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Abstract

We present structural and electronic properties of the cubic structure for different concentrations x of ternary alloy $B_xGa_{1-x}N$. The computational method is based on the full-potential linearised augmented plane wave method (FP-LAPW). The exchange and correlation energy is described in the local density approximation (LDA) and generalized gradient approximation (GGA). We have investigated the effect of composition on the ground state properties, lattice parameters, bulk modulus, pressure derivative and band gap of the zinc blend BN and GaN. The results obtained are in a good agreement with experimental and theoretical values concerning the variation of the gaps and crossover direct, indirect band gap and the bowing parameter. A reasonable agreement is found from the comparison of our results with other theoretical calculations.

Key Words: Lattice parameter, bulk modulus, pressure derivative and band gap, FP-LAPW, WIEN(2k).

1. Introduction

Semiconductor materials constitute the basic building blocks of emitters and receivers in cellular, satellite, and fibreglass communication components. Among these, the III-nitrides are nowadays widely used by the industry. With respect to "classical" III-V semiconductors, the group-III nitrides semiconductors have attracted much attention in recent years for their great potential for technological applications [1]. BN and GaN are regarded as promising wide band gaps semiconductors, ranging from the ultraviolet (UV) to the visible regions of the spectrum. They have a high melting point, high thermal conductivity, and a large bulk modulus [2]. These properties, as well as the wide band gaps are closely related to strong (ionic and covalent) bonding. These materials can therefore be used for short-wavelength light-emitting diodes (LEDs) laser diodes and optical detectors as well as for high-temperature, high-power and high-frequency electronic devices. Bright and highly efficient blue and green LEDs are already commercially available and diode lasers have been reported, emitting in the blue-violet range initially under pulsed conditions and subsequently under continuous operation.

2. Calculation Method

In our calculations we performed to use the scalar relativistic full-potential linearised augmented plane wave plus local orbitals (FP-L/APW+lo) [3] approach based on the density functional theory [4] within the

LDA and GGA using the scheme of Perdew, Brouke and Ernzerhof [5]. We adopt the Ceperley-Alder [6] forms for exchange correlation energy as parameterized by Perdew and Wang [7].

In the present calculations we apply the most recently version of Vienna package WIEN2k_2003 [8, 9]. In this new version, the alternative base sets (APW+lo) are used inside the atomic spheres for those chemically important l-orbitals (partial waves) that are difficulty converge (outermost valence p-, d-, or f-states), or for atoms where small atomic spheres must be used [10–11]. For all the other partial waves the LAPW scheme is used.

Moreover, we used the semi-relativistic approximation in that no spin orbit effects are included, but where the core levels are treated fully relativistically [12]. It is also expected Ga to contribute the semi core *d*electrons in the valence bands. In the following calculations, we specifically distinguish the Boron $1s^2$, Gallium $1s^2{\cdot}2s2{\cdot}2p6{\cdot}3s2{\cdot}3p^6$, and Nitrogen $1s^2$ inner-shell electrons from the valence electrons of Boron $2s^2{\cdot}2p^1$, Gallium $3d^{10}{\cdot}4s2{\cdot}4p^1$ and Nitrogen $2s^2{\cdot}2p^3$ shells.

The remaining core states are self-consistently relaxed in a spherical approximation. Inside the non-overlapping spheres of muffin-tin (MT) radius R_{MT} around each atom, spherical harmonics expansion is used. We chose the plane wave basis set for the remaining space of the unit cell. For BN and GaN we adopted as the MT radius, the values (in units of the hydrogen radius a_0) of 1.6, 1.90 and 1.4 for B, Ga and N, respectively.

