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Fundamental state quantities and high-pressure phase transition in beryllium chalcogenides

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Abstract

In this work we study the structural and electronic properties of Be chalcogenides (BeS, BeSe and BeTe) using two different methods: the full-potential linear augmented-plane wave (FP-LAPW) and the plane-wave pseudopotential (PPsPW). The exchange–correlation effects are treated in the local-density approximation (LDA) and the generalized-gradient approximation (GGA). We have evaluated the ground-state quantities such as equilibrium volume, bulk modulus and its pressure derivative as well as the elastic constants. Various structural phase transitions were considered here in order to confirm the most stable structure and to predict the phase transition under hydrostatic pressure. In addition we have studied the band structure and the density of states, which show a wide indirect band gap for these compounds. These results were in favourable agreement with previous theoretical works and the existing experimental data. To complete the fundamental characteristics of beryllium chalcogenide compounds we have analysed their bonding character in terms of charge transfer and the ionicity parameter. The latter is found to be in agreement with the charge transfer behaviour, which shows an important ionic localization.

1. Introduction

Wide-band-gap semiconductors have expanded the scope of device applications beyond those of silicon and gallium arsenide. Exploitation of wide-gap semiconductors holds promise for revolutionary improvement in the cost, size, weight and performance of a broad range of military and commercial microelectronic and optoelectronic systems. The inherent material properties of beryllium chalcogenides make them ideal candidates for light-emitting and laser diodes (LEDs and LDs) operating in the visible region of the spectrum and consequently

very attractive for various industrial applications such as optical disc storage and fibre-optical communication.

Recently, many interesting studies have been made to shed light on the structural and electronic properties of beryllium chalcogenides [1–14]. Luo *et al* [3] studied the structural phase transformation of BeSe and BeTe using a diamond anvil cell. Narayana *et al* [10] used the same technique to study the phase transformation of BeS. Some previous theoretical works, such as those of Van Camp and Van Doren [7], were devoted to the phase transformations of BeS using the *ab initio* pseudopotential method. The latter method was used by Munoz *et al* [4] to study the phase transitions for all beryllium chalcogenides. Gonzalez-Diaz *et al* [9] have investigated the elastic constants of beryllium chalcogenides using the same method as well. More recently Fleszar *et al* [11] studied the electronic excitations in beryllium chalcogenides from an *ab initio* GW approach [18, 19].

In this study, we have carried out *ab initio* calculations of the structural and electronic properties for three BeX compounds: BeS, BeSe and BeTe. We have considered various structural phases in order to get the most stable phase and to predict the phase transition under hydrostatic pressure. Moreover, a detailed analysis of the band structure, density of states and bonding behaviour are reported in order to achieve a complete study for these compounds. To this end, two different methods (FP-LAPW and PPsPW) were employed. The exchange–correlation effects are treated in the local-density approximation and the generalized-gradient approximation. This paper is organized as follows. The methods used are described in section 2. In section 3 we present and discuss our results. Section 4 is the conclusion.

2. Computational details

The structural and electronic properties of beryllium chalcogenides were calculated using both the all-electron full-potential linear augmented-plane-wave method (FP-LAPW) [31] and the plane-wave pseudopotential (PPs-PW) [32] scheme. The latter was used for comparison in all steps of this work except for the structural phase transitions.

For the FP-LAPW method, we have performed scalar relativistic calculations in which the exchange–correlation terms have been treated within both the local-density approximation (LDA) [33] and generalized-gradient approximation (GGA) [30]. To calculate the total energy we used a muffin-tin radius (R_{mt}) of 1.6, 2.0, 2.1 and 2.3 au for Be, S, Se and Te respectively. The plane wave cut-off is determined by $R_{\text{mt}}^* K_{\text{max}} = 8.75$. The Brillouin zone is sampled on a uniform mesh with 43, 36, 56 and 35 irreducible k -points for the zinc blende (ZB), NiAs, CsCl and NaCl phases, respectively. For each calculation, the energy convergence criterion is set to be 0.1 mRyd.

For the PPs-PW method, the pseudopotentials used are norm-conserving [23, 24] and they were generated using non-relativistic calculations except for Se and Te pseudopotentials, which were calculated scalar relativistically. Nonlinear core corrections were included for the Be atom. The Ceperley–Alder electron gas results [15] as interpolated by Perdew and Zunger [16] were used for the exchange correlation potential. The pseudo-wavefunctions were expanded in a plane-wave basis set with an energy cut-off of 60 Ryd for all the compounds treated in order to ensure convergence by an accuracy of 10^{-3} Ryd. At the equilibrium cell volume this corresponds to an expansion into approximately 1483, 1796 and 2307 plane waves for BeS, BeSe and BeTe respectively. For the primitive cell of the reciprocal lattice (first Brillouin zone) we used a Monkhorst–Pack [17] $4 \times 4 \times 4$ shifted grid, which corresponds to 10 special k -points.

