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Pressure dependence of electronic and optical properties of zincblende BP, BAs and BSb compounds

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We have performed first-principles full-potential linearized augmented-plane wave calculations with density functional theory in generalized gradient approximation, in aim to determine and predict the pressure dependence of energy band gaps and optical properties of BP, BAs and BSb compounds. First we present the main features of electronic properties, where the electronic band structure shows that the fundamental energy gap is indirect near X ($X_{15v} \rightarrow \Delta_{\min}$).The trends of the band gap pressure coefficients for these III-V compounds are investigated. The linear pressure coefficients compare well with previous theoretical results. The accurate calculation of linear optical function (refractive index and its pressure derivative, and the real part of dielectric function) is performed in the photon energy range up to 30 eV. Also, we have investigated the pressure dependence of the static dielectric function. The refractive index and its variation with hydrostatic pressure are well described. The predicted optical constants agree well with the available theoretical ones.

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1. Introduction

Boron compounds have attracted increasing research interest over the past few years, as wide gap semi-conductors. These materials are of great technological interest for high temperature, electronic and optical applications [1-8]. The electronic valence configuration is $1s^2 2s^2 2p^1$ for boron atoms and $ns^2 np^3$ for group V elements. They crystallize at low pressure in the four-fold coordinated zinc-blende structure. These materials possess a peculiar behaviour where compared to other III-V compounds, among this, is the inverse role between the cation and anion in terms of charge transfer, which is confirmed by Wentzcovich et al. [2,3] and Bouhafs et al. [4]. Their unusual behaviour appears to originate from the small core size and the absence of p electrons in B. Boron is expected to have a deep and localized pseudopotential compared with the atoms from other rows. The reason for these fundamental differences between these compounds and other III-V materials is apparent from band structures and charge density calculations.

The effect of pressure on the electronic properties of III-V compounds can be investigated experimentally in many ways [9-13]. On the other hand, both theoretical and technical developments in density functional theory (DFT) and pseudo potential calculations in recent decades have provided researchers with powerful methods for predicting electronic and energetic properties as revealed by novel experimental techniques. Meanwhile, the technical development of epitaxial growth at the end of the last century has provided the possibility for researchers to fabricate synthetic materials with expected compositions and structures. The situation has simulated extensive computational studies on high-pressure behaviour of various semiconductors [14-18]. In recent years, ab initio density-functional calculations based on the local density approximation (LDA) have been successful in describing the structural properties of solids [19]. However, the LDA bands gaps of semiconductors and insulators have been consistently underestimated by about 30-50% compared with experiments [20]. Despite the discrepancies between the calculated and measured band gaps, the pressure variations of the band gaps in semiconductors have been correctly described [21-23] and do not depend on the type or functional form of the exchange-correlation potential [7,23,24]. Under high pressure the boron compounds undergo a structural phase transformation to a high coordination phase. For BP, BAs and BSb the transition form zinc-blende to rocksalt phase occurs in range of 111 GPa , 93 GPa and 53GPa respectively [8]. For the same transition,Wentzcovitch et al.[3] have found the values of 160 GPa for BP and 110 GPa for BAs. As such, we have investigated the pressure dependence of the energy gap and static optical quantities using the FP-LAPW method within the generalized gradient approximation.

The paper is organized as follows. In Section 2 we briefly the method of calculation and the computational details. Moreover, in Section 3 we present our results and discussion of the pressure dependence of electronic and optical properties of our compounds. Finally, a general conclusion is given in Section 4.

2. Computational details

We apply the most recently developed Vienna package WIEN2k [25] for the full-potential augmented plane waves plus local orbitals (FP-APW+lo) method within density functional theory (DFT) [26,27], for which the electrons exchange correlation energy is described in the generalized gradient approximation (GGA) using the Perdew-Burke-Enzerhof functional parametrization [28]. The APW +l_0 method expands the Kohn-Sham orbitals in atomic like orbitals inside the atomic muffin-tin (MT) spheres and plane waves in the interstitial region. The details of the method have been described in the literature [29-31]. Basis functions, electron densities and potentials were expanded inside the muffin-tin spheres in combination with spherical harmonic functions with a cut off l_{max} = 10, and in Fourier series in the interstitial region. We use a parameter R_{MT} K_{max} = 8 which determine matrix size, where R_{MT} denotes the smallest atomic sphere radius and K_{max} gives the magnitude of the largest K vector in the plane wave expansion. Calculations of the optical properties need a very dense k-point mesh in order to take most of the transition into account, this circumstance requires the use of a fine k-point mesh(in our case k_{mesh} = 3000 in the full BZ). All of the calculations were carried out at the theoretical equilibrium lattice constants. We chose the muffin-tin radii of B, As, P and Sb to be 1.5, 2.0, 2.0 and 2.0 a.u. respectively. The k integration over the brillouin zone is performed using the Monkhorst-Pack scheme[32]. To correct the GGA error in the band gaps, a constant potential is applied to the conduction band states (using the scissors operator which rigidly shifts the conduction band states) in order to match the calculated band gaps with the experimental data. In our case, no scissors shift was performed due to no availability of experimental measurements.

