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THEME

Ab-initio calculation of the physical properties of some Beryllium based ternary semiconductors

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DEDICATION

Dedicate this work to my parents.

To my grandmother and grandfather.

To my brothers and sisters.

To all my family.

To my friends and all my teachers.

ACKNOWLEDGEMENTS

This dissertation could not have been written without the help of Allah and the support of many people who have contributed by many different ways.

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Finally, I wish to thank my parents for their support and encouragement throughout my study.

Table of Content

List of Abbreviations

DFT Density functional theory.

CASTEP Cambridge Serial Total Energy Package.

HSE **H**eyd–**S**cuseria–**E**rnzerhof.

LDA local density approximation.

GGA Generalized Gradient Approximation.

LSTO Linear Augmented Slater-Type Orbitals

So simple orthorhombic.

bct body center tetragonal.

fcc face center cubic.

VBM valence band maximum.

CBM conduction band minimum.

DOS density of state.

PP pseudo-potential

PW plane wave

List of figure

List of table

I. General introduction

A theoretical study of the structural, electronic, mechanical and optical properties of some ternary semiconductor compounds with chemical formula $BeAB_2$ (A: C Si and B: N P As) is presented in this dissertation. These, compounds that have non-centrosymmetric crystal structures show a variety of interesting physical properties. Therefore, these compounds have potential for many technological applications, such as photovoltaic, optoelectronic, nonlinearoptic, pyroelectric and electrooptic applications [5] [8].

Density functional theory (DFT) is among the most popular and useful Ab initio methods we have used this method with the pseudo potential plane wave (PPPW) approximation, which is implemented in the CASTEP [1], [2] and ABINIT codes, to determine the properties of BeAB2 compounds.

In the **first chapter,** I will present the physical characteristics and some applications of our compounds and describe the crystallographic structures. Moreover, I will present previous theoretical and experimental works for these compounds.

In the **second chapter**, I briefly describe the method that is used to perform electronic structure calculations, density functional theory DFT and some approximations I used in this dissertation.

In the **third chapter**, I present in the first part, the calculated structural properties: lattice parameter, stable phase and the formation enthalpy. The electronic structure studied in this dissertation are band structure (BS), density of states (DOS) and Mulliken population analysis.

The second part of **chapter III** is concerned with the mechanical properties: elastic constant and I used Debye model to calculate Debye temperature, which is related to melting point, and a discussion of the optical properties: dielectric function, the optical anisotropy and the second harmonic generation susceptibility of some compounds.

In the end, I close my dissertation with a general conclusion and some perspectives.

II. Chapter I

II.1.Introduction

In this chapter, I will present the importance, some application of Beryllium based ternary semiconductors and I describe the different structure of these compounds, the previous theoretical and experimental works also presented in this chapter.

II.2.Be based ternary semiconductors

Ternary semiconductors with the general chemical formula $A^{\mathrm{II}}B^{\mathrm{IV}}C_2^{\mathrm{V}}$ are used in numerous optical applications, such as solar cells, non-linear optical devices, infrared detectors, visible and invisible light emitting diodes etc. In addition, Beryllium based ternary are very hard because they have large elastic constants. Therefore, a large number of experimental [3] and theoretical works focus on the synthesis and understanding of $A^{\mathrm{II}}B^{\mathrm{IV}}C_2^{\mathrm{V}}$ternary properties. In this study, we are interested in Beryllium based compound of general formula $BeB^{\mathrm{IV}}C_2^{\mathrm{V}}$.

II.2.1. Previous works

It has come to our knowledge that the $BeSiN_2$ and $MgSiN_2$ were synthesized [3][4] in a structure derived from the wurtzite (WU) structure(space group *Pna*21 N ref) [5] .In [5]has adopted two strategies for the preparation of $BeCN_2$ films and suggested a possible structure, which is analogous to the WU phase of $BeSiN_2$ and $MgSiN_2$. Moreover, a number of theoretical papers have been published, in which the first-principle study of structural, electronic, mechanical and optical properties of the $A^{\mathrm{II}}B^{\mathrm{IV}}C_2^{\mathrm{V}}$ternary were reported.

II.2.2. Crystal structure $A^{\mathrm{II}}B^{\mathrm{IV}}C_2^{\mathrm{V}}$

According to crystallography data (crystallography open database (COD), Springer Materials and Material project)

Ternary $A^{\mathrm{II}}B^{\mathrm{IV}}C_2^{\mathrm{V}}$ compounds can be obtained in different structural phases. The most probable of these are:

a) A simple orthorhombic (SO) structure (space group*Pna*21) similar to the wurtzite structure.

b) A body-centered tetragonal (bct) chalcopyrite structure (space group *I*-42*d*),which consists of a doubled sphalerite structure, but with an ordered arrangement of cations in the corresponding sublattices.

c) A face-centered cubic (fcc) sphalerite structure (space group F43m) with an average statistical distribution of II- and IV-group atoms over two equivalent cation sublattices.

In this work, we focus on $BeBC_2$compounds, (B=Si, C and C=N, P, As).

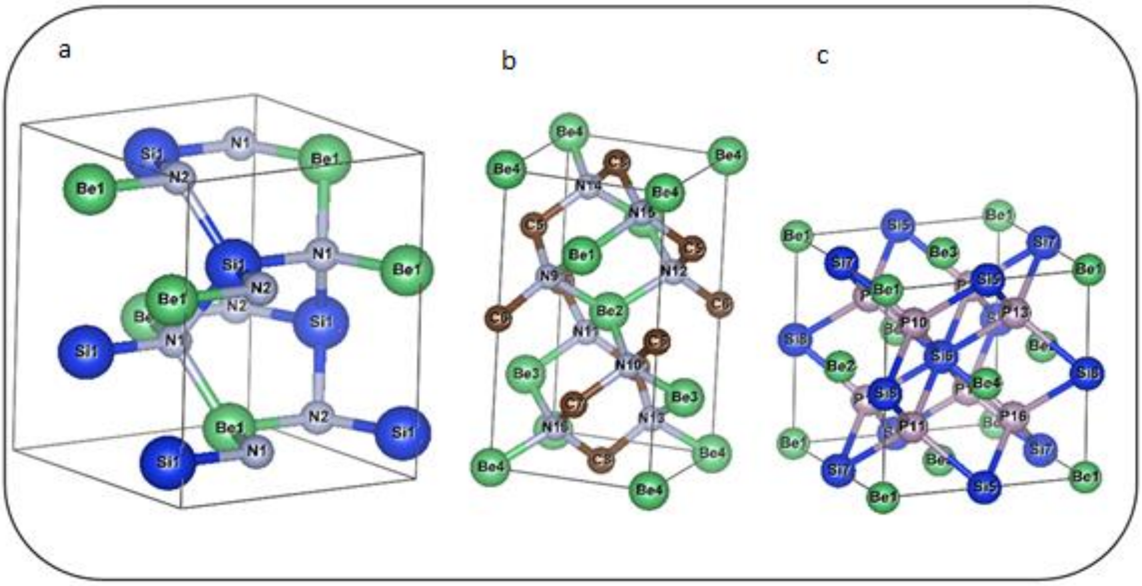


Figure II-1: Schematic representation of the Unit cells of $BeBC_2$. Drawn using VESTA package[6]. *a)* simple orthorhombic b) body-centered tetragonal, , c) face-centered cubic

The unit cells of fcc, bct and so phases contain 8, 8 and 16 atoms. In all of these structures, the elements Be and C or Si atom are tetrahedrally coordinated to four neighboring atoms N, P or As, Figure II-2.

Figure II-2: Tetrahedral coordination

II.2.3. $BeBC_2$ (B: Si, C and C: N, P, As) compounds

Now I am going to present all information I found (structural, mechanical, electronic and optical properties) about $\mathbf{BeBC_2}$ (B: Si, C and C: N, P, As) compounds.

II.2.3.1. $BeCN_2$

This compound is the most studied among all ternary materials of general chemical formula $BeBC_2$, (B= C, Si, Ge, Sn and C= N, P, As, Sb).

Information on the hypothetical $BeCN_2$ with a structure similar to the structure of chalcopyrite, the lattice parameters are (a= from 3.655Å to 3.78Å and c=from 6.829 to 7.272Å) was published in ([7]-[8]).

Table II-1: Structure and calculated equilibrium lattice constants, band Gap, elastic and optical properties for $BeCN_2$ compound.

Properties										
Structural				Electronic	elastic	Optic		XC	ref	
a(Å)	b(Å)	c(Å)	Structure	Gap (eV)		L	NLO			
3.65546		6.82942	Bct	7.34	-*	-	-	(B3LYP)	[7]	2017
3.71		7.27	Bct	4.63	+**	-	-	LDA	[9]	1994
4.373	5.278	4.224	So	5.56	+	+	-	LDA	[10]	2011
4.424	5.329	4.269	So		+	+	-	GGA	[10]	2011
3.746		6.904	Bct	3.72	+	+	-	LDA	[10]	2011
3.782		6.994	Bct		+	+	-	GGA	[10]	2011
3.710		7.272	Bct	3.90	-	+	+	LASTO	[8]	2008

**Previous works

* Not studied

In addition, the lattice parameters of the second structure (wurtzite structure) we found (a=4.373Å, b=5.278Å c=4.224Å) and (a=4.424Å b=5.329Å, c=4.269Å) was published in [10]. Furthermore the band gap was also predicted for two structures besides the optical and mechanical properties [8].. All this information are shown in Table II-1.

II.2.3.2. $BeSiN_2$

This compound is the only synthesized of this family with the chemical formula $BeBC_2$ with an orthorhombic unit cell (SO) with lattice parameters (a=4.977Å b=5.747 Å and c=4.674 Å). In addition hypothetical $BeSiN_2$ was obtained in different structural phases the first is SO with lattice parameter (a=4.999 Å b=5.772Å, c=4.699 Å and a=4.939 Å, b=5.697 Å, c=4.639 Å).The second is bct, (a=3.94554 Å c=7.99001 Å, (a=4.10 c= 8.364 Å) and (a=4.100 b=8.364) and finally fcc (a=4.080). Moreover, the calculated band gaps in the range from 3.60eV to 5.71eV. Furthermore, the mechanical properties were calculations proved that this compound is stable and hard [11]. [6] authors predicted the linear optical properties and in [8] the linear and second order optical properties calculated. See Table II-2.

Table II-2: Theoretical equilibrium lattice constants, band Gap, elastic and optical properties together with experimental data for $BeSiN_2$ compounds.

