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High pressure phases of Boron compounds using first principles approach

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Zero pressure properties and elastic constants and phase transition have been studied for BX (X= As, Sb and P). The possible high pressure phase transition from Zincblende (B3) to Rock-salt (B1) phase of BAs, BSb and BP are examined by comparing the total energies. The energies are calculated using the density functional formalism in the plane wave self consistence method. The generalized gradient approximation (GGA) is used for exchange and correlation along with Perdew and Wang pseudopotential parameter. Our results are in good agreement with numerous experimental and theoretical data wherever available, and provide predictions where they are absent

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1. Introduction

The behavior of metals, alloys and compounds under high pressures is of great current interest because high-pressure experiments are becoming more refined [1-2]. An accurate first-principles method of calculating the structural properties of all these matters are, therefore, very valuable. Such calculations can also predict pressure induced phase transitions. Specifically, the theoretical studies of such phase transitions in compounds have been of special interest over the last three decades [3-5]. Among the different compounds, Boron compounds namely Boron Arsenide (BAs), Boron Antimony (BSb) and Boron Phosphate (BP) are interesting in many ways, being Zinc-blend (ZB) structure under normal conditions and thus been the subject of numerous experimental and theoretical studies [6-11]. The Boron compounds are expected to find application in the area of optoelectronic devices due to some extreme physical properties, such as low ionicity, small band-gap, short bond lengths and high mechanical strength/or elastic moduli, and high melting point [6-9] .

The theoretical work on boron compounds have been extensively performed so far, mostly carried out by Ferhat et al [8, 12-14], within the various ab initio methods. Specifically, the structural and electronic properties of BX Compounds have been, recently, calculated by Ferhat et al [12-16], Zaoui et al [15], Carrier et al [17], and Meradji et al [18] by using the various first-principles methods based on the density functional theory (DFT). They reported that the zinc-blende (ZB) phase (B3) is the ground state of BSb, BSb and BP. The most recent work on these alloys is done by K. Boumama et al [19]. They theoretically predicted the phonons of these alloys and confirmed the experimental work by Sanjurjo et al [20]

From the structural point of view, it is assumed that BX(X=As, Sb, P) is stable in ZB phase (space-group 216/F-43 m) with two atom pairs per unit cell at ambient conditions. Here B and X (X= AS, Sb, P) ions occupy the positions (0, 0, 0) and (0.25, 0.25, 0.25), respectively. In rock-salt (RS) structure (space-group 225/Fm3 m), B and the other associated ions occupy the positions (0, 0, 0) (0.5, 0.5, 0.5), respectively. Here, we report the results of our first principles calculations on the structural properties of BAs, BSb and BP. Especially, we focus our attention to the much important bulk properties of solids, varying with/without pressure for these compounds. The layout of this paper is given as follows: the method of calculations is given in section 2. The results and overall conclusion are presented and discussed in sections 3 and 4.

2. Method of calculation

We used the plane-wave self consistence pseudopotential approach within the framework of density functional theory. The *ab initio* norm-conserving pseudopotentials were generated using the method of Troullier and Martins [21]. The electron-electron interaction was considered within the generalized gradient approximation (GGA) of the density functional theory, with the correlation scheme of Ceperley and Alder [22]. The electronic wave functions were expanded in a basis set of plane waves, up to a kinetic energy cutoff of 50 Ry. For the **k**-point sampling, we used 60 and 75 special points in the irreducible wedge of the Brillouin zone of the zinc-blende and rock-salt structures, respectively. For both the phases, the Kohn-Sham equations were solved using an iterative conjugate gradient scheme to find the total energy. These considerations allow total energies of competing phases to be compared within an accuracy of 2 meV/atom. Having obtained self-consistent solutions of Kohn-Sham equations, the other ground state properties were calculated within the framework of the self-consistent density functional perturbation theory. All the calculations have been performed by using the PWSCF code [23].

Table 1. Calculated equilibrium lattice constant (a_0), bulk modulus (B) and pressure derivative of bulk modulus (B'), the related experimental data, and other theoretical works for BAs, BSb and BP in zincblende (B3) (ZB) and rock-salt structure (B1) (RS).

	Parameter	Present	Experimental	Other Theoretical works
BAs				
B3 (ZB)	a_0(Å)	4.7422	4.777 [24]	4.726 [16], 4.777[7], 4.784[25]
	B (GPa)	148		147 [16], 145 [7], 137 [25]
	B'	3.45		3 [16], 3 [25]
B1 (RS)	a_0(Å)	4.617		4.619 [25], 4.583 [13]
	B (GPa)	138		135[25], 143 [13]
	B'	3.46		3.44[25]
BSb				
B3 (ZB)	a_0(Å)	5.241		5.21[26], 5.201 [16], 5.252 [25], 5.120 [12]
	B (GPa)	109		110[26], 109 [16], 103 [25], 105[12]
	B'	4.12		4.07 [26], 4.00[16], 3 [25], 5[12]
B1 (RS)	a_0(Å)	4.979		4.96[26], 4.92 [27],
	B (GPa)	110		116[26], 147 [27],
	B'	3.82		4.84[26], 3.30[27]
BP				
B3 (ZB)	a_0(Å)	4.514	4.538 [24,28]	4.558[7], 4.546[25],
	B (GPa)	170	173[24,28]	166[7], 166[25],
	B'	3.8		4[7], 3 [25]
B1(RS)	a_0(Å)	4.327		4.320[25], 4.339 [9]
	B (GPa)	1.51		1.71[25], 1.55[9]
	B'	2.98		2.82 [25]