The maximum $l$value for the wave function expansion inside the atomic spheres was confined to $l_{max} = 10$. In order to achieve energy eigenvalues convergence, the wave functions in the interstitial region are expanded in plane waves with a cutoff of $R_{MT}\ k_{max} = 7$, where R_{MT} is the average radius of the MT spheres and k_{max} is the maximum modulus for the reciprocal lattice vector. The k integration over the Brillouin zone is performed using Monkhorst and Pack [13] mesh, yielding to $73k$points in the irreducible wedge of the Brillouin zone for both zincblende structures. The iteration process is repeated until the calculated total energy of the crystal converges to less than 0.1 mRy.

Optical bowing is a well-known phenomenon in ternary semiconductor alloys; and was observed more than thirty years ago in the large band gaps of III-V semiconductor, by Larach et al. [14] on powder material, and by Ibina et al. [15] on bulk single crystal which has been reviewed in reference [7].

On the theoretical side, different methods have been applied in the calculation of the band structure of these alloys. These include methods based on the dielectric two band model [16], semi empirical tight-binding method [17, 18] semi empirical pseudo-potential method [19, 20], ab initio pseudo-potential method [21, 22] and full potential linearised augmented plane wave method [23, 24]. To our knowledge, except for the recent theoretical work of Baaziz et al. [25] and Grein et al. [26], there is no theoretical investigation of B_xGa_{1-x} N alloy in literature. To understand the structural and electronic properties of these ternary alloys, we carry out the present study, in which we used the first-principles full-potential linearised augmented plane wave method (FP-LAPW) within the (LDA) and (GGA) scheme [27–28].

The details of calculations are as follows: the charge density and the potential are represented inside the muffin-tin spheres (MTS) by spherical harmonics up to l_{max}=15. The k integration over Brillouin zone is performed using tetrahedron method [29]. The values of the sphere radii (MTS), number of plane waves (NPLW).

3. Results and Discussions

3.1. Structural properties

The calculated structural properties (lattice parameters a, bulk modulus B and B') of the binaries are summarized in Table 1. We have an underestimation of the lattice parameters and an overestimation of the bulk modulus in comparison to those of experiment (Table 1), due to the use of the LDA and GGA.

Table 1. The calculated lattice parameter (a), bulk modulus B and its pressure derivatives B' for $B_xGa_{1-x}N$ and its binary compounds. Available experimental and theoretical data are also given for comparison.

	a(Å)	B (GPa)	B'
BN	3.585	404	3.71
Our calc	3.627	375.4	3.27
LDA	3.575 [33]	386 [33]	3.6 [37]
GGA	3.576 [37]	397 [37]	2.91 [38]
Other calc.	3.649 [38]	366 [38]	3.94 [30]
Experiment	3.606[31][32]	367 [31][31]	3.97 [39]
	3.615[34][35][36]	369 [34]	4[34]
GaN			
Our calc			
LDA	4.463	204	4.68
GGA	4.553	179.2	3.57
Other calc	4.335 [40]	207 [40]	4.32 [40]
Experiment	4.464 [41]	-	4.3 [41]
	4.47 [42]	187 [42]	
	4.52[43] 4.50[46]	190[45]	-
$B_{0.25}Ga_{0.75}N$			
LDA	4.31	226.4	4.1
GGA	4.39	195.3	4.06
$B_{0.50}Ga_{0.50}N$			
LDA	4.13	261.13	3.88
GGA	4.19	234	3.86
$B_{0.75}Ga_{0.25}N$			
LDA	3.86	319	3.59
GGA	3.95	287	3.8

We have started our FP-LAPW calculation of the structural properties with the zinc-blend structure and let the calculation forces move the atoms to their equilibrium positions. We have chosen the basic cubic cell as the unit cell. In the unit cell there are four C anions and three A and one B, two A and two B, and one A and three B cations, respectively, for $x = 0.25$, 0.50 and 0.75. For the structures considered, we performed structural optimization by calculating total energies for different volumes around the equilibrium cell volume V_0 of the binary BN and GaN compound and their alloys. The calculated total energies are fitted to the Murnaghan's equation of state [44] to determine the ground state properties such as the equilibrium lattice constant a_0, the bulk modulus B_0 and its pressure derivative B'. The calculated equilibrium parameters a_0, B, and B' are given in Table 1. There is good agreement between our calculated results and the theoretical investigations. Also, there is small underestimation of the lattice parameters and overestimations of the bulk modulus compared to the experimental data; this is due essentially to the use of the local density approximation (LDA). Furthermore, the values of calculated bulks modulus using the LDA approximation decrease from BN to GaN, i.e. from the lower to the higher atomic number. This suggests that BN is more compressible than GaN.

