Pressure induced phase transition of XN (X=B, Ga) compounds

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Abstract. The pressure induced phase transition, volume collapse and elastic properties have been investigated by means of two different models (1) modified interaction potential model (MIPM) which includes the three body interaction, covalency effect, overlap repulsive interaction up to second neighbour ions and van der Waal interaction. (2) Interaction potential model (IPM) which exclude the covalency effect in previous (IPM) model. The BN and GaN transform from B3 to B1 structure under high pressure (p= 555 GPa and 37GPa) and show the volume collapse of 3.6% and 16.53%. The elastic constants have also been obtained. The results are in good agreement with the experimental and theoretical data where available.

1. Introduction
Group III- nitrides generally crystallize in wurtzite (W) structure, but zinc-blend (ZB) structure have been synthesized by epitaxial growth on suitable substrates [1]. The ZB phase has several advantages for device applications including easy cleavage, smaller band gap, and higher carrier mobilities [1]. Cubic BN exhibits three different structures hexagonal, cubic zinc-blend structure and wurtzite structure. But in zinc-blend structure the properties of BN such as high melting point, high thermal conductivity and extreme hardness make it useful for protective coatings which are related to their mixed ionic and covalent bonding [2]. The experimental studies on III-nitrides are less reported. Among these the elastic constants at zero pressure have been performed experimentally for BN only [3]. By using FP-LAPW method Zaoui et al.[4] found that the transition pressure from ZB (zinc-blend) →RS (rock-salt) is 550 GPa. Furthermore Christensen et al [5] concluded that the pressure was 850 GPa by using linear muffin-tin orbital (LMTO) calculation. The transformations from ZB→RS have also been reported by Serrano at pressure 42.1GPa for GaN [6]. N.E. Christensen et. al have been studied the optical and structural properties of III-V nitrides by using band structure and total energy calculations. These calculations were made by means of the linear muffin tin orbital (LMTO) method. They conclude that all nitrides transform from W →RS phase and BN transform from ZB→RS at pressure 850 GPa. First-principle pseudo potential method shows that BN transform from ZB→RS phase at pressure 1088 GPa with a volume reduction of 3.1% [7]. M.B. Kanoun et.al [8] was studied the pressure dependence of elastic constants of BN, AlN, GaN and InN by using first-principle full potential augmented-plane wave plus local orbital (FP-APW+lo) calculations with density functional theory in local density approximation.

The structural, mechanical and electronic properties of III- nitrides compounds have been studied by various first-principle calculations. Inspite of the above electronic, structure calculations, there is no study available using phenomenological model. The nature of interatomic forces is not well understood in these compounds. So phenomenological models based on various interatomic interaction energies to determine stable structures become important. First-principle calculations have their own disadvantages as generally van der Waals interactions are ignored in them. In the present paper, we report the structural and elastic properties of XN (X= B, Ga) compound by using modified interaction potential model (MIPM) and interaction potential model (IPM). Since the compounds are partially covalent in nature so the IPM is modified by taking covalency effect.
2 Present potential model and method of computation

To study the phase transition, elastic and thermo physical properties of XN (X=B, Ga) we have developed the (1) MIPM and (2) IPM. The MIPM consist of long-range coulomb attraction, three-body interaction modified by covalency effect, short-range overlap repulsive interaction and van der Waal interaction. A complete study has been made with IPM, which is similar to MIPM except that covalency effects have been excluded from it. The application of pressure on the crystal causes the decrease in their volume, which in turn leads to an increased charge transfer (or exchange) between the overlapping electron shells of the adjacent ions [9]. These TBI effects have been incorporated in the Gibbs free energy \( G = U + PV - TS \). Here, \( U \) is the lattice energy which at \( T=0K \) is equivalent to the lattice energy, \( S \) is the vibrational entropy at absolute temperature \( T \). At \( T=0K \) and pressure \( P \), the Gibbs free energy for the zinc-blend (B3, real) and NaCl (B1, hypothetical) structures are given by

\[
G_{B3}(r) = U_{B3}(r) + PV_{B3}
\]

\[
G_{B1}(r') = U_{B1}(r') + PV_{B1}
\]

