

First-principles study of cubic $B_xGa_{1-x}N$ alloys

A. Lachebi^{1,*}, H. Abid¹, M. Driz¹, Y. Al-Douri²

¹⁾ Applied Materials Laboratory, University of Sidi-Bel-Abbes, 22000 Algeria.

²⁾ CRISMAT, ENSICAEN/CNRS UMR 6508, 6 boulevard du Maréchal Juin, F-14050 Caen Cedex, France.

Abstract

We present first-principles calculations of the structural and electronic properties of cubic for different concentrations x of ternary alloy $B_xGa_{1-x}N$. The computational method is based on the full-potential linearized 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, 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.

Keywords: Structural properties, Electronic properties, FP-LAPW.

1. Introduction

Semiconductor materials constitute today basic building blocks of emitters and receivers in cellular, satellite, and fibreglass communication. 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 to 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, a 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

^{*}) Permanent adresse: Université Djillali Liabès, Faculté des Sciences de l'Ingénieur, Département d'Electronique, Sidi- Bel Abbès, 22000, Algérie. E-mail address: lachebi2005@yahoo.fr (M. Lachebi)

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 linearized/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 [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 (no spin orbit effects included) whereas the core levels are treated fully relativistically [12]. In particular, the Ga is considered in such as to include explicitly the semi core d electrons in the valence bands. In the following calculations, we distinguish the B ($1s^2$), Ga ($1s^2 2s^2 2p^6 3s^2 3p^6$), and N ($1s^2$) inner-shell electrons from the valence electrons of B ($2s^2 2p^1$), Ga ($3d^{10} 4s^2 4p^1$) and N ($2s^2 2p^3$) 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 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 is k_{MAX} the maximum modulus for the reciprocal lattice vector, and R_{MT} is the average radius of the MT spheres). The k integration over the Brillouin zone is performed using Monkhorst and Pack [13] mesh, yielding to 73 k 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.

In ternary semiconductor alloys, the optical bowing is a well-known phenomenon. This bowing in large band gap of III-V semiconductor has been observed more than thirty years ago by Larach and al. [14] on powder material and by Ebina et al. [15] on bulk single crystal which has been reviewed in Ref. [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 [21-32] and full potential linearized augmented plane wave method [33, 34]. To our knowledge, except the recent theoretical work of Baaziz et al. [35] and Grein et al. [36] where there is no theoretical investigation of $B_xGa_{1-x}N$ alloy appeared 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 linearized augmented plane wave method (FP-LAPW) within the (LDA) and (GGA) scheme [37-39].

The details of calculations are fellows: 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 [40]. The values of the sphere radii (MTS), number of plane waves (NPLW).

3. Results and discussions

3.1. Structural properties

We calculated the structural properties of the binary compounds BN and GaN in the zinc-blend structure. Then the semiconductor ternary alloy is the type $B_xA_{1-x}C$, we have started our FP-LAPW calculation of the structural properties with the zinc-blend structure and let the calculation forces to 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, 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 considered structures, we performed the structural optimization by calculating the total energies for different volumes around the equilibrium cell volume V_0 of the binary BN and GaN compound and their alloy. The calculated total energies are fitted to the Murnaghan's equation of state [48] to determine the ground state properties 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 a 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 [49].

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

where a_{AC} and a_{BC} are the equilibrium lattice constants of the binary compounds AC and BC respectively, $a(A_xB_{1-x}C)$ is the alloy lattice constant. However, violation of Vegard's law has been observed in semiconductor alloys both experimentally [50] and theoretically [51-52].

Hence, the lattice constant can be written as:

$$a(A_xB_{1-x}C) = x a_{AC} + (1-x) a_{BC} - x(1-x)b \quad (2)$$

where the quadratic term b is the bowing parameter.

