Structural and Piezoelectric Properties of BSb under High Pressure: a DFT Study

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Structural and piezoelectric properties of boron-antimonide (BSb) under high pressure up to 60 GPa were investigated using the pseudopotential plane wave method in the framework of the density functional theory within the local density approximation for the exchange-correlation functional. Both direct and converse piezoelectric coefficients were obtained using the density functional perturbation theory. Both direct and converse piezoelectric coefficients decrease gradually with pressure.

Keywords: DFPT, Boron-antimonide, Piezoelectric properties, LDA.

1. INTRODUCTION

Recently, boron pnictide materials have started gaining attention; these compounds have some particular characteristics, such as large hardness and high melting point [1]. As all crystals, under hydrostatic compression, the low-pressure phase of boron pnictide materials is destabilized and structural phase transition occurs. For boron-antimonide (BSb) compound, the generalized mechanical stability criteria show that the phase transition appears at a pressure of around 72 GPa [2]. Using first principles approach, Lindsay *et al.* [3] have investigated the temperature dependence of the thermal conductivity of cubic III-V boron compounds. At room temperature, they found that BSb has high thermal conductivity, it is of around 465 Wm $^{-1}$K $^{-1}$.

Yao *et al.* [4] have used *Ab initio* calculations of the electronic and phononic properties of bulk BSb compounds. They found that BSb material could be a good material candidate (with low cost and easily processed) for hot carrier absorbers in high-efficiency third generation solar cell.

Bouamama *et al.* [5] have used first principles approach to study the pressure dependence of the optical phonon frequencies, the high-frequency dielectric coefficient and the dynamic effective charge of a series of boron compounds.

In the present work, we report on first principles calculations of the high pressure effect on the structural and piezoelectric properties of BSb in the zincblende (B3) structure using the pseudopotential plane wave (PP-PW) method in the framework of density functional theory (DFT) [6], and the density functional perturbation theory (DFPT) [7], within the local density approximation (LDA).

2. COMPUTATIONAL METHODS

The calculations in the present study were carried out using the ABINIT code [8] based on the pseudopotential plane wave (PP-PW) approach in the framework of the DFT and the DFPT. ABINIT code is a package whose main program allows to find the total energy and several other physical properties of systems made of electrons and nuclei. It is a common project of the

University Catholique de Louvain, Corning Incorporated, the University de Liège, and other contributors.

The Troullier-Martins type norm-conserving pseudo-potentials, which have been generated thanks to the FHI98PP code [9] were used to describe the interactions between the valence electrons and the nuclei and core electrons, while the exchange-correlation energy was evaluated in LDA using Perdew-Wang parametrization [10].

The plane-wave energy cut-off to expand the wave functions used here was taken to be 80 Hartree. The Brillouin zone integrations were usually replaced by discrete summations over a special set of *k*-points. Using the standard *k*-point technique of Monkhorst and Pack [11], the *k*-point mesh used in our calculation is 8×8×8. Careful convergence tests show that with these parameters, the relative energy is converged to better than 10^{-5} Hartree.

3. DISCUSSION OF RESULTS

3.1 EOS Parameters

The lattice spacing between atoms is an important parameter, which affects several physical quantities of crystals, such as the width of the gap and the bands of the semiconductors, the volumetric mass density, the sound velocity, etc. Usually, the structural equilibrium parameters can be predicted from Ab-initio calculation, using the total energy – unit cell volume (*E-V*) data. In order to obtain the structural equilibrium parameters of boron-antimonide (BSb) compound in both cubic zincblende (B3) and cubic sodium chloride (B1) structures, the different values of the total energy were traced as a function of the unit cell volume. The equilibrium lattice constant, the bulk modulus and the pressure derivatives of the bulk modulus can be easily obtained by using the Murnaghan equation of state (EOS), which is given as follows [1].

Fig. 1a, b discern the variation of the total energy as a function of the unit cell volume of BSb compound in both zincblende and rock-salt structures, respectively.

Our predicted values of the equilibrium lattice parameter a_0, bulk modulus B_0, and its pressure derivative B_0' of both zincblende and rock-salt structures are

