Ab initio Study of Electronic, Mechanical and Structural Properties of Cubic Antiperovskite material Mn_3XN (X=Al, Ga, Zn)

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ABSTRACT

We report *ab initio study* of the electronic, mechanical and structural properties for the negative thermal expansion (NTE) application of antiperovskites manganese nitrides materials Mn_3XN (X=Al, Ga, Zn). Using first principle calculations based on generalized gradient approximation (GGA), the electronic, structural, and mechanical properties of the Mn_3XN (X = Al, Ga, Zn) phases were investigated. The optimized lattice parameters give the first reference to the upcoming theoretical and experimental studies. THERMO_PW as a post-processing code was used for the computation of elastic constants that were used to derive bulk modulus (B), shear modulus (G), Young's modulus (E), Poisson's ratio (õ), and hardness. The calculated elastic constants are in excellent agreement with the available data. Moreover, obtained elastic constants revealed that both the Mn_3ZnN and Mn_3GaN phases are brittle. The band structure and density of states analysis showed that these phases are electrical conductors, having strong directional bonding existing near the Fermi level between Mn -N atoms due to Mn-d and N-p hybridization. The Mn_3GaN compound has the highest Debye temperature (452.8K), while Mn_3ZnN has Debye temperature of (283.4K) indicating that they are thermodynamically and dynamically stable and can be synthesized experimentally. Mn_3AlN compound has Debye temperature (0.000K) indicating the system is unstable for compressional deformation. The stoichiometric Mn_3XN (X = Al, Ga, Zn) compounds are very similar in both structural and elastic properties hence their metallic behavior that exhibit both ionic and covalent characters.

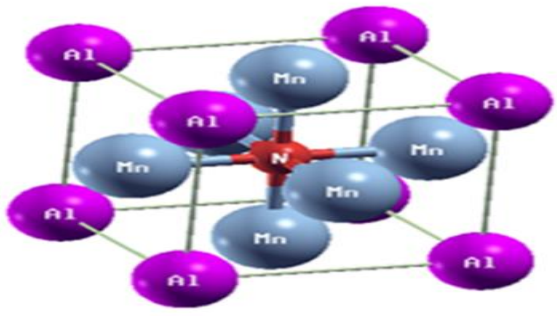
***Keywords**:* Antiperovskite, Band Structure, Density of States

I. INTRODUCTION

Antiperovskites are also known as inverse Perovskites. Their compounds consist of two types of anion and cation positions that are switched. The Mn-rich ternary nitrides Mn_3XN (X = Al, Ga, Zn, etc.) antiperovskite have captured a lot of interests with researchers having increased interest since the discovery of superconductivity (at 8K) for cubic antiperovskite MgCNi compound (He *et al.*, 2001). This discovery has strongly motivated the study of antiperovskite series. The studies of the family of manganese rich Carbides and Nitrides have been investigated theoretically and experimentally (Schaak *et al.*, 2004). In recent years, the investigations on some new antiperovskite type nitrides have gained wide interest in some biosensor applications in bioelectronics industry (Tong, P. *et al.*, 2006). Despite the fact that there are a number of studies related to their properties for some cubic antiperovskite type Mn-rich ternary nitrides, in particular, the mechanical properties of Mn3XN -type compounds with X= Ga, In, Zn, have not been studied computationally (Uehara *et al.*, 2006). The structural and mechanical properties of the antiperovskite $XNNi_3$ (X=Zn, Mg, Al) with pressure effect are studied by Aleksandrov *et al.* *(*2004) using CAmbridge Serial Total Energy Package (CASTEP) code. GaCMn3 is a widely studied antiperovskites material and is reported to be a metallic material with antiferromagnetic (AFM) behavior at ambient temperature. Studies especially on lattice dynamical properties, mechanical and electronic properties of Mn3XN (X= Zn and Al) have not been sufficiently predicted computationally so as to achieve the results that agrees well with the experimental data available hence prompting our study using Quantum espresso code. This study substitutes carbon (C) with Nitrogen (N) and analyses the effects of electronic and mechanical properties and compares with the existing experimental work.

The magnetic Mn atoms are located at the cubic face centers and form a tetrahedral cluster with N atoms at the body center. The Al atoms are at the cubic corners. Optimized lattice parameters and electronic band structures are reported by using ultra soft pseudo potential (Johannes *et al.*, 2004). In addition, anisotropic independent second order elastic constants (Cij) were computed using thermo_pw code interfaced within quantum espresso code that enabled us to find mechanical parameters of Mn3XN (X= Zn, Ga and Al). Fig 1 shows the body centered cubic structure of Mn_3XN (X = Zn, Ga and Al).

