Computational Investigation Of Elastic Properties Of Nitride Compounds

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Abstract: *An investigation into the elastic properties of the In GaN compound under high pressure and high temperature was conducted using first-principles calculations based on density functional theory. For the calculation of the elastic properties we have used the Vinet EOS theory of state based on the augmented plane wave (APW) and quantum statistical methods. In this work we have used the all-electron full-potential linear muffin tin orbital (FP-LMTO) method augmented by a plane-wave basis (PLW) to calculate the total energies as well as the basic ground state properties. Exchange-correlation has been accounted for within LDA using the exchange-correlation potential calculated by Vosko et al. and Perdew et al. The results of the calculated properties for the considered compound are discussed and compared to the theoretical works as well as to the experimental data. We have also applied this computational method to InGaN alloys to check its transferability to predict the linear optical and thermodynamic properties from those of their parent compounds.*

Keywords: *Elastics Properties, (In, Al, Ga) N, equation of state, LMTO methods.*

I. Introduction

III-nitride semiconductors have been realized for many commercial light emitters and detectors in short wavelength regime over the last decade. The InGaN semiconductors alloy is of considerable importance for short and medium wavelength optoelectronics and photonics. InGaN is used as tremendous impact on many important systems technologies [1], [2].

In the last few years a lot of progress has been made in developing ab initio methods to compute the total energy, electronic structure and elastic properties of molecules, clusters and solid state systems. The elastic constants of the materials at high pressures are essential in order to predict and understand material response, strength, mechanical stability and phase transitions. The accurate measurement of these quantities is a difficult task due to difficult experimental conditions at high pressure. With the advances in ab initio methods, it is possible to compute a systematic study of the elastic properties as well as electronic and optical properties of materials at elevated pressure conditions. InGaN system crystallizes in the cubic zincblende and wurtzite structures at ambient pressure. It is clear that pressure and temperature are certainly critical parameters for the structural stabilities, and electronic and optical properties. The aim of this present work therefore is to explore the influence of these effects on the electronic and optical properties of the InGaN system and to show their direct consequence on the optoelectronic devices.

The most important technical details of our calculations are discussed in Computational method. The core of the article appears in the results and discussion, where the results are presented and analyzed. The article ends with a short exposition of the main results in tables.

II. Computational Method

In the present work, the calculations were performed in two steps using different approaches based on the local density approximation LDA from the density functional theory using the parameterization of *Vosko et al* [3] and also of Perdew et al [4]. We use the Savrasov version of the full potential linear muffin-tin orbital (FP-LMTO) method augmented with a plane wave basis (PLW) [5]. The non overlapping muffin tin spheres potential is expanded in spherical harmonics inside the spheres and Fourier transformed in the interstitial regions.

In this work, the orbital $3d^{10}$, $4s^2$, $4p^1$ of Ga, $4d^{10}$, $5s^2$, $5p^1$ of In, $2s^2$, $2p^3$ of N , and $3s^2$, $3p^1$ of Al are all included into the self-consistent treatment, i.e viewed as valence electrons. We use for GaN, AlN and AlN the value 8 for the parameter RMK_{max} which determines the matrix size, where K_{max} is the PW cut-off and RM (R_{Ga}, R_N are Muffin-tin radius equal to 8 for the Ga and N atoms, respectively with RGa = *1.59* and *R*N=1.87), for the ternary alloys (example: InGaN, AlGaN) the value (R_N are muffin-tin radius equal to 8,75 au for the Ga and N atoms, respectively with *R*Ga = 2*.08*, *R*In = 2*.08* and *R*N = 1.71).

In order to overcome the complexity of the EOS, the common practice is that the temperature of the substance is raised first and then the substance is compressed along the isotherm of interest. The relevant equations are called the thermal and isothermal EOSs, respectively [6, 7]. The thermal EOS is used to calculate the volume at atmospheric pressure and temperature *T*, compressed along the isotherm of interest *V*0, *T*. It is also necessary to know the temperature effect on the bulk modulus, B0 (T). Using the values of the volume and the bulk modulus at the corresponding temperature the isothermal EOS calculates the effect of pressure by incorporating the first and second derivates of the bulk modulus, $(\partial B/\partial P)_T$ *and* $(\partial^2 B/\partial P^2)_T$, at the given temperature.