Figures 1 and 2, shows the variation of the calculated equilibrium lattice constants and the bulk modulus against concentration x for $B_xGa_{1-x}N$ alloy, respectively. It is very clear from fig. 2 that the value of the bulk modulus increase with increasing the x concentration, confirming the suggestion of Véiré [53], which states that the adding 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.

		a (Å)	B (GPa)	B'
BN				
Our cal.	LDA	3.585	404	3.7090
	GGA	3.627	375.4	3.2566
	Other cal.	3.575 [25]	386 [25]	3.6 [29]
		3.576 [29]	397 [29]	2.91 [30]
		3.649 [30]	366 [30]	3.94 [22]
		3.606 [23,24]	367 [23,24]	3.97 [31]
	Exp.	3.615[26-28]	369 [26]	4[26]
GaN				
Our cal.	LDA	4.463	203.6566	4.6835
	GGA	4.553	179.1803	3.5690
	Other cal.	4.335 [41]	207 [41]	4.32
		4.464 [42]	-	4.3
		4.47 [43]	187 [43]	-
Exp.	4.52[44]	190 [46]	-	
	4.50[47]			
	$B_{0.25}Ga_{0.75}N$			
LDA	LDA	4.31	226.4237	4.0725
	GGA	4.3886	195.264	4.063
$B_{0.5}Ga_{0.5}N$				
LDA	LDA	4.125	261.1289	3.8786
	GGA	4.187	253.6914	3.1789
$B_{0.75}Ga_{0.25}N$				
LDA	LDA	3.86	318.9293	3.5887
	GGA	3.948	285.02	3.978

Table 1: The calculated lattice parameter (a), bulk modulus B_0 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.

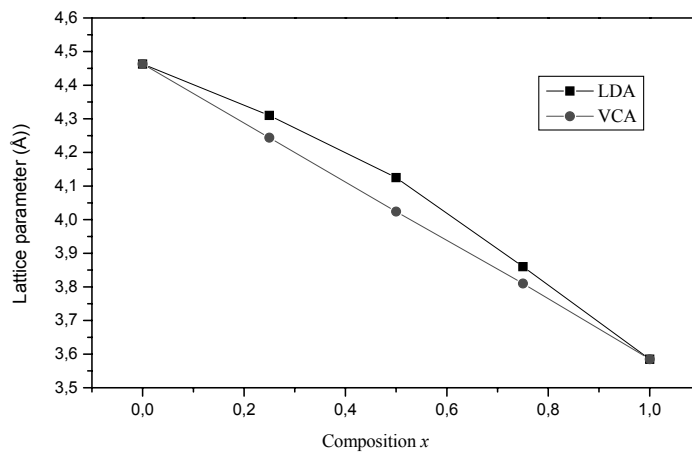


Fig.1: Composition dependence of the calculated lattice constant of $B_xGa_{1-x}N$ alloy (solid squares) and with VCA (dashed line).

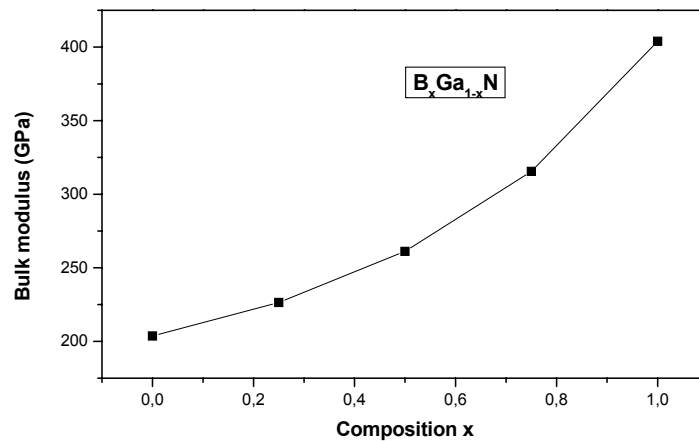


Fig. 2: Composition dependence of the calculated modulus of $B_xGa_{1-x}N$ alloy.

3.2. Electronic properties

Figure 3 (a-c) show 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 $B_xGa_{1-x}N$ with x varies from 0.25 to 0.75. For GaN, the valence band maximum (VBM) and the conduction band minimum (CBM) occurs at the Γ and X point, respectively. The main band gaps are given in table 2 as well as the theoretical and experimental ones. It is clearly seen that the band gaps are on the whole underestimated in comparison with experiments results. This underestimation of the band gaps is mainly due to the fact that the simple form of LDA does not take into account the quasiparticle self energy correctly which make 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 [59].