Figure 1:
Shows A Simple Cubic Structre Of Mn_3XN (X= Zn, Ga and Al) Compound Where Aluminum Element Can Be Replaced by Ga and Zn



II. METHODOLOGY

All the calculations of these compounds are performed in the framework of the density functional theory (DFT) (Hohenberg *et al*., 1964), where the projected augmented wave (PAW) method is implemented in the quantum espresso code (Giannozzi *et al.,* 2009*)*. The electronic exchange correlation energy has been taken into account under the generalized gradient approximation parameterized by Perdew, Burke & Ernzerhof [GGA-PBE] (Perdew *et al*., 1996) used for exchange and correlation. The Kohn-Sham orbitals are expanded using the plane wave energy cut off of 400 eV which was found to be sufficient to achieve a total-energy convergence. In structural optimization, we used the procedure in Jiang, (Jiang *et al*., 2003) and Schmalz's work (Schmalzl *et al*., 2007). For accurate Brillouin zone integration, Monkhorst-Pack K-point mesh with a grid size of 13x13x13 have been employed in this study to ensure well convergence of the computed structures and energies, structural optimization and total energy calculation. The elastic properties are exploited to estimate with stress-strain method (Mayer *et al.,* 2003). Bulk modulus *B*, Young's modulus *E* and shear modulus *G* are directly calculated within these elastic constants by the Voigt–Reuss–Hill method (Hill, 1952).

III. RESULTS

Structural and Electronic Properties

The unit cell of Mn3AlN compound is shown in Figure 1. The crystal structures of Mn_3GaN and Mn_3ZnN compounds are the same with Mn3AlN compound as shown. In order to understand the electronic structure of manganese nitrides antiperovskites Mn3XN (X = Ga, Al and Zn), the Wyckoff positions of atoms are located as follow: Al (0, 0, 0); N (0.5, 0.5, 0.5); and Mn (0, 0.5, 0.5). The plot for energy against lattice parameter for Aluminum manganese nitride antiperovskite is shown in Fig 2. The minimum point of lattice parameters was obtained for the Mn3XN (X=Al, Zn and Ga) compounds as 4.207 Å, 3.883 Å and 3.902 Å, respectively. These values compare well with other studies available as alluded by (Ennassiri *et al.,* 2018).

Table 1:

The Table Below Shows Lattice Parameter, A, Calculated Using Quantum Espresso as Compared with Other Existing Work in Experimental Data.

Method	Mn_3AlN	Mn_3GaN	Mn_3ZnN	Reference
Quantum espresso(GGA)	4.207 Å	4.191 Å	3.904 Å	Present work
Experimental	4.243 Å	3.883 Å	3.902 Å	
Reference	Kavitha *et al.* (2015)	Han *et al.* (2022)	Sun *et al.* (2013)	

Figure 2:
Shows A Curve of Energy (Ev) Against The Lattice Parameter A, In Atomic Units (a.u) For Mn3AlN. The Same Process Was Done for The Three Compounds Until the Convergence Was Arrived at The Minimum Point.