Both the energy cut-off and number of k -points were tested to be sufficient for the convergence in all cases for the two methods used (FP-LAPW and PPs-PW).

Table 1. Lattice parameters a and c/a (between square brackets), bulk modulus B_0 , and its pressure derivative B'_0 for the different phases studied for BeS, BeSe and BeTe.

Material	Phase	Reference	a (Å)[c/a]	B_0 (Mbar)	B'_0
BeS	ZB	Present work	4.80 ^a ; 4.88 ^b ; 4.81 ^c	0.98 ^a ; 0.90 ^b ; 0.91 ^c	3.64 ^a ; 4.04 ^b ; 3.60 ^c
		Theory	4.75 ^d ; 4.82 ^f ; 4.81 ^e	1.16 ^d ; 1.13 ^f ; 0.93 ^e	3.22 ^d ; 3.99 ^f ; 3.34 ^e
			4.77 ^g	1.02 ^g	3.70 ^g
		Experiment	4.86 ^h ; 4.87 ⁱ	1.05 ⁱ	3.5 ⁱ
	NiAs	Present work	3.25[1.59] ^a ; 3.31[1.58] ^b	1.16 ^a ; 1.06 ^b	3.48 ^a ; 3.53 ^b
		Theory	3.20[1.59] ^d	1.36 ^d	3.98 ^d
	NaCl	Present work	4.56 ^a ; 4.64 ^b	1.13 ^a ; 1.07 ^b	3.57 ^a ; 3.40 ^b
		Theory	4.49 ^d	1.26 ^d	3.20 ^d
	CsCl	Present work	2.87 ^a ; 2.93 ^b	0.91 ^a ; 0.81 ^b	3.45 ^a ; 3.34 ^b
		Theory	2.87 ^d	0.76 ^d	3.25 ^d
BeSe	ZB	Present work	5.09 ^a ; 5.19 ^b ; 5.12 ^c	0.85 ^a ; 0.74 ^b ; 0.76 ^c	3.23 ^a ; 3.47 ^b ; 3.68 ^c
		Theory	5.04 ^d ; 5.13 ^e	0.98 ^d ; 0.80 ^e	3.11 ^d ; 3.56 ^e
		Experiment	5.14 ^h	0.92 ^j	
	NiAs	Present work	3.46[1.58] ^a ; 3.53[1.57] ^b	1.03 ^a ; 0.86 ^b	3.31 ^a ; 3.70 ^b
		Theory	3.42[1.58] ^d	0.95 ^d	3.85 ^d
	NaCl	Present work	4.84 ^a ; 4.93 ^b	1.00 ^a ; 0.85 ^b	3.33 ^a ; 3.57 ^b
		Theory	4.80 ^d	0.91 ^d	4.03 ^d
	CsCl	Present work	3.05 ^a ; 3.11 ^b	0.87 ^a ; 0.70 ^b	3.43 ^a ; 3.72 ^b
		Theory	3.06 ^d	0.75 ^d	3.38 ^d
	BeTe	ZB	Present work	5.56 ^a ; 5.67 ^b ; 5.56 ^c	0.68 ^a ; 0.55 ^b ; 0.60 ^c
Theory			5.53 ^d ; 5.58 ^e	0.71 ^d ; 0.60 ^e	3.38 ^d ; 3.72 ^e
Experiment			5.62 ^h	0.67 ^j	
NiAs		Present work	3.79[1.55] ^a ; 3.86[1.56] ^b	0.83 ^a ; 0.66 ^b	3.30 ^a ; 3.88 ^b
		Theory	3.77[1.56] ^d	0.77 ^d	3.72 ^d
NaCl		Present work	5.27 ^a ; 5.37 ^b	0.78 ^a ; 0.65 ^b	3.41 ^a ; 3.76 ^b
		Theory	5.25 ^d	0.79 ^d	3.57 ^d
CsCl		Present work	3.30 ^a ; 3.36 ^b	0.69 ^a ; 0.60 ^b	3.84 ^a ; 4.52 ^b
		Theory	3.31 ^d	0.70 ^d	3.54 ^d

^a Present calculations using the FP-LAPW method within the LDA.

^b Present calculations using the FP-LAPW method within the GGA.

^c Present calculations using the PPsPW method within the LDA.

^d Reference [4].

^e Reference [5].

^f Reference [6].

^g Reference [7].

^h Reference [2].

