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# First principles prediction of the ground state crystal structures of antiperovskite compounds $A_3PN$ ( $A = \text{Be, Mg, Ca, Sr, Ba}$ and $\text{Zn}$ )

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## Abstract

In solids, crystal structure describes the orderly arrangement of constituent atoms. Knowing the crystal structure is absolutely mandatory for any further theoretical investigation of a material. Predicting the crystal structure of an unknown material from first principles, even before it is synthesized is still one of the most challenging and interesting issue in materials research and development. Here, we present the results from ab-initio calculations based on density functional theory on a series of ternary antiperovskite compounds:  $\text{Be}_3\text{PN}$ ,  $\text{Mg}_3\text{PN}$ ,  $\text{Ca}_3\text{PN}$ ,  $\text{Sr}_3\text{PN}$ ,  $\text{Ba}_3\text{PN}$  and  $\text{Zn}_3\text{PN}$ . We have predicted the equilibrium crystal structures of these compounds using structural optimization with stress and force minimization by considering the potential structures of 32 space groups in the calculation. The calculations were performed using the Vienna ab-initio Simulation Package (VASP) within the Generalized Gradient Approximation (GGA). We have predicted that the ground state of all the compounds have orthorhombic structure with a space group of  $P2_1ma$ , except  $\text{Be}_3\text{PN}$  which stabilizes in a space group of  $Pbmm$ . We have done a systematic study on the structural characteristics and the electronic properties to explain the bonding nature and stability in these compounds. Our results represent a step toward a more complete understanding of the structural and electronic properties of the mentioned compounds. This is the first quantitative theoretical prediction of structural and electronic properties of  $\text{Be}_3\text{PN}$ ,  $\text{Sr}_3\text{PN}$ ,  $\text{Ba}_3\text{PN}$  and  $\text{Zn}_3\text{PN}$  compounds that require experimental confirmation.

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## 1. Introduction

Crystal structure is one of the most important information about a system since the properties of a material normally depend very sensitively on its structure. It is therefore crucial to determine the correct structures of materials [1]. The prediction of crystal structures based only on chemical composition from completely first principles approach has been always one of the major issues in crystallography as well as in computational materials science and solid state theory [2–8]. But now, the increasing availability of computational resources and developments in the methods and robustness of the codes have led to the ability to perform the numerous Density Functional Theory (DFT) calculations. In addition, more accurate first-principles minimization techniques have made the structure prediction a very fast growing field of research. In this article, we have predicted the ground state crystal structures of six ternary antiperovskite compounds  $A_3\text{PN}$ , ( $A = \text{Be, Mg, Ca, Sr, Ba}$  and  $\text{Zn}$ ). Among these six compounds,  $\text{Ca}_3\text{PN}$  had been already synthesized experimentally, and the electrical conductivity measurements indicated that this compound is an insulator [9]. There are some more theoretical studies on this compound [10–12]. Eventhough the compound  $\text{Mg}_3\text{PN}$  is not synthesized experimentally yet, there is one reported study on the structural and electronic properties of this compound by means of the state-of-the-art *ab initio* self consistent full potential linearized augmented plane wave plus local orbitals method [13]. To the best of our knowledge, there are no experimental or theoretical works exploring the structural and other related physical properties of the remaining four compounds:  $\text{Ba}_3\text{PN}$ ,  $\text{Sr}_3\text{PN}$ ,  $\text{Be}_3\text{PN}$  and  $\text{Zn}_3\text{PN}$ . The aim of this paper is to predict the ground state structures of the considered ternary antiperovskite compounds. In order to take full advantage of the properties of these compounds and the predictive capability of this theoretical investigation, further experimental studies are also necessary.