Optical properties of a solid are usually described in terms of the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The imaginary part of the dielectric function in the long wavelength limit has been obtained directly from the electronic structure calculation, using the joint density of states and the optical matrix elements. The real part of the dielectric function can be derived from the imaginary part by the Kramers-Kronig relationship. The knowledge of both the real and the imaginary parts of the dielectric function allows the calculation of important optical functions. In this paper, we also present and analyse the refractive index $n(\omega)$, given by

$$n(\omega) = \left[\frac{\varepsilon_1(\omega)}{2} + \frac{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}}{2} \right]^{1/2} . \qquad (1)$$

At low frequency (ω=0), we get the following relation:

$$n(0) = \varepsilon^{1/2}(0) \qquad (2)$$

3. Results

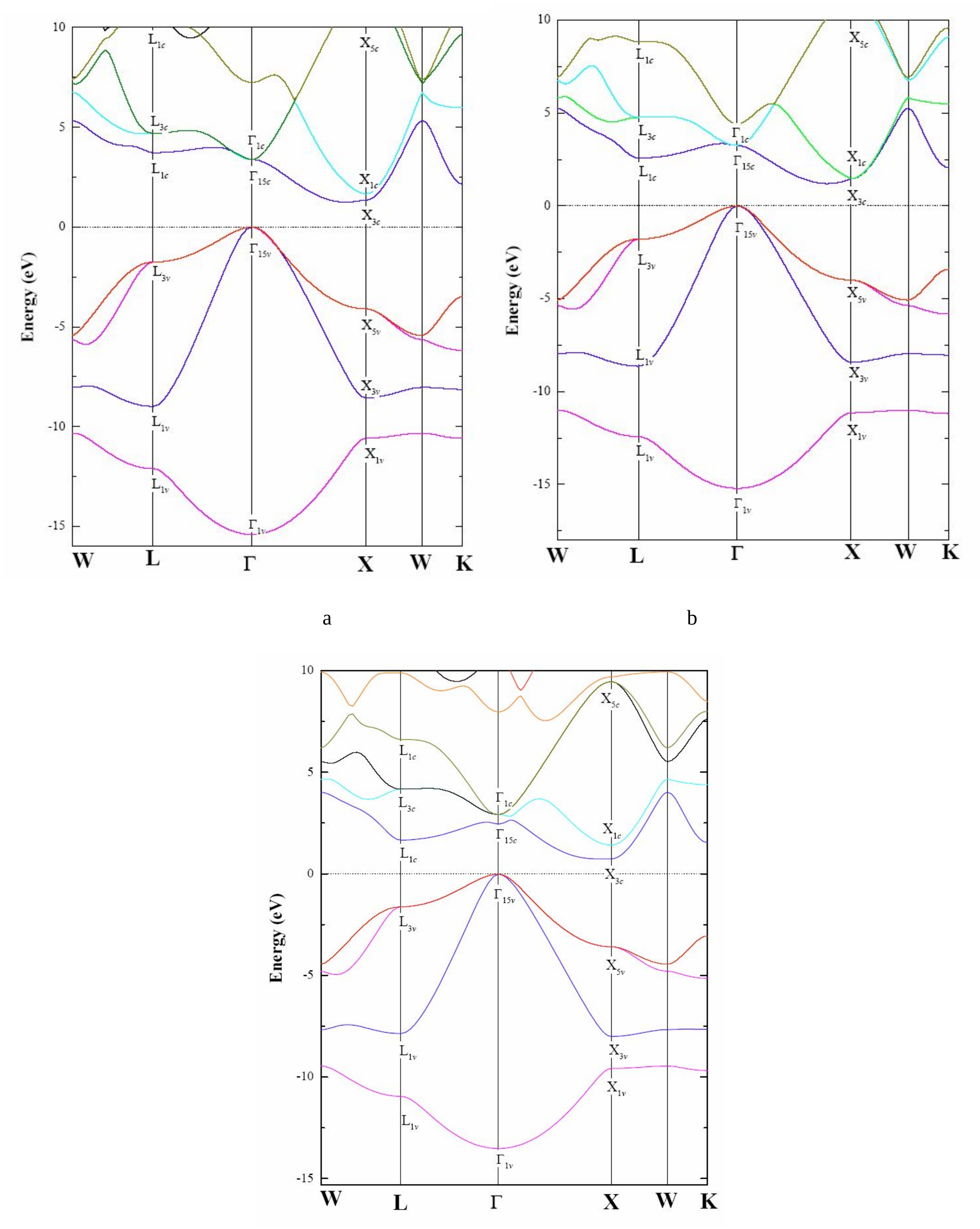
3.1. Electronic properties

The calculated band structures energies of binary compounds along the high symmetry directions in the Brillouin zone are given in Fig. 1. The overall band profile is found in agreement with the available theoretical works [1-3,5,7,8]. Our calculations of band structure show an indirect gap near X ($X_{15v} \rightarrow \Delta_{min}$) for all compounds. Using the equilibrium lattice parameters, we have obtained energy gaps of 1.24 eV for BP, 1.20 eV for BAs and 0.73 eV for BSb. This underestimation of energy gaps is caused, however by the generalized gradient approximation. This is mainly due to the fact that LDA and GGA have simple forms that are not sufficiently flexible to accurately reproduce both exchange-correlation energy and its charge derivative. Table 1 gives a summary for the most important calculated band-gaps in the zincblende structure of our compounds compared with the experimental and theoretical ones. The GW calculations give energy band gaps in excellent agreement with experiment, as shown by Surh et al [33] for these semiconductors. The results are in agreement with other ab initio calculations.

Table1. Calculated indirect band gap ($\Gamma_{15v} \rightarrow \Delta_{min}$), direct band gap ($\Gamma_{15v} \rightarrow \Gamma_{15c}$) and valence bandwidth for BP, BAs and BSb. All the energies are in eV.

		Present work	*Experiment*	Other calculations	
				PWPP [7]	LMTO [6]
BP	E_g ($\Gamma_{15v} \rightarrow \Gamma_{15c}$)	3.38	5.0^a		3.55
