequencies.\textsuperscript{13} The intensities are determined by calculating the macroscopic dielectric polarizability tensors for each normal mode eigenvector.\textsuperscript{14} The atomic charges and bond orders are calculated using density derived electrostatic and chemical charges (DDEC) method implemented in VASP.\textsuperscript{15}

**Results and discussion**

At 0 GPa, no negative formation enthalpy Ag\textsubscript{a}N\textsubscript{b} compounds exist, therefore, a concave hull consists of metastable structures with positive formation enthalpies. This is in agreement with the fact that at ambient conditions only two known silver-nitrogen compounds, silver nitride (Ag\textsubscript{3}N) and silver azide (AgN\textsubscript{3}), possess very high positive formation enthalpies.

At 50 GPa, the stoichiometries with negative formation enthalpy are thermodynamically stable AgN\textsubscript{5}, AgN\textsubscript{6}, and metastable AgN\textsubscript{9}, and AgN\textsubscript{4}, see the convex hull in Fig. 1. At 60 GPa and 70 GPa only AgN\textsubscript{5}-P\textsubscript{2}1/c is on the convex hull while AgN\textsubscript{6}-P\textsubscript{2}1\textsubscript{2}1\textsubscript{2} becomes metastable with 1.93 meV/atom and 17.4 meV/atom above the convex hull at each pressure respectively.

Both AgN\textsubscript{5}-P\textsubscript{2}1/c and AgN\textsubscript{6}-P\textsubscript{2}1\textsubscript{2}1\textsubscript{2} follow the pattern of NaN\textsubscript{5} which contains a single phase of XN\textsubscript{5} over the entire pressure range\textsuperscript{10} whereas KN\textsubscript{5}, RbN\textsubscript{5}, and CsN\textsubscript{5} consist of a low pressure and a high pressure phases.\textsuperscript{10,11,13,19} The formation enthalpy of AgN\textsubscript{5}-P\textsubscript{2}1/c becomes negative for the first time at 41.5 GPa. At 57.5 GPa, AgN\textsubscript{5}-P\textsubscript{2}1/c reaches its lowest formation enthalpy of −0.095 eV/atom. Finally, at 79.4 GPa, the formation enthalpy of AgN\textsubscript{5}-P\textsubscript{2}1/c becomes positive again. Similarly, the formation enthalpy of AgN\textsubscript{6}-P\textsubscript{2}1\textsubscript{2}1\textsubscript{2} becomes negative at 41.7 GPa. At 57.5 GPa, the formation enthalpy of AgN\textsubscript{6}-P\textsubscript{2}1\textsubscript{2}1\textsubscript{2} reaches the lowest value of −0.086 eV/atom. The formation enthalpy of AgN\textsubscript{6}-P\textsubscript{2}1\textsubscript{2}1\textsubscript{2} becomes positive again at pressures exceeding 68 GPa.
Figure 1: Ag-N convex hulls at 50, 60, and 70 GPa. Filled squares indicate thermodynamically stable structures; open circles – metastable structures.

Figure 2: Crystal structure of a) AgN$_5$-P2$_1$/c and b) AgN$_6$-P2$_1$2$_1$2 pentazolates. The Ag atoms are depicted in gray and the N atoms are depicted in blue.

The crystal structures of the two new compounds are depicted in Fig. 2. There are 24 atoms in the AgN$_5$-P2$_1$/c unit cell and 28 atoms in the AgN$_6$-P2$_1$2$_1$2 unit cell. In AgN$_5$-P2$_1$/c, nitrogen atoms form 5 membered cyclo-N$_5$ pentazolate rings with the silver atoms not covalently bonded to the nitrogen rings or other silver atoms. The packing efficiency of AgN$_5$-
$P2_1/c$ is 43.8%. The distance between the molecular centers of nearest neighboring cyclo-$N_5^-$ pentazolate rings in AgN$_5$-$P2_1/c$ is approximately 5 Å. In AgN$_6$-$P2_1 2_1 2$, nitrogen atoms form cyclo-$N_5^-$ with extra, isolated N$_2$ dimers and standalone silver atoms. The packing efficiency of AgN$_6$-$P2_1 2_1 2$ is 24.6%. The molecular centers of nearest neighboring cyclo-$N_5^-$ pentazolate rings in AgN$_6$-$P2_1 2_1 2$ are separated by approximately 5.2 Å. The cyclo-$N_5^-$ pentazolate rings of both AgN$_5$-$P2_1/c$ and AgN$_6$-$P2_1 2_1 2$ are isolated with bonding only occurring between the nitrogen atoms within each individual ring. The electronic band structure of both predicted silver pentazolate crystals display insulator character at all pressures studied, see Figs. S1 and S2 in the supplementary information.