## 2. Structure Prediction Methodology and Computational details

All physical properties are related to the total energy of a system. For instance, the equilibrium lattice constant of a crystal is the lattice constant that corresponds to the minimum the total energy. Once the total energy is obtained accurately, any physical property related to the total energy can be determined. For the study of structural phase stability, we have considered thirty two potential structure types:  $\text{CaCO}_3(\text{Ama}2)$ ;  $\text{BaTiO}_3(\text{Amm}2)$ ;  $\text{ZnSiO}_3(\text{C12C1})$ ;  $\text{PbZrO}_3(\text{Cm}2m)$ ;  $\text{CaSnO}_3(\text{Fm-}3c)$ ;  $\text{KSbO}_3(\text{Fd}3m)$ ;  $\text{SrZrO}_3(\text{I4/mcm})$ ;  $\text{CdGeO}_3(\text{B11b})$ ;  $\text{NaNbO}_3(\text{P2}_1ma)$ ;  $\text{SrZrO}_3(\text{Bmmb})$ ;  $\text{BaPbO}_3(\text{I12/m1})$ ;  $\text{BaPbO}_3(\text{Ibmm})$ ;  $\text{LaMnO}_3(\text{P121/a})$ ;  $\text{PbSeO}_3(\text{P121/m1})$ ;  $\text{NaClO}_3(\text{P123})$ ;  $\text{BaSiO}_3(\text{P212121})$ ;  $\text{NaTaO}_3(\text{P4/mbm})$ ;  $\text{BaTiO}_3(\text{P4/mmm})$ ;  $\text{LiIO}_3(\text{P63})$ ;  $\text{BaNiO}_3(\text{P63/mmc})$ ;  $\text{CuGeO}_3(\text{Pbmm})$ ;  $\text{YFeO}_3(\text{Pbn}21)$ ;  $\text{LaTiO}_3(\text{Pbnm})$ ;  $\text{CaZrO}_3(\text{Pcmm})$ ;  $\text{SrTiO}_3(\text{Pm-}3m)$ ;  $\text{NaNbO}_3(\text{Pmmm})$ ;  $\text{GdVO}_3(\text{Pmnb})$ ;  $\text{NgSeO}_3(\text{Pnma})$ ;  $\text{BiFeO}_3(\text{R}3c)$ ;  $\text{LaCuO}_3(\text{R-}3c)$ ;  $\text{BaTbO}_3(\text{R-}3cR)$ ; and  $\text{BaRuO}_3(\text{R-}3m)$ .

The DFT calculations are performed with the Vienna *ab initio* simulation package (VASP) code [14,15] implementing the projector-augmented-wave (PAW) [16] method, with the generalized gradient approximation (GGA) for the exchange correlation energy, in the form known as Perdew-Burke Ernzerhof (PBE) [17]. All the considered 32 structures were fully relaxed using force as well as stress minimization. A plane wave cut off energy of 520 eV and the total energies were calculated over a Monkhorst-Pack mesh of k-points [18] in the Brillouin zone with sufficient k-point density. The total energy change was set to  $1 \times 10^{-6}$  eVatom<sup>-1</sup> and the maximum ionic Hellmann-Feynman force within 0.01 eVÅ<sup>-1</sup>. The input parameters were sufficient in leading to well converged total energy and geometrical configurations. We have plotted the energy volume curve for the compounds to find the

energetically lowest structural configurations for the compounds and the calculated volume vs total energy curve was fitted to Murnaghan equation of states.

### 3. Results and discussion

#### 3.1. Structural properties and stability

From the optimization, we have predicted that the ground state of all the compounds have orthorhombic structure with a space group of  $P2_1ma$  (space group 26), except  $\text{Be}_3\text{PN}$  which stabilizes in a space group of  $Pbmm$  (space group 51). The unit cells of orthorhombic phases ( $P2_1ma$  and  $Pbmm$ ) of the compounds are visualized in Fig 1(a) and (b) respectively. In all the orthorhombic phases, it is clear that nitrogen is octahedrally coordinated with the corresponding  $A$  atoms. The optimized structural parameters and formation energies are depicted in Table 1. In order to determine the stability of the predicted compounds we have calculated the formation energy [19] [20–23]. The negative values of formation energy confirm the thermodynamic stability of all the structures predicted here.

