Transactions of the Nigerian Association of Mathematical Physics
Volume 13, (October – December, 2020 Issue), pp39 –44

ELECTRONIC, STRUCTURAL, MAGNETIC AND MECHANICAL PROPERTIES OF $Mg_{1-x}Sr_xN$ ROCKSALT FROM FIRST-PRINCIPLES

O. R. Jolayemi [1] and S.A. Ekong [1, 2]

[1] Department of Physics, University of Benin, Benin City, Edo State, Nigeria.
[2]Department of Physics, Akwa Ibom State University, Ikot-Akpaden, Nigeria.

Abstract

The structural and elastic properties of $Mg_{1-x}Sr_xN(x = 0.00, 0.25, 0.50, 0.75, 1.00)$ in the cubic rocksalt structure are studied using first-principles pseudopotential method within the generalized gradient approximation (GGA-PBEsol) for the exchange-correlation energy and potential. Though from previous reports, the extreme compounds MgN and SrN are known to be half-metallic, the $Mg_{0.75}Sr_{0.25}N$, $Mg_{0.50}Sr_{0.50}N$ and $Mg_{0.25}Sr_{0.75}N$ compositions are found to be metallic.

***Keyword*:** Nitrides, Rocksalt, Half-metallic, Composition.

INTRODUCTION

The growing technology of nitride compounds has attracted enormous attention due to their high breeding ratio, high density, high thermal conductivity, and excellent compatibility as well as reprocessing behaviour in several outstanding physical applications [1–4]. Their high hardness, mechanical strength, high melting point and electrical conductivity that vary from metallic to semiconducting combining behaviour are of high significance in probing the material's behaviour. As a result, these materials can be used extensively in technological applications such as optical coatings, hard ware-resistant coatings, etc. Nitrides are becoming an exciting class of ceramic fuel because of their use in the development of fast nuclear reactors. Also, they are found as superlattices expected to have promising applications in future thermoelectric devices [3–6]. Furthermore, Ciriello *et al.* [7] and Basim *et al.* [8] reported new experimental data regarding the thermophysical properties of zirconium nitride. In addition, some of these transition metal nitrides have been found to possess half-metallic (HM) behaviour, which useful in spintronic applications [9, 10]. Alkaline earth metal nitrides have also been reported to exhibit half-metallicity [11–13]. According to literature, Ozdogan *et al.*[14] studied the electronic and magnetic properties of XY (X = Mg, Ca, Sr and Y = N, P, As, Sb) compounds in the zincblende (ZB) phase and reported that the Ca and Sr alkaline-earth metal monopnictides are found to be half-metallic with a total spin magnetic moment of 1.0 μB per formula unit. They further explained that in the case of the Mg alloys, the p-d hybridization effect is much weaker and only MgN is a half-metal. The method of full-potential non-orthogonal local-orbital minimum basis band structure method (FPLO) was employed by Palanichamy *et al.* [15] to investigate the structural, electronic, mechanical and magnetic properties of 3 alkaline-earth metal nitrides (XN: X= Ca, Sr, and Ba). With the VASP code, they reported that at ambient pressure, all the three nitrides are stable in the ferromagnetic state with a cubic NaCl structure. The electronic structure revealed that the materials are half-metallic ferromagnets at standard pressure. A pressure-induced structural phase transition from NaCl (B1) to CsCl (B2) phase was reported for CaN, SrN and BaN. Also, with a further increase in pressure, a half-metallic to metallic transition was observed in the nitrides. They concluded that ferromagnetism is quenched in all the three nitrides at high pressures. Recently, Mazouz *et al.* [16] investigated the structural, electronic, magnetic, lattice dynamics, and thermodynamic properties of ferromagnetic alkaline earth metal nitrides CaN, SrN, and BaN in the rocksalt structure using the techniques of plane-wave pseudopotential. They calculated the phonon dispersion spectra of nitride compounds using the linear response approach. They reported that the electronic structure and magnetic properties confirmed that rocksalt CaN, SrN, and BaN are half-metallic ferromagnets. Very recently, Benaissa *et al.* [11] investigated the structural, elastic, mechanical, and thermal properties of MgN compounds in different phases using the full-potential linearized augmented plane wave method in WIEN2K code.