Structural				Electronic	Elastic	Optic		XC	Ref	Year
a(Å)	b(Å)	C(Å)	Structure	Gap(eV)		L	NLO			
3.94554		7.99001	Bct	5.71	-	-	-	(B3LYP)	[7]	2017
4.10		8.364	Bct	4.47	+	-	-	LDA	[9]	1994
			Bct	3.60	-	-	-	(LDA)	[12]	2004
4.080		8.092	Fcc	-	+	+	-		[11]	2008
4.073		8.164	Bct	-	+	-	-		[11]	2008
4.999	5.772	4.699	So	5.19	+	+	-	GGA	[11]	2008
4.939	5.697	4.639	So	-	+	-	-	LDA	[11]	2008
4.977	5.747	4.674	So	-	-	-	-		**EXP** [13]	1967
4.100		8.364	bct	3.67	-	+	+	LASTO	[8]	2008

II.2.3.3. $BeSiP_2$

This compound was also theoretically studied in three structure bct, so and fcc. The lattice constants of bct calculated in [14],[15] are presented in Table II-3, fcc with lattice parameter (a=5.1198Å, a=5.9021Å) and SO with (a=7.0008Å,b=6.1792Å and c=8, 6824Å) [15]. Moreover,[16] calculated the band gap of the fcc with GGA Eg=2.29eV and[17] calculated the band gap of different functional (1.2eV GGA, 1.84eV MBJ and 1.75eVGW). In addition the linear optical properties predicted in [17], the mechanical properties was also calculated in[14] [15] and [18] , see Table II-3.

Table II-3: Theoretical equilibrium lattice constants, band Gap , elastic and optical properties for $BeSiP_2$ compounds.

Structural				Electronic	elastic	Optic		XC	ref	Year
a(Å)	b(Å)	C(Å)	structure	Gap(eV)		L	ONL			
5.10		10.173	bct	+	+	-	+	GGA	[14]	2015
5.121		10.217	bct	1.2 GGA 1.84 mBJ 1.75 GW	-	+	-		[17]	2012
5.1853		10.3369	bct	+	+	-	-	GGA	[15]	2014
7.0008	6.1792	8.6824	so	+	+	-	-	GGA	[15]	2014
5.9021			fcc	+	+	-	-	GGA	[15]	2014
5.135		10.255	bct	-	+	-	-	GGA	[18]	2014

II.2.3.4. BeSiAs$_2$

The only hypothetical structure of this compound is bct with lattice constants (a=[5.265 to 5.369] and b=[10.5195 to 10.732]). The calculated band gaps range from 1.05eV to 1.68eV.Moreover, this compound has also a good mechanical properties[14][18], all these information are shown in Table II-4.

Table II-4: Theoretical equilibrium lattice constants, Band Gap , elastic, and optical properties for BeSiAs$_2$ compound.

Structural			Electronic	Elastic	Optic		approximation	ref	Year
a(Å)	c(Å)	Structure	gap(eV)		L	ONL			
5.32	10.625	Bct		+	+	-	GGA	[14]	2015
5.36	10.711	Bct	1.07 GGA 1.68 mBJ 1.33GW	-	+	-		[17]	2012
5.36	10.73	Bct	1.05	-	-	-	GGA	[19]	2008
5.369	10.732	Bct	-	-	+	-	-	[20]	2015
5.265	10.5195	Bct	-	+	-	-	GGA	[18]	2014

II.2.3.5. BeCP$_2$ BeCAs$_2$

For these two compounds, we didn't find any experimental or theoretical data.

II.3.Conclusion

The ternary compounds with the chemical formula BeAB$_2$, (A= C, Si, Ge, Sn and B= N, P, As, Sb) have gained much interest in recent years. These materials offer a wide range of possible optical applications and they are very hard and **noncentrosymmetric.** Therefore, a large number of experimental and theoretical works for these compounds but there is no works for the last two compounds (BeCP$_2$ and BeCAs$_2$).

III. Chapter II: Theoretical frame work

II.1.Introduction

This chapter is concerned with the method used for our study; density functional theory, All properties of a quantum system; atom, molecule, solids determined by its wave function Ψ and corresponding energy, which can be obtained by solving the generalized Schrödinger equation.

II.2.Schrödinger equation

Consider a solid to consist of N nucleus and Ne electrons, we can write the time-independent Schrödinger equation for this system, this state called stationary states,

$$\hat{H}\psi(R,r) = E\psi(R,r) \qquad \text{III-1}$$

Where

- E is the total energy of the system and H is the Hamiltonian operator , given by relation

$$\hat{H} = T_e + T_n + V_{e-e} + V_{n-n} + V_{e-n} \qquad \text{III-2}$$

Relation for multi electron atoms is hard to solve, practically is **impossible.** Therefore, eqIII-1is solved using approximate methods.

II.3.Born-Oppenheimer Approximation

Born and Oppenheimer propose the common and the very reasonable approximation used in the solution of equation II-1, since the nuclei are much heavier than electrons (the mass of a proton is about 1836 times the mass of an electron). Therefore, the nuclei moves much slower than the electrons, hence the movement of nuclei and electron can be separated, so $V_{n-n} = constant$, T_n =0 and we can consider that the electrons are moving in a static external potential V_{ext} formed by the nuclei.

II.4.Density functional theory

Density functional theory (DFT)[21] is a highly competitive method for a wide range of applications in solid state physics. Moreover, is formally exact theory, the principal feature of density functional method is that the many problems solved directly for the charge density n(r). Rather than, for the many-electron wave function ψ. This is a massive simplification, as we only need consider a function of three variables x, y and z rather than the 3N variable problem above, its basis is the well-known Hohenberg-Kohn (HK) theorem.

II.4.1. The Hohenberg-Kohn (HK) Theorems

Hohenberg and Kohn in 1964 used the electron density as a fundamental variable, showed that this method may enable the calculation of the exact ground-state energy and created the following theorems on which the D.F.T is based on them:

1) The external potential is a unique functional of the density, this means that the density uniquely determines all properties of the system completely.

2) The exact ground state energy of the system is functional of the exact and 'unique' ground state density $n_0(r)$.

The HK theorems puts the particle density n(r) as the basic variable, it is still impossible to calculate any property of a system, this difficulty was overcome by Kohn and Sham [22] in 1965.

II.4.2. The Kohn-Sham equation

Kohn and Sham [22] give a practical method to calculate the grounds state energy and by replacing the original many-body system by an auxiliary independent-particle system and assume that the two systems have exactly the same ground state densityFig I I-4.

Are introducing an auxiliary system containing N non-interacting electrons in an effective background potential$V_{eff}\left(r\right)$.

$$V_{eff}\left(r\right)=V_H\left(r\right)+V_{xc}\left(r\right)+V_{ex}\left(r\right) \qquad \text{III-3}$$

Where $V_H$is Hartree potential

V_{xc} andV_{ext}arexchange and externe potential respectively.

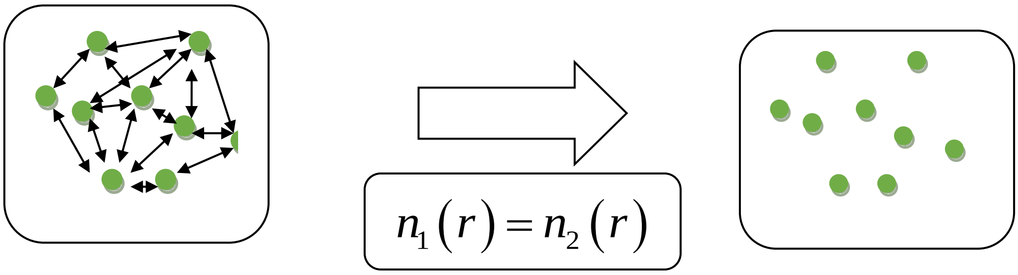


Figure III-1: The real system and the effective system with the same density.

Kohn-Sham equations in atomic unit given by:

$$\left[-\frac{1}{2}\nabla^2+V_{eff}(r)\right]\Psi_i=\varepsilon_i\Psi_i$$

III-4

Right now DFT is an exact theory we don’t forget the first approximation “born oppenhiemer”, It is simple to calculate the kinetic energy of the non-interacting system, is also simple to calculate Hartree potential and the potential applied by the nucleus. The difficult part to this day is $V_{xc}(r)$. We will now review some of the common approximations made for it.

II.4.3. Approximation

II.4.3.1. Local Density Approximations (LDA)

Kohn and Sham introduced this simple approximation for a slowly varying density, this approximation treats the density as a uniform electron gas.

The exchange-correlation energy for a density n(r) can be written as:

$$E_{XC}^{LDA}\left[n(r)\right]=\int n(r)\varepsilon_{XC}^{\hom}\left(n(r)\right)dr$$

III-5

LDA fails in situations where the density undergoes rapid changes.

II.4.3.2. Generalized-Gradient Approximation (GGA)

The electron density is inhomogeneous therefore; XC energy depends on the gradient of the electron density, the so-called Generalized Gradient Approximation (GGA).

The exchange-correlation energy for a density n(r) can be written as

$$E_{XC}^{GGA} = \int f(n, \nabla n) d^3 r \qquad \text{III-6}$$

II.4.3.3. Hybrid functional HSE

The **H**eyd–**S**cuseria–**E**rnzerhof HSE functional is very successful to treat the band structure and predict band gap energy. It is used exact Hartree-Fock exchange (so is computationally expensive) and two GGA-functional, the exchange-correlation energy for a density n(r) can be written as:

$$E_{XC}^{\omega PBEh} = aE_X^{HF,SR}(\omega) + (1-a)E_x^{PBE,SR}(\omega) + E_x^{PBE,LR}(\omega) + E_c^{PBE} \qquad \text{III-7}$$

- a is a mixing parameter
- ω is an adjustable parameter controlling the short-rangeness of the interaction.

for HSE06 a=0.25 and ω =0.189 .