Usually, in the treatment of alloys, it is assumed that the atoms are located at the ideal lattice sites and the lattice constant vary linearly with composition x according to the so-called Vegard's law [47]:

$$a\ (A_xB_{1-x}C) = x\ a_{AC} + (1-x)\ a_{BC}. \tag{1}$$

Here, a_{AC} and a_{BC} are the equilibrium lattice constants of the binary compounds AC and BC respectively, $a(A_x\ B_{1-x}C)$ is the alloy lattice constant.

However, violation of Vegard's law has been observed in semiconductor alloys both experimentally [48] and theoretically [49, 50]. Hence, the lattice constant is, instead, written as

$$a\ (\mathrm{A}_x\mathrm{B}_{1-x}\mathrm{C}) = x\ a_{\mathrm{AC}} + (1-x)\ a_{\mathrm{BC}} - x\ (1-x)b, \tag{2}$$

where the quadratic term b is the bowing parameter.

Figure 1 and Figure 2, shows the variation of the calculated equilibrium lattice constants and the bulk modulus against concentration x for $\mathrm{B}_x\mathrm{Ga}_{1-x}\mathrm{N}$ alloy, respectively. It is very clear from Figure 2 that the value of the bulk modulus increase with increasing the B concentration, confirming the suggestion of Véiré [51]: addition of beryllium to III-V compounds improve their hardness. A large deviation from the Vegard's law is clearly visible, with upward bowing parameter for the lattice constant and downward bowing for the bulk modulus.

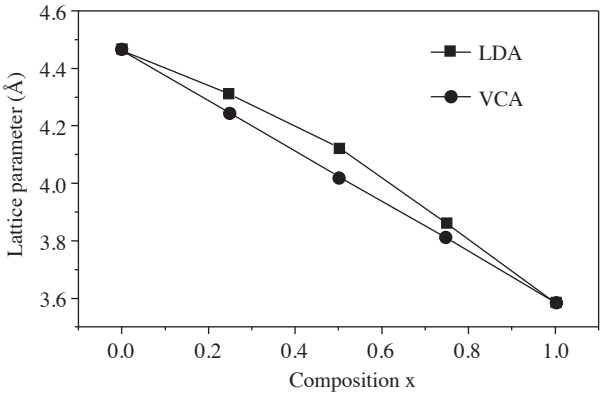

Figure 1. Composition dependence of the calculated lattice constant of $\mathrm{B}_x\mathrm{Ga}_{1-x}\mathrm{N}$ alloy (Solide Squares) and with VCA (dashed line).

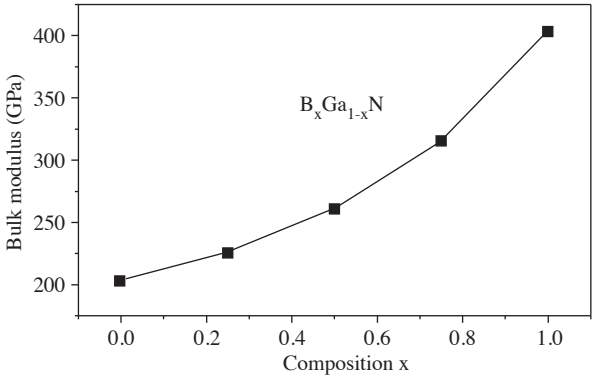

Figure 2. Composition dependence of the calculated modulus of $\mathrm{B}_x\mathrm{Ga}_{1-x}\mathrm{N}$ alloy.

