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First principles calculations of structure parameters and transition pressures of $GaN_{1-x}Bi_x$ alloys

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In this work, we have studied the structural properties of $GaN_{1-x}Bi_x$ ternary alloys using the pseudopotentiel method. We have calculated properties of these alloys in zinc blende, rocksalt and wurtzite structures at atmospheric and under hydrostatic pressure. The calculated lattice parameters increase by increasing bismuth composition, while a little deviation from Vegard's law is observed. We have shown that for $x = 0$ and 0.25, the wurtzite phase is the most stable, whereas for Bi concentration 0.375, 0.5, 0.75 and 1 the zinc blende phase is the most stable one. We have calculated for each case the transition pressure and we have found that our calculated values were in good agreement with those in the literature.

1. Introduction

In the last few years, bismuth containing III–V semiconductors have attracted much attention due to its possible application in different researches topics such as optoelectronic devices, laser, etc. Ternary and quaternary alloys such as InSbBi, InAsBi and InAsSbBi have been synthesized by different methods, such as Czochralski, molecular beam epitaxyand vapor phase epitaxy [1–3]. It has been demonstrated that the band gap reduction of InAsBi and InAsSbBi decreases with the addition of Bi, where the gap reduction is in the order of 55% meV/%Bi and 46 meV/%Bi for each case [3]. Oe and Okamato were the first researchers to study the incorporation of Bi into GaAs matrix [4]. It has been found that incorporation of small amount of Bi in GaAs matrix can lead to large reduction of the gap energy by about 90 meV/%Bi [5–7]. Furthermore, it has been suggested that incorporation of Bi gives rise to temperature-insensitive band gaps. Indeed, GaAsBi compound with 2.6% Bi was found to have temperature dependence $\delta E_g/\delta T = -0.15$ meV/K, or third of the temperature sensitivity of GaAs [8]. These properties have significant potential to develop heterostructure devices such as lasers for communication systems where emission wavelengths are required to remain constant under ambient temperature variation. So far most experimental studies have been focused on growth of GaAsBi, but very little on GaNBi. Levander et al. show that the addition of 11% of Bi in GaN produces a large reduction of the band gap energy of GaNBi [9], of about 200 meV/%Bi. While a gap reduction of 96 meV/%Bi has been obtained in our previous work [10]. On the other hand, a large band gap bowing of GaNBi (~ 25 eV) has been reported by Belabbes et al. [11]. This value is larger than those obtained for GaAsN and GaAsBi. The strong energy gap reduction compared to those observed for GaAsBi and InAsBi confirms our interest in this material.

In this work, we have focused on the calculation of structural properties of GaNBi alloys at atmospheric and under hydrostatic pressure. Particularly, our work's focus is in the phase transition of GaNBi with respect to Bi concentration.

2. Calculation method

In order to calculate the structural properties of $GaN_{1-x}Bi_x$ alloys, we have used the pseudo potential method as implemented in Quantum-Espresso code [12]. In this work we have adopted the local density approximation (LDA) to treat the exchange correlation effects.The kinetic energy cutoff for the plane-wave basis set is equal to 50 Ryd for the binary compounds GaN and GaBi and for their ternary alloys $GaN_{1-x}Bi_x$. The k integration over the Brillouin zone (BZ) is performed using the Monkhorst and Pack mesh [13]. A mesh of 28 special k-points in the irreducible Brillouin zone is used for the binary compounds in the cubic and wurtzite structure respectively. While a mesh of 27 k-points was used for the supercell calculations. Four compositions $x = 0.25$, 0.375, 0.5 and 0.75 have been studied in our present work.

In our case, we model the alloys at some selected compositions with the ordered structures described in terms of periodically repeated supercells containing 8 and 16 atoms per unit cell. And we also substitute one atom of the host material by one atom of Bi. Many researchers have used this method to investigate the properties of alloys [14]. For the considered structures, we peform the structural optimization by calculating the total energies for different volumes around the equilibrium cell volume V_0 of the binary compounds and their alloys. The calculated total energies are fitted by the empirical Murnaghan equation of state [15] to obtain an analytical interpolation of our computed points from which we determine the ground state properties such as the equilibrium lattice parameter (a) and bulk modulus (B).