With \( V_{B3} \) (3.08 \( r^3 \)) and \( V_{B1} \) (2.00 \( r'^3 \)) as unit cell volumes for B3 and B1 phases, respectively. The first term in (1) and (2) are lattice energies for B3 and B1 structures and they are expressed as

\[
U_{B3}(r) = -\frac{\alpha M e^2 Z^2}{r} - \frac{4\alpha M e^2 Z f_m(r)}{r} - \left[ \frac{C}{r^6} + \frac{D}{r^8} \right] + 4b\beta_{ij} \exp(r_i + r_j - r_{ij}/\rho) + 6b\beta_{ij} \exp(2r_i - 1.63r_{ij}/\rho) + 6b\beta_{ij} \exp(2r_j - 1.63r_{ij}/\rho)
\]

\[
U_{B1}(r') = -\frac{\alpha' M e^2 Z^2}{r'} - \frac{6\alpha' M e^2 Z f_m'(r')}{r'} - \left[ \frac{C}{r'^6} + \frac{D}{r'^8} \right] + 6b\beta_{ij} \exp(r_i + r_j - r_{ij}/\rho) + 6b\beta_{ij} \exp(2r_i - 1.414r_{ij}/\rho) + 6b\beta_{ij} \exp(2r_j - 1.414r_{ij}/\rho)
\]

With \( \alpha_M \) and \( \alpha'_M \) as the Madelung constants for ZnS and NaCl structures, respectively. \( C \) \((C') \) and \( D \) \((D') \) are overall van der Waal coefficients of B3 (B1) phases, \( \beta_{ij} \) \((i,j=1,2) \) are the Pauling coefficients defined as \( \beta_{ij} = 1 + (Z_i/n_i) + (Z_j/n_j) \) with \( Z_i \) \((Z_j) \) and \( n_i \) \((n_j) \) are the valence and the number of electrons of the \( i \) \((j) \)th ion. Ze is the ionic charge and \( b \) \((\rho) \) are the hardness \((range) \) parameters, \( r(r') \) are the nearest neighbour separation for ZnS (NaCl) structure. \( f_m(r) \) is the modified three-body force parameter which includes the covalency effect with three-body interaction \( r_i \) \((r_j) \) are the ionic radii of ions \( i \) \((j) \). These lattice energies consist of long range Coulomb energy \((first \ term) \), modified three-body interactions corresponding to the nearest neighbour separation \( r \) \((r') \) \((second \ term) \), van der Waal interaction \((third \ term) \), energy due to the overlap repulsion represented by Hafemeister and Flygare \((HF) \) type potential and extended up to the second neighbour ions \((forth, fifth and sixth terms) \).

We have included the effect of covalent forces in three-body force parameter \( f(r) \) on the lines of Motida [10]. In the present model \( f_m(r) \) is assumed to be constructed by two parts, i.e.

1. due to covalency \( f_{cov}(r) \)
2. due to overlap distorted effect \( f_{TBI}(r) \)

Now modified three-body parameter \( f_m(r) \) becomes

\[
f_m(r) = f_{TBI}(r) + f_{cov}(r)
\]

3. Results and discussion

The present interaction potential model (IPM) contains three model parameters \( b, \rho \) and \( f(r) \), namely hardness, range and three-body force parameter. We have modified the three-body force parameter \( f_m(r) \) by including covalency effect in the modified interaction potential model (MIPM). These parameters are calculated by using the first derivative of lattice energy \((U) \) and equilibrium condition expressed as:
\[ \frac{dU}{dr}, \ldots = 0 \quad \text{and} \quad B1 + B2 = -1.261 \ Z \ [Z + 8 \ f(r)] \] (6)

The input data and model parameters are given in table 1. As the stable phase is always associated with minimum of energy, we have minimised \( G_{B3}(r) \) and \( G_{B1}(r') \) at different pressures in order to obtain inter ionic separations \( r \) and \( r' \) for B3 and B1 phases respectively associated with minimum energies.