3.2. Electronic properties

Figures 3–5 show that the calculated band structure energies of binary compounds, as well as their alloy using FP-LAPW method within LDA approximation, give a direct band gap for GaN and $\mathrm{B}_x\mathrm{Ga}_{1-x}\mathrm{N}$ for $x = 0.25$ to 0.75. For GaN, the valence band maximum (VBM) and the conduction band minimum (CBM) occurs at the Γ and X points, respectively. The main band gaps are given in Table 2, together with their theoretical and experimental values. It is clearly seen that the band gaps are, on the whole,

underestimated in comparison with experimental results. This underestimation of the band gaps is mainly due to the fact that the simple form of LDA do not correctly take into account the quasiparticle self energy, which makes it not sufficiently flexible to accurately reproduce both exchange correlation energy and its charge derivative. It is important to note that the density functional formalism is limited in its validity and the band structure derived from it cannot be used directly for comparison with experiment. The band edge emission of $B_xGa_{1-x}N$ varies from 3.451 eV for $x = 0\%$ with FWHM of 39.2 meV to 3.465 eV for $x = 1.5\%$ with FWHM of 35.1 meV [54].

Table 2. Direct ($\Gamma - \Gamma$) and indirect (Γ-X) band gaps of BN and GaN and their alloy at equilibrium volume (all energies are in eV).

		$E_{\Gamma\Gamma}$ (eV)	$E_{\Gamma X}$ (eV)
GaN	Our calculation	3.52	3.5
	Experiment	3.3 [52] 3.35 [53]	
$B_{0.25}Ga_{0.75}N$		2.95	4.45
$B_{0.5}Ga_{0.5}N$		3.4	5.36
$B_{0.75}Ga_{0.25}N$		3.9	6.3
BN	Our calculation	8.89	4.75
	Other calculations	8.6 [31] 9.09 [52]	4.24 [52]

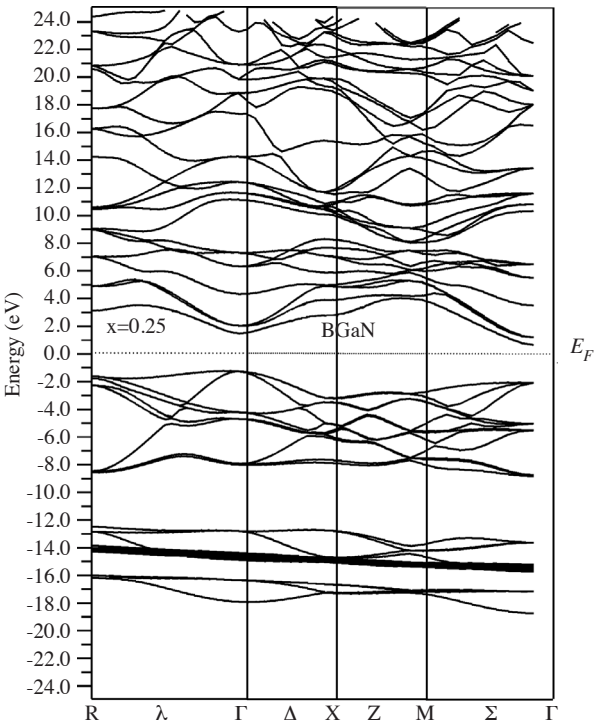

Figure 3. The band structure of the ternary alloy $B_{0.25}Ga_{0.75}N$.