ⁱ Reference [10].

^j Reference [3].

3. Results and discussion

3.1. Structural properties

The results of our total-energy calculations for the three BeX ($X = \text{S, Se and Te}$) compounds are illustrated in figure 1. We confirm from these curves that the ZB phase is the most stable. In order to obtain the equilibrium atomic volume, the bulk modulus and its pressure derivative, we have fitted the total energy versus volume curves from the Murnaghan equation of state [20]. The results are listed in table 1 and are compared with some available theoretical values and experimental data. We may notice for the obtained equilibrium lattice constant a net concordance between the two methods used within the LDA approximation and the

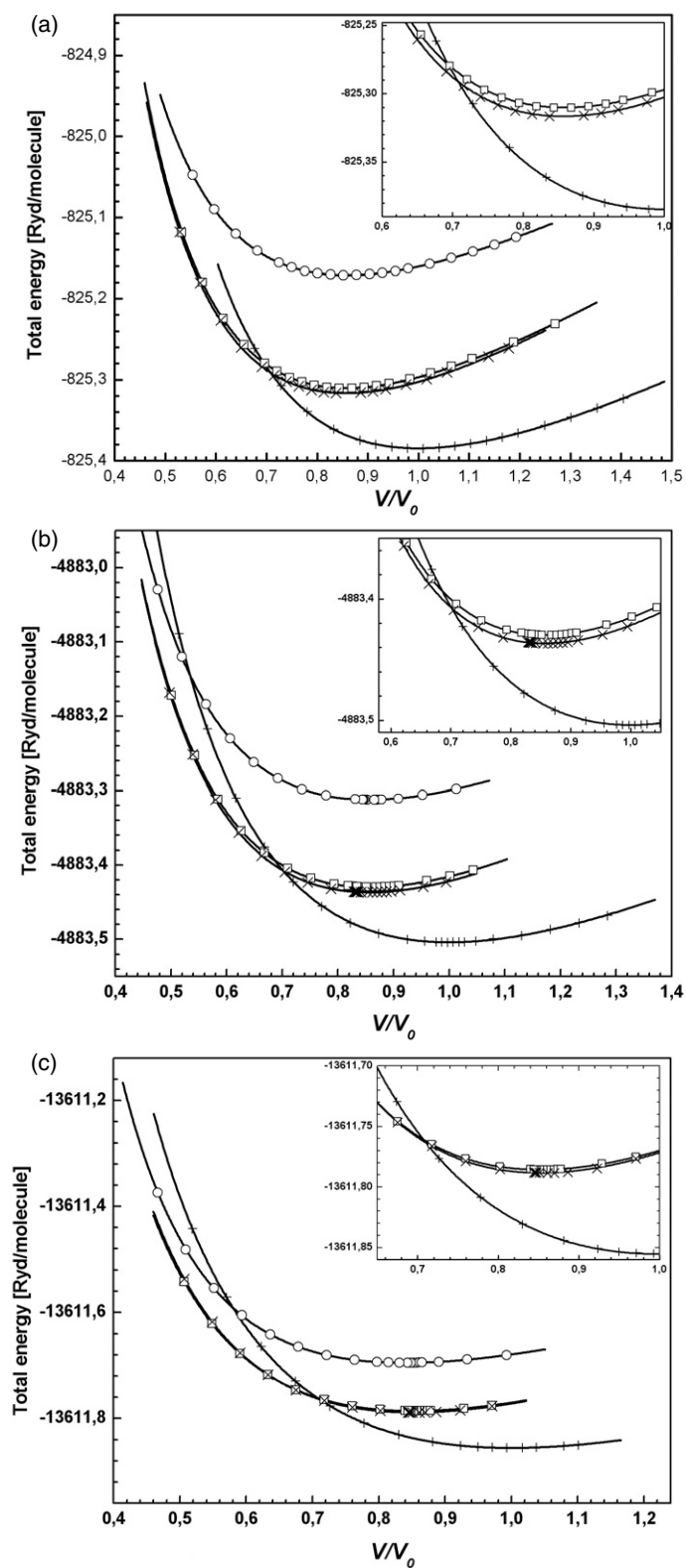


Figure 1. Calculated total energy versus volume for ZB (cross (+)), NiAs (cross (x)), NaCl (open square), and CsCl (open circle) phases for BeS (a), BeSe (b), and BeTe (c). For the BeSe and BeTe compounds, V_0 is the calculated zero-pressure volume for the ZB phase.

Table 2. Transition volumes and transition pressures for the ZB to NiAs structures. Volumes are normalized to the calculated equilibrium volumes in the ZB structures.