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For Bi compositions $x = 0.25, 0.5$ and 0.75, 8 atom supercells have been used for both cubic and wurtzite structures, corresponding respectively to $1 \times 1 \times 1$ a conventional cubic cell and $1 \times 1 \times 2$ the size of the primitive wurtzite unit cell. Whereas for Bi composition $x = 0.375$, a 16 atom supercells corresponding respectively to $1 \times 1 \times 2$ a conventional cubic cell and $2 \times 2 \times 1$ the size of the primitive wurtzite unit cell. The structures were optimized with respect to lattice constants, and atomic relaxation is fully included via the Hellman–Feyman theorem [16].

3. Results and discussions

In the present study, we have focused on the calculation of the stability in three phases namely, zinc blende (B_3), rocksalt (B_1) and wurtzite (B_4) for the GaN and GaBi binary compounds and for their $GaN_{1-x}Bi_x$ ternary alloys.

We have started our calculation by studying the stability of the binary compounds GaN and GaBi in the three phases indicated below. In Fig. 1, *a* we represent the variation of the total energy (E) as function of volume (V) for the B_3-GaN, B_1-GaN and B_4-GaN. We remark that the ground state structure of GaN is the wurtzite and is slightly favored to the zinc blende one. However, the rocksalt structure is the least stable. Our result is in good agreement

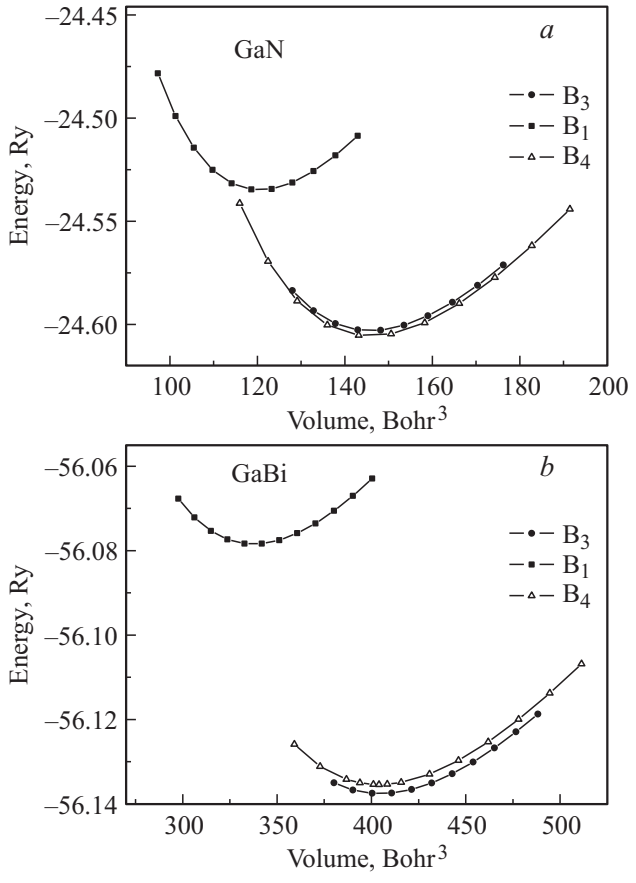

Figure 1. The variation of the total energy as a function of volume for GaN (*a*), and for GaBi (*b*).