The indium gallium nitride (InGaN) semiconductor materials have received much attention in the past few years due to their important applications in the blue-green light emitting diodes (LED) and the short wavelength laser diodes [8,9].The phase behaviour, structural parameters, bulk modulus, its pressure derivative and the equilibrium lattice parameters have been obtained by fitting Birch-Murnaghan EOS [10].

The elastic constants of the materials at high pressures are essential in order to predict and understand material response, strength, mechanical stability and phase transitions.

The EOS of a III-V can be described in a general form as a functional relationship between the pressure, volume, and temperature as

$$P(V,T) = P_{St}(V,300) + P_{th}(V,T) \quad (1)$$

Where $P(V,T)$ represents the pressure and volume V and temperature T, $P_{St}(V,300)$ and $P_{th}(V,T)$ represent the static pressure at volume V and 300K, and the thermal pressure at volume V and temperature T, respectively.

The modification has been incorporated such that the Vinet EOS becomes consistent with the extreme compression behaviour of solids predicted from the quantum statistical models [11.12] which can be formulated as follow:

$$P = 3B_0 \times K^{\frac{-5}{3}} \times G \times \exp\left[\frac{3}{2}\left(B_0^{'} - 3\right) \times G + \left(Y - \frac{3}{2}\right) \times G^2\right] \quad (2)$$

Where $K = \frac{V}{V_0}$, $G = \left(1 - K^{\frac{1}{3}}\right)$ and

$$Y = \left(\frac{3}{8}\left(B_0^{'} - 1\right)\left(B_0^{'} + 3\right) + \frac{3}{2}B_0 B_0^{''} + \frac{1}{3}\right)$$

Here B_0, $B_0^{'}$ and $B_0^{''}$ are respectively the values of isothermal bulk modulus *B* and its pressure derivatives (dB/dP) and $(d^2B/dP^2)_V$. The value of T_0 is 300K.

III. Results and Discussion

The theoretical ground-state parameters B_0, $B_0^{'}$ and B_0 $B_0^{''}$ of $In_{0.5}Ga_{0.}$ Are obtained and listed in Table I,

V (bohr3)	B_0(GPa)	B_0'	$-B_0.B_0$''
763.93	72.21	4.9813	18,34062
763.99	72.13	4.9956	18,56807
764.50	71.56	5.0606	19,22574
766.58	69.74	5.2216	20,335
769.20	67.64	5.3936	21,3526
771.90	65.52	5.5718	22,38563
775.14	63.15	5.7735	23,49767
778.54	60.71	5.9899	24,64583
782.10	58.21	6.2236	25,8616
785.89	55.60	6.4789	27,14525
789.77	52.97	6.7527	28,50215
794.33	50.04	7.0700	29,96375

Table 1. Elastic parameters of Cubic $In_{0.5}Ga_{0.5}N$

Figure 1 illustrates curve of the $-B_0.B_0$''calculated as a function of pressure derivatives bulk modulus B_0' according to Eq (2). An expression for the isothermal bulk modulus B_T is obtained by differentiating the Vinet EOS (Eq (2).

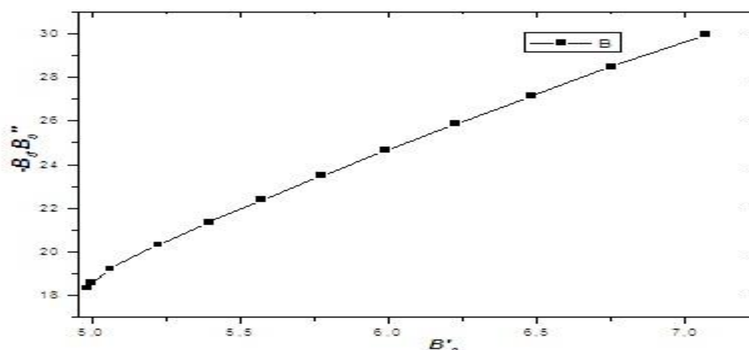

Figure 1. Relationship between B'_0 and B_0B_0''

To analyze the structural properties, the equilibrium lattice parameters are calculated within the method seen previously using the habitual minimization procedure. The total energy was calculated for different values of the lattice constant, and the ground state corresponds to the lowest value of the total energy. Fig. 2 shows the total energy as a function of volume for In0.5Ga0.5N, AlN and InN in the zincblende (8 atoms). The curves were obtained by calculating the total energy E at many different volumes around equilibrium and by fitting the calculated values to the Murnaghan/Birch [10] equation of state. In order to make easier the comparison of our results, we have plotted the E-V diagram for the zincblende phase.