Material	Reference	V_T (ZB)	V_T (NiAs)	ΔV (%)	P_T (GPa)
BeS	Present work [FPLAPW]				
	LDA	0.752	0.661	12.07	49.24
	GGA	0.745	0.649	12.85	51.15
	Other calculation	0.757 ^a , 0.727 ^c	0.651 ^a , 0.648 ^c	14.03 ^a , 10.7 ^c	52.35 ^a , 58.5 ^c
	Experimental data	0.724 ^e		11.0 ^e	51 ^e
BeSe	Present work [FPLAPW]				
	LDA	0.743	0.659	11.20	42.4
	GGA	0.715	0.635	11.12	47.32
	Other calculation	0.759 ^a , 0.716 ^b	0.659 ^a , 0.632 ^b	13.25 ^a , 11.7 ^b	42.76 ^a , 45.7 ^d
	Experimental data	0.733 ^d	0.658 ^d	10.2 ^d	56 ± 5 ^b
BeTe	Present work [FPLAPW]				
	LDA	0.753	0.669	11.21	31.26
	GGA	0.732	0.647	11.58	31.77
	Other calculation	0.758 ^a , 0.714 ^b	0.665 ^a , 0.633 ^b	12.41 ^a , 11.3 ^b	32.21 ^a , 34.7 ^d
	Experimental data	0.742 ^d	0.668 ^d	10 ^d	35 ± 5 ^b

^a Reference [4].^b Reference [3].^c Reference [7].^d Reference [8].^e Reference [10].

experimental results, which corresponds to about 1%–1.2%, 0.4%–1% and 1% for BeS, BeSe and BeTe respectively in the ZB phase.

The corresponding calculation based on the GGA is overestimated by 0.4%, 1% and 0.9%. Our calculated bulk moduli within the FP-LAPW scheme based on the LDA are 0.98, 0.85, and 0.68 Mbar (BeS, BeSe and BeTe), which are very close to the experimental values of 1.05, 0.92 and 0.67 Mbar. In addition, our results concerning the different phases studied are close to those obtained previously by Munoz *et al* [4], where they used *ab initio* pseudopotential technique with the same approximation of exchange–correlation effects (LDA). Using the full-potential calculation, we notice the best agreement between our calculated bulk moduli and the experimental data for the LDA approximation rather than for the GGA. This unexpected agreement probably comes from the fit based on the use of Murnaghan’s equation.

Since the pressure-induced phase transition of usual semiconductors, including Be chalcogenides, is known to be insensitive to temperature (at least up to room temperature) experimentally, it is a common practice to neglect the entropy contribution ($-TS$) to the Gibbs free energy and minimize the enthalpy ($H = E + PV$) to predict the transition. The pressure-induced transition occurs along the common tangent line connecting the tangential points on the two total-energy curves. The negative of its slope is the transition pressure (P_T). All the studied compounds follow the same first phase transition, i.e. from the ZB phase to the NiAs one, as shown in figure 1. The calculated transition volumes (V_T) and transition pressures are given in table 2 along with previous theoretical and experimental values. The differences between our LDA results and experiment are only 1.36%, 1.48% for V_T in the ZB structure and 0.15% for V_T in the NiAs structure for BeSe and BeTe, respectively, whereas the transition pressures show a larger discrepancy (3.45%, 7.22% and 9.91% for BeS, BeSe and BeTe respectively). In fact this difference occurs when we are dealing with a quantity involving derivatives, like for the calculated P_T , which is quite sensitive to a small error in energy.

Table 3. The elastic constants C_{ij} , the bulk modulus B_0 , and the shear modulus $C_s = (C_{11} - C_{12})/2$ for BeS, BeSe and BeTe.

Material	Reference	C_{11} (Mbar)	C_{12} (Mbar)	C_{44} (Mbar)	B_0 (Mbar)	C_s (Mbar)
BeS	Present work	1.87 ^a ; 1.56 ^b	0.59 ^a ; 0.59 ^b	0.93 ^a ; 0.95 ^b	0.98 ^a ; 0.91 ^b	0.64 ^a ; 0.49 ^b
	Theory	1.84 ^c	0.75 ^c	0.99 ^c	1.11(1.16) ^c	0.55 ^c
	Experiment				1.02 ^d 1.05 ^e	
BeSe	Present work	1.45 ^a ; 1.29 ^b	0.51 ^a ; 0.49 ^b	0.61 ^a ; 0.79 ^b	0.85 ^a ; 0.76 ^b	0.47 ^a ; 0.40 ^b
	Theory	1.49 ^c	0.59 ^c	0.81 ^c	0.89(0.98) ^c	0.45 ^c
	Experiment				0.92 ^f	
BeTe	Present work	1.02 ^b	0.39 ^b	0.63 ^b	0.68 ^a ; 0.60 ^b	0.32 ^b
	Theory	1.11 ^c	0.43 ^c	0.60 ^c	0.66(0.70) ^c	0.34 ^c
	Experiment				0.67 ^f	

^a Present calculations using the FP-LAPW method within the LDA.