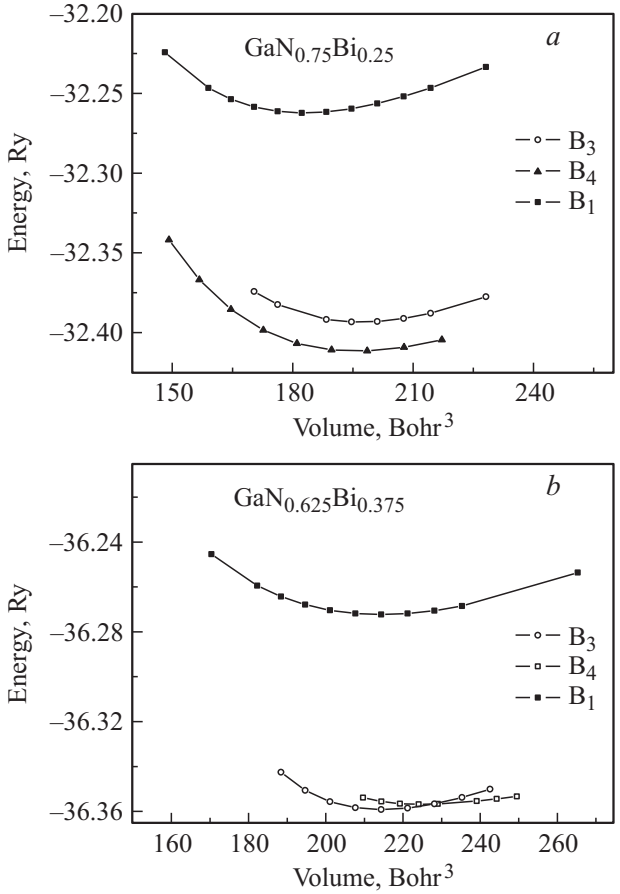

Figure 2. The variation of the total energy as a function of volume for $GaN_{0.75}Bi_{0.25}$ (*a*), $GaN_{0.625}Bi_{0.375}$ (*b*).

with those reported in the literature [17,18]. However, as shown in Fig. 1, *b* the ground state structure for GaBi is the zinc blende. This result is in agreement with those calculated by Ferhat and al [19]. On the other hand, we focused our work on the calculation of the stability of the ternary alloys $GaN_{1-x}Bi_x$ for four compositions x of Bi, $x = 0.25, 0.375, 0.5$ and 0.75. As an example, we report in Fig. 2 the result of calculation for $x = 0.25$ and 0.375. It should be noted that the zinc blende structure for the $GaN_{1-x}Bi_x$ alloys remain favored over the wurtzite and the rocksalt structure for Bi composition of 0.25. But from a composition $x = 0.375$, we can note that the zinc blende structure for $GaN_{0.625}Bi_{0.375}$ alloys becomes slightly favored over the wurtzite and the rocksalt structures. This phase transition that occurred for a composition $x = 0.375$ is also confirmed for $x = 0.5$ and 0.75, where the zinc blende structure is the most stable among the other structures. Our calculated values for each composition are summarized in Table 1.We noticed that our calculated lattice parameters for both B_3-GaN and B_3-GaNBi are underestimated with respect to those reported in our previous work [10]. This difference is mainly attributed to the difference in the calculation methods adopted in each case. On the other hand, in our present study, atoms have been relaxed the around their equilibrium position but we are neglected

Table 1. Equilibrium lattice parameter a_0, bulk modulus B_0, and pressure derivative B_0' for the B_3, B_1, and B_4 phases of $GaN_{1-x}Bi_x$ alloys

Composition x	a_0 (Å)			c_0/a_0	B_0 (GPa)			B_0'		
	B_3	B_1	B_4		B_3	B_1	B_4	B_3	B_1	B_4
0	4.42[a]	4.15[a]	3.14[a]	1.608[a]	205.7[a]	248.7[a]	201.3[a]	4.48[a]	4.30[a]	4.34[a]
	4.497[i]	4.157[i]	3.18[i]	1.632[i]	196[i]	263[i]	196[i]	4.2[i]	4.5[i]	4.3[i]
	4.50[b,c]	4.225[i]	3.16[i]	1.627[i]	205[c]	240[i]			4.6[d]	
	4.48[d]		3.14[m]	1.629[m]	206.3[d]				4.32[f]	
	4.46[f]		3.20[n]	1.631[n]	202[f]					
					190[e]					
0.25	4.88[a]	4.76[a]	3.48[a]	5.55[a]	123.1[a]	112.8[a]	101.3[a]	5.34[a]	4.80[a]	4.48[a]
	5.21[k]	–	–		99.59[k]	–	–	4.27[k]	–	–
0.375	5.04[a]	5.02[a]	3.62[a]	5.82[a]	102.8[a]	61.7[a]	60.4[a]	4.40[a]	3.44[a]	15[a]
	5.44[k]	–	–		91.41[k]	–	–	3.73[k]	–	–
0.5	5.30[a]	5.24[a]	3.82[a]	6.15[a]	80.2[a]	75.3[a]	68.1[a]	5.62[a]	4.78[a]	4.66[a]
	5.61[k]	–			92.58[k]	–	–	3.42[k]	–	–
0.75	5.77[a]	5.56[a]	4.17[a]	6.63[a]	57.9[a]	61.6[a]	50.1[a]	4.18[a]	5.32[a]	3.63[a]
	5.83[k]	–	–		105.4[k]	–	–	3.22[k]	–	–
1	6.21[a]	5.84[a]	4.40[a]	7.12[a]	45.4[a]	53.1[a]	45.3[a]	4.64[a]	4.70[a]	4.83[a]
	6.33[g]				–			–		
	6.47[h]				39.1[h]			–		
	6.32[d]				45.1[d]			4.9[d]		
	6.18[j]				46.9[j]			–		