	E_g ($\Gamma_{15v} \rightarrow \Delta_{min}$)	1.24	2.40^b	1.12	1.35
	Valence bandwidth	15.40	<17^c	15.78	15.55
BAs	E_g ($\Gamma_{15v} \rightarrow \Gamma_{15c}$)	3.25	1.46^d	3.30	
	E_g ($\Gamma_{15v} \rightarrow \Delta_{min}$)	1.20	0.67^d	1.06	
	Valence bandwidth	15.21	16.0^e	15.71	
BSb	E_g ($\Gamma_{15v} \rightarrow \Gamma_{15c}$)	2.45		3.06	
	E_g ($\Gamma_{15v} \rightarrow \Delta_{min}$)	0.73		0.52	
	Valence bandwidth	13.52		14.35	

^{a} Ref [34], ^{b} Ref [35], ^{c} Ref [36], ^{d} Ref [37], ^{e} Ref [38]



a

b

c

Fig. 1. The electronic band structure of (a) BP, (b) BAs and (c) BSb at the calculated equilibrium volume.

3.2. Pressure dependence of band gaps

Photoluminescence spectra of semiconductors are sensitive to hydrostatic pressure. Theoretical investigation of the pressure dependence of the energy band structure provides a way to understand the chemical trends and dielectric behaviours of the compound. Figure 2 shows the calculated variation of the band gaps with the pressure. In order to calculate the pressure coefficients, we have fitted $E_g(p)$ to a quadratic function:

$$E(p) = E(0) + bp + cp^2 \tag{3}$$

Where a and b are the first and the second order pressure derivatives respectively which are given in Table 2 for BP, BAs and BSb. When analyzing more carefully these results, there is a good agreement between our results and the PWPP calculations of Bouhafs et al [7]. The small differences seen in table2 can be: the accuracy of the method used, e.g. pseudo potential and full potential, the choice of the functional for the exchange-correlation energy of the electrons and the computational parameters such as the energy cutoff. It is found that in Fig. 2, the indirect ($\Gamma \rightarrow \Delta_{min}$) and ($\Gamma \rightarrow X$) band gaps decrease with increase in pressure, thus BX(X=P,As,Sb) have negative pressure coefficient (dE_g / dP). On the other hand, the direct ($\Gamma \rightarrow \Gamma$) and the indirect ($\Gamma \rightarrow L$) band gaps increase with increase in pressure giving rise to positive linear pressure coefficient. This trend is in good agreement with the calculations of Bouhafs et al [7]. The behaviour of the band-gap variation under pressure is very similar to that found in all III-V materials. For the second- order pressure derivatives of the different band gaps (Table2), we have observed that there is a difference between our results and those obtained by Bouhafs et al, it is due probably to the method used.