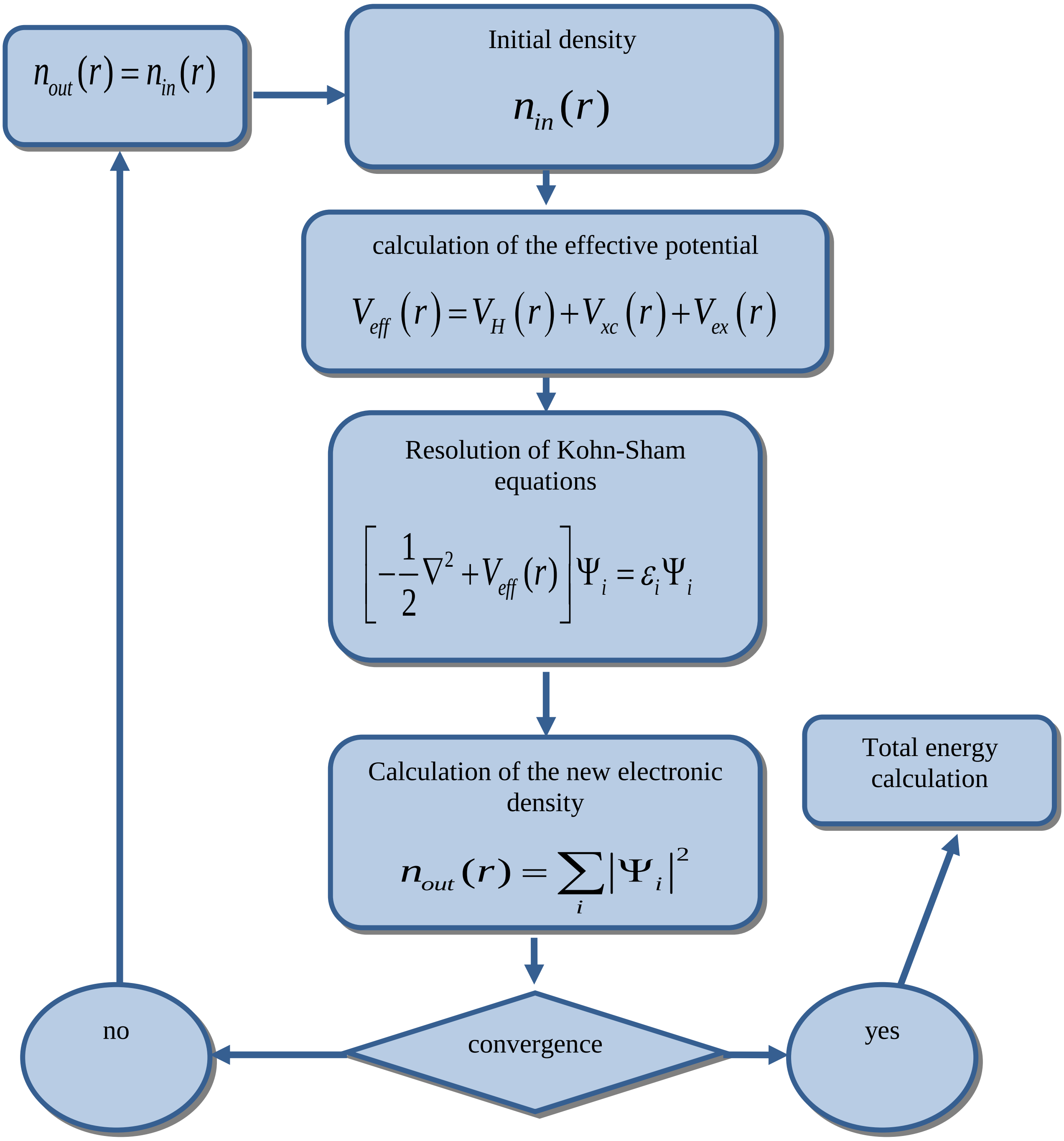


Figure III-2: Self-consist field

II.4.4. Calculation methods

In this work, and in order to calculate the physical properties, I use the pseudo-potential plane wave (PPPW) method as implemented in the CASTEP and ABINIT codes.

In this part, I'm going to talk about the most important concepts for this method and the particularity of the solid crystals.

II.4.4.1. Bloch's Theorem and Plane Wave Basis Sets

Bloch Theorem stipulates that in a perfect crystal (at 0K), the atoms are arranged in a regular periodic way. Therefore, the external potential will also be periodic which can be expressed as:

$$V(\vec{r}) = V(\vec{r} + \vec{R}) \qquad \text{III-8}$$

As by this theorem, it is possible to express the wave function of the infinite crystal in terms of wave functions at reciprocal space vectors of a Bravais lattice. The wave function is written as:

$$\Psi_i\left(\vec{r}\right) = e^{i\vec{k}.\vec{r}} f_i(\vec{r}) \qquad \text{III-9}$$

The second term is the cell periodic part of the wave function. This can be expressed as:

$$f_i(\vec{r}) = \sum_{\vec{G}} C_{\vec{G}}(k) e^{i\vec{G}.\vec{r}} \qquad \text{III-10}$$

Where $\vec{G}$ are the reciprocal lattice vectors

By the equations II-7 and II-8 we obtain the mono-electronic wave function written as a sum of plane wave functions.

$$\Psi_i(\vec{r}) = \sum_{\vec{G}} C_{\vec{G}}(\vec{k}) e^{i(\vec{k}+\vec{G})\vec{r}} \qquad \text{III-11}$$

This Fourier series is infinite. Therefore, we need to make a limit for the wave number, this number is limited by a cutoff energy noted E_cut.

$$\frac{\hbar^2}{2m}\left|\vec{K} + \vec{G}\right|^2 \leq E_{cut} \qquad \text{III-12}$$

The computing cost strongly increases with the increase of E_{cut} value. In the convergence study, we chose the cut off energy for which the total energy converges with the required precision.

II.4.4.2. Sampling of the Brillouin zone

Bloch theorem simplifies a system with infinite number of equations in one finite system, but for an infinite number of k-points. To calculate the energy of the system, it must be integrated over the (finite) first Brillouin zone in reciprocal space.

A finite number of points in the Brillouin zone, called the **k**-point mesh. we choose a sufficiently dense mesh of integration points which is crucial for the convergence of the results. This is the objectives when performing convergence tests on K-points.

II.4.4.3. Pseudopotential

The pseudopotential approximation (PPA) is to replace complicated interactions between core electrons of a physical system by pseudopotential.

The most important reason for using this method that only the valence electrons are chemically active. Most of the properties of a solid are related to the valence electrons. Therefore, we can replace the effect of the core electrons on a valence system by a pseudopotential.

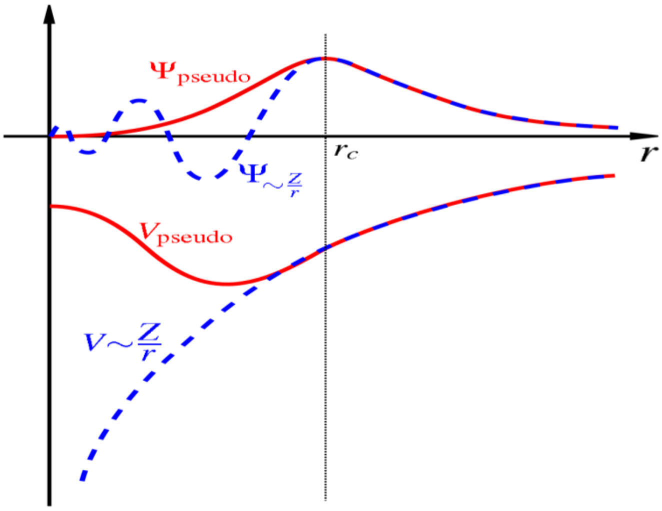


Figure III-3: Schematic illustration of pseudo-potential. Comparison of a wave function in the Coulomb potential of the nucleus (blue) to the one in the pseudo-potential (red). The real and the pseudo wave function and potentials match above a certain cutoffradius r

II.5.Nonlinear optics:

For noncentrosymmetric crystals and only at very high light intensities such as those provided by lasers, the responds nonlinearly to the electric field observed equation III-13.

$$P(t) = \varepsilon_0(\chi^{(1)}E(t) + \chi^{(2)}E^2(t) + \chi^{(3)}E^3(t) + \ldots) \qquad \text{III-13}$$

They are many nonlinear optical processes but we are interested in the frequency doubling (second harmonic generation SHG), for example, Second harmonic generation is used by the laser industry to make green 532 nm lasers from a 1064 n m source.

Figure III-4: Second harmonic generation used by the laser industry

This process can be efficient only when the propagation velocity of the generated second harmonic (2ω) is equal to the propagation velocity of the fundamental signal (ω) (inside the crystal).This is known as phase matching condition.

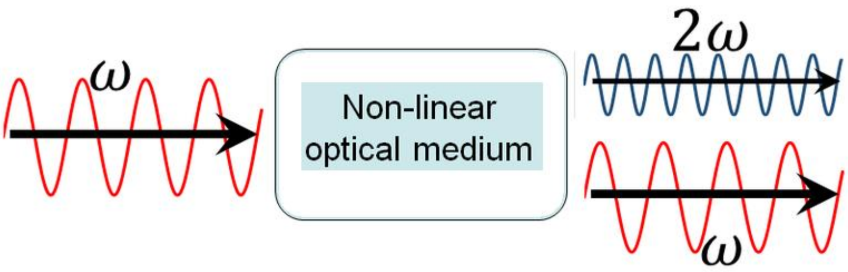


Figure III-5: Second harmonic generation processes.

IV. Chapter III Result and discussion

IV.1. Introduction

In this part, I will present calculation results of structural, electronic, mechanical and optical properties related to the Be based compounds of general formula $BeBC_2$ (B=C, Si, C=N, P, As).

This work was carried out in the LPM laboratory "laboratoire physique des materiaux". The calculations were performed with licensed CASTEP module of the Materials Studio package. It was used for calculating the structural, elastic, electronic and linear optical properties and open source ABINIT code for calculate the nonlinear optical properties.

The generalized gradient approximation (GGA) with the Perdew-Burke -Ernzerhof functional and Heyd-Scuseria-Ernzerhof (HSE06) functional, were used to treat the exchange correlation effects. The valence states considered in our calculations for different atoms of ternary compounds are as follows: Be: $2S^2$, C: $2S^2$ $2P^2$, Si: $3s^2$ $3p^2$, N: $2s^2$ $2p^3$, P: $3s^2$ $3p^3$ and As: $4s^2$ $4p^3$.

IV.2. Convergence study

For Ab-initio method, we need to optimize two parameters that are very important to balance between calculation time and precision of our study.

The first one is the cut-off energy (E_cut), this parameter is used to fix the number of plane wave in the basis set, and the second one is the reciprocal grid spacing, which means the number of K points in reciprocal space (Nkpt) used to sample the first Brillouin zone.

IV.2.1. The tetragonal structure of $BeCN_2$

a) The cut off energy

Table IV-1: Convergence study: Total energy Vs Ecut of $BeCN_2$ with tetragonal phase.

E_{cut}(eV)	E_{tot}(eV)	$\Delta \boldsymbol{E_{tot}} / \boldsymbol{E_{tot}}$
200	-1453.959807927	0.004
300	-1458.858424796	0.0002
400	-1459.011124999	0.0001
500	-1459.065078483	6.371E-05

600	-1459.075211563	5.677E-05
700	**-1459.094610017**	**4.347E-05**
800	-1459.127144231	2.117E-05
1000	-1459.158040112	0

b) reciprocal grid density

Table IV-2: Convergence study: Total energy Vs separation of $BeCN_2$ with tetragonal phase

Separation(1/Å)	E_{tot}(eV)	$\Delta E_{tot}/E_{tot}$
0.07	-1458, 89406	2, 25E-07
0.04	**-1458, 89344**	**-2, 03E-07**
0.02	-1458, 89366	-5, 05E-08
0.01 [303037]	-1458, 89374	

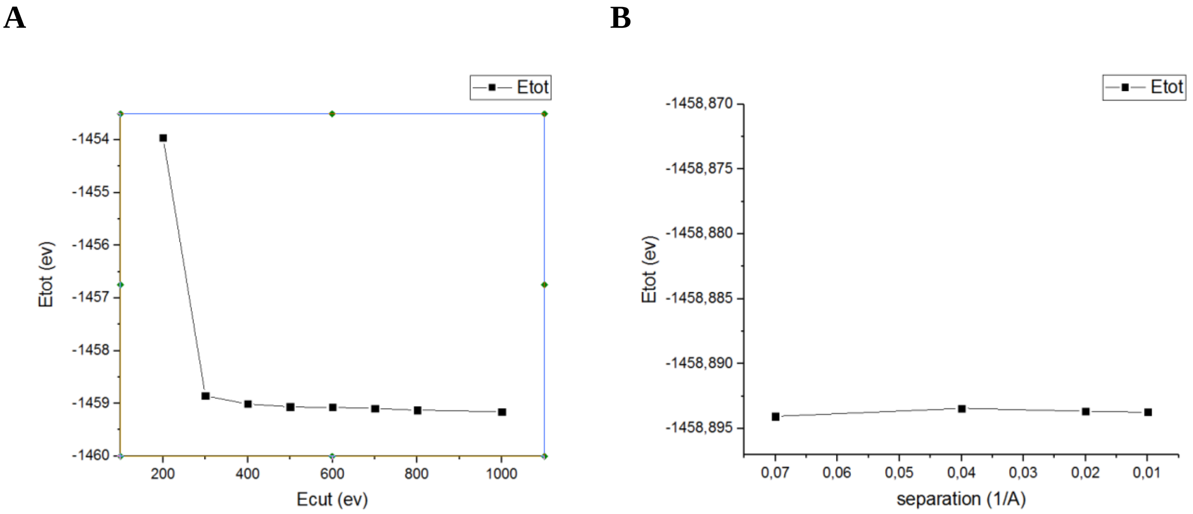


Figure IV-1: Convergence study of $BeCN_2$ with tetragonal phase: (a) Total energy Vs Ecut (b) total energy Vs separation.