**Table 1** Input and model parameters of XN (X=B, Ga) compounds.

|                  | Input parameters | Model parameters |
|------------------|------------------|------------------|
|                  | \( r_1 (\text{Å}) \) | \( r_2 (\text{Å}) \) | \( a (\text{Å}) \) | \( b (10^{-12} \text{ ergs}) \) | \( \rho (\text{Å}) \) | \( f(r) \) | \( f_m(r) \) |
| BN               | 1.2              | 1.71             | 3.615           | 0.076           | 0.314           | -0.0647 | -0.0053 |
| GaN             | 0.62             | 1.71             | 4.50            | 0.1557          | 0.160           | -0.0234 | -0.0364 |

We have evaluated the corresponding \( G_{B3}(r) \) and \( G_{B1}(r') \) and their respective differences \( \Delta G = G_{B3}(r) - G_{B1}(r') \). A positive value of \( \Delta G \) at zero pressure justifies the stability of B3 phase. As the pressure is increased these values of \( \Delta G \) decrease and approach to zero at the transition pressure (\( P_t \)). Beyond this pressure \( \Delta G \) becomes negative as the phase B1 become stable. It is found that the phase transition pressures from MIPM (IPM) is at 555 (556) GPa and 37 (38) GPa for BN and GaN are presented in table 2 and compared with the available results. The first order phase transition involving discontinuity in volume take place at the phase transition pressure. At elevated pressures, the materials undergo structural phase transition associated with a sudden change in the arrangement of the atoms. The atoms are rearranged in new position leading to a new structure. Experimentally one usually studies the relative volume change associated with the compressions. The discontinuity in volume at the transition pressure is obtained from the phase diagram. The compression curves are plotted in figure 1 to show equation of state (EOS). The values of the volume collapses (%) are depicted in table 2. It is clear from figure 1 that the volume of BN decreases up to 555 GPa, an abrupt decline in volume is observed at this pressure which is observed in first-order transformation associated with structural change from B3 \( \rightarrow \) B1 phase. Similar trend is observed in GaN too. The EOS obtained from MIPM show good agreement with available theoretical results [7, 11] than IPM, which show a small deviation from MIPM and others [7, 11]. This difference is due to the exclusion of covalency effect in IPM.

**Table 2** Input and model parameters of XN (X=B, Ga) compounds.

|                  | Phase transition pressure (GPa) | Volume collapse (%) | Elastic constants (GPa) |
|------------------|--------------------------------|---------------------|------------------------|
|                  |                                | \( C_{11} \) | \( C_{12} \) | \( C_{44} \) |
| BN               | MIPM                           | 555                | 3.6                   | 819                 | 189.6               | 475 |
|                  | IPM                            | 556                | 3.7                   | 817                 | 188                 | 474 |
|                  | Exp. [3]                       | -                  | -                     | 820                 | 190                 | 480 |
|                  | Other [7, 4]                   | 1088, 555          | 3.1                   | 801.26              | 159                 | 456.9 |
| GaN             | MIPM                           | 37                 | 16.53                | 278                 | 177                 | 186.9 |
|                  | IPM                            | 38                 | 16.0                 | 277                 | 176                 | 185  |
|                  | Exp.                           | -                  | -                    | -                   | -                   | -    |
|                  | Other [11, 8]                  | 37                 | 17                   | 274.2               | 166.1               | 199  |

and give important information about nature of forces operating in solids. The study of elastic properties is also essential to understand the chemical bonds and cohesion of material. In order to obtain the values of elastic constants we have used the method reported in our earlier work [9]. The second order elastic constants (SOECs) have been obtained and they are given in table 2. The calculated SOECs are compared with experimental data and others [3, 7-8]. It is clear from table 2
that values of SOECs obtained from MIPM are good agreement with experimental data than IPM and others [7-8] where available.

4. Conclusion
We have applied Modified interaction potential model (MIPM) and interaction potential model (IPM) to investigate the structural phase transition and elastic properties of XN (X=B, Ga) compounds. An overall assessment shows that, our values of MIPM near to available experimental data and they are in general better matching than other theoretical results and IPM. Finally it may be concluded that the present MIPM has successfully predicted the compression curves giving the phase transition pressures, volume collapse and elastic constants for XN compounds. Our results where no experimental results are available may be tested with different theoretical and experimental methods in future.

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