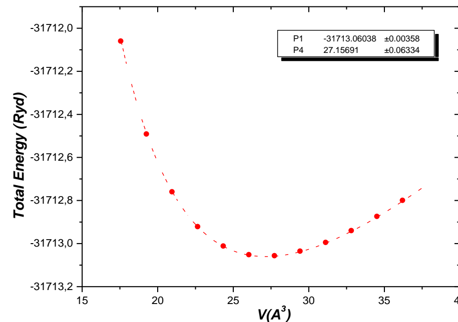

Figure 2. Calculated total energy versus relative volume for $In_{0.5}Ga_{0.5}N$

The results of the site-projected partial density of states are shown in Fig. 3. There is not just one way to perform this atom and orbital decomposition, so the results should be interpreted qualitatively. The lower valence bands ranging from 2.51 to -3.50 eV has significant contribution from Ga-d orbitals.

The intermediate subband between -4.4 and -2 eV, originates from In/Ga-s orbitals. The higher-energy set of valence bands can be further divided into two subbands. The lower-energy subband from -4.6 to -0.6 eV is originates from In/Ga/N-p band. The higher-energy subband from -2.4eV up to Fermi level (EF) are consists of N/s and In/Ga-p states. The conduction band running from 0.5 eV consists of admixture of Sb- s/p/, In-s/p/d and Ga-s/p states. From the partial density of states one can see that there exist a strong hybridization between Ga-p and Ga-s between -4 eV up to E_F.

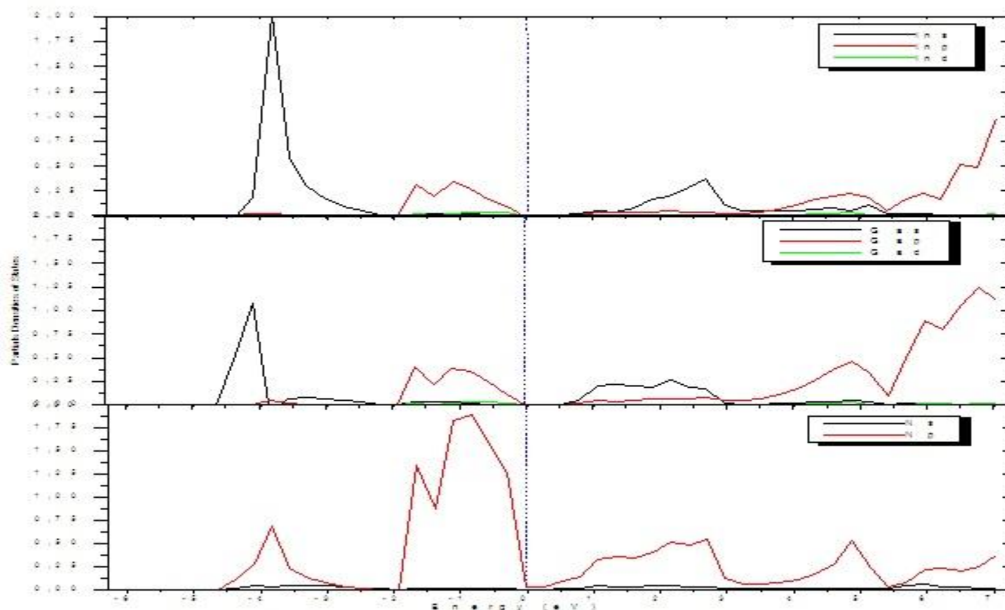

Figure 3. Partial densities of states of Cubic $In_{0.5}Ga_{0.5}N$.

The results of the fit of our *Pressure-Volume-Temperature (P-V-T)* data to the thermal pressure EOS are summarized in Table 3. Figure 4 shows the *P-V-T* data from both the experiments and calculations carried out in our study. The values of $\alpha B_T(V_0,T)=\frac{\partial P}{\partial T}$ where $\alpha=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)$ was 0.00244236. This result is in general agreement with previous studies [13, 14and 15].