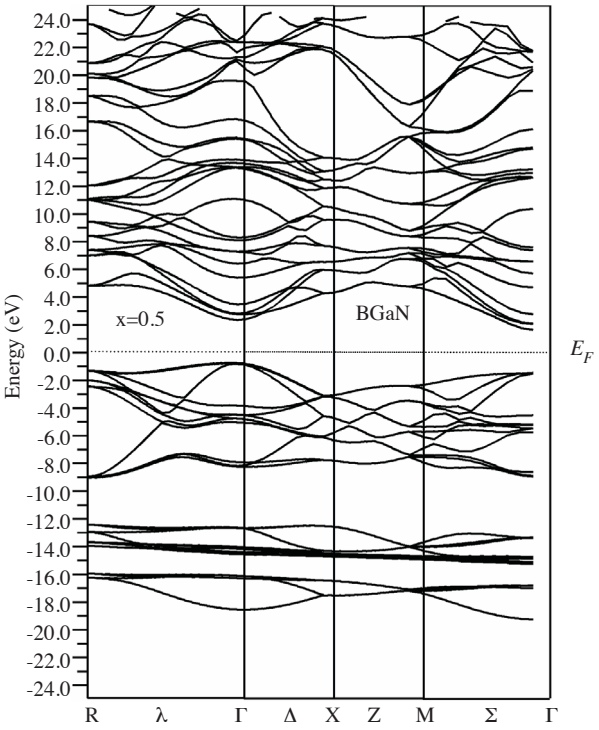

Figure 4. The band structure of the ternary alloy $B_{0.50}Ga_{0.50}N$.

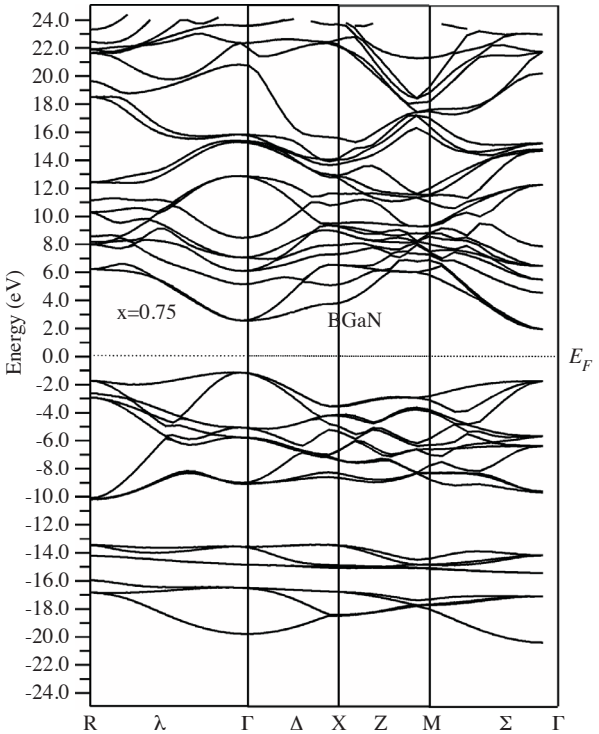

Figure 5. The band structure of the ternary alloy $B_{0.75}Ga_{0.25}N$.

The variation of the direct $E_{\Gamma-\Gamma}$and indirect $E_{\Gamma-X}$ band gaps against alloy composition is shown in Figure 6. Note the presence of a crossover between direct and indirect band gaps at concentration $x \approx 0.77$. Through Figure 6, we note that, to about $x \sim 0.21$, the fundamental gap $E_{\Gamma-\Gamma}$ increases with concentration

x, while $E_{\Gamma-X}$ decreases; and above $x \sim 0.21$, both gaps increase with concentration. The increase in direct energy gap is remarkable beyond $x = 0.50$. We note that between $0 \leq x \leq 0.50$, the variation is linear with the respect to the average slope of 3.4 eV/x; however, in reference [55], the average slope is found equal to 5.041 eV/x. This is due to the method of calculation used. The total bowing parameter is calculated by fitting the non linear variation of the calculated direct and indirect band gaps in terms of concentration with a polynomial function. The results are shown in Figure 7 and found to obey the relations