![Diagram](attachment:image.png)

**Figure 3:** a) The charges and bond order in the cyclo-$N_5^-$ pentazolate in the AgN$_5$-$P2_1/c$ crystal. The N-N bond lengths in cyclo-$N_5^-$ pentazolate between each silver atom is between 1.33 Å and 1.33 Å. b) The charges and bond order in the cyclo-$N_5^-$ pentazolate in the AgN$_6$-$P2_1 2_1 2$ crystal. The N-N bond lengths in the cyclo-$N_5^-$ pentazolate is between 1.31 and 1.34 Å. c) The charges and bond order in the N$_2$ dimer in the AgN$_6$-$P2_1 2_1 2$ crystal: the N-N bond length is 1.10 Å.
To understand the bonding of these novel compounds, the charges and bond orders were calculated, see Fig. 3. The N-N bond lengths in the pentazolate cyclo-N$_5^-$ anions in AgN$_5$-P$_2$$_1$/c are between 1.32 Å and 1.33 Å. The charges, beginning from the atom at the top point of the pentazolate ring shown in Fig. 3(a) and moving clockwise, are: -0.088e, -0.027e, -0.029e, -0.086e, and -0.106e. The silver atom carries charge +0.33e, the corresponding negative charge is on N$_5^-$ anion. The aromatic nature of the cyclo-N$_5^-$ can be deduced from the N-N bond orders which range from 1.34 to 1.42, i.e. between those corresponding to single and and double bonds. The average charge and average N-N bond order in the cyclo-N$_5^-$ in AgN$_5$-P$_2$$_1$/c are similar to their counterparts in the cyclo-N$_5^-$ in XN$_5$ \{X = Na, K, Rb, Cs\} compounds.

The N-N bond lengths in cyclo-N$_5^-$ in AgN$_6$-P$_2$$_1$2$\text{1}_2$ crystal are between 1.31 and 1.34 Å which are slightly smaller than those of its pure pentazolate counterpart, AgN$_5$-P$_2$$_1$/c. As seen in Fig. 3(b), the charges on the nitrogen atoms in the AgN$_6$-P$_2$$_1$2$\text{1}_2$ pentazolate are also smaller on average than those in AgN$_5$-P$_2$$_1$/c crystal, ranging from $-0.033e$ to $-0.078e$. The N$_2$ dimer of AgN$_6$-P$_2$$_1$2$\text{1}_2$ is almost electroneutral, as the atomic charges on N atoms $-0.017e$ and 0.014e compensate each other, see Fig. 3(c). The silver atoms in AgN$_6$-P$_2$$_1$2$\text{1}_2$ carry a charge of 0.27e. Though the charges are smaller in AgN$_6$-P$_2$$_1$2$\text{1}_2$ crystal than in AgN$_5$-P$_2$$_1$/c, the N-N bond orders are comparable, ranging from 1.32 to 1.47 in case of AgN$_6$-P$_2$$_1$2$\text{1}_2$. The N-N bond of the N$_2$ dimer in AgN$_6$-P$_2$$_1$2$\text{1}_2$ is close to a triple bond in isolated diatomic N$_2$ molecule with N-N bond length 1.1 Å and bond order 2.73.
In principle, the new compounds can be synthesized via compression of silver azide and nitrogen in a diamond anvil cell (DAC). Several attempts have been made to produce pentazolate salts via traditional DAC experiments whereby a combination of a metal azide and molecular nitrogen is cold compressed to high pressures and then laser heated. CsN$_5$ was synthesized, having first been guided by first-principles crystal structure prediction, by Steele et al. via compression of CsN$_5$ + N$_2$ in DAC to 60 GPa. Zhou et al. compressed lithium azide and molecular nitrogen in DAC to pressure of only 41.1 GPa and report the formation of a new phase of LiN$_5$-P$_{21}$m. Zhou et al.’s results are consistent with predictions of the transition pressure of 40 GPa by Yi et al. and Peng et al. Recently, the formation of two new pentazolate salts, NaN$_5$ and NaN$_5$·N$_2$, were observed via DAC experiments of sodium azide and molecular nitrogen compressed to $\sim$50 GPa. Notably, the NaN$_5$·N$_2$ crystal synthesized by Bykov et al. contains both cyclo-N$_5^-$ pentazolate rings and N$_2$ dimers similar to what is predicted here for AgN$_6$-P$_{21}2_12$.