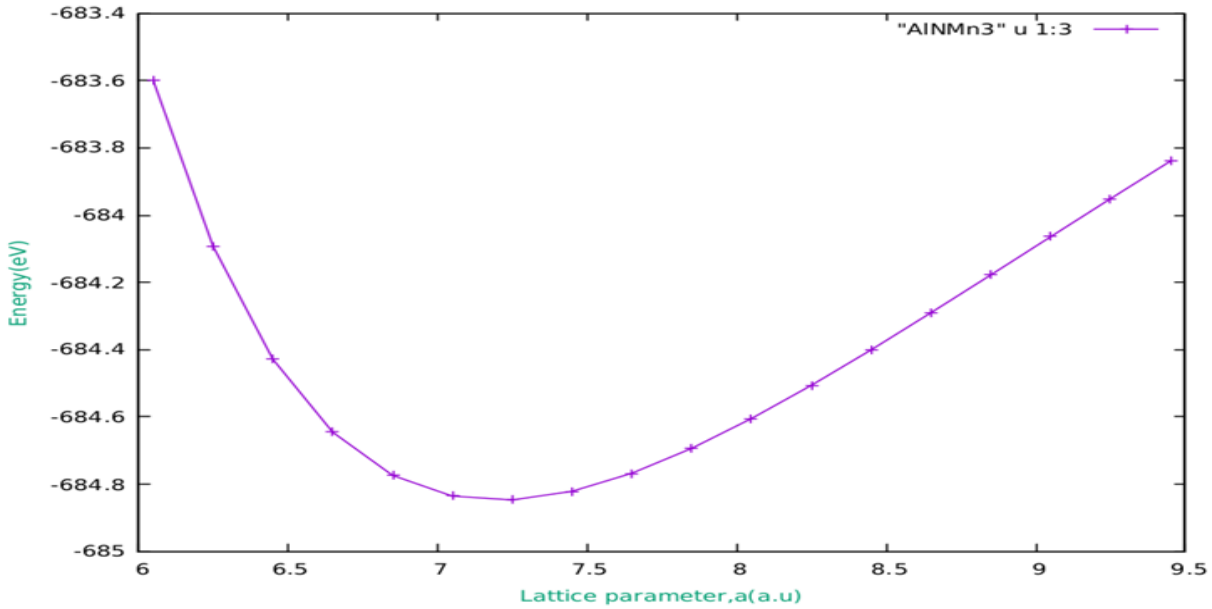


Figure 3a:
Density of States Against Energy for $AlNMn_3$ Compound

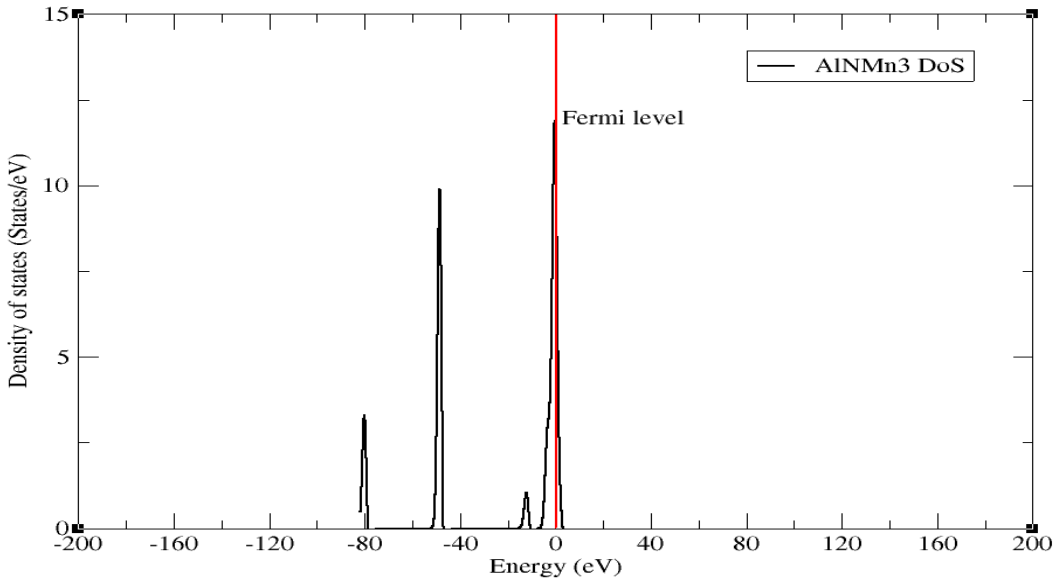


Figure 3(b):
Density of States Against Energy for $GaNMn_3$ Compound.