		$E_{\Gamma\Gamma}$ (eV)	$E_{\Gamma X}$ (eV)
BN	Our cal.	8.89	4.75
	Other cal.	9.09 [60]	4.24 [60]
gaps			
equili-			
$B_{0.25}Ga_{0.75}N$		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
GaN	Our cal.	3.52	3.56
	Exp.	3.3 [57]	-
		3.35[58]	

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

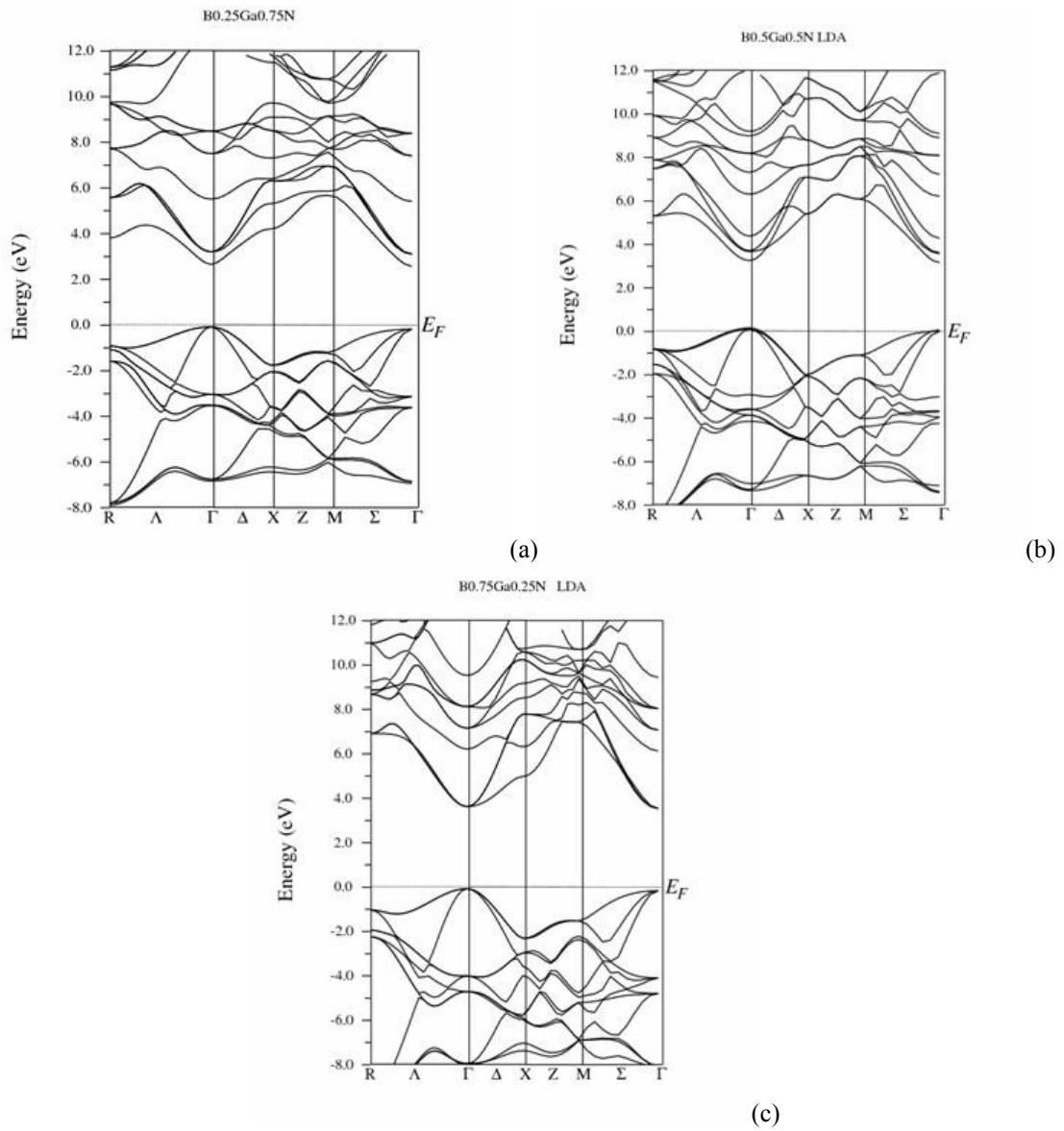


Fig 3: The band structure of the ternary alloy $B_{0.25}Ga_{0.75}N$ (a) the band structure of the ternary alloy $B_{0.50}Ga_{0.50}N$ (b) the band structure of the ternary alloy $B_{0.75}Ga_{0.25}N$ (c).