Correspondence Author: Jolayemi O.R., Email: omamuyovwiakemu@yahoo.com, Tel: +2347061602488

Nevertheless, to the best of our knowledge information with regards to variations in the concentration of these pnictide compounds are still scarce in the literature. Thus the motivation for this study, the structural studies have shown that alkaline earth metal nitride in the rocksalt (RS) phase is the most stable when compared to other cubic structures [11,17]. We present in the current paper, an alkaline earth metal nitride study of the electronic structural and magnetic properties of MgN, SrN and $Mg_{1-x}Sr_xN$ at different concentrations. Furthermore, we aim to carefully apply the DFT techniques in providing accurate elastic constants of MgN, SrN, and $Mg_{1-x}Sr_xN$; and using the Voigt approach, the bulk, shear and Young moduli, Poisson ratios for the compounds are calculated [18–20].

2. COMPUTATIONAL METHOD

The calculations are based on the implementation of plane-wave density functional theory (DFT) in the Kohn–Sham framework [21] using Quantum Espresso simulation package [22]. The wave functions describe only the valence and the conduction electrons, while the core electrons are taken into account for pseudopotentials. We have used the plane wave self-consistent field (PWSCF) implementation of DFT, with a generalized gradient approximation (GGA-*PBEsol*) [23, 24]to exchange correlation energy and ultrasoft pseudopotential [25] to represent the interaction between ionic cores and valance electrons. PWs with a basis-set cutoff energy of 75 Ry was used to describe the electronic wave functions, while PWs with an energy of 750 Ry were included for the description of charge density. The occupation numbers are treated according to the Marzari-Vanderbilt smearing [26] scheme with a broadening of 0.02 Ry. Integration over the Brillouin zone was carried out using the Monkhorst–Pack scheme [27] with a 16 x 16 x 16 mesh of k-points. The equilibrium lattice parameters are obtained using the fitted energy-volume method proposed by Birch–Murnaghan [28].

$$E = E_0 + \frac{9B_0V_0}{16}\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^2 \left\{6 + B_0'\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right] - 4\left(\frac{V_0}{V}\right)^{\frac{2}{3}}\right\} \quad (1)$$

where V_0 is the equilibrium volume at zero pressure, E_0 is the equilibrium energy, B_0 is the bulk modulus, and $B_0'$is the pressure derivative of the bulk modulus.

The application of Hooke's law to small strains (ε_{ij}) gives the elastic energy Eapproximated by a quadratic function of the strain components:

$$\frac{E}{V} = \frac{1}{2}C_{11}\left(\varepsilon_{xx}^2 + \varepsilon_{yy}^2 + \varepsilon_{zz}^2\right) + C_{12}\left(\varepsilon_{xx}\varepsilon_{yy} + \varepsilon_{xx}\varepsilon_{zz} + \varepsilon_{yy}\varepsilon_{zz}\right) + 2C_{44}\left(\varepsilon_{xy}^2 + \varepsilon_{xz}^2 + \varepsilon_{yz}^2\right) \quad (2)$$

An applied strain with ε_{xx}being non-zero gives a quadratic energy variation in ε_{xx}, from which C_{11} can be fitted. In a similar approach, with $\varepsilon_{xy} \neq 0$the C_{44}can be fitted. For $\varepsilon_{xx} = \varepsilon_{yy}$being non-zero, an expression that depends on C_{11} and $C_{12}$is fitted to a second-order polynomial [21]. In all cubic systems, there are only three independent elastic constants, namely, C_{11}, C_{12}, and C_{44} thus, only a set of three equations is needed to determine all the constants, meaning that three types of strain must be applied to the crystal.