We choose the k-points grid separation=0.04 1/(Å) and an cutoff energy E_cut=700eV.

IV.2.2. The orthorhombic structure of $BeSiN_2$

a) The cut-off energy

Table IV-3: Convergence study: Total energy Vs Ecut of $BeSiN_2$ with orthorhombic phase.

E_{cut}	E_{tot}	$\Delta E_{tot}/E_{tot}$
200	-2735, 62586	-0, 0020
300	-2741, 10082	-0, 0001

400	-2741, 27651	-9, 4E-05
500	-2741, 36424	-6, 2E-05
600	-2741, 37498	-5, 8E-05
800	-2741, 47938	1, 96E-05
1000	-2741, 53311	0

b) Reciprocal grid density

Table IV-4: Convergence study: Total energy Vs separation of $BeSiN_2$ with orthorhombic phase.

Separation(1/Å)	E_{tot}(eV)	$\Delta E_{tot}/E_{tot}$
0.1	-2741.118712541	2, 23E-05
0.08	-2741.121360142	2, 32E-05
0.06	-2741.055829752	-6, 76E-07
0.04	**-2741.057817109**	**4, 88E-08**
0.02[10 9 11]	-2741.057683439	0

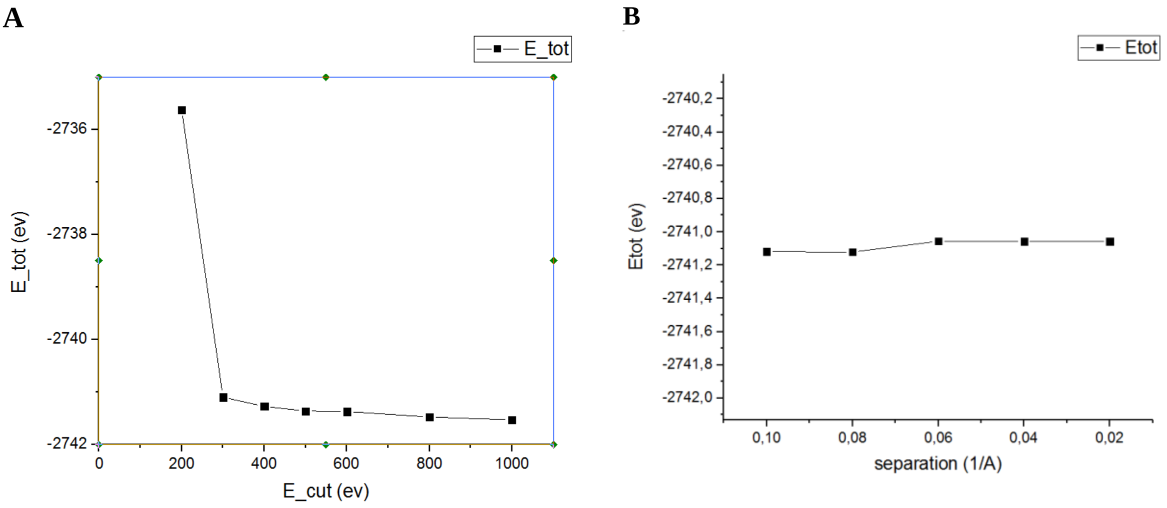


Figure IV-2: Convergence study of $BeSiN_2$ with tetragonal phase: (a) Total energy Vs Ecut of and (b) total energy Vs separation.

We choose the k-points grid separation=0.04 1/Å and an cutoff energy E_{cut}=600eV

IV.3. Structural properties

IV.3.1. Geometric optimization

The first step in the theoretical study of a molecule or a solid, is the relaxation of the structure, by the minimization of forces and stress associated to a minimal energy. Therefore, a good optimization gives the minimum energy or the "ground state energy". The algorithm used by CASTEP module changes the lattice parameter and move the atoms starting from the chosen configuration by the user until the structure is fully relaxed.

This is done when forces acting on atoms are below a certain chosen thresholds, In the elementary cells of the compounds the atomic positions are: Be (0, 1/2, 1/4), Si (1/2, 0, 1/4), C (1/2, 0, 1/4), these atomic positions are not affected by the optimization, because they are fixed by symmetry. However, it was necessary to relax the position of Nitrogen atoms in both compounds because of its general position (x, y, z).

The convergence criteria of total energy and structure optimization are; the energy tolerance of 10-6eV/ atom. BFGS (Broydene-Fletchere-Goldarbe-Shanno) optimization method was performed to obtain the equilibrium crystal structures of $BeBC_2$ with maximum atom displacement and force set to 0.002 Å and 10-4 eV/Å. and with maximum stress 0.005GPa.

IV.3.1.1. Tetragonal structure

The calculated lattice constants of tetragonal phase present in Table IV-5.

Table IV-5: Calculated lattice constants and volume per unit formula compared to data from previous theoretical studies of tetragonal structures.

Compounds	Lattice constants		Unit cell volume (Å)^3	
	a(Å)	c(Å)	This work	Unit cell volume (other works)
$BeSiN_2$	4, 08	8, 17	34, 012	31, 1 [7]**, 35, 2** [9]
$BeSiP_2$	5, 11	10, 20	66, 664	66, 14993[14]**,** 66, 98429[17]
$BeSiAs_2$	5, 35	10, 69	76, 460	75, 17825[14]**,** 76, 93069[17]
$BeCN_2$	3, 78	6, 99	24, 973	24, 22012[10]**,** 25, 00971[10]
$BeCP_2$	4, 64	8, 92	47, 9797	/
$BeCAs_2$	4, 91	9, 52	57, 3547	/

These results shows that the calculated structure parameters are in good agreement with the theoretical values calculated in [7][9][14][17][10]**.** Maximum forces and maximum stress after the optimization and relaxation of structure presents in the following table.

IV.3.1.2. Orthorhombic structure

The calculated lattice constants of orthorhombic phase present in Table IV-6.

Table IV-6: Lattice constants and volume per unit formula calculated compared with other work, and experimental data of orthorhombic structure.

Compounds	Lattice constants			Cell volume per unit formula(Å)^3	
	a(Å)	b(Å)	c(Å)	This work	other works
$BeSiN_2$	5.01	5.78	4.71	34, 065	32, 63245[11]**,** 33, 42239[3]
$BeSiP_2$	6.23	7.20	5.95	66, 669	/
$BeSiAs_2$	6.52	7.53	6.23	76, 444	/
$BeCN_2$	4.42	5.33	4.27	25, 128	24, 37321[10]**,** 25, 16095[10]
$BeCP_2$	5.53	6.53	5.35	48, 281	/
$BeCAs_2$	5.89	6.90	5.66	57.507	/

These results show that the calculated structure parameters are in good agreement with the experimental value for $BeSiN_2$ [3]and the theoretical values calculated in ref [10][11].Again it should be noted here that no previous theoretical or experimental work is reported on $BeCP_2$ or $BeCAs_2$ in the both phases.

The volume decreases are caused by the replacement of atoms in the C →Si and N→P →As that explained by the number of electrons and the electronegativity.

IV.3.2. Stable phases

The ground state energy of all crystals are shown in Table IV-7, this results proved that the most of this compounds are more stable with the tetragonal structure except $BeCN_2$ and $BeSiN_2$.

Table IV-7: Ground state energy and the sable phase

Compounds	Energy (eV)		Stable phase
	So	Ct	
$BeSiN_2$	-685, 33**304075275**	-685, 33**71183945**	-
$BeSiP_2$	-499, **09463639425**	-499, **1365685702**	Tetragonal
$BeSiAs_2$	-483, 5**0973430925**	-483, 5**5403448465**	Tetragonal
$BeCN_2$	-729, 5**54561389**	-729, 5**473051365**	-
$BeCP_2$	-545, 2**1257276025**	-545, 2**56348892**	Tetragonal
$BeCAs_2$	-529, 1**4744618975**	-529, 1**81341877**	Tetragonal

IV.3.3. Formation Enthalpy

We have calculated formation enthalpy of two structures by the following relation [10].

$$\Delta H_f = \text{E}\ (BeB^{\text{IV}}C_2^{\text{V}}) \text{- E}\ (Be) \text{- E}\ (B^{\text{IV}}) \text{-2 E}\ (C^{\text{V}})$$

The calculated energies for isolates atoms are Be=-27.2593eV, Si=-101.9044eV, C=-145.8348eV, N=-262.7321eV, P=-174.2056eV and As=-167.4554. This energies used for calculate the formation enthalpy. This negative values means that possible of syntheses these compounds.

Table IV-8: Calculated formation enthalpy

Compounds	Enthalpy	
	So	Ct
$BeSiN_2$	-30, 70514	-30, 70922
$BeSiP_2$	-21, 51974	-21, 56167
$BeSiAs_2$	-19, 43523	-19, 47953
$BeCN_2$	-30, 99626	-30, 98901
$BeCP_2$	-23, 70727	-23, 75105
$BeCAs_2$	-21, 14255	-21, 17644

IV.4. Electronic structures

IV.4.1. Band structure

One of the most important reasons for calculating the electronic band structure is to determine the band gap. This value describes the solid nature (conductor, semi-conductor...), the values obtained by solving the Kohn-Sham equations along specific directions in the Brillouin zone can be used to generate energy band structure diagrams and the electronic density of states.

The electronic band spectra calculated by CASTEP code within GGA and HSE06 along some high-symmetry directions of the body centered tetragonal and the simple orthorhombic Brillouin zone are shown in Figure IV-3.The calculated band gaps reveal that all our compounds are semiconductors.

The band gap values obtained in the HSE06 approximation have a high degree of reliability. In addition, when we used this method to calculate diamond and Silicon band gaps, the results were 5.349eV for diamond and 1.168eV for silicon in total agreement with experimental 5.47eV and 1.12eV. For diamond and silicon. However, when this gap is calculated using GGA approximation it drops to 4.126eV and 0.6eV for C and Si respectively.