Note. [a] Present work, [b] Ref. [20] (Expt.), [c] Ref. [21], [d] Ref. [22], [e] Ref. [24] (Expt.), [f] Ref. [23], [g] Ref. [25], [h] Ref. [19], [i] Ref. [17], [j] Ref. [27], [k] Ref. [10], [l] Ref. [28], [m] Ref. [29], [n] Ref. [30].

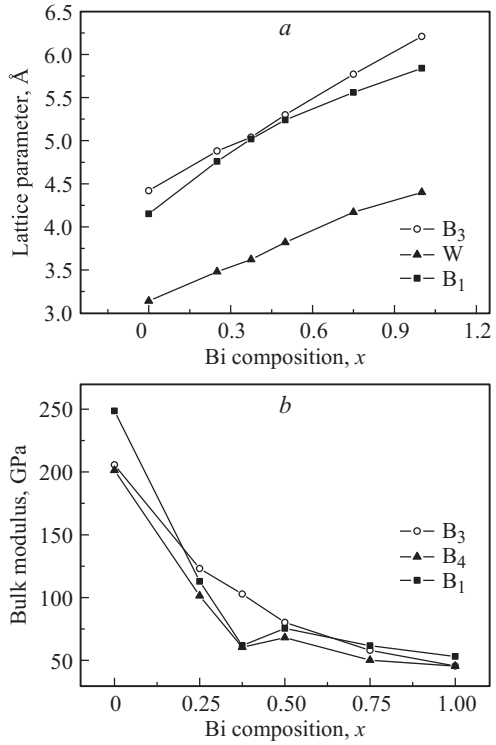

Figure 3. *a* — lattice parameter of $GaN_{1-x}Bi_x$ as function of Bi concentration x, *b* — bulk modulus of $GaN_{1-x}Bi_x$ as function of Bi concentration x.

relaxation in our previous work. Therefore, we think that our present result is the most accurate. Unfortunately, there are no results for GaNBi in the rocksalt and in the wurtzite structure for comparison.

In Fig. 3, *a*, we represent the variation of the equilibrium lattice parameter as function of Bi composition for the three phases of the $GaN_{1-x}Bi_x$ alloys. We remark that the lattice parameter increases with increasing the Bi concentration for all structures B_3, B_1 and B_4.

A quadratic fitting of the lattice parameter for the cubic structure give the following equations:

$$a_0(x) = 4.42 + 1.71x + 0.082x^2, \quad (1)$$

for zinc blende phase B_3,

$$a_0(x) = 4.15 + 2.63x - 0.96x^2, \quad (2)$$

for the rocksalt phase B_1.

For the wurtzite phase two parameters are fitted, the $a_0(x)$ and the $c_0(x)$. We obtain the following results:

$$a_0(x) = 3.14 + 1.46x - 0.17x^2, \quad (3)$$

$$c_0(x) = 5.05 + 2.2x - 0.11x^2. \quad (4)$$

We remark that the lattice parameters for the three phases show a deviation with respect to the Vegard's law, and this deviation is the most important in the case of the rocksalt