^b Present calculations using the PPsPW method within the LDA.

^c Reference [9]: the first value uses $B = (C_{11} + 2C_{12})/3$; the second value (in brackets) uses B from Murnaghan's equation.

^d Reference [7].

^e Reference [10].

^f Reference [3].

3.2. Elastic constants

In order to investigate the mechanical properties of the studied compounds we have used the PPsPW method and applied the method developed by Mehl *et al* [21]. The elastic constants of a cubic crystal (ZB in our case) may be divided into two classes, the bulk modulus $B = (C_{11} + 2C_{12})/3$, and the two shear moduli, $(C_{11} - C_{12})/2$ and C_{44} . The bulk modulus is related to the curvature of $E(V)$, which can be determined using the Murnaghan equation of state [20]. The shear modulus requires the knowledge of the derivative of the energy as a function of lattice strain [22]. This strain can be chosen so that the unit-cell volume is conserved. Thus for the calculation of $C_{11}-C_{12}$ we used the volume-conserving orthorhombic strain tensor,

$$\vec{\varepsilon} = \begin{pmatrix} \delta & 0 & 0 \\ 0 & -\delta & 0 \\ 0 & 0 & \delta^2/(1 - \delta^2) \end{pmatrix}.$$

Applying this strain involves change in the total energy from its unstrained value to

$$E(\delta) = E(-\delta) = E(0) + (C_{11} - C_{12})V\delta^2 + O[\delta^4],$$

where V is the unit-cell volume and $E(0)$ is the energy of the unstrained lattice at volume V .

For the elastic modulus C_{44} , we used the volume-conserving monoclinic strain tensor

$$\vec{\varepsilon} = \begin{pmatrix} 0 & 1/2\delta & 0 \\ 1/2\delta & 0 & 0 \\ 0 & 0 & \delta^2/(4 - \delta^2) \end{pmatrix}.$$

This changes the total energy to $E(\delta) = E(-\delta) = E(0) + 1/2C_{44}V\delta^2 + O[\delta^4]$. Besides, the results were also obtained from the FPLAPW scheme following the method implemented in the WIEN2K package by Charpin [31]. Our calculated and earlier theoretical values of elastic constants for BeS, BeSe and BeTe are listed in table 3. We notice that except for the bulk modulus there are no available experimental values for elastic constants for these compounds. The agreement with previous theoretical works is good for all the calculated values in both cases (FPLAPW and PPsPW). From the bulk modulus and shear modulus obtained for

Table 4. Calculated and experimental direct and indirect band gaps for the ZB compounds (all values are given in eV).

Material	Reference	Direct gap (Γ - Γ)	Indirect gap (Γ -X)
BeS	Present work	5.50 ^a ; 5.42 ^b	2.83 ^a ; 2.85 ^b
	Theory	5.51 ^c ; 5.67 ^d ; 5.40 ^e	2.75 ^c ; 2.98 ^d ; 2.82 ^e
	Experiment		>5.5 ^f
BeSe	Present work	4.38 ^a ; 4.52 ^b	2.41 ^a ; 2.43 ^b
	Theory	4.72 ^c ; 4.04 ^d	2.39 ^c ; 2.31 ^d
	Experiment		4-4.5 ^f
BeTe	Present work	3.56 ^a ; 3.57 ^b	1.76 ^a ; 1.80 ^b
	Theory	3.28 ^d	1.6 ^d
	Experiment	4.2 ^g	2.7 ^f , 2.8 ^h

^a Present calculations using the FP-LAPW method within the LDA.

^b Present calculations using the PPsPW method within the LDA.

^c Reference [9].

^d Reference [11].

^e Reference [7].

^f Reference [14].

^g Reference [12].

^h Reference [13].

each compound, we may confirm the good prediction of the calculated phase transition under pressure. The latter decreases with decreasing of the rigidity of the system, which is reflected by the bulk modulus, and the shear modulus, which is an indication of hardness. The more the system is rigid and hard, the more difficult it is to compress it and to change its structural phase. BeS has the highest phase transition under hydrostatic pressure and the highest bulk modulus and shear modulus.

3.3. Band structure

The band structure and densities of states (DOSs) for ZB beryllium chalcogenides BeS, BeSe, and BeTe are compiled in figure 2. They have been calculated by solving the LDA equations by means of a pseudopotential plane-wave basis set as described above. From the figures obtained we notice the similarity of the topology in all compounds.