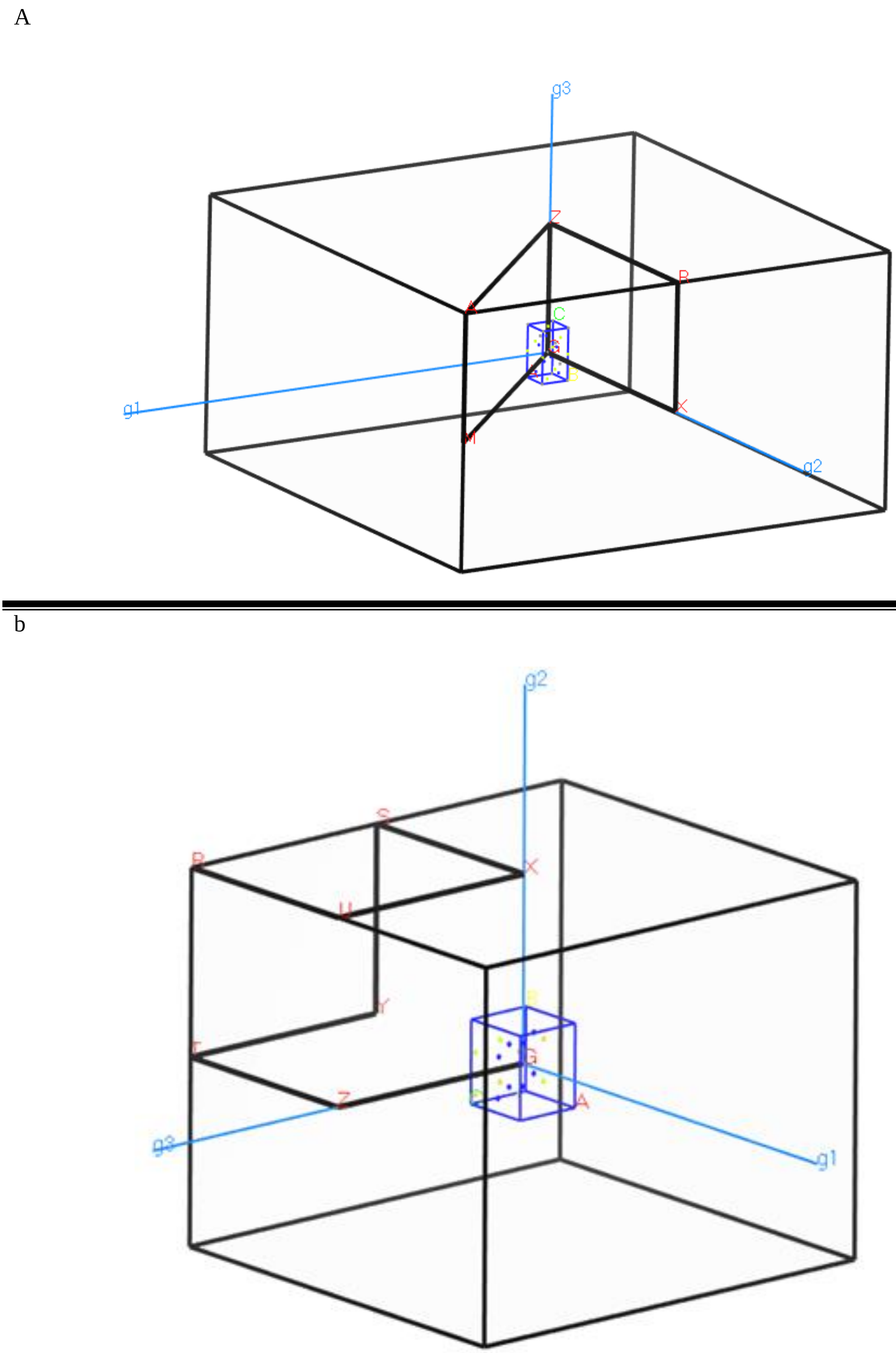


Figure IV-3: Brillouin Zone, high symmetry points and high symmetry lines for studied crystals (a): tetragonal and (b): orthorhombic.

We are using the primitive cell of tetragonal crystal presented in Figure IV-4 in the calculation of the electronic properties. Therefore, points of high symmetries, path and the number of band are change but the electronic properties are the same, we are using this structure just for the time of our study, the first Brillion zone show in Figure IV-4.

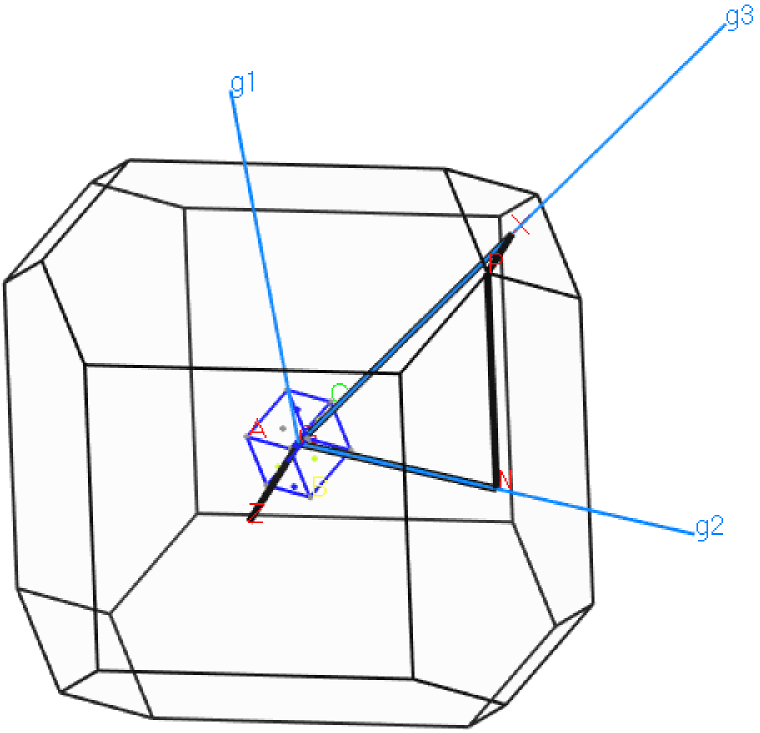


Figure IV-4: Brillouin Zone, high symmetry points and high symmetry lines for studied crystals; the primitive cell of tetragonal crystal.

IV.4.2. Density of state and Mullikan population analysis

The density of states (DOS) counts the number of electronic states having on each atomic orbital like bands as function of energy, the analysis of the density of state is very important for understanding and determining the nature of chemical bonds between atoms of a crystal and gives an idea about the elements that create the gap energy. In the calculation of $BeAB_2$ density of states we used GGA.

On the other hand, population analysis expresses the bonding nature between two atoms. It takes a value between 0 and 1. The trend towards 0 indicates that the character of the bond is ionic, and the trend towards 1 indicates that the bond is dominated by covalent nature.

IV.4.3. Tetragonal

The calculated energy band structure obtained for the chalcopyrite crystals are shown in Figure IV-5 and Figure IV-6. From the analysis of the band spectra E(k),the $BeCN_2$, $BeSiN_2$, $BeSiP_2$ and $BeSiAs_2$ are found to be direct-gap semi-conductor.

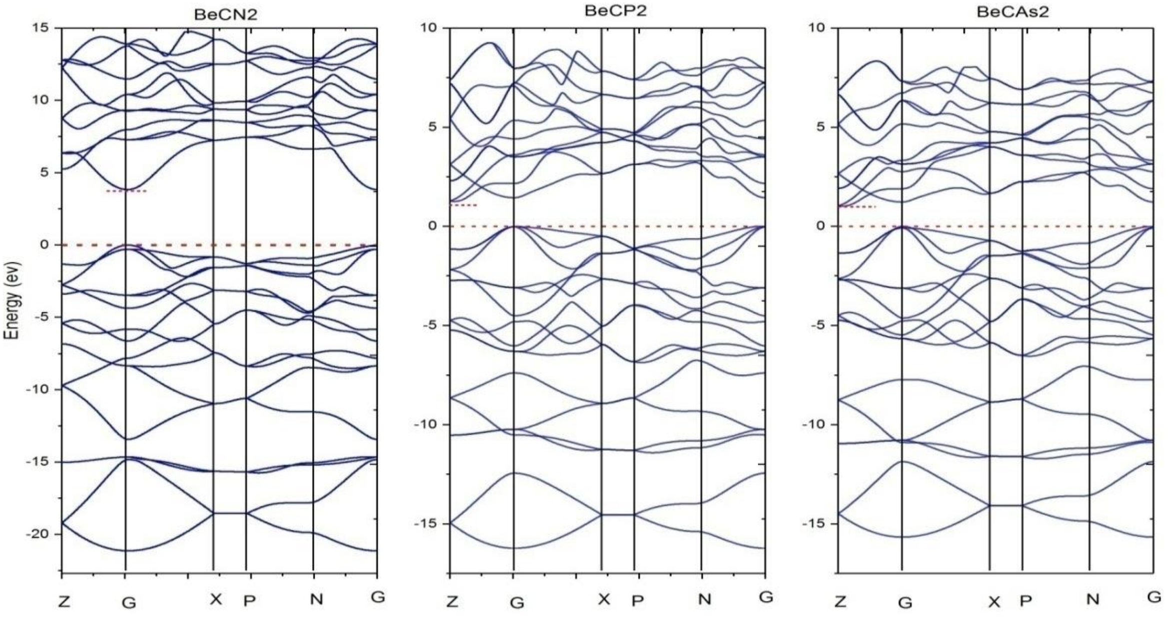


Figure IV-5: Calculated band structures of $BeCN_2$, $BeCP_2$ and $BeCAs_2$, for tetragonal structure.

The valence band maximum VBM and the conduction band minimum CBM are both located at the G-point. The first two semiconductors characterized by wide gaps of 3.841eV (5.102eV), for $BeCN_2$ and 3.637 eV (4.802eV) for $BeSiN_2$ using GGA (HSE06) respectively. The results obtained by GGA in agreement with values predicted by the LDA (**3.72**eV[10]**,** 3.60eV[12])and the LASTO methods (3.90 eV, 3.67eV) [5] for $BeCN_2$ and $BeSiN_2$ respectively.

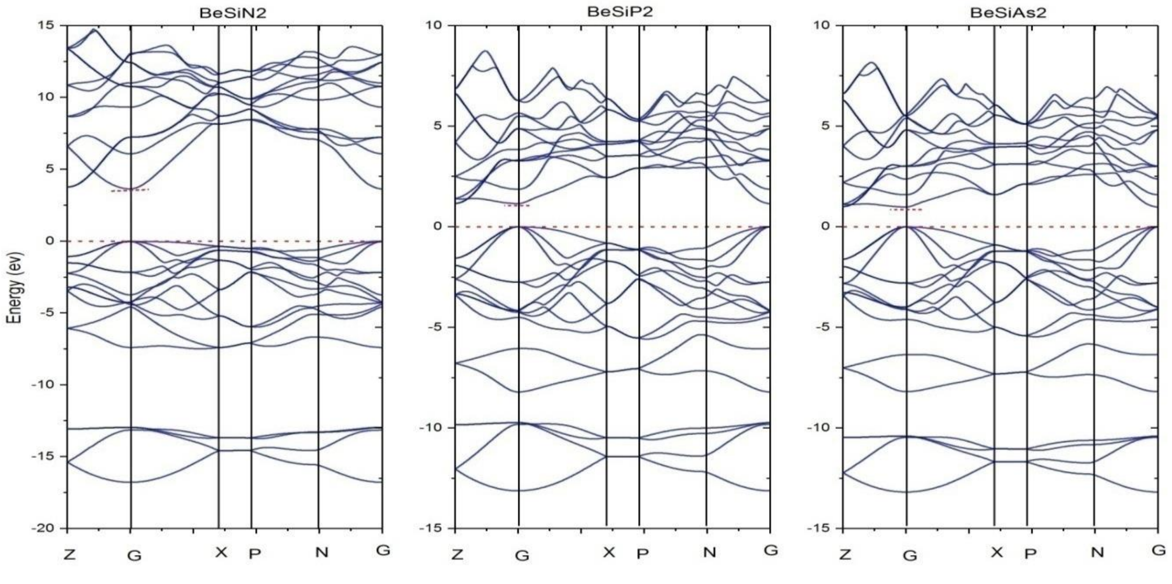


Figure IV-6: Calculated band structure of $BeSiN_2$, $BeSiP_2$ and $BeSiAs_2$, for tetragonal structure.