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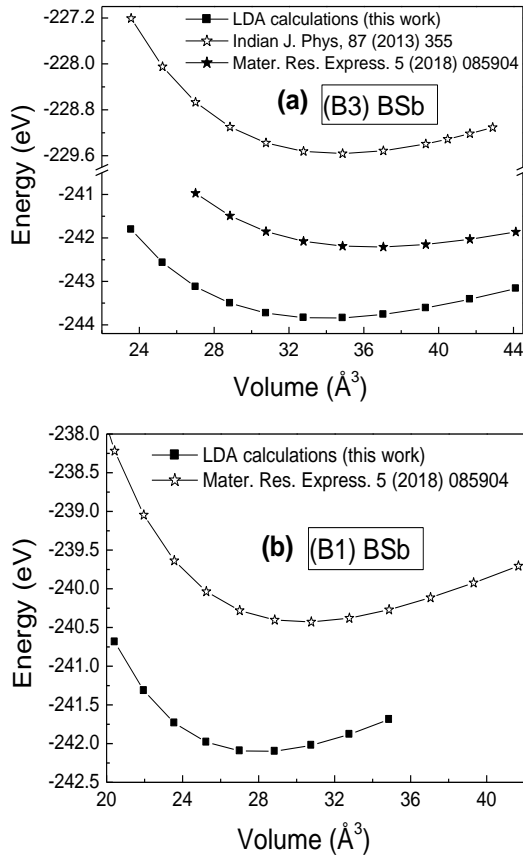summarized in Table 1 compared with other theoretical results [1, 2].

Fig. 1 – Total energy versus volume for B3 phase of BSb (a), total energy versus volume for B1 phase of BSb (b)

Table 1 – EOS parameters of BSb at zero-pressure in comparison with other theoretical values [1, 2]

Phase	Parameter	Our work	Other works
B3	a_0 (Å)	5.139	5.265 [1] GGA 5.18 [2] LDA
	B_0 (GPa)	107.7	95.30 [1] GGA 108.4 [2] LDA
	B'_0	3.99	3.99 [1] GGA 3.743 [2] LDA
B1	a_0 (Å)	4.8244	4.9565 [1]
	B_0 (GPa)	117.7	97.4 [1]
	$B'_0{}^-$	4.47	4.60 [1]

From the results summarized in Table 1, it is observed that the equilibrium lattice constant a_0 of BSb compound in both cubic zincblende and cubic sodium chloride structures are in good agreement compared to other theoretical results [1, 2]. Where for example, our obtained value (5.139 Å) of cubic zincblende structure underestimates the theoretical value (5.18 Å) obtained in Ref. [2] only by less than 0.8 %. It is important to note that the lattice parameter is one of the fundamental structural quantities in solid state physics; it is related directly with the bond length parameter, which was determined by the density of valence electrons between the atoms of crystal.

Our predicted values of the bulk modulus B_0 and its pressure derivative B_0' of both zincblende and rock-salt structures are also in good agreement compared to other theoretical results [1, 2]. For example, our obtained value 4.47 of B_0' for the cubic sodium chloride structure underestimates the theoretical value 4.60 obtained in Ref. [1] by less than 2.87 %.

Fig. 2 discerns the variation of the crystal density as a function of the pressure of BSb compound in cubic zincblende phase. The results obtained in the previous works [2, 12] are also represented and traced in Fig. 2.
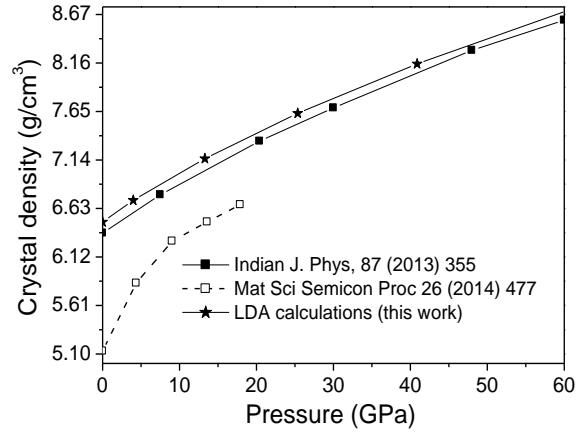

Fig. 2 – Crystal density versus for B3 phase of BSb compound

The crystal density of BSb compound at zero-pressure is 6.488 g/cm³, it is in good agreement with the value 6.37 g/cm³ obtained from the LDA [2]. It is important to note also that the value 5.13 g/cm³ of the crystal density reported by Salehi *et al.* [12] is not correct. By using the numerical value 5.2809 Å of the equilibrium lattice parameter obtained by Salehi *et al.* [2], the correct value of the crystal density is 5.979 g/cm³ which is in general in agreement with our obtained value 6.488 g/cm³ and with the value 6.37 g/cm³ obtained from the LDA [2].

3.2 Piezoelectric Coefficients

As we know, piezoelectric effect does not exist in all structures. Among the five symmetry classes belonging to the cubic system, only $\bar{4}$ 3m and 23 classes exhibit the piezoelectric effect. In the first case, the piezoelectric tensor contains only one constant e_{14} (in the direct piezoelectric effect), it is expressed in C/m². The piezoelectric tensor is given as [13]

$$\underline{e} = \begin{pmatrix} 0 & 0 & 0 & e_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & e_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & e_{14} \end{pmatrix}. \qquad (1)$$