Table 2. Calculated linear and quadratic pressure coefficients of important band gaps for BP, BAs and BSb compounds.

$E_i(p) = E_i(0) + bp + cp^2, b = \partial E_i / \partial p \; in \; eV \; Mbar^{-1},$

$c = \partial^2 E_i / \partial p^2 \; in \, eV \; Mbar^{-2}$

	$\Gamma_{15v} \rightarrow \Delta_{n}$		$\Gamma_{15v} \rightarrow \Gamma_{15}$		$\Gamma_{15v} \rightarrow L_{1}$		$\Gamma_{15v} \rightarrow X_{3}$	
	b	*c*	*b*	*c*	*b*	*c*	**b**	**c**
BP	-0.82	0.23	0.76	-0.019	3.07	-1.96	-1.10	0.41
This work	-0.72	0.37	1.01	-0.17	3.98	-4.66	-1.03	0.53
PWPP								
BAs								
This work	-0.58	0.18	0.80	-0.24	3.54	-1.21	-0.77	0.22
PWPP	-0.58	0.31	0.79	0.07	3.99	-2.36	-0.52	-0.11
BSb								
This work	-0.92	0.61	4.20	-4.98	4.16	-2.57	-0.95	0.65
PWPP	-0.90	0.80	1.77	-1.09	4.73	-3.71	-0.91	0.83

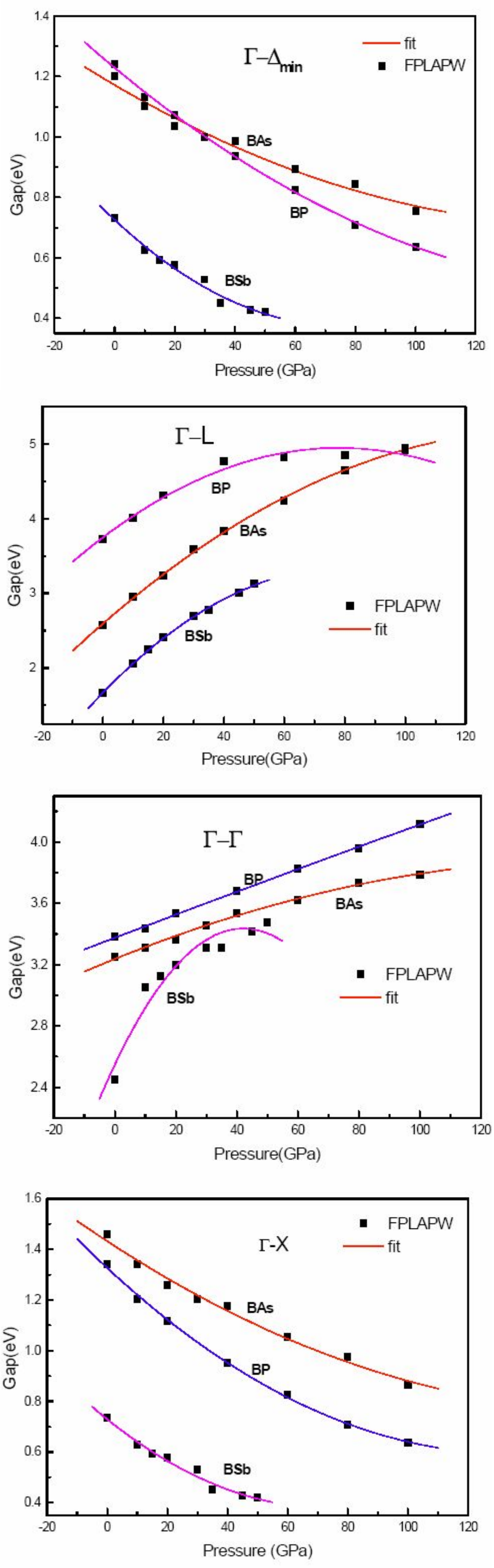


Fig. 2. calculated dependence of the band gaps $\Gamma_{15v} \rightarrow \Delta_{min}$, $\Gamma_{15v} \rightarrow \Gamma_{15c}$, $\Gamma_{15v} \rightarrow L_{1c}$ *and* $\Gamma_{15v} \rightarrow X_{3c}$ *of boron compounds BP, BAs and BSb as a function of pressure.*