3. Results and discussion

The equilibrium lattice parameter has been computed by minimizing the crystal total energy calculated for different values of lattice constants. Murnaghan equation of state is used to fit total energy as a function of volume. Equilibrium parameters at zero temperature have been obtained by minimization of the crystal total energy, without including the zero-point energy. The bulk moduli and the equilibrium lattice parameters have been obtained by fitting the equation of state by the Murnaghan expression [24],

$$E(V) = E_0 - \frac{B_0 V_0}{B' - 1} + \frac{B_0 V}{B'}\left[\frac{\left(V_0/V\right)^{B'}}{B' - 1} + 1\right] \quad (1)$$

wehere B_0 and B' are the bulk modulus and its pressure derivative, E_0 is the ground-state total energy, and V_0 is the equilibrium volume. The calculated equilibrium unit cell parameters, bulk moduli, and pressure derivative for both of structures, as well as available referenced experimental and theoretical data for boron compounds for both the phases are listed in Table 1 for all the three compounds. Both phases have high bulk moduli that indicate a very hard and not easily compressible compound. The results show a good agreement in computed and experimental data for ambient phase. The estimated lattice parameters 4.7420 Å for BAs, 5.241 Å for BSb and 4.514 Å for BP fall within the range of experimental values as well as recent theoretical results.

One can obtain the information for transition pressure directly from energy – volume-pressure curve by determining the common tangent between the thermodynamically stable structures as pressure is increased (or volume is decreased). The slope of the common tangent, which is the derivative of the total energy with respect to the volume, corresponds to minus the coexistence pressure for the low- and high-pressure phases, and the volume of each phase at the transition (the transition volume) corresponds to that at the tangent point. It is straightforward to verify that the enthalpies of the two phases are equal at these points. The calculated transition pressure (P_t) using aforesaid method for zincblende (B3) to rock-salt (B1) phase is reported in table 2. The early studies on high-pressure structural phase transitions of BP and BAs were discussed by Wentzcovitch et al [7-9], it can be verified from the table that our results for both the BP and BAs are also in line with their results.

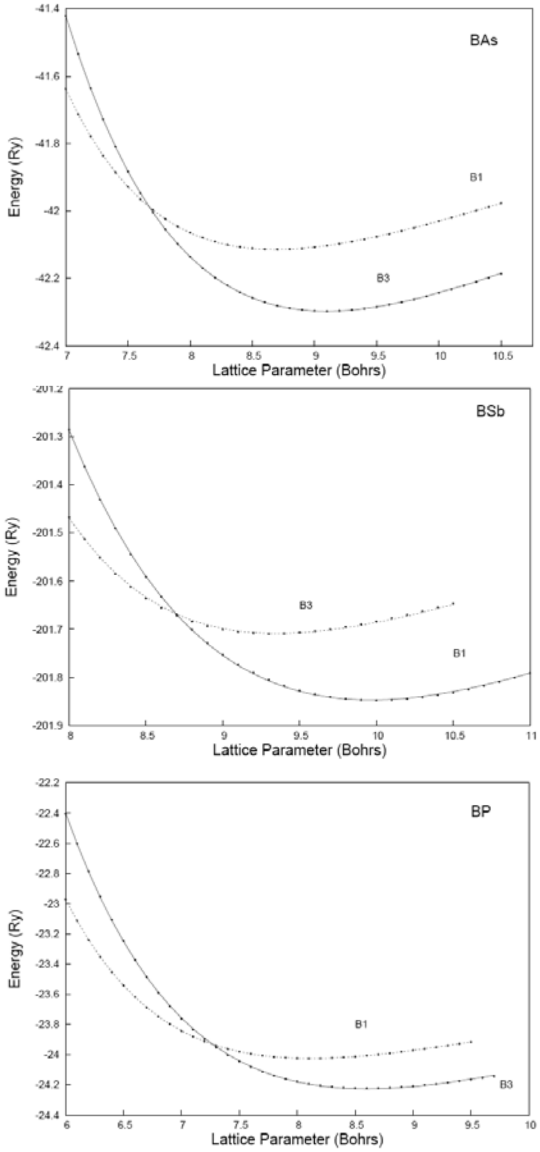

Fig. 1. Total Energy – lattice parameter curve for the BAs, BSb and BP in Zincblende (B3) and Rocksalt (B1) Structures, line represents computed and dot is fitted data.

Table: 3 Calculated value for transition pressure from ZB to RS structures for BAs, BSb and BP compared with other reported results.