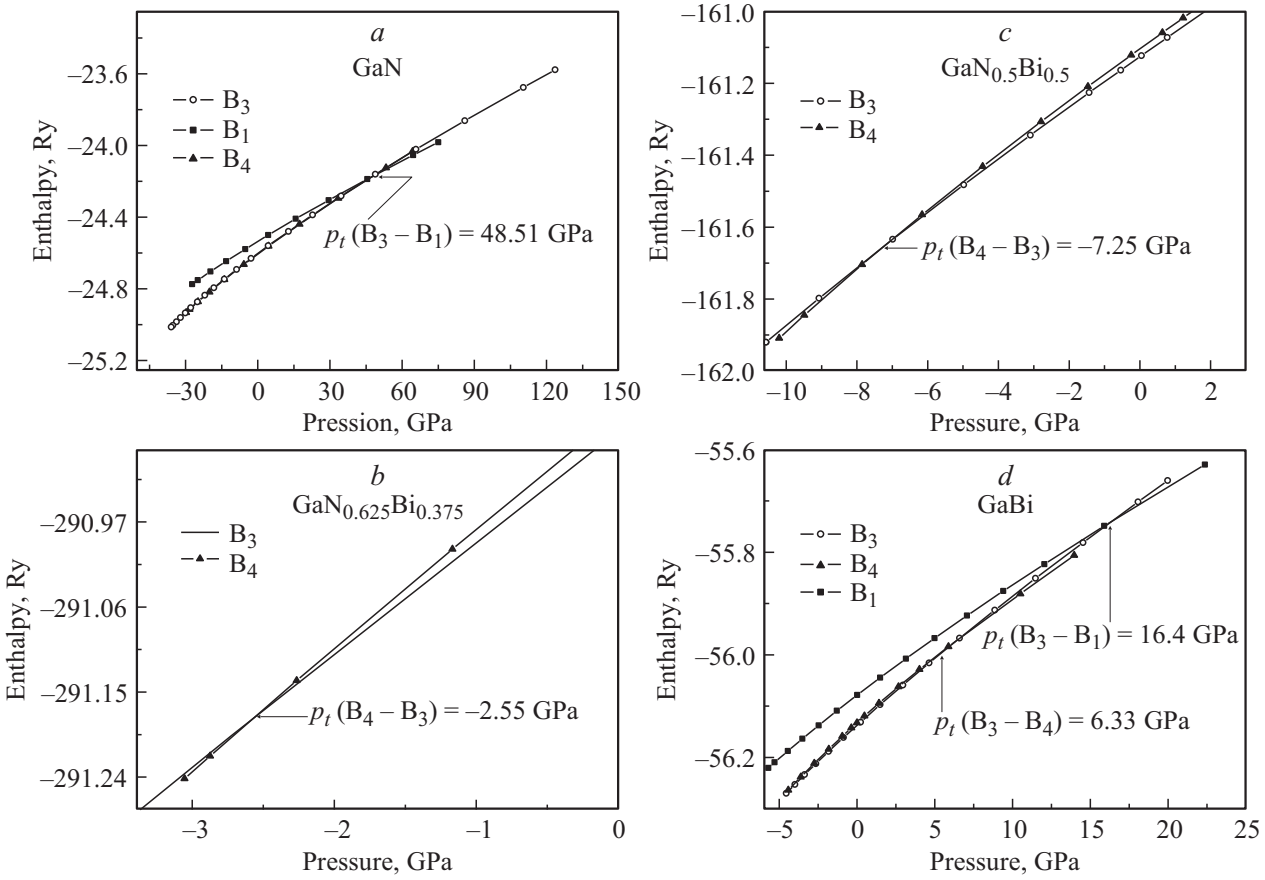

Figure 4. Enthalpy versus pressure for GaN (a), $GaN_{0.625}Bi_{0.375}$ (b), $GaN_{0.5}Bi_{0.5}$ (c), GaBi (d).

phase. We attribute the violation of Vegard's law to the relaxation effect that is not included in Vegard's law. On the other hand, we have calculated the bulk modulus (B_0) for the binary and ternary alloys for the different phases studied in this work. B_0 is property of material, which defines its resistance to volume change when compressed. It is expressed by:

$$B_0 = -V(dP/dV)_T. \tag{5}$$

We remark that our calculated values of the bulk modulus corresponding to the binary compounds GaN and GaBi in the zinc blende phase matches very well other calculated values [21–24]. When compared to experiment, our value is slightly larger than reported in reference [23]. In fact the bulk modulus is generally overestimated by the LDA approximation. Furthermore, we have studied the evolution of the bulk modulus B_0 of the three phases as function of the Bi composition. As mentioned in Fig. 3, b, as the Bi composition increases from 0 corresponding to GaN to 1 corresponding to GaBi, the bulk modulus B_0 for the three phases decreases. This result is consistent with the evolution of the lattice parameter, where the bulk modulus B_0 generally varies inversely with respect to the lattice parameter a_0.