Another way of representing the effect of pressure on the band gap is through the use of a second-order polynomial fit [39-41] to the calculated values with:

$$E_g^{\alpha}(a) = E_g^{\alpha}(a_0) + B\left(\frac{-\Delta a}{a_0}\right) + C\left(\frac{-\Delta a}{a_0}\right)^2 \qquad (4)$$

Where Δa is the change in the lattice constant, a_0 the equilibrium lattice spacing and α is either the indirect $\Gamma \rightarrow \Delta_{min}$, $\Gamma \rightarrow L$, $\Gamma \rightarrow X$ or direct $\Gamma \rightarrow \Gamma$ band gap. The values of the coefficients obtained from this quadratic fit are tabulated in Table3. Figure 3 shows the calculated variation of the band gaps with the relative variation in lattice constant. It is seen that the band gaps $\Gamma \rightarrow \Delta_{min}$ and $\Gamma \rightarrow X$ decrease with increase in the relative change of the lattice constant for the three compounds since both coefficients B and C are negative. This is in agreement with the variation of the band gap with lattice constant deduced for the compounds GaAs [41] and SiC [42]. The band gaps $\Gamma \rightarrow L$ and $\Gamma \rightarrow \Gamma$ increase with the increase in the relative variation of the lattice constant for all the compounds. This behaviour confirms well our analyses on the variation of the band gaps according to the pressure.