$$E_{\Gamma-\Gamma} = 2.363 - 3.122\ x + 9.085\ x^2 \tag{3}$$

$$E_{\Gamma-X} = 3.426 + 0.864x + 2.08\ x^2. \tag{4}$$

These relations make it clear both the direct ($\Gamma - \Gamma$) and indirect (Γ-X) band gaps express non linear behaviour. This behaviour is also observed by Baaziz et al. [25] and Tsai et al. [56] by using the ab initio FP-LAPW and Pseudo-potential methods, respectively. The direct gap ($\Gamma - \Gamma$) versus concentration has a downward bowing with a value of $b = 9.085$, while the indirect gap (Γ-X) has an upward bowing of $b = 2.08$. The values of these bowings are much closed to those obtained by using the full-potential linearised augmented plane wave.

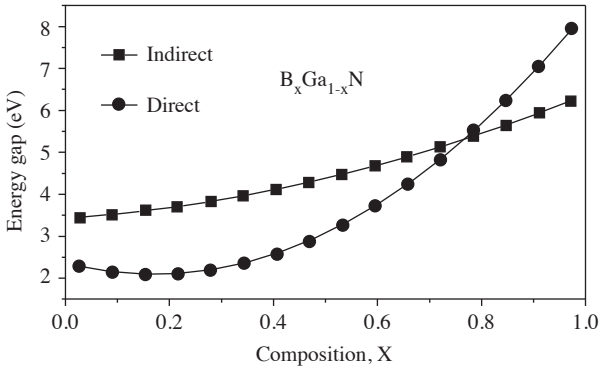

Figure 6. Composition dependence of the direct ($\Gamma - \Gamma$) and indirect (Γ-X) band gaps in $B_xGa_{1-x}N$ alloy.

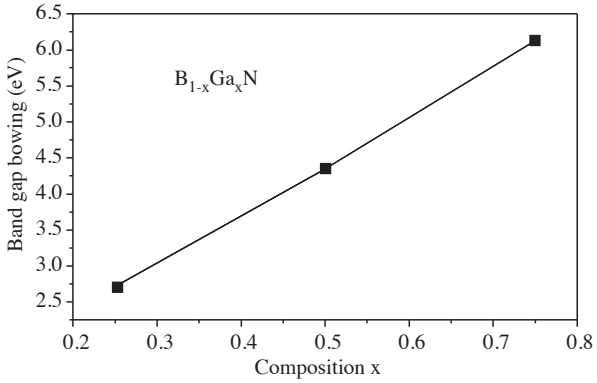

Figure 7. The calculated optical bowing parameter as a function of composition x

4. Conclusion

We have used the FP-LAPW method within the LDA for exchange-correlation potential to investigate the structural and electronic properties of the cubic $B_xGa_{1-x}N$ alloy. We have calculated the equilibrium lattice constants, bulk modulus and its pressure derivative. The bowing of the lattice constant, bulk modulus and energy band gap are also investigated. Our results are compared with previous calculations using different

methods. In particular, a good agreement is found with the GGA study of this alloy [25], using FP-LAPW (Wien2k code). Our results show a strong dependence of the band gap bowing factor on composition and lattice parameter.

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References

[1] S. Nakamura, M. Senoh, S. Nagahma, N. Iwasa, T. Yamada, T. Matsuahita, H. Kiyoku, and Y. Sugimoto, *Jpn. J. Appl. Phys.,* **35**, (1996), 174.

[2] H. W. Leite Alves, J. L. A. Alves, R. A. Nogueira, and J. R. Leite*, Braz. J. Phys.*, **4**, (1999), 29.

[3] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka and J. Luitz, *WIEN2k, An Augmented- Plane-Wave + Local Orbitals Program for Calculating Crystal Properties,* (Karlheinz Schwarz, Techn Wien, Austria, 2001).

[4] R. Dreizler and E. K. U. Gross, *Density-Functional Theory* (Springer, New York, 1990).