The three compounds have an indirect band gap with the minimum band gaps located between Γ and X, which is in agreement with previous calculations and experimental measurements. The energy gaps at high-symmetry points are given in table 4 along with the results of the earlier theoretical and experimental studies. We notice the good agreement between our results and the previous calculations. This was expected, since it is well known that the LDA underestimates the band gap. From the band structure curves we may also notice the important splitting in the valence bands at the X-point, which is an indication of the importance of the ionicity of the bond. This splitting does not exist for the elemental semiconductors such as Si and Ge, it is small for the III-V semiconductors with low ionicity, and pronounced for the more ionic systems, which seems to be the case of the BeX compounds.

In figure 3 we present a detailed calculation of partial DOS, where we show the contributions of each atomic orbital for each band. The lowest valence bands originate from the s orbital of S, Se and Te atoms for BeS, BeSe and BeTe, respectively. The highest bands come from s and p hybridization, which originate from the Be cation in all cases. However, the main contributions in the anti-bonding states come from the d orbital of the anion (S, Se and Te) for each compound and in a lowest magnitude, the p orbital of Be.

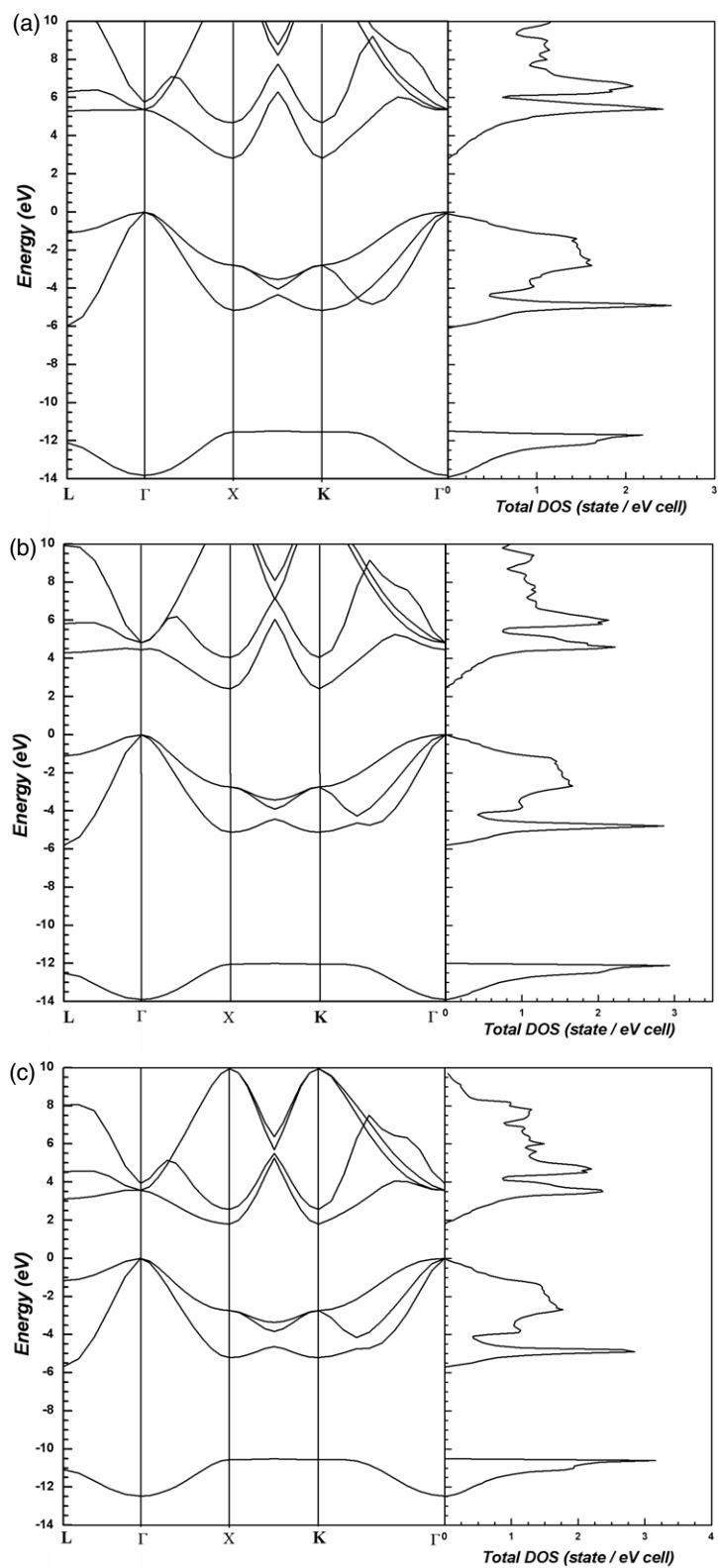


Figure 2. Left panel: calculated energy band structure; right panel: calculated total density of states (DOS) for BeS (a), BeSe (b), and BeTe (c). The energy scale has been adjusted to zero at the valence band maximum at the Γ -point.