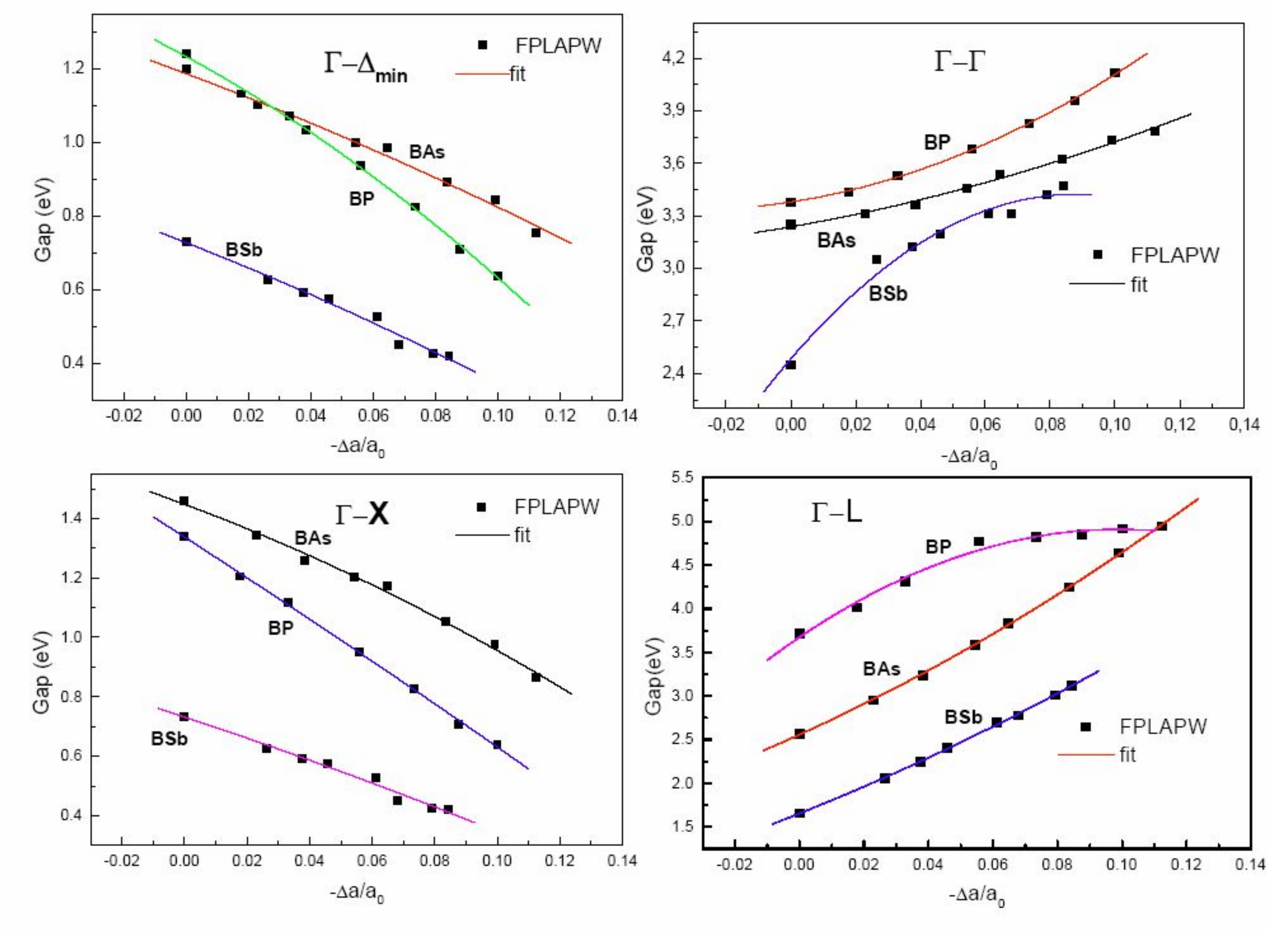


Fig. 3. calculated dependence of the band gaps $\Gamma_{15v} \rightarrow \Delta_{min}$, $\Gamma_{15v} \rightarrow \Gamma_{15c}$, $\Gamma_{15v} \rightarrow L_{1c}$ *and* $\Gamma_{15v} \rightarrow X_{3c}$ *of boron compounds BP, BAs and BSb as a function of relative variation of lattice constant.*

From our band structure studies, the behaviour of the various band gaps can be understood in terms of the relative changes in the energies of the various bands as pressure is varied. It is found that in these compounds, the band gaps $\Gamma \rightarrow \Delta_{min}$ and $\Gamma \rightarrow X$ decrease with increase in pressure due to the lowering in energy of the conduction band (B p and X p, X=P,As,Sb)**.**

On the other hand, the band gaps $\Gamma \rightarrow L$ and $\Gamma \rightarrow \Gamma$ increase as the pressure is increased because energy of the conduction band at the points L and Γ increase.