Silver azide, in spite of its volatility, is well studied with a known phase transition from low pressure AgN$_3$-Ibam to high pressure AgN$_3$-I$_4$/mcm at 2.7 GPa. The theoretical study presented by W. Zhu et al. predicts this transition to occur at nearly 7 GPa.
ever, our results are closer to what was found in experiments with AgN$_3$-I$_4/mcm$ becoming energetically favorable near 1.5 GPa.

The enthalpy difference between AgN$_5$-P$_{21}/c$ and AgN$_6$-P$_21212$ and the possible precursors, AgN$_3$-I$_4/mcm$ and N$_2$-R3-c, was calculated over increasing pressure as a zero-temperature estimate of potential transformation of the precursors to the pentazolate product, see Fig. 4. AgN$_3$-I$_4/mcm$ is taken as the precursor due to the phase transition from AgN$_3$-Ibam to AgN$_3$-I$_4/mcm$ that occurs at such a low pressure. The results show that AgN$_5$-P$_{21}/c$ and AgN$_6$-P$_21212$ are thermodynamically favorable to the mixture of the precursors at 0 K and pressures exceeding 21 GPa and 26 GPa respectively.

It is important to note that 0 K data are the lowest pressure estimates. The transition pressures at high temperatures are determined by a complex interplay of thermodynamics and kinetics of solid-state reactions. On the one hand, temperature helps to activate kinetics, thus potentially lowering transition pressure. On the other hand, temperature might thermodynamically stabilize the molecular precursors compared to solid reactants due to entropic -TS contribution to the Gibbs free energy, thus increasing transition pressure upon increase of temperature. Due to extreme complexity of the phenomena involved a meaningful predictions of finite temperature effects seem to be impractical to make within the scope of the current work.
Figure 5: Calculated Raman spectra of AgN$_5$-P2$_1$/c, black curve, and AgN$_6$-P2$_1$2$_1$2, red curve, at 0 GPa zoomed to show smaller peaks. The tallest peak of AgN$_5$-P2$_1$/c at 1183.4 cm$^{-1}$ is nearly 7 times larger than the next tallest peak at $\sim$106 cm$^{-1}$. The tallest peak of AgN$_6$-P2$_1$2$_1$2 at 1200.2 cm$^{-1}$ corresponding to the symmetric stretching of the N$_5$ molecule is 1.42 times larger than the next tallest peak at 2355.9 cm$^{-1}$ corresponding to the symmetric stretching of the N$_2$ dimer. The specific bending and stretching modes are labeled in the high frequency range.