When pressure is applied, the ternary alloys $GaN_{1-x}Bi_x$ is expected to transform from the wurtzite structure to the zinc blende one. The transition pressures (p_t) of $GaN_{1-x}Bi_x$ at various Bi contents ranging from 0 to 1 have been determined by calculating the Gibbs free energy (G). The latter is expressed as follows:

$$G = E_0 + PV - TS. \tag{6}$$

Since the Gibbs free energy is calculated at $T = 0\,\mathrm{K}$, therefore the Gibbs free energy is reduced to the enthalpy, i. e., $H = E_0 + PV$. Since the variation of H versus pressure allowed us to obtain the transition pressure for the $GaN_{1-x}Bi_x$, the latter has been calculated for each phase as function of pressure for different Bi compositions. As an example, we have plotted in Fig. 4 the enthalpy evolution with respect to the pressure for the binary compounds GaN and GaBi and for their ternary alloys and $GaN_{0.75}Bi_{0.25}$ and for $GaN_{0.625}Bi_{0.375}$. For GaN, we can note that the pressure transition from B_3 to B_1 phase is occurred at $p_t = 46.5\,\mathrm{GPa}$ (see Fig. 4, a). While from B_4 to B_1, transition has been occurred at $p_t = 48.27\,\mathrm{GPa}$. We remark that our calculated value of the pressure transition from B_3 to B_1 is in agreement with that reported in references [17,18,26]. On the other hand, our calculated value for the pressure transition from B_4 to B_1 phase agree very well with the experimental one (47−50 GPa range) [27]. We can note that the two curves representing the enthalpy variation of the

Table 2. Transition pressures (p_t) for $GaN_{1-x}Bi_x$ at various Bi compositions x

Composition (x)	p_t (GPa)	Transition
0	48.27[a]	$B_4 \to B_1$
	47–50[b]	$B_4 \to B_1$
	42.9[e]	$B_4 \to B_1$
	46.50[a]	$B_3 \to B_1$
	42.98[c]	$B_3 \to B_1$
	37.15[d]	$B_3 \to B_1$
	42.1[e]	$B_3 \to B_1$
0.25	–	–
0.375	−2.55[a]	$B_4 \to B_3$
0.5	−7.25[a]	$B_4 \to B_3$
0.75	−8.77[a]	$B_4 \to B_3$
1	6.33[a]	$B_3 \to B_4$
	16.4[a]	$B_3 \to B_1$

Note. [a] Present work, [b] Ref. [18] (Expt.), [c] Ref. [25], [d] Ref. [26], [e] Ref. [17].

wurtzite and zinc blende are almost confused. This is not surprising, because the curves representing the zinc blende and the wurtzite phases of GaN are almost indistinguishable as shown in Fig. 1, *a*. For the $GaN_{0.625}Bi_{0.375}$, $GaN_{0.5}Bi_{0.5}$ and $GaN_{0.25}Bi_{0.75}$ alloys, the pressure transition from B_4 to B_3 is occurred at -2.55 GPa, -7.25 GPa and -8.77 GPa respectively. In this case, negative pressure indicates that these materials have undergone an expansion. For GaBi the transition pressures from B_3 to B_1 and from B_3 to B_4 as derived by our results are respectively, 16.4 and 6.33 GPa. In Table 2, we have summarized the pressure transition for various Bi contents. Unfortunately, there are no theoretical or experimental results of pt for $GaN_{1-x}Bi_x$ in the entire composition range.

4. Conclusion

In summary, we have investigated the structural properties of $GaN_{1-x}Bi_x$ alloys in zinc blende, rocksalt and wurtzite phases for Bi concentrations varying from 0 up to 1. We have determined the lattice parameters, the bulk modulus for each composition x of Bi. Our result shows that the lattice parameters increase with Bi composition, while the bulk modulus decreases. We have demonstrated that the wurtzite phase is the most stable among the three phases for Bi concentrations of 0 and 0.25, whereasfor Bi concentrations of 0.375, 0.5, 0.75 and 1 the zinc blende phase is the most stable one. On the other hand, we have calculated the transition pressures from the wurtzite to the zinc blende structures for each concentrations of Bi.

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