3. RESULTS AND DISCUSSION

3.1 Electronic structure

We have performed the structural optimization for the lattice constants of MgN, SrN and $Mg_{1-x}Sr_xN$ intermetallic alloy through energy minimization. The obtained total energies and lattice constants data are then fitted to third-order Birch–Murnaghan equation of state [28], to obtain the equilibrium lattice parameter (a_0), bulk modulus B_0 and pressure derivative of the bulk modulus B'. The summary of our calculated electronic structure properties compared to available data from other works are presented in Table 1. Our results for the structural properties of MgN and SrN as observed from Table 1, are in good agreement with the reported theoretical data [1, 11,13,17]. In addition, we present for the first time the structural properties of the $Mg_{1-x}Sr_xN$ alloys in Table 1. An observation from our result shows that lattice constants of composition $Mg_{1-x}Sr_xN$ alloys with concentration x = 0.25, 0.50 and 0.75 fit in range of the lattice parameter of the parent nitrides; MgN and SrN respectively.

From Fig. 1, we present the energy diagrams of the nitrides under study for spin-polarized and non-spin-polarized phases. It is found that the ferromagnetic phase is of MgN and SrN have lower energies compared to the non-magnetic phases. It is thus an indication that MgN and SrN are ferromagnetic in nature. This result is in good agreement with other theoretical reports [1,11,13]. Though the parent alloys were found to be ferromagnetic, the composition alloys from Fig 1c to 1e, shows that they are non-ferromagnetic. We thus consider investigating the half-metallic properties of the parent alloys. It is a known fact all half-metallic materials are ferromagnetic, but not all ferromagnetic material are half-metallic. A half-metal is characterized by two distinct band structures, such that one band exhibits a gap around the Fermi level while the other band structure displays metallic properties. From our study, the majority charge carriers (spin-up) of MgN and SrN are semiconducting while the minority charge carriers (spin down) are metallic.

Table 1: Calculated lattice constant (a_0), bulk modulus (B_0) and pressure derivative (B') of MgN, SrN and $Mg_{1-x}Sr_xN$ alkaline-earth metal nitrides at ambient condition.

Alloy	Ref.	a_0 (Å)	B_0 (GPa)	B'
MgN	Present work Others	4.374, 4.429[a], 4.380[b]	131.6, 114.26[a], 131.0[b]	3.948, 4.010[b]
$Mg_{75}Sr_{25}N$	Present	4.597	100.9	3.949
$Mg_{50}Sr_{50}N$	Present	4.840	84.9	4.067
$Mg_{25}Sr_{75}N$	Present	5.072	74.5	3.734
SrN	Present work Others	5.271, 5.28[c], 5.379[d]	73.6, 75.0[c], 64.08[d]	3.857 3.86[c]

[a]Mankad *et al*. (2012) Ref. [1]
[b]Benaissa *et al*. (2018) Ref. [11]
[c]Beldi *et al*. (2018) Ref. [13]
[d]Sharifzadeh *et al*. (2013) Ref. [17]