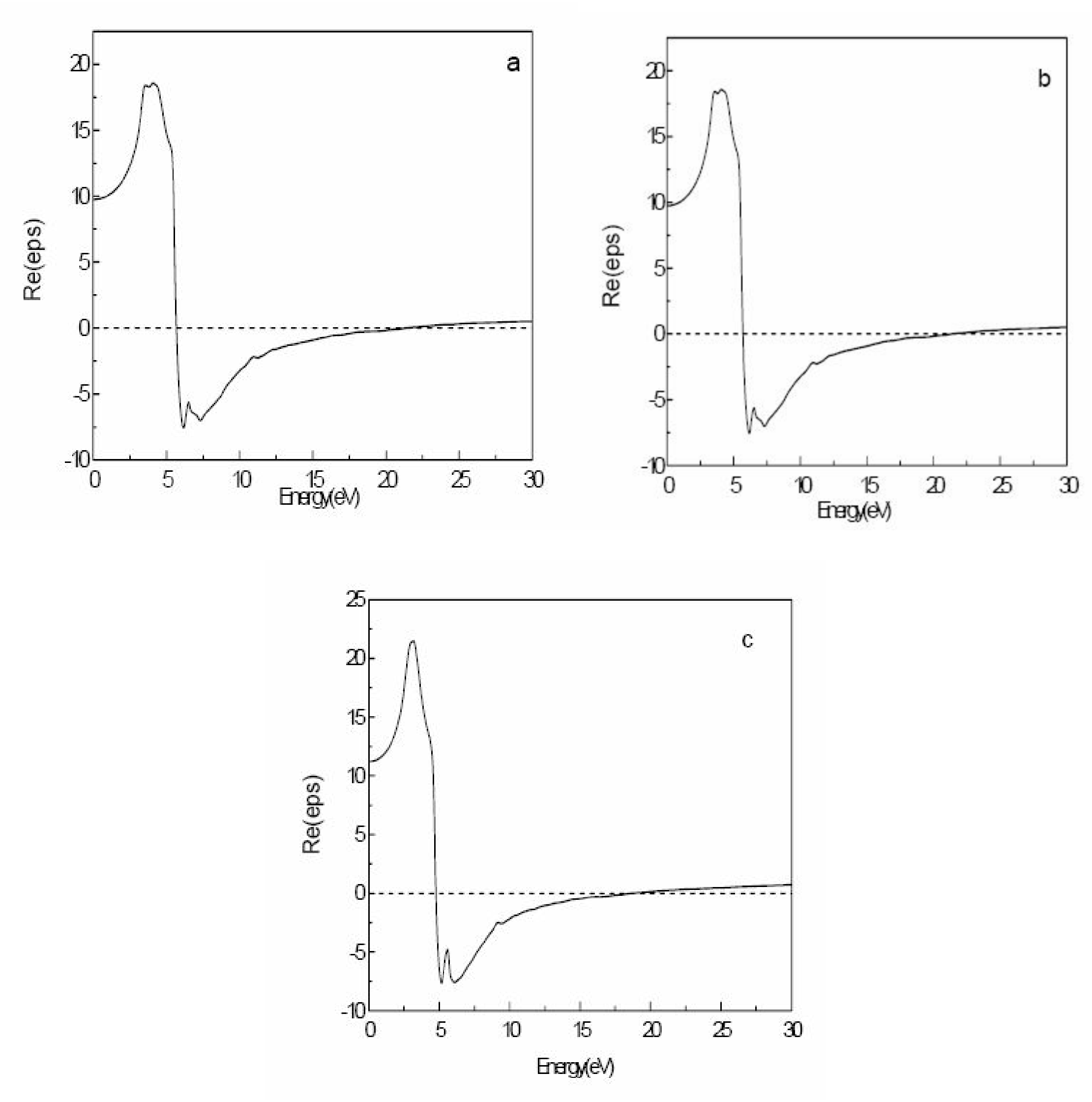


Fig. 4. Calculated real parts of dielectric function for (a) BP, (b) BAs and (c) BSb.

3.3. Optical properties

The most important measurable quantity we address in this section is the static dielectric constant $\varepsilon_1(0)$ and the refractive index n(0) which is obtained by the relation **2**. Fig. 4 shows the real part of the dielectric function in the energy range up to 30 eV. Generally, it is seen that the dielectric spectra for the boron compounds BP, BAs and BSb are similar.

Table3. Coefficients obtained from least-square fits with $E_g^{\alpha}(a) = E_g^{\alpha}(a_0) + B\left(\frac{-\Delta a}{a_0}\right) + C\left(\frac{-\Delta a}{a_0}\right)^2$ *to the calculated values of the indirect* $\Gamma \rightarrow \Delta_{\min}$, $\Gamma \rightarrow L$, $\Gamma \rightarrow X$ *and direct* $\Gamma \rightarrow \Gamma$ *band gaps of boron compounds BP, BAs and BSb.*

	$\Gamma_{15v} \rightarrow \Delta_{\min}$			$\Gamma_{15v} \rightarrow \Gamma_{15c}$			$\Gamma_{15v} \rightarrow L_{1c}$			$\Gamma_{15v} \rightarrow X_{3c}$		
	E(a$_0$)	*B*	*C*	*E(a$_0$)*	*B*	*C*	*E(a$_0$)*	*B*	*C*	E(a$_0$)	B	C
BP	1.23	-4.59	-14.13	3.37	2.84	44.40	3.67	24.9	-125.80	1.33	-6.80	-2.63
BAs	1.19	-3.18	-4.51	3.23	3.21	16.27	2.55	16.70	2.55	1.44	-3.91	-10.01
BSb	0.72	-3.33	-4.98	2.48	21.45	-122.58	1.65	14.71	30.98	0.73	-3.48	-3.73

Table 4. Calculated static optical properties and pressure coefficient of refractive index for BP, BAs and BSb.

Compounds	$\varepsilon(0)$	*n(0)*	$\frac{1}{n_0}\frac{dn}{dp}$ (10^{-2}GPa^{-1})
BP	9.03^a 10.55^b 11^d	3.004^a 3.25^b 3.1^c	-0.031^a -0.0029
BAs	9.67^a 11.19^b	3.10^a 3.35^b	-0.042^a -0.019
BSb	11.17^a 6.37^b	3.34^a 2.52^b	-0.19^a -0.035

In Table 4, we present the different optical properties of the three binary compounds at normal pressure and the pressure coefficients of refractive index ($\alpha = \frac{1}{n_0}\frac{dn}{dp}$).

Fig. 5 shows the calculated results for the pressure dependence of the dielectric constants $\varepsilon(0)$ for all compounds considered. As can be seen, the dielectric constants decrease with increase in pressure. We can also notice that the calculated dielectric constants values increase when the atomic number of the group –V element increases ($P \rightarrow As \rightarrow Sb$).