[5] J. P. Perdew, S. Burke and M. Ernzerhof, *Phys. Rev. Lett.,* **77**, (1996), 3865.

[6] D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.,* **45**, (1980), 556.

[7] J. P. Perdew and Y. Wang, *Phys. Rev.*, **B 45**, (1992), 13 244.

[8] K. Schwarz and P. Blaha, Comput, *Mater. Sci.,* **28**, (2003), 259.

[9] K. Schwarz, *J. Solid. Stat. Chem.*, **176**, (2003), 319.

[10] G. H. K. Madsen, P. Blaha, K. Schwarz, E. Sjöstedt and L. Nordström, *Phys. Rev.*, **B64**, (2001), 195134-1.

[11] G. H. K. Madsen, B. B. Iversen, P. Blaha and K. Schwarz, *Phys. Rev.*, **B64**, (2001), 195102-1-6.

[12] D. D. Koelling and B. N. Harmon, *J. Phys*, **C10**, (1977), 3107.

[13] H. J. Monkhorst and J. D. Pack, *Phys. Rev.*, **B13**, (1976), 5188.

[14] S. Larach, R. E. Shrader and C. F. Stocker, *Phys. Rev.*, **108**, (1957), 587.

[15] A. Ebina, M. Yamamoto and T. Takahashi, *Phys. Rev.*, **B6**, (1972), 3786.

[16] J. A. Van Vachten and T. K. Bergstresser, *Phys. Rev.*, **B1**, (1970), 3351.

[17] D. J. Chadi, *Phys. Rev.*, **B 16**, (1977), 790.

[18] M. Rabah, B. Abbar, Y. Al-Douri, B. Bouhafs and B. Sahraoui, *Mater. Sci. Eng.*, **B100**, (2003), 163.

[19] A. Baldereschi, E. Hess, K. Maschke, H. Neumann, R. K. Schulze and K. Unger, *J. Phys.*, **10**, (1977), 4709.

[20] Z. Charifi, H. Baaziz, N. Bouarissa, *Int. J. Mod. Phys*, **B 18**, (2004), 137; *Mater. Chem. Phys.,* **84**, (2004), 273.

[21] A. Zaoui, *J. Phys., Condens. Matter,* **14**, (2002), 4025.

[22] G. Q. Lin, H. Gong and P. Wu, *Phys. Rev.*, **B71**, (2005), 085203.

[23] Z. Charifi, F. El Haj Hassan, H. Baaziz, Sh. Khosravizadeh, S. J. Hashemifar, H. Akbarzadeh, *J. Phys. Condens. Matter.*, **17**, (2005), 7077.

[24] S. H. Wei and A. Zunger, *Phys. Rev.*, **B 43**, (1991), 1662.

[25] H. Baaziz, Z. Charifi, F. El Haj Hassan, S. J. Hashemifar and H. Akbarzadeh, *Phys. Stat.Sol. (b).*, (2006), 1-10.

[26] C. H. Grein, R. G. Radtke, H. Ehrenreich, C. Chauvet, E. Tournié and J. P. Faurie, *Solid State. Commun.*, **123**, (2002), 209.

[27] S. Savrasov and D. Savrasov, *Phys. Rev.*, **B46**, (1992), 12181.

[28] J. P. Perdew and Y. Wang, *Phys. Rev.*, **B 46**, (1992), 12947.

[29] P. Blochl, O. Jepsen, and O. K. Andersen, *Phys. Rev.*, **B49**, (1994), 16223.

[30] W. Sekkal, B. Bouhafs, H. Aourag, and M. Certier, *J. Phys. Condens. Matter.*, **10**, (1998), 4975.

[31] R. M. Wentzcovitch, K. J. Chang and M. L. Cohen, *Phys. Rev.*, **B 34**, (1986), 1071.

[32] R. M. Wentzcovitch, M. L. Cohen, and Pui K. Lam, *Phys. Rev.*, **B36**, (1987), 6058.