$BeSiP_2$ is characterized by gaps of 1.155 eV and 1.841 eV within GGA and HSE06 respectively. Moreover the $BeSiAs_2$ is also characterized by narrow band gaps of 0.987 eV 1.817 eV within GGA and HSE06 respectively. These results are also in good agreement with the theoretically predicted direct gaps (1, 2 GGA 1, 84 mBJ 1, 75 GW)[17] $BeSiP_2$ and an indirect gaps (1, 07GGA 1, 68 mBJ 1, 33GW)[17]for $BeSiAs_2$.

$BeCP_2$ and $BeCAs_2$ are characterized by indirect gaps the MBV located at G point and MCB located at Z point. The gap band energy of $BeCP_2$ and $BeCAs_2$ respectively 1.260 eV,1.024eV with GGA and 2.11 eV, 1.825 eV with HSE06.

The valence band of $BeSiN_2$ and $BeCN_2$ compounds consists of two allowed energy bands instead of three bands as in most compounds. In addition, MBV off all compound formed by three bands, moreover the topology of the conduction band edge, proved that the $BeCN_2$ and $BeSiN_2$ have a light electronic effective mass than another compounds. All this result are shown in TableIV-9.

Table IV-9: Band gap, compared with other works, for tetragonal structure.

Compounds	This work		Gap nature	location	Other work
	GGA	HSE06			
$BeSiN_2$	3.637	4.802	Direct	G	**3, 60ev LDA**[12]**3, 67eV LASTO**[8]
$BeSiP_2$	1.155	1.841	Direct	G	1, 2 GGA 1, 84 mBJ 1, 75 GW[17]
$BeSiAs_2$	0.987	1.817	Direct	G	1, 07GGA 1, 68 mBJ 1, 33GW[17]
$BeCN_2$	3.841	5.102	Direct	G	**3.72evLDA**[10] **3.90ev LASTO** [8]
$BeCP_2$	1.260	2.110	indirect	G-Z	-
$BeCAs_2$	1.024	1.825	indirect	G-Z	-

We note here that it is the first time that this band gaps have been calculated for the$BeCP_2$and $BeCAs_2$.

The band-gap width regularly decreases Figure IV-7, which correlates with an increase in the atomic number.

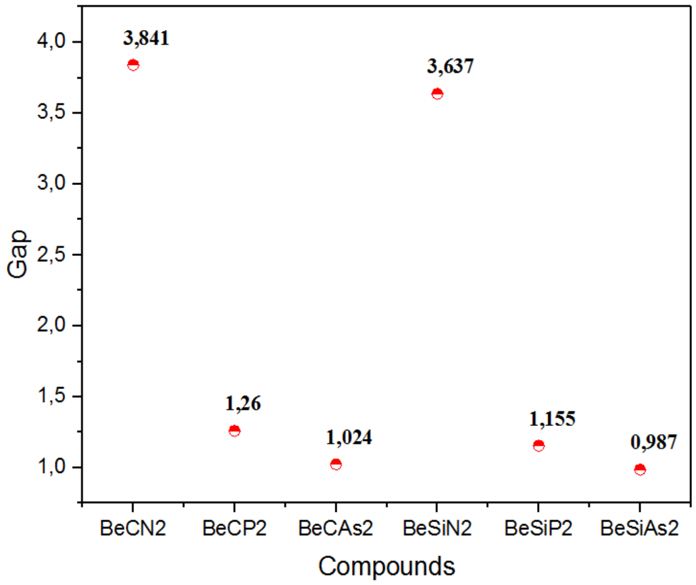
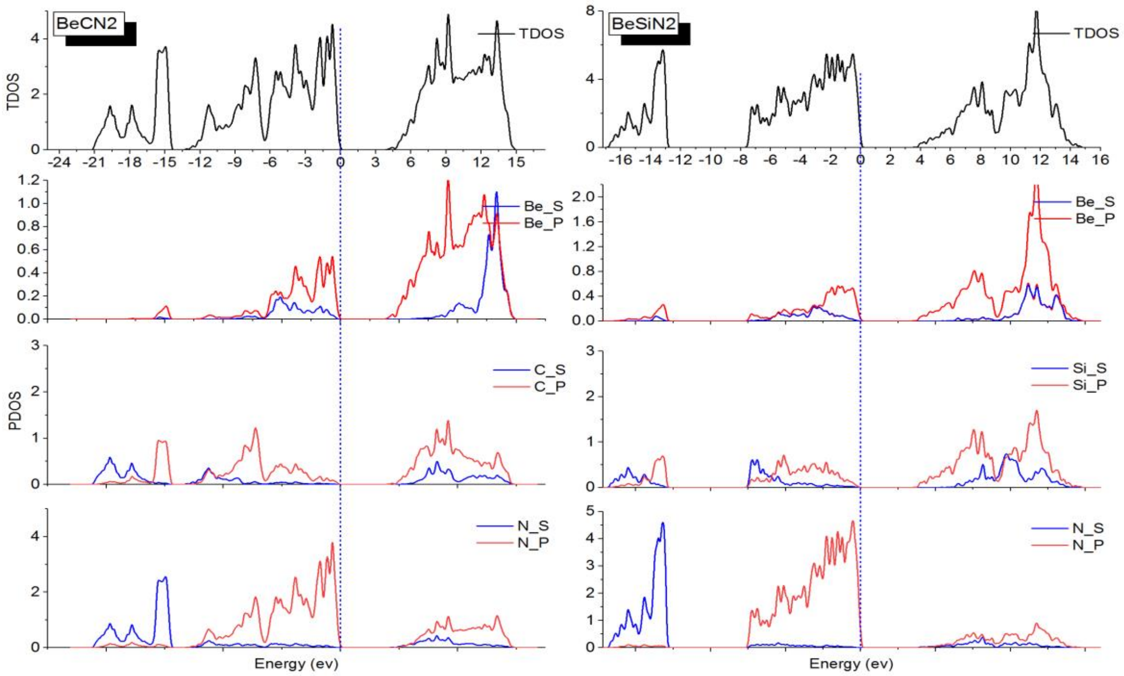


Figure IV-7: Band gap variation

The calculated density of state for the tetragonal compounds are shown in Figure IV-8. Total DOS formed by the contribution of orbital noted PDOS of all atoms.



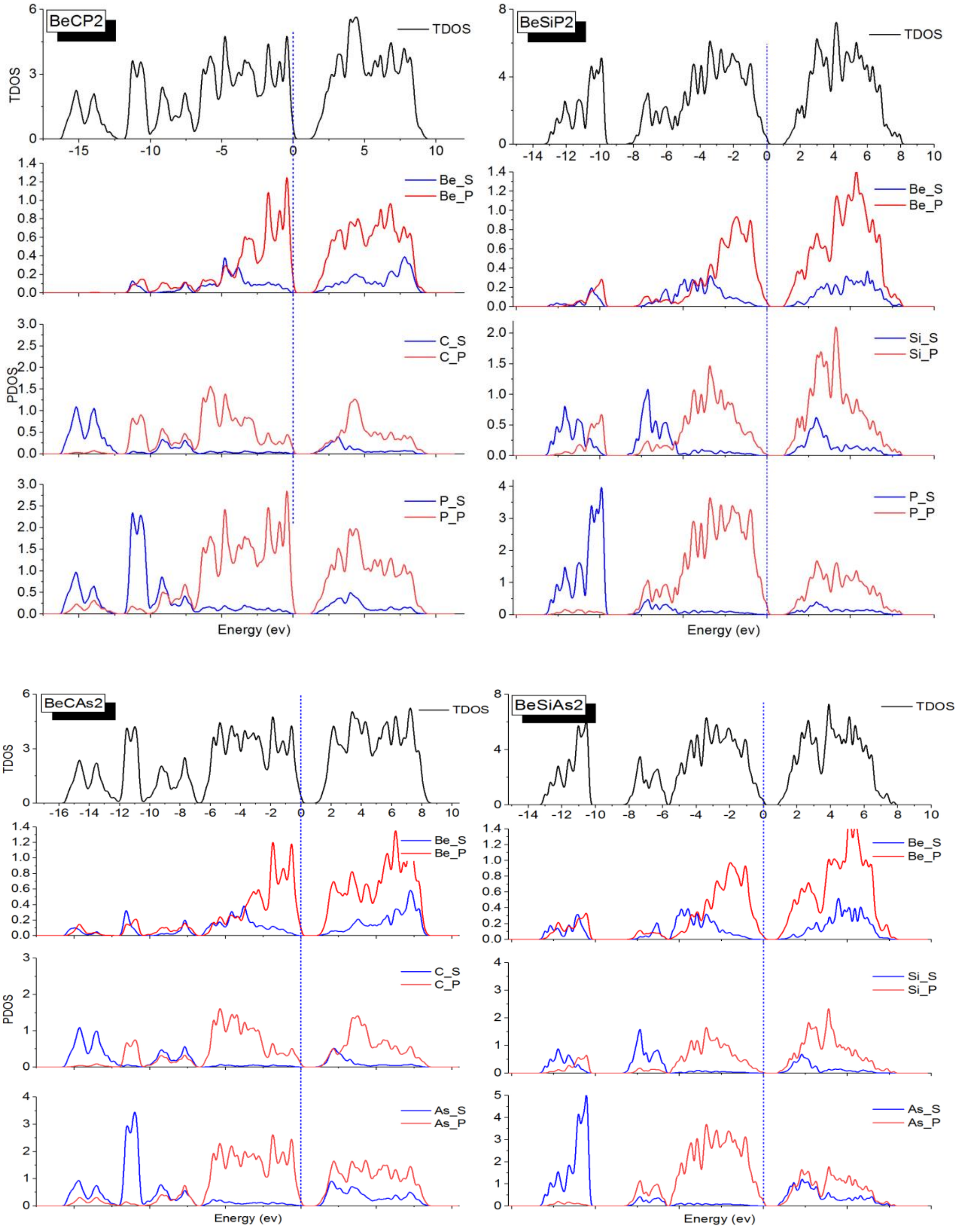


Figure IV-8: Total and partial density of state, $BeCN_2$, $BeCP_2$, $BeCAs_2$, $BeSiN_2$, $BeSiP_2$ and $BeSiAs_2$, for tetragonal structure.

The analysis of these curves reveals that contributions of states of beryllium are relatively small, which is explained by small number of valence electrons in Be atoms. In addition the electron of s-Be state transfer to the p-Be and we can see clearly the hybridization between these states.