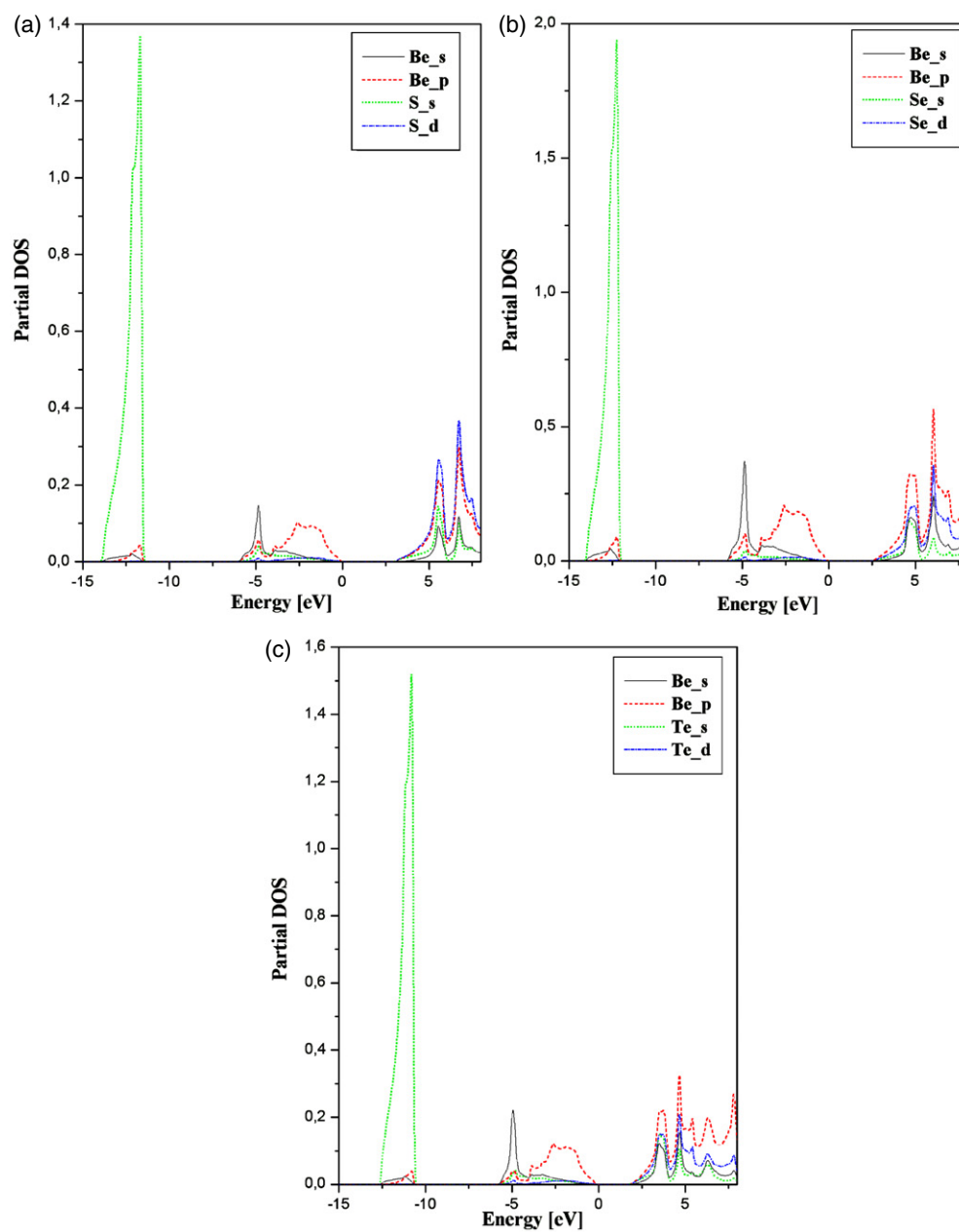


Figure 3. Partial density of states showing the s, p, and d orbital contributions for BeS (a), BeSe (b), and BeTe (c).