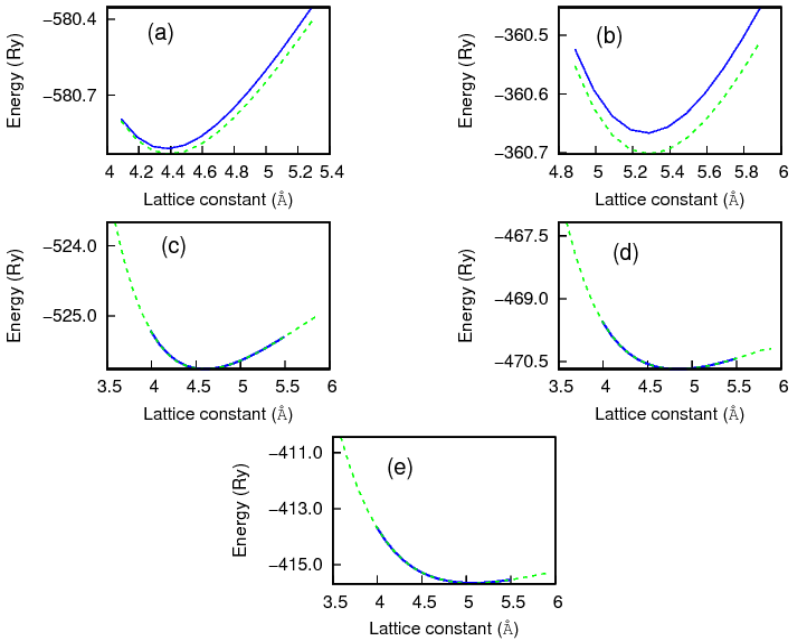

Fig. 1: Total energies as functions of lattice constants for the spin-polarized (dashed green lines) and non-spin-polarized (solid blue lines) configurations of the (a) MgN, (b) SrN, (c) $Mg_{75}Sr_{25}N$, (d) $Mg_{50}Sr_{50}N$ and (e) $Mg_{25}Sr_{75}N$ compounds in the rocksalt phase.

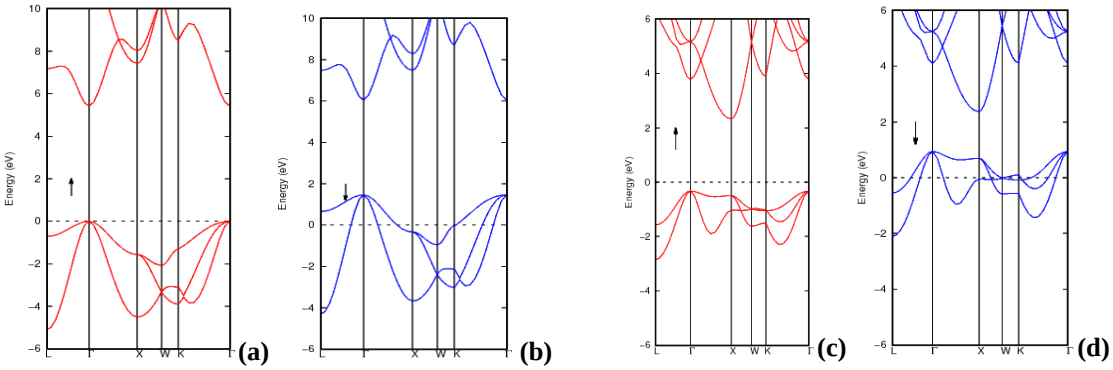

Fig 2: Spin-up (↑) and Spin-down (↓) bands for MgN (a) and (b) and for SrN(c) and (d) respectively.

3.2 Elastic constants and Mechanical properties

Our calculated elastic constants for the five rocksalt configurations are listed in Table 2 with the poisson ratio, bulk, Shear and Young moduli computed [20]. The elastic constants for cubic structure consists of three independent components: C_{11}, C_{12} and C_{44} as presented in Table 2. We have shown clearly in this study that the Born-Huang mechanical stability criteria were met as required by the relation: $C_{44} > 0$; $C_{11} > |C_{12}|$; $(C_{11} + 2C_{12}) > 0$ and $C_{12} < B < C_{11}$ for cubic structures [30]. The calculated results presented in Table 2 are indications that the considered rocksalt structures are elastically stable.

Table 2: Calculated elastic constants (C_{ij}), Voigt Bulk (B), Voigt Shear (G) and Voigt Young (E) Moduli and Voigt Poisson's ratio (μ) for MgN, SrN and $Mg_{1-x}Sr_xN$ alkaline-earth metal nitrides.