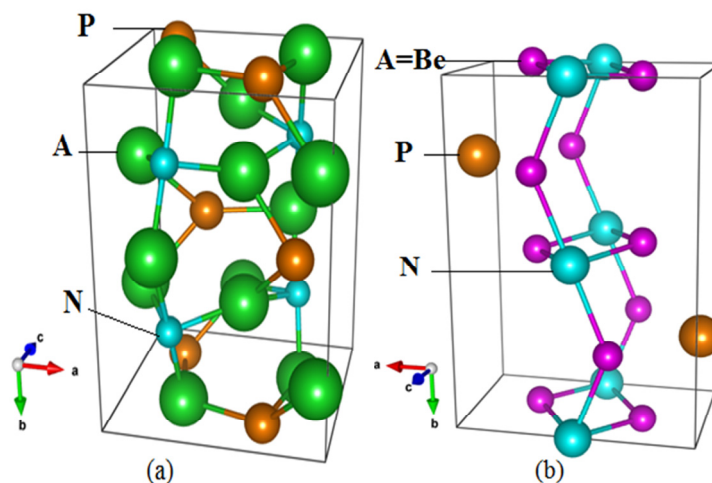


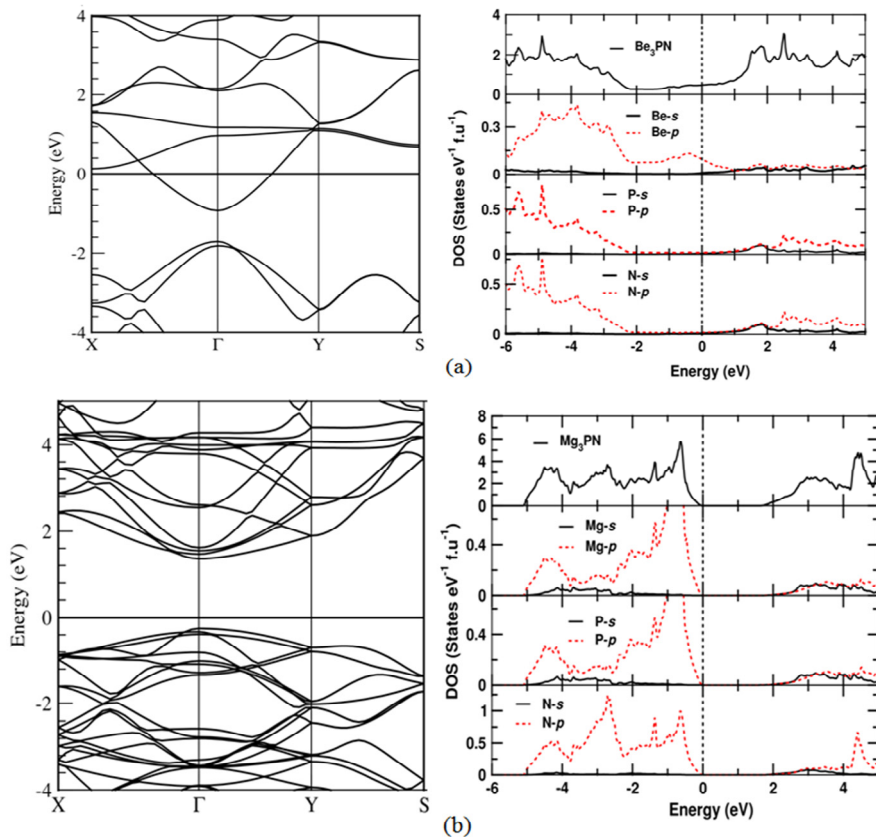
Fig 1. The crystal structures of  $A_3\text{PN}$  with orthorhombic phase (a) in  $P2_1ma$  (b) in  $Pbmm$

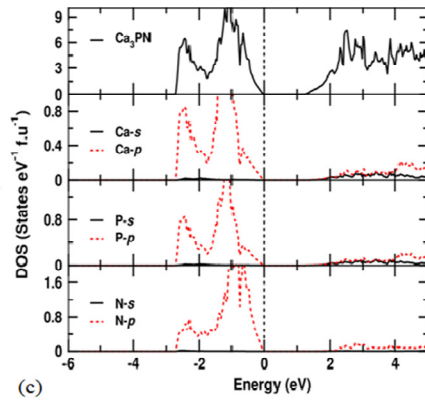
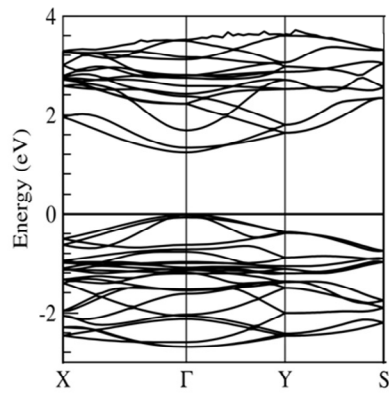
Table 1 Optimized Structural Parameters and Formation Energies of compounds

Compound	Lattice Parameters ( $\text{\AA}$ )			Volume ( $\text{\AA}^3$ )	Formation Energy (KJ/mol)
	a	b	c		
$\text{Be}_3\text{PN}$	4.6561	6.8102	2.9602	46.11	-107.75
$\text{Mg}_3\text{PN}$	5.9214	8.3693	5.9324	72.82	-302.55
$\text{Ca}_3\text{PN}$	6.7192	9.4213	6.6346	101.05	-418.29
$\text{Sr}_3\text{PN}$	7.2870	10.0875	7.0490	130.99	-1270.19
$\text{Ba}_3\text{PN}$	7.8377	10.7371	7.4021	158.78	-715.69
$\text{Zn}_3\text{PN}$	6.4054	7.9235	6.3636	105.34	-400.46