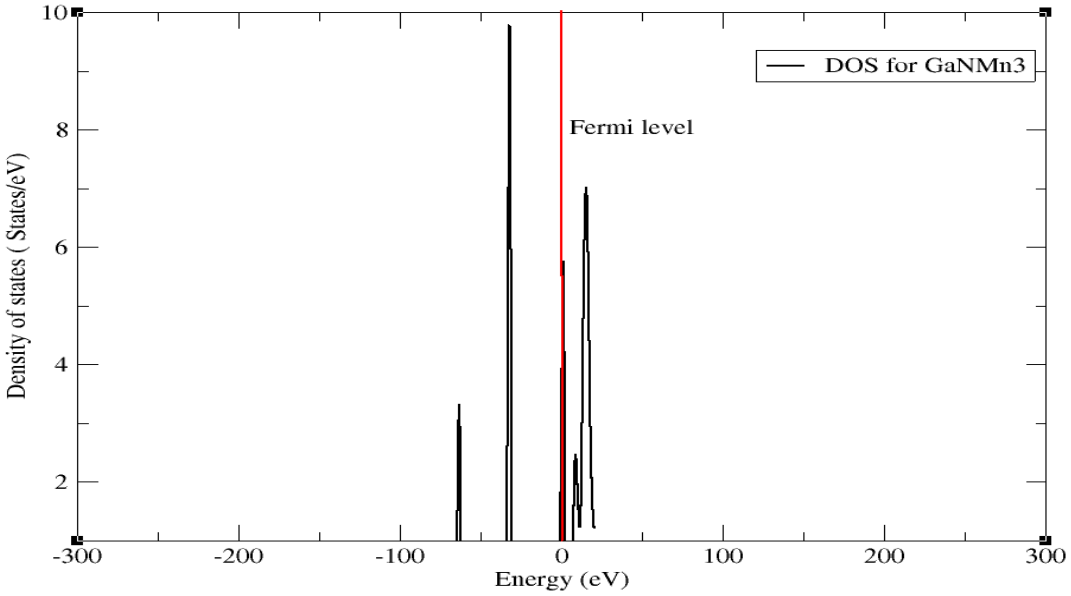
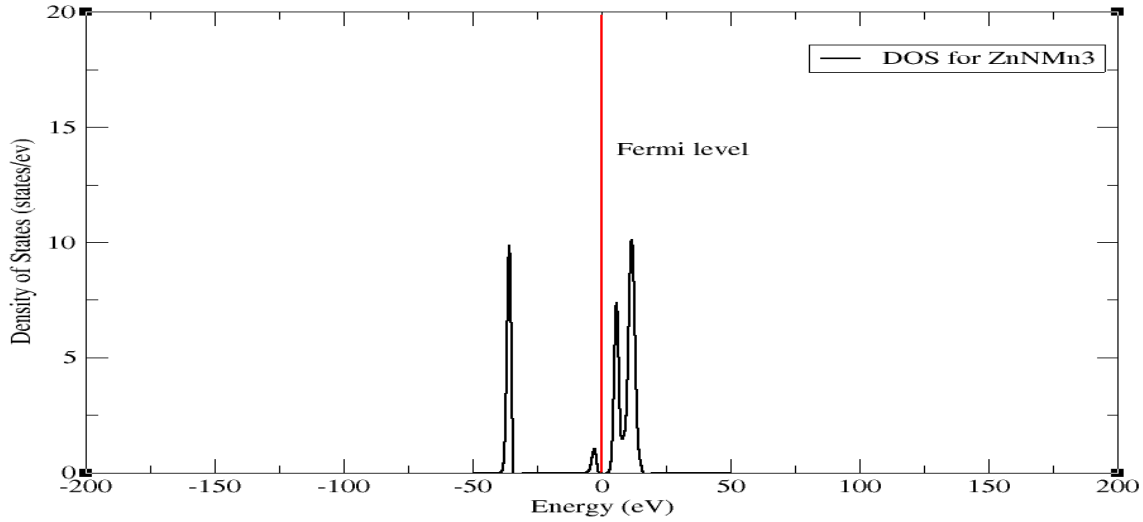


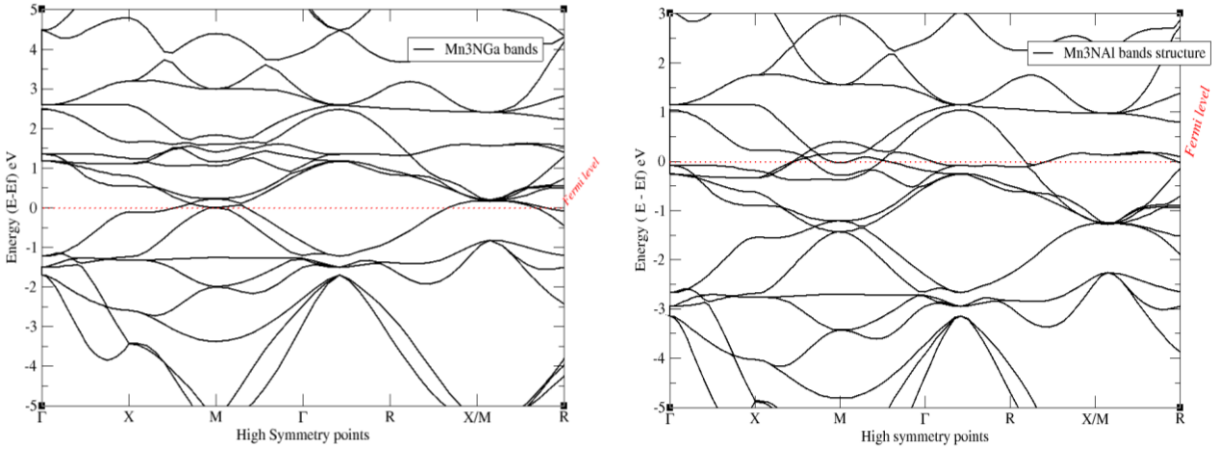
Figure 3(c):
Density of States Against Energy for $ZnNMn_3$ Compound.