A Vinet EOS fitted to the room temperature data fielded an isothermal bulk modulus of *BT0* = 67.64GPa and a pressure derivative of *BT0'* = 5.3936. The high-temperature data from the first-principles calculations were fitted to the thermal pressure EOS. The resulting calculated parameter of the thermal pressure αBT *(V0, T)* was 2.44 x 10-3 (GPa/K).
To assess the influence of different EOSs, we calculated the parameters from our pressure volume
data using different EOSs. The difference in parameters is significant. As InGaN is unstable at pressures lower than 25 GPa [16,17 and 18].

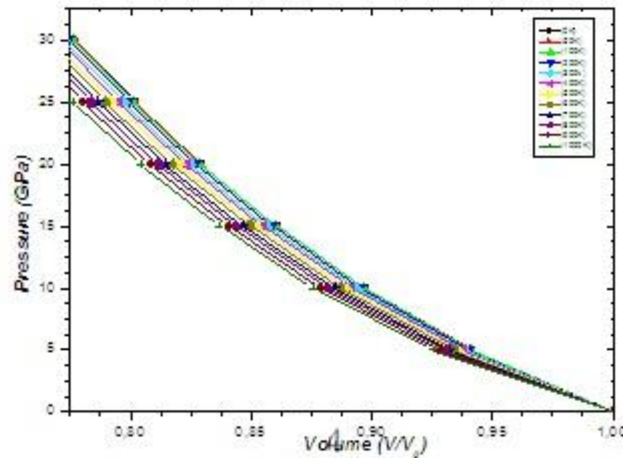

Figure 4. Pressure-volume data for $In_{0.5}Ga_{0.5}N$. The circles and diamonds denote the volumes from the first-principle calculations at temperatures from 0 to 1000 K.

Parameters For V_0 at 0GPa and 300K	Values
$V_0(Bohr)^3$	769.20
B_{T0} (GPa)	67.64
B'_{T0} (GPa)	5.3936
$\alpha B_T(V_0,T)=\frac{\partial P}{\partial T}$ (GPa/K)	0.002442360

Table 2. The thermoelastic parameters of Cubic $In_{0.5}Ga_{0.5}N$

We calculate the elastic properties of InN, GaN and InGaN by computing the components of the stress tensor for small strains, using the method developed recently by Charpin [19, 20]. It is well known that a cubic crystal has only three independent elastic constant C11, C12 and C44. So a set of three equations is needed to determine all the constants, which means that three types of strain must be applied to the starting crystal. The first type involves calculating the elastic modulus (C11 + 2C12), which are related to the bulk modulus *B:*

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

The elastic constants of the cubic materials are shown in Table 3. we compare our main finding of zincblende AlN and GaN, this table also shows the elastic constants obtained from first-principles LAPW computations and calculations works [21,22,23,24]. The accuracy of the elastic constants C11, C12 and C44 is remarkably good.
For comparison, the first-principles results also differ from the calculations works by less than 3%,.

	GaN[25]	GaN	AlN[25]	AlN	InN[25]	InN	InGaN[26,27]	InGaN
C11(Gpa)	293	277	304	311	187	170	240	233.5
C12(Gpa)	159	162	160	155	125	131	159.5	145
C44(Gpa)	155	171	193	200	86	93	120.5	133

Table 3. Elastic parameters of Cubic $In_{0.5}Ga_{0.5}N$

IV. Conclusion

Full potential linear muffin-tin orbital method (FP-LMTO) within the density functional theory has been applied to study the electronic and thermal properties of ternary alloys InGaN in cubic phase using the density functional theory with LDA. The local density approximation has been used with and without generalized gradient correction based on exchange-correlation energy optimization. The calculated energy allowed us to investigate several structural properties such as lattice

parameter, bulk modulus and its pressure derivative. Our calculated lattice parameter is found to be in reasonable agreement with other theoretical works.

The numerically calculated values showed generally reasonable agreement with the available experimental and other calculations for the electronic and thermal properties only (Dos, three independent elastic constant C11, C12 and C44…).

The results obtained for the P-V-T relationships in the present study give information regarding higher order thermodynamic likes the isothermal P-V relationship which yields the bulk modulus. It is found from the results that bulk modulus increases with the increase in pressure whereas it decreases with the increase in temperatures. The additional advantages of the EOS are that the expression is simple and allows calculating some required variables.

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