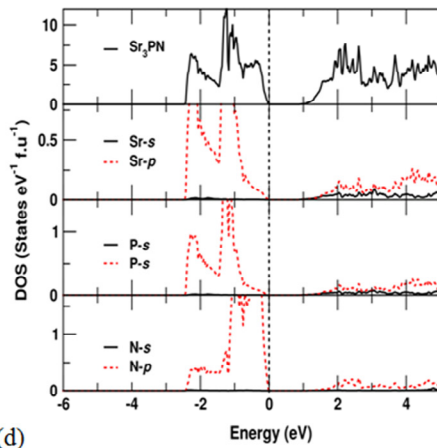
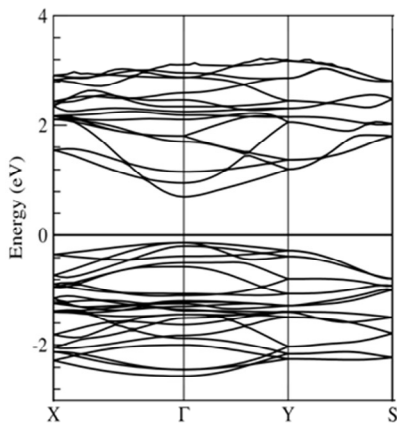
### 3.2. Electronic properties

The calculated band structures and the corresponding density of states for  $\text{Be}_3\text{PN}$ ,  $\text{Mg}_3\text{PN}$ ,  $\text{Ca}_3\text{PN}$ ,  $\text{Sr}_3\text{PN}$ ,  $\text{Ba}_3\text{PN}$  and  $\text{Zn}_3\text{PN}$  at the equilibrium lattice parameter, along the high symmetry directions in the Brillouin zone are shown in Fig 2(a), (b), (c), (d), (e) and (f) respectively. From the band structure analysis, it is clear that for the compounds  $\text{Ba}_3\text{PN}$ ,  $\text{Sr}_3\text{PN}$ ,  $\text{Ca}_3\text{PN}$  and  $\text{Mg}_3\text{PN}$ , the valence band maximum (VBM) and conduction band minimum (CBM) occur at gamma point and so these compounds are direct band gap semiconductors. The calculated values of the band gap ( $\Gamma$ -  $\Gamma$ ) for  $\text{Ba}_3\text{PN}$ ,  $\text{Sr}_3\text{PN}$ ,  $\text{Ca}_3\text{PN}$  and  $\text{Mg}_3\text{PN}$ , are 0.34, 0.81, 1.23 and 1.62 eV respectively. It is well known that the GGA calculations underestimate the fundamental gap of semiconductors; so these compounds may have larger gaps than the predicted values. From above, it is noticeable that the energy band gap of these four compounds decreases as increase in the atomic number of the compounds, or in other terms the band gap value decreases with the decrease of electro negativity of the cations. Among these four direct band gap compounds, the bands of  $\text{Mg}_3\text{PN}$  and  $\text{Ca}_3\text{PN}$  are well dispersed and they have band gap value near to the optimum band gap value, so these compounds can be used in optoelectronic applications. But for  $\text{Zn}_3\text{PN}$ , the VBM and CBM occur at different symmetry points leading this material as an indirect band gap semiconductor. It can be noted that for  $\text{Be}_3\text{PN}$ , the conduction band is crossing the Fermi level and more bands from the conduction region are coming down with increasing energy cut-off and there is no band gap at the Fermi level. This finding indicates the metallicity of this material.

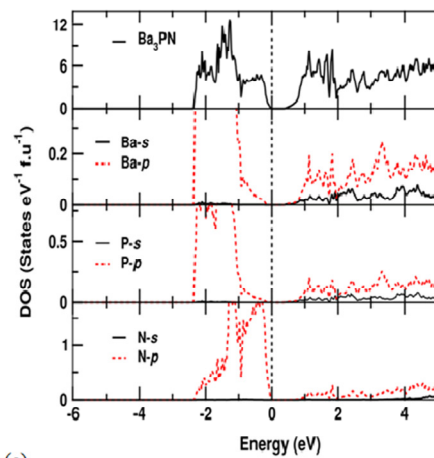
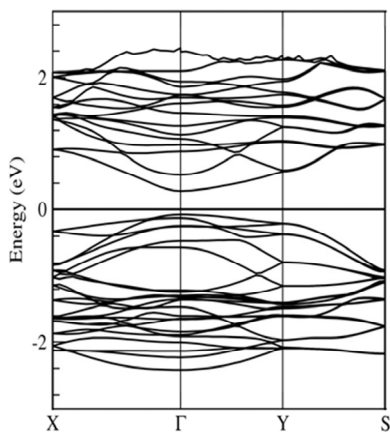