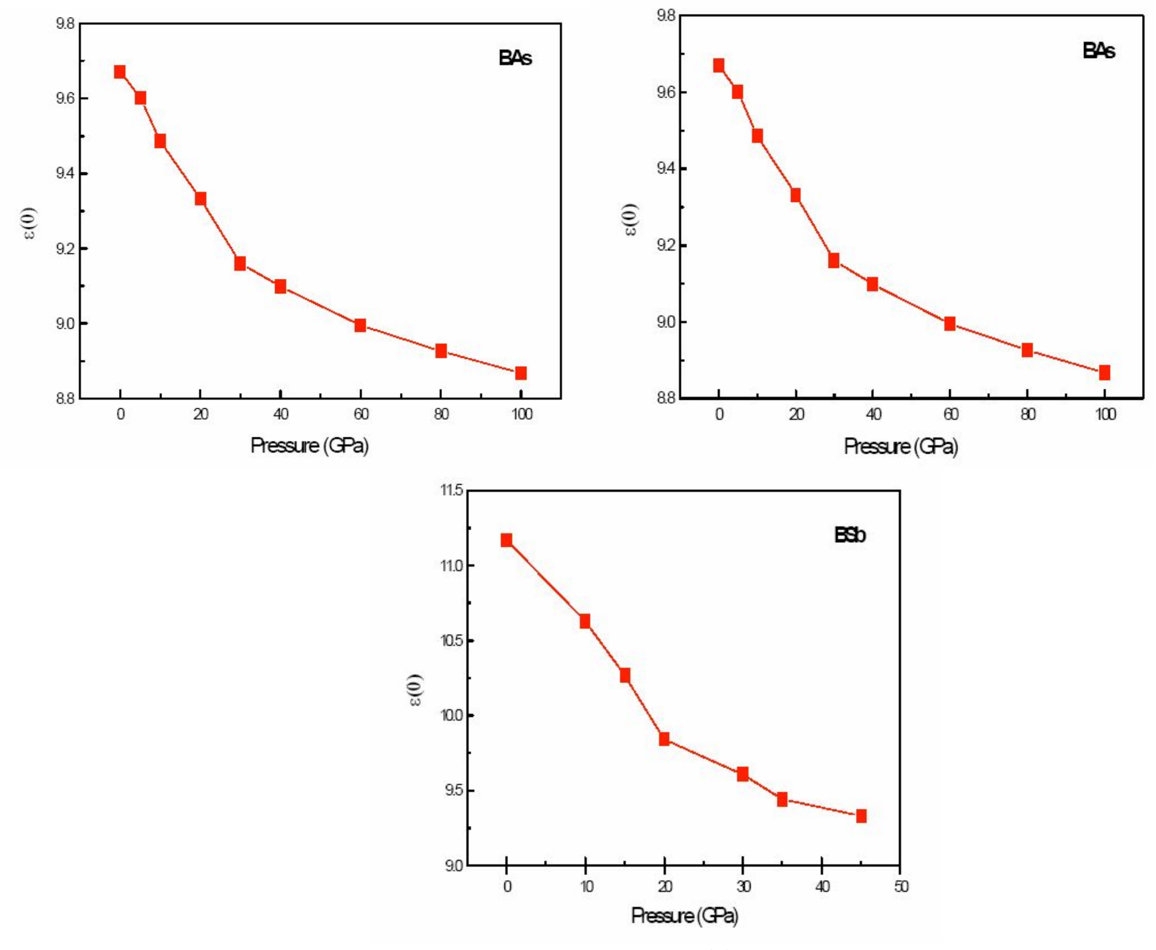


Fig. 5. Pressure dependence of $\varepsilon(0)$ *of BP, BAs and BSb*

The pressure derivative of the refractive index n of BP, BAs and BSb is determined by a linear fit. We have a negative value of pressure coefficients of refractive index, in good agreement with previous calculations [43]**.** This result could be expected knowing that the dielectric constant (and the refractive index) is related to the microscopic polarizability, which has the same dimension and characteristics of a volume: then, the increase in pressure or the decrease in the size of the atom (from Sb to P), leads to a decrease in the polarizability and the refractive index. From our results, the first derivative of n versus p, which is negative, is all the more large when the atoms in the alloys are big.

4. Conclusions

We have used the generalized gradient approximation within the full potential linearized augmented plane wave method to study the electronic and optical properties of zincblende boron compounds under pressure. A summary of our results follows:

1. Our calculated band gaps, using GGA, are in a good agreement with the other computational works, but lower than the experimental work.

2. Our investigation of the effect of pressure on the main band gaps, show that the band gaps $\Gamma \rightarrow \Delta_{min}$ and $\Gamma \rightarrow X$ decrease with increase in pressure, on the other hand, the band gaps ($\Gamma \rightarrow \Gamma$) and ($\Gamma \rightarrow L$) increase with increase in pressure. The calculated pressure coefficients close the available theoretical results.

3. The optical properties of the compounds have been investigated at normal and under hydrostatic pressure. It is shown that the static dielectric constant decreases under pressure. We are not aware of any published data on the static dielectric constant under pressure, so our calculations can be used to cover the lack of data for these compounds.

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