Moreover, bonds are formed between the new hybrid Be state and p state of N, P and As atoms. This results are confirmed by Mullikan population Table IV-10.

Table IV-10: Bond, Mullikan population, Bond nature and bond length

Compounds	Atom	Population	Bond nature	Bond length A
$BeCN_2$	Be---N	0.43	Near ionic	1.710
	C---N	0.74	Near covalent	1.497
$BeCP_2$	Be---P	0.63	Near covalent	2.081
	C----P	0.63	Near covalent	1.895
$BeCAs_2$	Be---As	0.63	Near covalent	2.186
	C---As	0.60	Near covalent	2.028
$BeSiN_2$	Be---N	0.46	Near ionic	1.788
	Si---N	0.63	Near covalent	1.748
$BeSiP_2$	Be---P	0.62	Near covalent	2.167
	Si----P	0.67	Near covalent	2.260
$BeSiAs_2$	Be---As	0.64	Near covalent	2.256
	Si----As	0.62	Near covalent	2.379

The VBM create by the contribution of all states.in addition the deep bond formed between s p state of C, Si atoms and s p state of N, P and As atoms. These chemical bonds are stronger than the first bonds and take the covalent character (Mullikan population),C and Si cations affect the total width of the valence band. The total width of the valence band decreases with increasing atomic number of C and Si cations. The same remarks hold for other compounds; the principal change is the decreases of band gap width.

IV.4.4. Orthorhombic

The results of calculations of the energy band structure obtained for the orthorhombic crystals are shown in Figure IV-9 and Figure IV-10 From the analysis of the band spectra E(k), the $BeCN_2$, $BeSiN_2$ are wide gap semi-conductor.

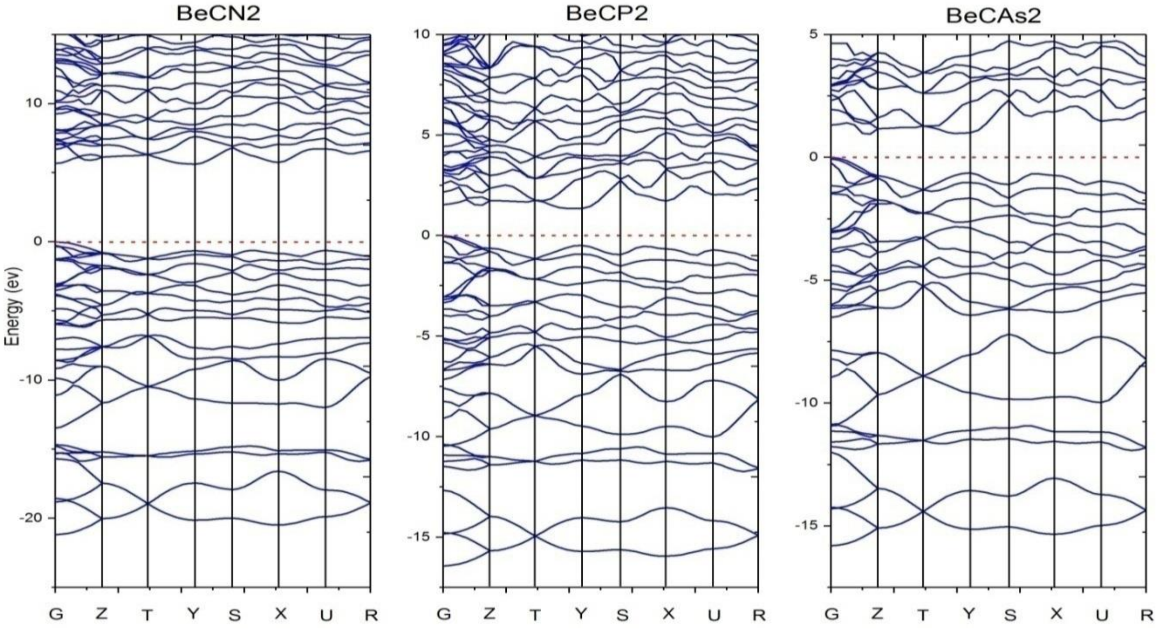


Figure IV-9: Calculated band structure for $BeCN_2$, $BeCP_2$ and $BeCAs_2$, for orthorhombic structure

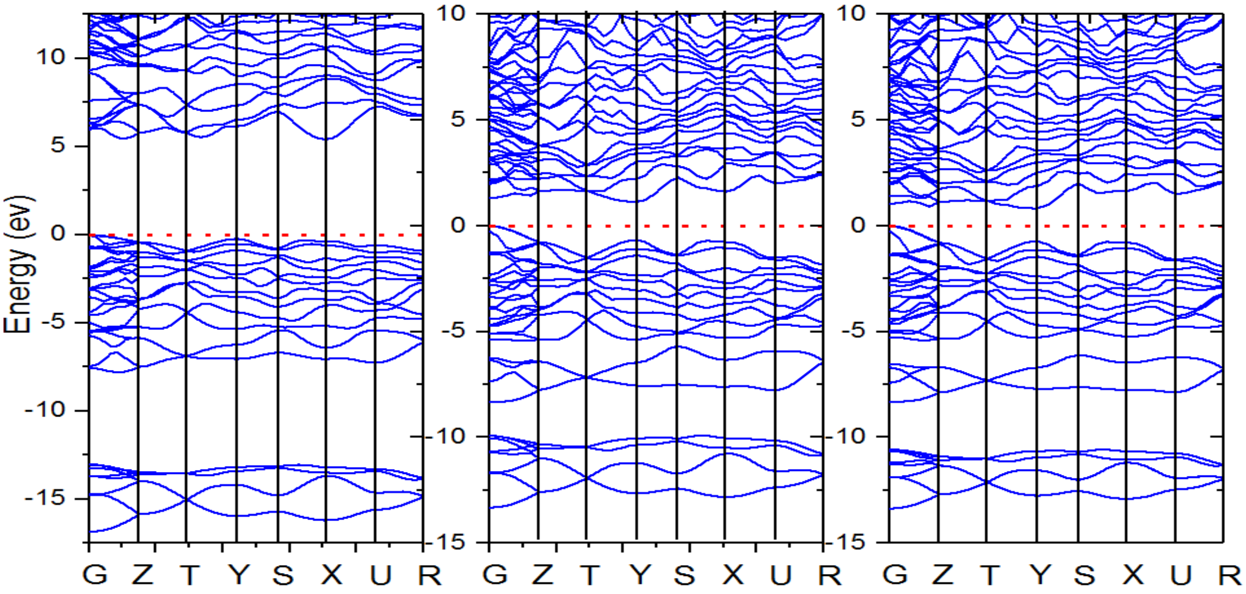


Figure IV-10: Calculated band structure for $BeSiN_2$, $BeSiP_2$ and $BeSiAs_2$ for orthorhombic structure.

All compounds are found to be indirect-gap semi-conductor, the valence band maximum VBM located at G point and the conduction band minimum CBM located at the X Y or Z points see Table.IV.11.

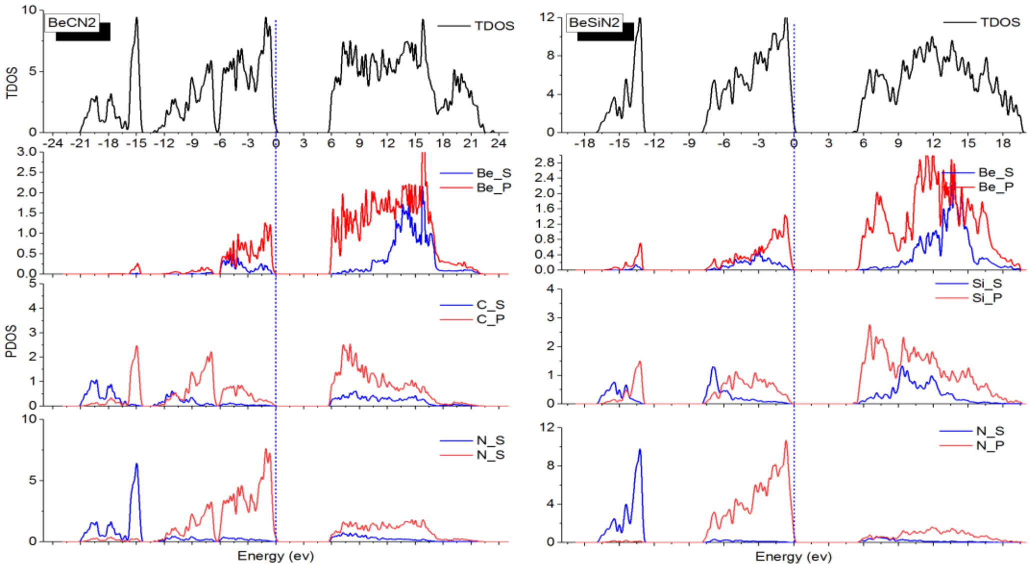
Table IV-11: Band gap compared with other works, for orthorhombic structures.

Compounds	This work		Gap nature	location	Other work
	GGA	HSE06			
$BeSiN_2$	5, 402	6.611	Indirect	G X	5,19 eV GGA [11]
$BeSiP_2$	1, 133	1.821	Indirect	G Y	/
$BeSiAs_2$	0, 827	1.611	Indirect	G Y	/
$BeCN_2$	5, 629	7.073	Indirect	G Y	5,56eVLDA[10]7,34 eV B3LYP [7]
$BeCP_2$	1, 344	2.127	Indirect	G Y	/
$BeCAs_2$	0, 956	1.773	indirect	G *Z	/

The value obtained using GGA 5,402eV for $BeSiN_2$ are in good agreement with 5,19eV GGA[11]. in addition the gap for $BeCN_2$ 5.629eV 7.073eV with GGA and HSE06 respectively, are also in good agreement with 5,56eV LDA[10] and 7,34eV B3LYP [7]. The valence band of $BeSiN_2$ and $BeCN_2$ compounds consists of two or one allowed energy bands.

We note here that it is the first time that this band gaps have been calculated for the four compounds namely $BeSiP_2$, $BeSiAs_2$, $BeCP_2$ and $BeCAs_2$.

The calculated density of state for the orthorhombic structure are shown in Figure IV-11.