(This figure is in colour only in the electronic version)

3.4. Bonding analysis

In figure 4 we display both the charge density contour in the $(1\bar{1}0)$ plane and the charge density profile along the $\langle 111 \rangle$ directions for BeTe as representative compound for the remaining beryllium chalcogenides. The calculation was conducted using the pseudopotential method

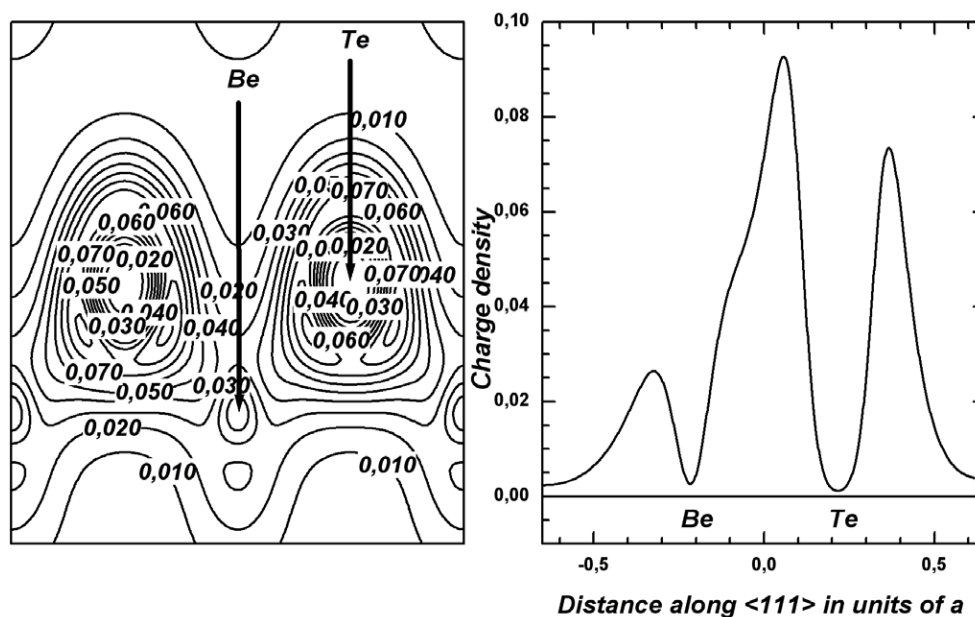


Figure 4. Valence charge density contours in the $[1\bar{1}0]$ plane (left panel), and charge density along the $\langle 111 \rangle$ directions (right panel) for BeTe. The positions of the anion and cation along this direction are indicated.

Table 5. Calculated ionicity parameters compared with those obtained from the models of Phillips, Pauling and Coulson *et al.*

Compound	BeS	BeSe	BeTe	
Ionicity	Present work	0.729	0.677	0.563
	Phillips [26]	0.312	0.299	0.169
	Pauling [27]	0.61	0.59	0.55
	Coulson <i>et al</i> [28]	0.6	0.6	0.6

with the LDA approximation. We may see from the obtained charge density the important delocalization of charges around the anion site, which reflects a pronounced ionic character for these compounds. BeS and BeSe follow the same trends and confirm the same character as well.

The best way to analyse the bond in a given system is to calculate its corresponding ionicity value. There are several ways to define ionicity [25–29], and here we use the model of Zaoui *et al* [25], which is based on a simple formulation of the ionicity of the bond, taking into account two parts of the charge density profile (anionic space and cationic space) with respect to the bond centre. The calculated ionicity parameter using this model is reported in table 5 for the BeX compounds and compared with the values obtained with other models. The first remark to make is about the importance of our values compared to others, in spite of the agreement between ours and those of Pauling [27] and Coulson *et al* [28]. Those obtained by Phillips [26] are much lower. The important values of the ionicity are explained by the charge density behaviour and is mainly due to the small core size of Be and the larger one of S, Se and Te.

4. Conclusion

In conclusion, we have studied the structural and electronic properties of beryllium chalcogenides (BeS, BeSe and BeTe) using both the full-potential linear augmented-plane-

wave (FP-LAPW) and the plane-wave pseudopotential (PPsPW) methods. The two methods were used for comparison in almost all the steps of our work. The ground-state parameters, such as equilibrium volume, bulk modulus and its pressure derivative, were calculated and compared with preceding theoretical works as well as with the available experimental data, and show good agreement. We have additionally predicted the high-pressure phase transition. This calculation was completed by the evaluation of the elastic constants. The band structure and the density of state show a wide indirect band gap for these compounds. All results were in favourable agreement with previous theoretical works and the existing experimental data. Finally, the analysis of the bonding character in terms of charge transfer was confirmed by the important ionicity value. This is supported by the important delocalization of charges around the anionic site.

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