The variation of the direct $E_{\Gamma-\Gamma}$ and indirect $E_{\Gamma-X}$ band gaps against alloy composition is given in fig. 4. A crossover between the direct and indirect band gaps is located at a concentration of 0.77. Through fig. 4 we note that the fundamental gap $E_{\Gamma-\Gamma}$ increases according to the concentration and fall in good term with the evaluation from the lattice constant which decreases when the concentration increases. However it is noted that the increase is remarkable beyond $x=0.50$, while between $0 \leq x \leq 0.50$ variation remains linear and marks an average slope of 3.4 eV what is verifiable in the surrounding of others calculations 5.041 eV [54]. 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 polynomial function. The results are shown in fig. 5 and obey the following variations:

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

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

It is shown from the above equations the variation of direct ($\Gamma-\Gamma$) and indirect ($\Gamma-X$) band gaps as a function concentration has a non linear behaviour. This behaviour is also observed by Baaziz et al. [35] and Tsai et al. [55] by using the *ab initio* FP-LAPW and pseudopotential methods, respectively. The direct gap ($\Gamma-\Gamma$) versus concentration has a downward bowing with a value of $b=9.085$, while the indirect gap ($\Gamma-X$) has an upward bowing of $b=2.08$. The values of these bowings are much closed to those obtained by using the full-potential linearized augmented plane wave.

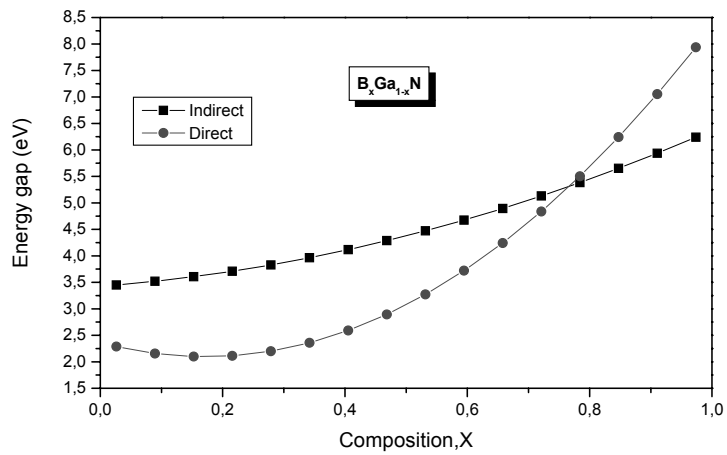


Fig.4: Composition dependence of the direct ($\Gamma-\Gamma$) and indirect ($\Gamma-X$) band gaps in $B_xGa_{1-x}N$ alloy.

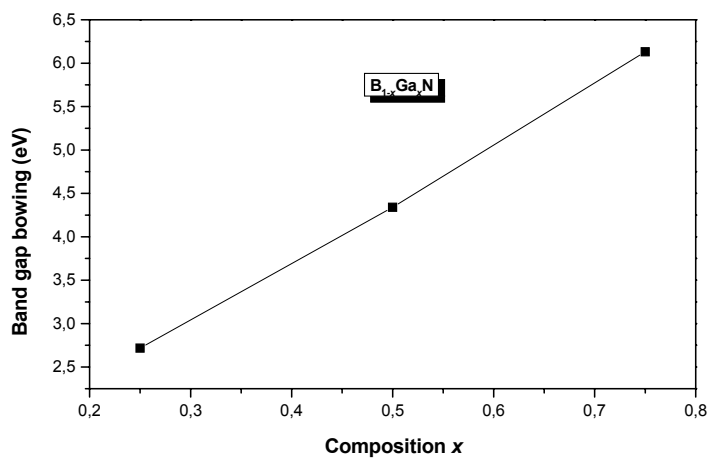


Fig. 5: The calculated optical bowing parameter as a function of concentration.