All of the three total densities of states have nearly similar features. The Fermi level lies at the energy of 7.83 eV for Mn_3AlN. All these compounds exhibit metallic character. It is clearly seen that Mn-d state and N-p state contribute at Fermi level, and this emerges to be a dp-hybridization between metal-d state and N-p states. This is shown by the band structure in Fig 4 below. Band structure for all compounds resemble each other. The red line indicates Fermi energy level.
The GGA electron energy band structure of the antiperovskite Mn_3AlN, Mn_3ZnN and Mn_3GaN at zero pressure along principal symmetry points in the Brillouin zone is shown in the figures below.

Fig 4:

Shows the Band Structure of (a) Mn_3AlN and (b) Mn_3GaN Compounds. Band Structure Along the Symmetry Lines of the Brillouin Zone at the Equilibrium Lattice Constant. The Position of the Fermi Level is Shown by the Red Dotted Horizontal Line. The Bands for Mn_3ZnN Compound was Exactly Resembling that of Mn_3AlN Compound Shown Below



(a) (b)

Mechanical Properties

The mechanical stability is analyzed by computing the elastic constants. The elastic constants Cij are calculated within the total-energy method, where the unit cell is subjected to a number of finite-size strains along several strain directions. Cubic lattices have three independent elastic constants, namely, C_{11}, C_{12} and C_{44}. The bulk and shear moduli are calculated using the following relations.

$$B = \frac{1}{3}(C_{11} + 2C_{12}) \quad \ldots (1)$$

$$G = \frac{1}{2}(C_{11} - C_{12}) \quad \ldots (2)$$

Shear modulus (G) can also be calculated by use of the following formula

$$G = \frac{(G_V + G_R)}{2} \quad \ldots (3)$$

$G_V = Voight's\ shear\ modulus (related\ with\ the\ upper\ bound\ of\ G\ values)$

$G_R = Reuss's\ shear\ modulus\ (related\ with\ the\ lower\ bound\ of\ G\ values)$

$$G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5}, G_B = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})} \quad \ldots (4)$$

The Zener anisotropy factor (A), Poisson ratio (õ), and Young's modulus (E) are important parameters to see all image of elastic properties. These parameters are given by eqns. (5 – 7);

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \quad \ldots (5)$$

$$\tilde{o} = \frac{3B - 2G}{2(3B + G)} \quad \ldots (6)$$

$$E = \frac{9BG}{3B + G} \quad \ldots (7)$$

In bulk materials, to see the elastic anisotropy behavior, the Zener anisotropy factor is calculated to determine the degree of anisotropy. For an isotropic crystal A is equal to 1, while any value smaller or larger than 1 indicates anisotropy. The magnitude of the deviation from 1 is a measure of the degree of elastic anisotropy possessed by the crystal. The three manganese nitrides are entirely anisotropic since they exhibit greater deviation than 1.

Using the calculated Bulk Modulus B, shear modulus G, and Young's modulus E, the Debye temperature Θ_D can be calculated using the formula below.

$$\Theta_D = \frac{h}{k_B}\left[\frac{3n}{4\pi V_a}\right]^{1/3} V_M \quad \ldots (8)$$

Where V_m is the average sound velocity, $\hbar$ is Plank's constant, k_B is Boltzmann's constant and Va is the atomic volume and n is the number of atoms per formula unit.

The obtained elastic stiffness constants are given in Table 2. For a stable cubic structure, the independent elastic constants should satisfy the well-known Born Huang criterion, given by:

$$C44 > 0,\ C11 > |C12|,\ C11 + 2\ C12 > 0.$$

Table 2:

Shows Calculated Elastic Parameters of Mn_3XN (X = Al, Ga, Zn) Structure C_{11}, C_{12} and C_{44} in GPa and Zener Anisotropy Factor (A).