Alloy	Ref.	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	B (GPa)	G (GPa)	E (GPa)	μ
MgN	Present work Others	276.4 213.9[a], 253.0[b]	65.1 64.4[a], 72.0[b]	7.9 66.0[a], 35.0[b]	135.5	46.9	126.4	0.34
$Mg_{75}Sr_{25}N$	Present work	164.3	70.8	30.4	101.9	36.9	98.9	0.34
$Mg_{50}Sr_{50}N$	Present	135.4	80.6	50.6				0.32
$Mg_{25}Sr_{75}N$	Present	83.2	73.5	32.0	76.7	21.1	58.0	0.37
SrN	Present work Others	90.8 80.0[c], 106.2[d]	67.2, 66.0[c], 43.0[d]	24.5 21.0[c], 25.1[d]	75.1	53.6	19.4	0.38

[a]Mankad *et al*. (2012) Ref. [1]
[b]Benaissa *et al*. (2018) Ref. [11]
[c]Beldi *et al*. (2018) Ref. [13]
[d]Sharifzadeh *et al*. (2013) Ref. [17]

4. CONCLUSION

We have investigated the structural, half-metallic and mechanical properties of binary and ternary in the rocksalt structure by using density functional theroy within GGA approximation. We predict for the first time that $Mg_{75}Sr_{25}N$, $Mg_{50}Sr_{50}N$ and $Mg_{25}Sr_{75}N$ compounds are metals though MgN and SrN are half-metals. This is also in agreement with the Poisson ratio for these compounds.

REFERENCE

[1] V. Mankad, S.K. Gupta, P.K. Jha (2012). Ab initio investigation on structural, electronic and lattice dynamical properties of MgN and GdN crystals. *Results in Phys*. 2, 34-40.

[2] B. Saha, T.D. Sands, U.V. Waghmare (2011). Electronic structure, vibrational spectrum, and thermal properties of yttrium nitride: A first-principles study. J. Appl. Phys. 109, 073720: 1 – 6.

[3] V. Rawat, Y.K. Koh, D.G. Cahill, T.D. Sands (2009). Thermal conductivity of (Zr,W)N/ScN metal/semiconductor multilayers and superlattices. J. Appl. Phys. 105, 024909:1 – 6.

[4] B. Saha, J. Acharya, T.D. Sands, U.V. Waghmare (2010). Electronic structure, phonons, and thermal properties of ScN, ZrN, and HfN: A first-principles study. J. Appl. Phys. 107, 033715: 1 – 8.

[5] V. Mankad, S.K. Gupta , H.R. Soni, P.K. Jha (2012). Density functional theoretical study of lattice-specific heat and thermal properties of magnesium nitride. J Therm Anal Calorim 107: 45–48.

[6] M. Zebarjadi, Z. Bian, R. Singh, A. Shakourie, R. Wortman, V. Rawat, T. Sands (2009). Thermoelectric Transport in a ZrN/ScN Superlattice. J. Electron. Mater. 38, 960–963.

[7] A. Ciriello, V.V. Rodinella, D. Staicu, J. Somers (2007). Thermophysical characterization of nitrides inert matrices: preliminary results on zirconium nitride. J Nucl Mater. 371: 129–33.

[8] V. Basini, J.P. Ottaviani, J.C. Richaud, M. Streit, F. Ingold (2005). Experimental assessment of thermophysical properties of (Pu, Zr)N. J Nucl Mater. 344:186–90.

[9] M. Foroughpour, S. Davatolhagh, A-H. Tabatabaeifar (2013). Antiferromagnetic half-metallicity of transition metal nitrides under volume expansion. Eur. Phys. J. B 86: 78.

[10] A. Houari, S.F. Matar, V. Eyert (2010). Semiconducting (half-metallic) ferromagnetism in Mn(Fe) substituted Pt and Pd nitrides. Physical Review B 82, 241201(R).

[11] H. Benaissa. H. Bendaoud, S. Amari, K. O. Obodo, L. Beldi, B. Bouhafs (2018). Electronic and mechanical properties of MgN compound: Prediction of stable half-metallic ferromagnet in NaCl and ZB phases. Journal of Magnetism and Magnetic Materials, Vol. 466, 28–37.