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 (Ref. [35]), using FP-LAPW (Wien2k). Our results show a strong dependence of the band gap bowing factor on composition and lattice parameter.

Acknowledgements

We would like to thank Dr. S.Beah from Bejaia University, Algeria, for his documentation material help.

References

- [1] H. Kawnishi, T. Honda, *Photonics Based on Wavelength Integration and Manipulation*, pp. 19–24 (2005)
- [2] H. Okuyama, T. Miyajima, Y. Morinaga, F. Hiei, M. Ozawa, K. Akimot, *Electron. Lett.* **28** (1992)1798
- [3] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, WIEN2k, *an Augmented-Plane-Wave + Local Orbitals Program for Calculating Crystal Properties* (Karlheinz Schwarz, Techn Wien, Austria, 2001)
- [4] R. Dreizler, E. K.U. Gross, *Density-Functional Theory* (Springer, New York, 1990)
- [5] J. P. Perdew, S. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77** (1996) 3865
- [6] D. M. Ceperley, B. J. Alder, *Phys. Rev. Lett.* **45** (1980)556
- [7] J. P. Perdew, Y. Wang, *Phys. Rev. B* **45** (1992)13244
- [8] K. Schwarz, 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, L. Nordström, *Phys. Rev. B* **64** (2001)195134,
- [11] G. H. K. Madsen, B.B. Iversen, P. Blaha, K. Schwarz, *Phys. Rev. B* **64** (2001)195102
- [12] D. D. Koelling, B.N. Harmon, *J. Phys. C* **10** (1977)3107
- [13] H. J. Monkhorst, J.D. Pack, *Phys. Rev. B* **13** (1976)5188
- [14] S. Larach, R. E. Shrader, C. F. Stocker, *Phys. Rev.* **108** (1957) 587
- [15] A. Ebina, M. Yamamoto, T. Takahashi, *Phys. Rev. B* **6** (1972) 3786
- [16] J. A. Van Vachten, T. K. Bergstresser, *Phys. Rev. B* **1** (1970)3351
- [17] D. J. Chadi, *Phys. Rev. B* **16** (1977)790
- [18] M. Rabah, B. Abbar, Y. Al-Douri, B. Bouhafs, B. Sahraoui, *Mater. Sci. Eng. B* **100** (2003) 163
- [19] A. Baldereschi, E. Hess, K. Maschke, H. Neumann, R. K. Schulze, K. Unger, *J. Phys. C* **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] W. Sekkal, B. Bouhafs, H. Aourag, M. Certier, *J. Phys.: Condens. Matter* **10** (1998) 4975
- [23] R. Wentzcovitch, K.J. Chang, M. L. Cohen, *Phys. Rev. B* **34** (1986) 1071