Material	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	Lattice parameter, a,(Å)	Zener anisotropy A	Debye temperature(Θ_D) *K*
Mn_3AlN	-8213.600	5808.743	321.806	4.207	-0.046	0.000
Mn_3GaN	225.413	58.824	59.585	4.191	0.715	452.800
Mn_3ZnN	40.139	5.086	34.391	3.904	1.962	283.400

Using ratio of isotropic shear modulus and bulk modulus, elastic manners of materials are estimated. Ratios of G/B is called Pugh ratio of Mn3XN (X=Al, Zn and Ga) compounds and are given in Table 3.

Table 3:

Shows The Calculated Results of Bulk Modulus, Young Modulus, Shear Modulus in Gpa Respectively Under Voigt, Reuss and Hill Averaging Scheme, Poisson's Ratio (Õ) and Pugh Ratio (G_H/B_H) are also Indicated

Material	B_V	B_R	B_H	G_V	G_R	G_H	E_H	Õ	G_H/B_H
Mn3AlN	-661.03	-661.03	-661.03	-28.7887	65.2819	18.246	58.691	0.6082	-0.0276
Mn_3GaN	114.354	114.354	114.354	69.06881	67.2409	68.155	170.573	0.2514	0.5960
Mn_3ZnN	16.7703	16.7703	16.7703	27.64525	24.8332	26.239	51.7021	-0.0148	1.5708

IV. DISCUSSION

Firstly, the equilibrium lattice constants, bulk modulus and its pressure derivative have been obtained by minimizing the total crystal energy calculated for different values of lattice constants using the Birch-Murnaghan equation of states, (Birch, 1978), and the calculations results are given in Table 1 above for cubic antiperovskite structure (space group *Pm3m* (#221)) of Mn3XN (X=Al, Zn and Ga). The present lattice constants were optimized by varying the lattice parameter slightly and calculating corresponding energy. The convergence was reached after several calculations of energies.

The electronic properties of these materials showed that they are all metallic since there are no gaps between the conduction band and the valence band. The band structure and density of states analysis showed that these phases are electrical conductors, having strong directional bonding existing near the Fermi level between Mn -N atoms due to Mn-d and N-p hybridization.
The Shear and Young's modulus are calculated with their Voigt and Reuss values and Poisson ratios with maximum and minimum values at zero pressure by Quantum espresso for anisotropic behaviors of three manganese nitrides.

From the literature it is well-known that, if the rate of Poisson is less than 0.25, the material shows covalent bond character, otherwise it is bigger than or equal to 0.25 it shows ionic bond character (Kavitha *et al.,* 2015). From the results obtained shows Mn_3AlN and Mn_3GaN are ionic bond characters while Mn_3ZnN portrays a covalent bond character. Mechanical properties of materials are important in order to study binding characteristics between the adjacent atomic plane, specific heat, Debye temperature, thermal expansion and many other properties. The knowledge of elastic constants Cij is useful and valuable to obtain information about the anisotropic character of the bonding, the structural stability and stiffness of materials.

The computed elastic constants indicate that Mn_3XN (X = Ga, and Zn) materials are mechanically stable whereas Mn_3AlN is unstable for compressional deformations. Provided that $G/B<0.5$ the material exhibits a ductile behavior while, the material with $G/B>0.5$ exhibits a brittle behavior, (Bannikov *et al.,* 2007). These findings show that Mn_3GaN and Mn_3ZnN exhibits brittleness in which Mn_3GaN behavior is near brittle/ductile border-like whereas Mn_3AlN is ductile since the ratio is greatly less than 0.5.

Conclusion

In this work, the structural, electronic and mechanical properties of manganese nitrides are investigated. The calculated equilibrium lattice constant is in good agreement with the previous experimental work. Results analysis shows that the computed lattice constants for Mn_3AlN, Mn_3ZnN and Mn_3GaN has percentage errors of -0.8484%, +1.079% and +0.051% respectively as compared with the existing experimental work. In elastic calculations, isotropic shear modulus, Poisson's ratios and Young's modulus were estimated using Voigt and Reuss approximations. From our first-principles calculations, the stoichiometric Mn_3XN (X = Al, Ga, Zn) compounds are very similar in both structural and elastic properties. The three ternary nitrides have metallic behavior and exhibit both ionic and covalent characters. The mechanical behavior of Mn_3XN (X = Al, Ga, Zn) compounds are corroborated with electronic properties as given in the results section.

Recommendations

Cubic manganese nitrides antiperovskites materials shows promise for a wide range of applications for example as gas sensors, catalysts for various chemical reactions, magnetic storage in hard disks etc. Therefore, we recommend all these compounds to be synthesized experimentally so as to allow industrial application. The compounds studied here can also be promising candidates for the study of optical properties.

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