[33] P. Rodriguez-Hernandez, M. Gonzalez-Diaz, and A. Munoz, *Phys. Rev.*, **B51**, (1995), 14705.

[34] E. Knittle, R. M.Wentzcovitch, R. Jeanloz and M. L. Cohen, *Nature (London).*, **337**, (1989), 349.

[35] S. Fahy, *Phys. Rev.,* **B51**, (1995), 12873.

[36] R. M. Wentzcovitch, K. J. Chang, and M. L. Cohen, *Phys. Rev.*, **B34**, (1986), 1071.

[37] V. A. Pesin, *Sverktverd. Mater.*, **6**, (1980), 5.

[38] P. E. Van Camp, V. E. Van Doren, and J. T. Devreese, *Phys. Stat. Sol. (b).,* **146**, (1988), 573.

[39] K. Karch, and F. Bechstedt, *Phys. Rev.*, **B56**, (1997), 7404.

[40] S. Q. Wang and H. Q. Ye, *J. Phys. Condens. Matter.,* **14**, (2002), 9579.

[41] A. F. Wright and J. S. Nelson, *Phys. Rev.*, **B51**, (1995), 7866; *Phys. Rev.*, **50**, (1994), 2159.

[42] M. Fuchs, J. L. Da Silva, C. Stampfl, J. Neugebauer and M. Scheffler*, Phys. Rev.,* **B65**, (2002), 245212.

[43] A. Trampert, O. Brandt and K. H. Ploog, *in Crystal structure of group III Nitrides,* edited by J. I. Pankove and T. D. Moustakas*, Semiconductors and Semimetals,* Vol., **50**, (Academic, San Diego, 1998).

[44] F. D. Murnaghan, *Proc. Natl. Acad. Sci.*, **30**, (1947), 244; J. R. Macdonald, D. R. Powell, *J. Res. Nat. Bur. Stand.,* **A75**, (1971), 441.

[45] W. A. Harison, *Electronic Structure and the properties of Solids*, 176 (Dover, New York, 1989).

[46] I. Vurgaftman, J. R. Meyer and L. R. Ram-Mohan, *J. Appl. Phy.*, **89**, (2001), 5815.

[47] L. Vegard, *Z. Phys.*, **5**, (1921), 17.

[48] S. N. Rashkeev and W. R. L. Lambrecht, *Phys. Rev.*, **B63**, (2001), 165212.

[49] F. El Haj Hassan and H. Akbardadeh, *Mater. Sci. Eng.*, **B21**, (2005), 170.

[50] Z. Dridi, B. Bouhafs and P. Ruterana, *Comput. Mat. Sci.*, **33**, (2005), 136.

[51] C. Vèrié, *Mater. Sci. Eng.*, **B43,** (1997), 60; *J. Cryst. Grouth.,* **184**, (1998), 106.

[52] F. Chiker, B. Abbar, B. Bouhafs and P. Ruterana, *Phys. Stat. Sol. (b).,* **241**, (2004), 305.

[53] I. Vurgaftmana and J. R. Meyer L. R. Ram-Mohan, *J. Appl. Phys.*, **89,** (2001), 5815; I. Vurgaftman and J. R. Meyer, *J. Appl. Phys.*, **94**, (2003), 3675.

[54] C. H. Wei, Z. Y. Xie, J. H. Edgar, K. C. Zeng, J. Y. Lin, H. X. Jiang,C. Ignatiev, J. Chaudhuri and D. N. Braski, *J. Nitride Semicond. Res.*, **4S1**, (1999), G3.79.

[55] S. N. Rashkeev and W. R. L. Lambrecht*, Phys. Rev.*, **B63**, (2001), 165212.

[56] M. H. Tsai, F. C. Peiris, S. Lee and J. K. Furdyna, *Phys. Rev.*, **B65**, (2002), 235202.