- [24] R. Wentzcovitch, M. L. Cohen, Pui K. Lam, Phys. Rev. B **36** (1987) 6058
- [25] P. Rodriguez-Hernandez, M. Gonzalez-Diaz, A. Munoz, Phys. Rev. B **51** (1995) 14705
- [26] E. Knittle, R. M. Wentzcovitch, R. Jeanloz, M. L. Cohen, (London) Nature **337** (1989)349
- [27] O. Madelung, *Numerical Data and Functional Relationships in science and Technology*, Physics of Group IV Elements and III-V Compounds, Landolt-Börnstein, Vol. 17, Springer, Berlin, (1982)
- [28] O. Madelung, *Numerical Data and Functional Relationships in science and Technology -Crystal and solid state physics*, Vol. III, Landolt-Börnstein, (Springer, Berlin, 1972)
- [29] V. A. Pesin, Sverktverd, Mater. **6** (1980)5
- [30] P. E. Van Camp, V. E. Van Doren, J. T. Devreese, Phys. Stat. Sol. (b) **146**(1988) 573
- [31] K. Karch, F. Bechstedt, Phys. Rev. B **56** (1997)7404
- [32] G. Q. Lin, H. Gong, P. Wu, Phys. Rev. B **71** (2005) 085203
- [33] Z. Charifi, F. El Haj Hassan, H. Baaziz, Sh. Khosravizadeh, S. J. Hashemifar, H. Akbarzadeh, J. Phys.: Condens. Matter **17** (2005) 7077
- [34] S. H. Wei, A. Zunger, Phys. Rev. B **43** (1991)1662
- [35] H. Baaziz, Z. Charifi, F. El Haj Hassan, S. J. Hashemifar, H. Akbarzadeh, Phys. Stat. Sol. (b) **1** (2006)10
- [36] C. H. Grein, R. G. Radtke, H. Ehrenreich, C. Chauvet, E. Tournié, J. P. Faurie, Solid State. Commun. **123** (2002)209
- [37] S. Savrasov, D. Savrasov. Phys. Rev. B **46** (1992) 12181
- [38] S. Y. Savrasov, Phys. Rev. B **54** (1996) 16470
- [39] J. P. Perdew, Y. Wang, Phys. Rev. B **46** (1992) 12947
- [40] P. Blochl, O. Jepsen, O.K. Andersen, Phys. Rev. B **49** (1994) 16223
- [41]- S. Q. Wang, H. Q. Ye. J. Phys. Condens. Matter **14** (2002) 9579
- [42] A. F. Wright and J. S. Nelson, Phys. Rev. B **51** (1995) 7866 Phys. Rev. B **50** (1994) 2159
- [43] M. Fuchs, J. L. Da Silva, C. Stampfl, J. Neugebauer, M Scheffler, Phys. Rev. B **65** (2002) 245212
- [44] A. Trampert, O. Brandt, K. H. Ploog, in *Crystal structure of group III Nitrides*, Vol. 50 (Academic, San Diego, 1998)
- [45] M. E. Sherwin, T. J. Drummond, J. Appl. Phys. **69** (1991)8423
- [46] W. A. Harison, *Electronic Structure and the properties of Solids*, pp. 176, (Dover, New York, 1989)
- [47] I. Vurgaftman, J. R. Meyer, L. R. Ram-Mohan, J. Appl. Phys. **89** (2001) 5815
- [48] F. D. Murnaghan, Proc. Natl. Acad. Sci. USA **30** (1947) 244 J. R. Macdonald, D. R. Powell, J. Res. Nat. Bur. Stand. A **75** (1971) 441
- [49] L. Vegard, Z. Phys. **5** (1921)17
- [50] S. N. Rashkeev, W. R. L. Lambrecht, Phys. Rev. B **63** (2001) 165212
- [51] F. El Haj Hassan, H. Akbarzadeh, Mater. Sci. Eng. B **21** (2005) 170
- [52] Z. Dridi, B. Bouhafs, P. Ruterana, Comput. Mat. Sci. **33** (2005)136
- [53] C. Vérié, Mater. Sci. Eng. B **43** (1997) 60; J. Cryst. Growth **184** (1998) 106
- [54] S. N. Rashkeev, W. R. L. Lambrecht, Phys. Rev. B **63** (2001) 165212
- [55] M. -H. Tsai, F. C. Peiris, S. Lee, J. K. Furdyna, Phys. Rev. B **65** (2002) 235202
- [56] J. E. Bernard, A. Zunger, Phys. Rev. B **36** (1987) 3199
- [57] W. R. L. Lambrecht, B. Segall, S. Strite, G. Martin, A. Agarwal, H. Morkoc, A. Rockett, Phys. Rev. B **50** (1994)14155
- [58] I. Vurgaftmana, J. R. Meyer L. R. Ram-Mohan, J. Appl. Phys. **89** (2001) **5815** I. Vurgaftman, J. R. Meyer, J. Appl. Phys. **94** (2003) 3675

- [59] C. H. Wei, Z. Y. Xie, J. H. Edgar, K. C. Zeng, J. Y. Lin, H. X. Jiang, C. Ignatiev, J. Chaudhuri,
D. N. Braski, “*Growth and Characterization of $B_xGa_{1-x}N$ on 6H-SiC (0001) by MOVPE*”, MRS Internet J. Nitride Semicond. Res. **4S1** (1999) G3.79
- [60] F. Chicker, B. Abbar, B. Bouhafs, P. Ruterana, Phys. Stat. Sol. (b) **241** (2004) 305