In the converse piezoelectric effect (application of an electrical field creates mechanical deformation in the crystal), the piezoelectric tensor contains also only one constant called d_{14}, it is usually expressed in 10^{-12} m/V, or in pC/N. The piezoelectric properties of the present compound have been calculated for the first time. The converse piezoelectric coefficient d_{14} is related to the

elastic constant C_{44} and the direct piezoelectric coefficient e_{14} by the following formula [13, 14]:

$$d_{14} = e_{14}/C_{44}. \qquad (2)$$

Attempting to predict the effect of hydrostatic pressure on the direct and converse piezoelectric coefficients of BSb with cubic zincblende structure, the different results along these of boron phosphide (BP) semiconducting material [13] are presented in Fig. 3 and Fig. 4, respectively. As shown in Fig. 3 and Fig. 4, both the direct and converse piezoelectric coefficients decrease gradually with pressure; the first begins with a value of -0.134 C/m^2 at zero-pressure and reaches a value of about -0.865 C/m^2 at a pressure of 60.7 GPa, while the second one begins by -1.17 pm/V at zero-pressure and reaches a value of about -5.70 pm/V at the same pressure.
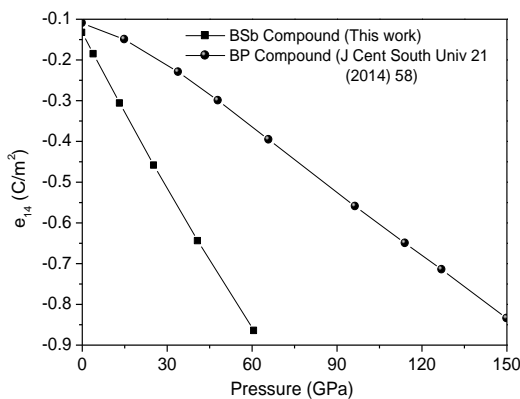

Fig. 3 – Direct piezoelectric coefficient of BSb and BP [13] versus applied pressure

It can be noted that a similar qualitative behavior of both the direct and converse piezoelectric coefficients versus pressure has been reported for boron phosphide (BP) [13], boron bismuth (BBi) [14], and aluminum phosphide (AlP) [15, 16] semiconducting materials.

Two analytical relations for the pressure (given in GPa) dependence of BSb direct and converse piezoelectric

Fig. 4 – Converse piezoelectric coefficient of BSb compound along this of BP [13] versus applied

coefficients are given by the following linear fits:

$$e_{14} \, (\text{C/m}^2) = -0.142 - 0.012p, \qquad (3)$$

$$d_{14} \, (\text{pm/V}) = 1.27 - 0.075p. \qquad (4)$$

To the best of the authors' knowledge, the pressure dependence of piezoelectric coefficients has never been previously reported in BSb material.

4. CONCLUSIONS

In conclusion, the DFT and DFPT methods have been used to obtain the EOS parameters and both the direct and converse piezoelectric coefficients of BSb under pressure up to a pressure of 60 GPa. It is found that both the direct and converse piezoelectric coefficients decrease with increasing pressure. It can be noted that a similar qualitative behavior has been reported in the literature for BP, BBi, and AlP materials.

At $P = 0$, the direct piezoelectric coefficient e_{14} was found at around -0.134 C/m^2, while the converse piezoelectric coefficient d_{14} was found at around -1.17 pm/V.

The results obtained for the Debye temperature and the melting temperature agree well with other experimental and theoretical data.

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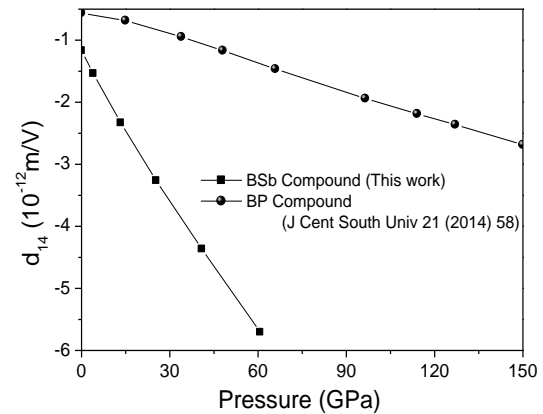8. ABINIT code is a common project of the Université Catholique de Louvain, Corning Incorporated, and other contributors. http://www.abinit.org.
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Структурні та п'єзоелектричні властивості BSb під високим тиском: дослідження DFT

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Структурні та п'єзоелектричні властивості бору-антимоніду (BSb) під високим тиском до 60 ГПа були досліджені за допомогою методу псевдопотенціальної плоскої хвилі в рамках теорії функціональної щільності в межах локального наближення густини для обмінно-кореляційного функціоналу. Як прямі, так і зворотні п'єзоелектричні коефіцієнти були отримані за допомогою теорії функціональних збурень щільності. Виявлено, що прямі і зворотні п'єзоелектричні коефіцієнти поступово зменшуються з тиском.

Ключові слова: DFPT, Бор-антимонід, П'єзоелектричні властивості, LDA.