		BAs	BSb	BP
P_t	Present	98	63	118
	Others	93 [25], 110 [7]	59 [26], 53 [25], 68 [29]	110[25], 160[9]

The elastic constants were obtained by straining the equilibrium lattice at fixed volumes, using volume-conserving strains and then computing the free energy as a function of strain. The primitive vectors a_i (i = 1, 2, 3) of crystals are transformed to new vectors under the strain by

$$\begin{pmatrix} a'_1 \\ a'_2 \\ a'_3 \end{pmatrix} = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} \cdot \left(I + \varepsilon \right) \tag{2}$$

where ε is the strain tensor. This relates to the strain vector **e** by

$$\varepsilon = \begin{pmatrix} e_1 & e_6/2 & e_5/2 \\ e_6/2 & e_2 & e_5/2 \\ e_6/2 & e_5/2 & e_3 \end{pmatrix} \tag{3}$$

It is well known that a cubic crystal such as the rock-salt structure has only three independent elastic constants, namely C_{11}, C_{12} and C_{44}. Thus, a set of three equations is needed to calculate these constants. Firstly, the bulk modulus B is determined by a linear combination of the elastic constants:

$$B = \frac{C_{11} + 2C_{12}}{3} \; . \tag{4}$$

To determine the bulk modulus, we calculated the total energy of the system as a function of crystal volume and then fitted it to Murnaghan's equation of state [24]. The second equation involves applying volume-conserving tetragonal strain [25]

$$e = (\delta, \delta, (1 - \delta)^{-2} - 1, 0, 0, 0) \; , \tag{5}$$

where δ is the stress tensor and the corresponding strain energy is given by

$$E(\delta) = E(0) + 3(C_{11} - C_{12})V_0\delta^2 + O(\delta)^3 \tag{6}$$

where $E(0)$ and V_o are the unstrained energy and the volume of the unstrained unit cell respectively. Finally C_{44} can be calculated under the volume-conserving monoclinic strain [25, 26] as

$$e = (0, 0, \frac{\delta^2}{(4 - \delta^2)}, 0, 0, \delta) \; \cdot \tag{7}$$

The corresponding strain energy is given by

$$E(\delta) = E(0) + \frac{1}{4}C_{14}V_0\delta^2 + O(\delta)^4 \; \cdot \tag{8}$$

Using the bulk modulus and the above volume-conserving strains, C_{11}, C_{12} and C_{44} are calculated. Our calculated elastic constants using volume-conserving strains method are presented in table 3 for all boron compounds. The results from this method are in good agreement with the other such published experimental and theoretical results. In particular, our calculated C_{44} for BP is in good agreement with the experimental value of 3.15 Mbar [24]. Although our calculated $C_{11}-C_{12}$ values from both the methods are similar to each other, these values for BSb show a difference of nearly 20% from the corresponding theoretical value. This disagreement indicates that new experimental work is needed on the elastic properties of BAs and BSb. To our knowledge, there are no experimental data available for elastic constants of BAs. However, our calculated values are in good agreement with the corresponding results from recent theoretical calculations.

Table 2. Calculated elastic constants C_{11}, C_{12}, $C_{44}$for BAs, BSb and BP in Zincblende phase

		Bas	BSb	BP
C_{11} (Mbar)	Present	2.52	1.92	3.29
	Experimental	-	-	3.15 [24]
	Theoretical	2.79[25] 2.51[26]	1.93 [27] 2.05 [28] 1.92 [29] 2.23 [30]	3.59 [25] 3.60 [26]
C_{12} (Mbar)	Present	0.78	0.585	0.975
	Experimental	-	-	1.00 [24]
	Theoretical	1.20 [25] 0.798 [26]	0.68[27] 0.62 [28] 0.58[29] 0.62[30]	0.81 [25] 1.55 [26]
C_{44} (Mbar)	Present	1.28	1.04	1.54
	Experimental	-	-	1.60 [24]
	Theoretical	1.13 [25] 1.27 [26]	1.12[27] 1.05[28] 1.40[29] 1.05[30]	2.02 [25] 1.46 [26]

4. Conclusion

We have performed a plane wave pseudopotential density functional approach with GGA scheme for BAs, BSb and BP compounds. We have obtained zero pressure lattice constant and bulk Modulus that match well with experimental and other theoretical reported values. From our volume vs. energy curve, it is clear that zincblende phase is the stable phase at ambient conditions. At high pressures the phase transition from zincblende to rocksalt occurs, the transition pressure calculated by using common tangent method yields results in agreement with the other published work. The reported calculation provides new ab-initio structural results for Boron compounds. The results, estimated for in this work, such as on the bulk modulus and transition pressure, make significant contributions to the existing data and stimulate the experimental and other works on the basic properties of the hypothetical BSb compound. The comparison of presently computed results with available theoretical and experimental findings is encouraging for ground state phase of zincblende. This confirms the applicability of plane wave potential density functional theory in explaining the phase transition. Study on the electronic, elastic properties and phonons of these compounds are in progress.

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