

# Supporting Information

## Pressure-Induced Stability and Polymeric Nitrogen in Alkaline Earth Metal N-Rich Nitrides( $\text{XN}_6$ , X = Ca, Sr and Ba): A First-Principles Study

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**Table S1.** We have summarized the pressure ranges of the stable structures for alkali metals, alkaline earth metals and transition metals nitrides, as follows:

Azide	Pressure range of stable structure		
$\text{LiN}_3$ [1]	$C2/m$ (9-38GPa)	$P6/m$ (38-100GPa)	
$\text{NaN}_3$ [2]	$I4/mcm$ (6.5-58GPa)	$P6/m$ (58-152GPa)	$C2/m$ above 152GPa
$\text{KN}_3$ [3,4]	$C2/m$ (15.7-41.4GPa)	$P6/mmm$ (41.4-298.6GPa)	$C2/m(\text{II})$ above 298.6GPa
$\text{RbN}_3$ [5]	$P-1$ (30-50GPa)	$P6/mmm$ (50-200GPa)	$C2/m$ above 200GPa
$\text{CsN}_3$ [6]	$C2/m$ (6-13GPa)	$P2_1/m$ (13-51GPa)	$P-1$ (51-200GPa)
$\text{MgN}_3$ [7]	$P-1$ (89-156GPa)		
$\text{CaN}_3$ [8]	$Pmma$ (8-38GPa)	$C2/c$ (38 -100GPa)	
$\text{SrN}_3$ [9]	$C2/m$ (60-100GPa)		
$\text{BaN}_3$ [10]	$C2/c$ (99-100GPa)		
$\text{FeN}_3$ [11]	$P2_1/c$ (30-100GPa)		
$\text{ZnN}_3$ [12]	$C2/m$ (14.5-30GPa)		
$\text{AgN}_3$ [13]	$Ibam$ (0-2.7GPa)	$I4/mcm$ (2.7-5GPa)	
$\text{ScN}_3$ [14]	$P1$ (25.7-40.8GPa)		

By comparing the pressure ranges of nitrides for alkali metals, alkaline earth metals and transition metals, we found that the stable structures exist in the medium and low pressure ranges. So this provides powerful help for our theoretical prediction of  $\text{XN}_6$  (X = Ca, Sr, Ba) to search for stable structures and obtain their pressure ranges.

Through the above reports, we predict that there will be stable structures in the  $\text{XN}_6$  ( $\text{X} = \text{Ca}, \text{Sr}, \text{Ba}$ ) system within the above pressure ranges.

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**Transition pressure to decrease for the formation of Polymeric Nitrogen when**

**we move from ionic to covalent azides.**

Among the above mentioned azides, there are ionic azides and covalent azide, we explained the reason for the transition pressure to decrease for the formation of Polymeric Nitrogen when we move from ionic azide to covalent azide. The main differences between the ionic azide compound and the covalent azide compound are the degree of ionization and the structure of the chemical bond. Generally, ionic azides contain azide groups with a symmetric linear structure. Alkali metal and alkaline earth metal (such as Li, K, Na, Rb, Cs, Ca, Sr and Ba) azides are ionic compounds, and their ionic properties are between 70% and 90%. The ionic properties of transition metals Cu, Ag, Hg, Cd and heavy metals Tl, Pb azides are 30% to 50%.[1] In essence,  $\text{AgN}_3$  and  $\text{HgN}_6$  are covalent azides, and  $\text{AgN}_3$  can obtain a stable structure at 3.1 GPa,[1] which formation of Polymeric Nitrogen requires lower pressure than alkali metal and alkaline earth metal azides. Therefore, the pressure that covalent azides for the formation of Polymeric Nitrogen required will be reduced. Secondly, the azides of alkali metals and alkaline earth metals are ionic compounds, and their structural stability is low, and high pressure is required to maintain stability to synthesize the ionic azides. The covalent azides has high structural stability, and the pressure required to maintain its stability is lower. Therefore, the transition pressure for the formation of Polymeric Nitrogen in covalent azides will be reduced.

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**The structure we predict can be used as a potential high energy-density material.**

In this paper, the  $P-1\text{-SrN}_6$  at 22 GPa and  $C2/m\text{-BaN}_6$  at 110 GPa were predicted to be stable under the corresponding high pressure conditions. After theoretical prediction and calculation, we found that the infinite nitrogen chain structure in the  $P-1\text{-SrN}_6$

structure is formed by polymerization when the *Fddd*-SrN<sub>6</sub> structure is under pressure of 22 GPa. Besides, the six-membered annular network structure in the *C2/m*-BaN<sub>6</sub> structure is formed by polymerization when the *Fmmm*-BaN<sub>6</sub> structure is under pressure of 110 GPa. The bonding manner of nitrogen atoms for *P*-1-SrN<sub>6</sub> under high pressure is nitrogen-nitrogen single bond and double bonds, and the polymeric nitrogen form is an infinite nitrogen chain structure. In the previously reported article, through the prediction of high pressure theory found, *P*-1-MgN<sub>4</sub> have this structure, and the energy density is 2.08 kJ/g,[1] for *P*2<sub>1</sub>/*c*-FeN<sub>3</sub> and *P*-1-FeN<sub>4</sub>, the energy density is 1.37-2.02 kJ/g,[6] for *P*1-ScN<sub>3</sub>, the energy density is 2.4 kJ/g,[5] for *C*2/*c*-GaN<sub>6</sub>, the energy density is 5.71 kJ/g,[3] and the calculated *P*4/*mbm*-CaN<sub>4</sub> can also be used as an energy carrier.[7] The polymeric form of nitrogen atoms for *C*2/*m*-BaN<sub>6</sub> in high pressure is six-membered annular network structure, and the bonding manner of nitrogen atoms is nitrogen-nitrogen single bond. In the previously reported article, through the prediction of high pressure theory found, *P*-1(I)-MgN<sub>3</sub> have this structure, the energy density is 2.87 kJ/g,[1] for *C*2/*m*-SrN<sub>3</sub> energy density is 1.08 kJ/g,[8] for *P*2<sub>1</sub>-LiN<sub>5</sub>, the energy density is 2.72 kJ/g,[2] and for *C*2/*m*-ScN<sub>5</sub> energy density is 4.23 kJ/g,[5] for *P*-1-CaN<sub>10</sub> and *Ibam*-BaN<sub>10</sub>, the energy densities are 2.35 kJ/g and 1.33 kJ/g,[9] *P*1-Zn(N<sub>5</sub>)<sub>2</sub> energy density is 6.5 kJ/g.[4] As can be seen from the previous references, the metal nitrogen-rich compound having the above structure can be used as a potentially high energy-density material. Therefore, we predicted that the high pressure *P*-1-SrN<sub>6</sub> and *C*2/*m*-BaN<sub>6</sub> structure may also serve as potential high energy-density materials.

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