[12] R.M. Shabara, S.H. Aly, S.Z. Yehia (2011). Half-Metallicity, Elasticity and Magnetic Moment of MgN: A First-Principles Study. Intl. J. Pure and Appl. Phys., Vol. 7 (1), pp. 39–48.

[13] L. Beldi, H. Bendaoud, K.O. Obodo, B. Bouhafs, S. Méçabih, B. Abbar (2018). First-principles study of the electronic structure, magnetism, and phonon dispersions for CaX (X = C, N) compounds. Computational Condensed Matter, Vol. 17, e00336.

[14] K. Özdogan, I. Galanakis (2012). First-Principles Computed Electronic and Magnetic Properties of Zincblende Alkaline-Earth Pnictides. Journal of Advanced Physics Vol. 1, pp. 69–77.

[15] R.R. Palanichamy, G.S. Priyanga, A.J. Cinthia, A. Murugan, A.T.A. Meenaatci, K. Iyakutti (2013). Half metallic ferromagnetism in alkaline-earth metal nitrides XN (X = Ca, Sr and Ba): A first principles study. Journal of Magnetism and Magnetic Materials 346, 26–37.

[16] M.H.A. Mazouz, A. Aiche, D. Bendouma, A. Tadjer (2017). First-Principles Study of Lattice Dynamics and Thermal Properties of Alkaline-Earth Metal Nitrides CaN, SrN, and BaN. Journal of Superconductivity and Novel Magnetism – Springer.

[17] H.S. Sharifzadeh, S.S. Sharifzadeh, F. Kanjouri, A. Esmailian (2013). Mechanical properties of CaN, SrN, and BaN compounds by density functional theory. Journal of Theoretical and Applied Physics, 7:16.

[18] W. Voight (1928). Lehrbook Der Kristallphysik. 2nd ed. Teubner, Leipzig, 962.

[19] A. Reuss (1929). Berechnung der fliessgrenze von mischkristallen auf grund de plastizitaettsbediengung fuer einkristalle. Z. Angew. Math. 9, 49–58.

[20] R. Hill (1952). The elastic behavior of a crystalline aggregate. Proc. Phys. Soc. London, Sect. A. 65, 349–354.

[21] S. Cottinier (2017). Computational Material Physics: Elastic constants stress tensor approach *http://compmatphys.epotentia.com/courses/computational-materials-physics/*

[21] W. Kohn, L.J. Sham (1965). Self-Consistent Equation Including Exchange and Correlation Effects. Physical Review 140, 1133 – 1138.

[22] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, etc. (2009). QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. Journal of Physics: Condensed Matter 21, 395502– 95521.

[23] J.P. Perdew, K. Burke, M. Ernzerhof, (1996). Generalized Gradient Approximation Made Simple, Phys. Rev. Lett. 77, 3865.

[24] X. Hua, X. Chen, W.A. Goddard (1997). Generalized generalized gradient approximation:An improved density-functional theory for accurate orbital eigenvalues, Phys. Rev. B 55, 16.

[25] D. Vanderbilt (1990). Soft self-consistent pseudopotentials in a generalized eigenvalue formalism, Phys. Rev. B 41, 7892.

[26] N. Marzari, D. Vanderbilt, A.D. Vita, M. C. Payne (1999). Thermal Contraction and Disordering of the Al(110) Surface, Phys. Rev. Lett. **82**, 3296.

[27] H. J. Monkhorst and J. D. Pack (1976). Special points for Brillouin-zone integrations, Phys. Rev. B 13, 5188.

[28] F.D. Murnaghan (1944). Proc. Natl. Acad. Sci. USA 30, 244.

[29] O.R. Jolayemi, S.A. Ekong, B.I. Adetunji, U.A. Iboh (2019). First-principles Study Of Half-Metallic Ferromagnetism In (1 1 1) Surface Of Csse. J. NAMP, 51, 157–162.

[30] Mouhat, F., and F. Couder, (2014). Necessary and Sufficient Elastic Stability Conditions in Various Crystal Systems, Phys. Rev. B 90, 224104, pp. 1–4.