(c)



(d)



(e)

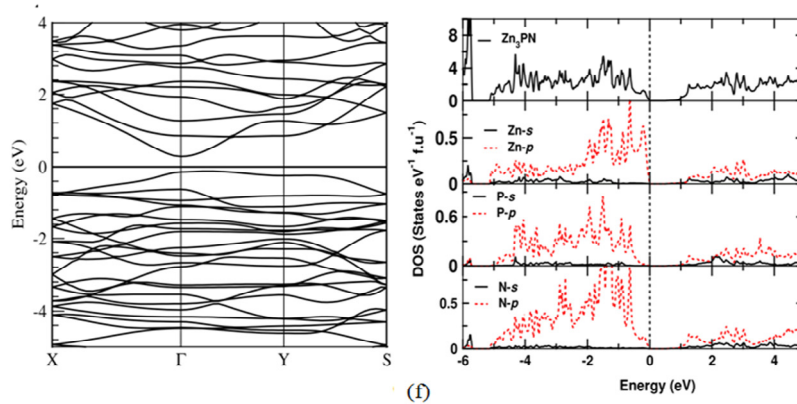


Fig. 2 (a), (b), (c), (d), (e) and (f) correspond to the band structures and the density of states of the compounds: Be<sub>3</sub>PN, Mg<sub>3</sub>PN, Ca<sub>3</sub>PN, Sr<sub>3</sub>PN, Ba<sub>3</sub>PN and Zn<sub>3</sub>PN respectively.

In order to illustrate the main contribution of orbitals in the band structures and the chemical bonding between atoms, we presented total and partial density of states for the compounds. The plotted energy range is from -6 to 5 eV and the Fermi level is set to zero. For the compounds in  $P2_1ma$ : Ba<sub>3</sub>PN, Sr<sub>3</sub>PN, Ca<sub>3</sub>PN, Mg<sub>3</sub>PN and Zn<sub>3</sub>PN, the DOS spectra and the relative heights of their peaks are rather similar, indicating similarity in chemical bonding. For these compounds, the upper valence bands mainly consist of *p* orbitals of *A*-site and nitrogen atoms, also *s* and *p* orbitals of phosphorous. It is evident that in the energy range from -2.3 eV upto Fermi level a covalent interaction occurs between the constituent elements due to the fact that the states are degenerate. N-*p* and P-*p* states are hybridized. Also due to the difference in the electro negativity between the elements, some ionic character can be expected. So the bonding character may be described as a mixture of covalent-ionic for the above mentioned five compounds. For Be<sub>3</sub>PN, it is clear from the partial density of states that the metallic nature is originated from the Berlium *p* orbitals with significant covalent character.

#### 4. Conclusion

In summary, we have predicted the crystal structures of six antiperovskite compounds  $A_3PN$  ( $A = \text{Be, Mg, Ca, Sr, Ba and Zn}$ ) using first principle calculations by considering potential structures of 32 space groups in to the calculation. From the elaborative prediction study, we have studied that all the six compounds are in orthorhombic structure and five of them Mg<sub>3</sub>PN, Ca<sub>3</sub>PN, Sr<sub>3</sub>PN, Ba<sub>3</sub>PN and Zn<sub>3</sub>PN stabilize in the space group of  $P2_1ma$ , but Be<sub>3</sub>PN crystallizes in  $Pbmm$  space group. The study of formation energies reveals their stable nature. We have also calculated the band structure, density of states in order to know the ground state electronic properties of the compounds. The electronic structure calculation show that four compounds: Mg<sub>3</sub>PN, Ca<sub>3</sub>PN, Sr<sub>3</sub>PN and Ba<sub>3</sub>PN are direct band gap ( $\Gamma - \Gamma$ ) semiconductors, Zn<sub>3</sub>PN is an indirect band gap material whereas Be<sub>3</sub>PN has metallic nature. The chemical bonding between the constituent elements is mainly covalent, but due to the difference in the electro negativity between the elements, ionic bonding also can be expected. Among the studied six compounds, the direct band gap semiconductors Mg<sub>3</sub>PN and Ca<sub>3</sub>PN can be used as better candidates in optoelectronic applications due to the presence of their dispersed bands and optimum band gap. It is our ambition that these calculations will inspire further experimental research on these predicted compounds.

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