A material must be at least dynamically stable at ambient conditions to be considered as a viable candidate for experimental synthesis. The dynamical stability of AgN$_5$-P2$_1$/c at 0 GPa is confirmed via the absence of negative phonon frequencies in phonon band structure, see Fig. S3 in the supplementary information. To aid in the experimental identification of AgN$_5$-P2$_1$/c, its Raman spectrum is calculated at 0 GPa, see Fig. 5. The lattice and N$_5$ librational modes are in the low frequency range of the Raman spectra, i.e. from 37.6 to 225.4 cm$^{-1}$. There are six bending modes in the Raman spectra: two twisting modes at 728.4 and 742.6 cm$^{-1}$ and four scissoring modes at 984.2, 1054.8, 1083, and 1101.3 cm$^{-1}$. The most intense peak is the symmetric stretching mode at 1183.4 cm$^{-1}$ while the last mode at 1222 cm$^{-1}$ is an anti-symmetric stretching mode. These results appear to agree well with experimental Raman spectra presented by Sun et al.$^{17}$. Specifically, both structures show symmetric stretching modes, with the mode reported in this study at 1183.4 cm$^{-1}$ and Sun
et al. reporting theirs at 1187 cm$^{-1}$[17]. There are also two bending modes reported in each study that are close in frequency, those at 1054.8 and 1101.3 cm$^{-1}$ in this study and at 1020 and 1122 cm$^{-1}$ in Sun et al.’s work.[17]

Negative phonon frequencies at ambient conditions are also not present in case of AgN$_6$-P$2_12_12$, see Fig. S4 in the supplementary information. The Raman spectra of this crystal are also calculated at 0 GPa to aid in its experimental identification, see Fig. 5. The lattice and N$_5^-$ librational modes are found in the low frequency range of 55.4 to 293.2 cm$^{-1}$. Unlike AgN$_5$-P$2_1/c$, there are no N$_5^-$ bending modes present in AgN$_6$-P$2_12_12$. The most frequent type of mode is anti-symmetric stretching of the N$_5^-$ molecule with a total of 6 modes at 990.7, 1005.1, 1089.7, 1097.6, 1214.3, and 1259.2 cm$^{-1}$. There are two symmetric stretching modes in the Raman spectra. The mode at 1200.2 cm$^{-1}$ is the symmetric stretching of the N$_5^-$ molecule and the mode at 2355.9 cm$^{-1}$ is the symmetric stretching of the N$_2$ dimer. In comparing the Raman spectra of AgN$_5$-P$2_1/c$ and AgN$_6$-P$2_12_12$, it can be seen that the crystals possess very different characteristics. The last modes for both AgN$_5$-P$2_1/c$ and AgN$_6$-P$2_12_12$ are anti-symmetric stretching modes but differ in frequency by about 37 cm$^{-1}$. The most intense peak of both crystals is the symmetric stretching mode found at 1183.4 cm$^{-1}$ for AgN$_5$-P$2_1/c$ and at 1200.2 cm$^{-1}$ for AgN$_6$-P$2_12_12$. AgN$_6$-P$2_12_12$ contains no bending modes compared to the six found in AgN$_5$-P$2_1/c$. Therefore, the correspondence between AgN$_5$-P$2_1/c$ crystal and that synthesized by Sun et al.’s[17] can unambiguously rule out the appearance of AgN$_6$-P$2_12_12$ in experiment.

Conclusions

Using first-principles evolutionary structure prediction calculations, we discovered two novel silver pentazolate compounds: AgN$_5$-P$2_1/c$ and AgN$_6$-P$2_12_12$, which are predicted to be thermodynamically stable at pressures 41.5 Pa and 41.7 GPa, respectively. These structures are proved to be dynamically stable at 0 GPa. In contrast to AgN$_5$ novel pentazolate AgN$_6$
compound contains N$_2$ diatomic molecules in addition to cyclo-N$_5^-$. Synthesis of AgN$_5$-$P2_1/c$ may be possible by compressing mixture of N$_2$ and AgN$_3$ to pressures above 21.42 GPa at which point AgN$_5$-$P2_1/c$ is becoming thermodynamically favorable. Synthesis of AgN$_6$-$P2_12_12$ may be possible at pressures above 25.58 GPa via the same route. The Raman spectra of both AgN$_5$-$P2_1/c$ and AgN$_6$-$P2_12_12$ are presented. We report agreement between calculated Raman spectrum of and experimental data from Sun et al.$^{[17]}$ and is therefore strong evidence that this structure was synthesize in experiment.

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Conflict of Interest Statement

The authors declare there are no competing financial interests.

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