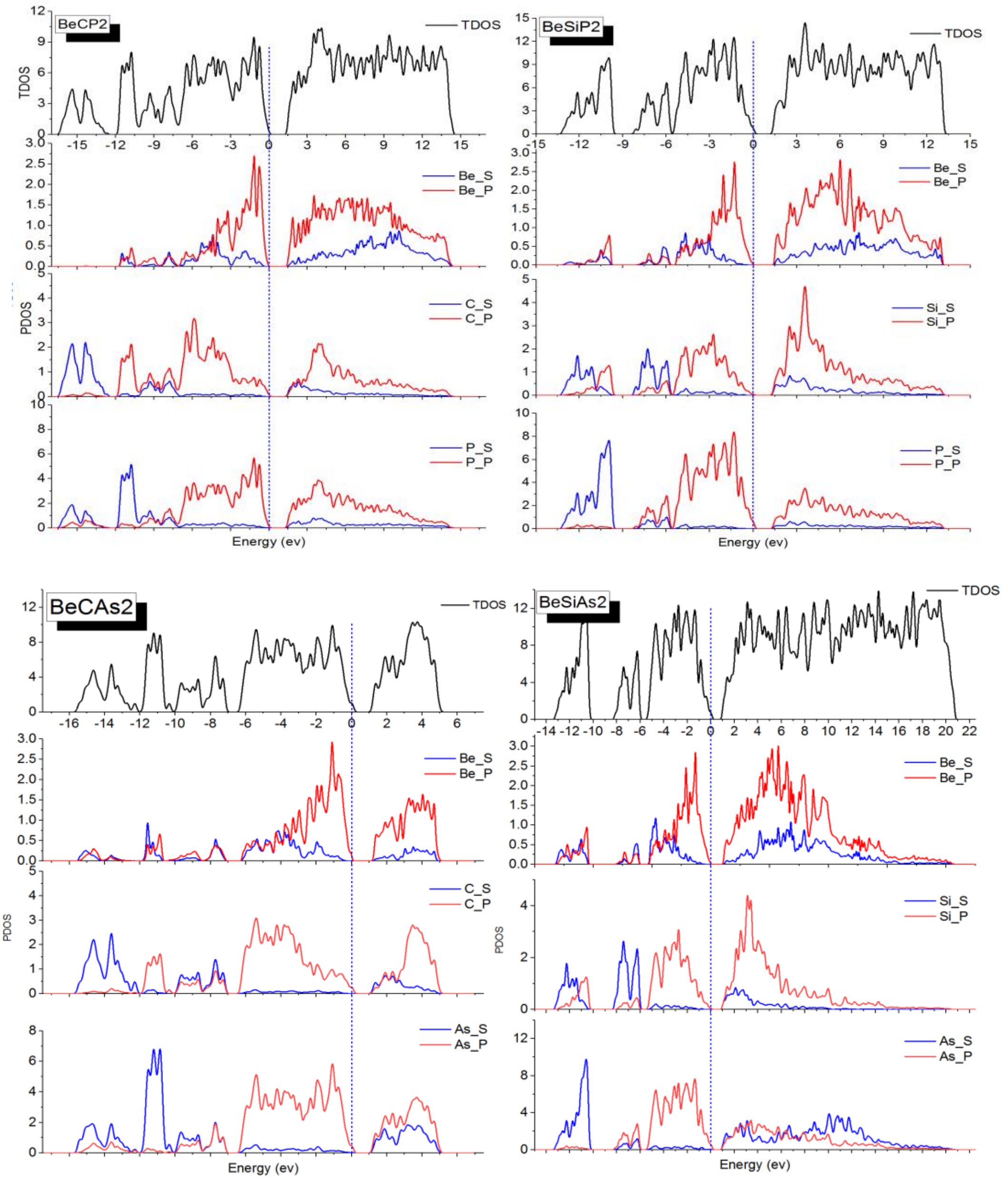


Figure IV-11: Total and partial density of state, ofBeCN$_2$, BeCP$_2$, BeCAs$_2$, BeSiN$_2$, BeSiP$_2$ and BeSiAs$_2$, for orthorhombic structure.

From the analysis of these results, the same thing happed for Be atom. The total density are complicated than the tetragonal phase. The TDOS formed by three and tow domain for BeCN2 and BeSiN$_2$ respectively, the electrons of Be, C, and Si atoms transfer to N atom.

Tow bonds are formed the first between hybrid s-p-Be state and s-N state. The second is between s-p C Si and s-p N P As states. The last are stronger than the former bonds.

The electrons of Be and C transfer to N. in other words, N attracts electrons towards it because N is more electronegative than Be and C. The same remark holds for other compounds. The principal change is the band gap value.

IV.5. The mechanical properties

The mechanical properties (elastic constants, elastic module, and elastic stability etc.) of the two structures are important for the potential industrial applications. They define the behavior of the solid when it undergoes stress, deformations, then recovers, and returns to its original shape after stress ceases.

IV.5.1. Elastic constant

The elastic constants describe all elastic properties of material this important tenser calculated by Hooke's law eqIII 1.

$$\sigma_{ij} = \sum_{k,l=1}^{3} C_{ijkl} e_{kl} \qquad \textbf{IV-1}$$

- e_{kl} strain tensor and σ_{ij} stress tensor

$$e_{ij} = \begin{pmatrix} e_{11} & e_{12} & e_{13} \\ e_{21} & e_{22} & e_{23} \\ e_{31} & e_{32} & e_{33} \end{pmatrix} \sigma_{ij} = \begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{pmatrix} \qquad \textbf{IV-2}$$

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{bmatrix} \qquad \textbf{IV-3}$$

C_{ijkl} is a tenser of 6*6 eqIII 3but the number of independent parameter reduces by the symmetry of the crystal Table IV 12.

Table IV-12: Number of independent parameter for different structure

Symmetry	**Number of independent parameter**
Cubic	**3**
Hexagonal	**5-7**
Rhomboedric	**6-7**
Tetragonal	**6-7**
Orthorhombic	**9**

Monoclinic	**13**
Triclinic	**21**

The Cij tensor for tetragonal and orthorhombic systems respectively written as follows:

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & & & \\ C_{12} & C_{11} & C_{13} & & & \\ C_{13} & C_{13} & C_{33} & & & \\ & & & C_{44} & & \\ & & & & C_{44} & \\ & & & & & C_{66} \end{bmatrix} \begin{bmatrix} C_{11} & C_{12} & C_{13} & & & \\ C_{12} & C_{22} & C_{23} & & & \\ C_{13} & C_{23} & C_{33} & & & \\ & & & C_{44} & & \\ & & & & C_{55} & \\ & & & & & C_{66} \end{bmatrix} \qquad \textbf{IV-4}$$

IV.5.2. Tetragonal structure

The calculated elastic tensors of our compounds are presented in Table IV 13.

Table IV-13: Calculated elastic constant of Tetragonal structure in GPa.

Compounds	**BeSiN$_2$**	**BeSiP$_2$**	**BeSiA$_2$**	**BeCN$_2$**		**BeCP$_2$**	**BeCAs$_2$**
				This work	**Other work[23]**		
C_{11}	**362.71**	**167.87**	**133.48**	**616.42**	**641**	**258.51**	**201.35**
C_{33}	**397.99**	**168.21**	**135.14**	**555.35**	**565**	**257.4**	**201.41**
C_{12}	137.55	57.37	46	98.65	101	63.08	56.18
C_{23}	150.6	57.95	46.18	198.95	206	74.125	62.42
C_{44}	239.44	84.78	70.75	370.87	384	142.72	109.98
C_{66}	225.89	86.37	72.01	370.87	361	146.23	112.08

For BeCN2 our result is in good agreement with other work [23].

IV.5.2.1. Elastic stability for tetragonal structure

The elastic stability is a necessary condition, for a stable tetragonal structureC_{ij} has to satisfy the elastic stability criteria:

$$C_{11} > 0, C_{33} > 0, C_{44} > 0, C_{66} > 0, (C_{11} - C_{12}) > 0, (C_{11} + C_{33} - 2C_{13}) > 0$$

$$and\ 2(C_{11} + C_{12}) + C_{33} + 4C_{13} > 0$$

These conditions are clearly satisfied for the tetragonal structure, confirming that this structure is mechanically stable.

IV.5.3. Orthorhombic structure

The calculated elastic tensors of our compounds are presented in Table IV 14

Table IV-14: Calculated elastic constant of orthorhombic structure in GPa

Compounds	$BeSiN_2$	$BeSiP_2$	$BeSiAs_2$	$BeCN_2$		$BeCP_2$	$BeCAs_2$
				This work	**Other work[23]**		
C_{11}	**492.11**	**197, 93**	**162.29**	**718, 68**	**741**	**314.51**	**240.09**
C_{12}	113.75	46.43	38.54	143.43	143	54.02	46.18
C_{13}	76.71	29.41	25.06	64.11	63	29.61	28.03
C_{22}	**449.56**	**194, 75**	**162.60**	**659, 71**	**670**	**306.26**	**237.93**
C_{23}	76.14	29.01	24.90	88.73	80	30.36	25.53
C_{33}	**495.44**	**223, 46**	**186.90**	**789, 43**	**804**	**342.00**	**269.55**
C_{44}	154.97	57.07	47.52	278.45	281	99.14	76.55
C_{55}	147.48	56.83	46.00	250.19	265	101.54	78.04
C_{66}	181.87	74.68	61.33	315.64	322	121.97	95.78

For BeCN2 our result is also in good agreement with other work [23]**.**

IV.5.3.1. Elastic stability for orthorhombic structure

For a stable orthorhombic structure C_{ij} has to satisfy the elastic stability criteria:

$$C_{11} > 0, C_{22} > 0, C_{33} > 0, C_{44} > 0, C_{55} > 0, C_{66} > 0,$$

$$C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}) > 0, (C_{11} + C_{22} - 2C_{12}) > 0, C_{11} + C_{33} - 2C_{13} > 0$$

$$\text{And } C_{22} + C_{33} - 2C_{23} > 0$$

These conditions are clearly satisfied for orthorhombic phase, confirming that this structure is mechanically stable.

The elastic constants C_{11}, $C_{22}$and C_{33} represent, respectively the resistance to linear compression in the a-direction b-direction and c-direction. The large $C_{11}, C_{22}$and C_{33}manifest that the a-axial, b -axial and c-axial directions of these two structures are extremely stiff. All these compounds have also a high shear constants.

IV.5.4. Bulk module

The calculated bulk modulus are shown in the Table IV-15, for the tetragonal and the orthorhombic structures respectively.

Table IV-15: Calculated Bulk module of our compounds for tetragonal and orthorhombic structure in GPa.

Compounds		$BeSiN_2$	$BeSiP_2$	$BeSiAs_2$	$BeCN_2$	$BeCP_2$	$BeCAs_2$
Bulk model	Orthorhombic	218.61	91, 72	76.48	306, 46	132.28	105.18
	Tetragonal	221.57	94.50	75.42	308.70	132.97	107.33

Our results are in good agreement with

The decreases of elastic constants and bulk model are caused by the replacement of atoms C →Si and N→P →As. Therefore, the lightest element have the largest values.

IV.5.5. Debye temperature

Deby temperature is the highest temperature that can be achieved due to a single normal vibration, mainly depending on the type of bonds. The rigid chemical bond means the acoustic velocity is high. Therefore, the θ_D will be high, the thermal conductivity and melting temperature are also high.

The Debye temperature can be estimated from the average sound velocity by the following equation based on elastic constant evaluations.

$$\theta_D = \frac{h}{K_B}\left[\frac{3n}{4\pi}\left(\frac{N_A\rho}{M}\right)\right]^{1/3} v_m \qquad \textbf{IV-5}$$

The calculated Debye temperatures of our compounds are listed in Table IV-16.

Table IV-16: Calculated Debye temperature of our compounds for tetragonal and orthorhombic structure.

Compounds		$BeCN_2$	$BeCP_2$	$BeCAs_2$	$BeSiN_2$	$BeSiP_2$	$BeSiAs_2$
Debye temperature	North	1676.3	912.3	573.8	1181.3	684.8	464.1
	Tetra	1658.4	924.2	579.1	1181.7	690.2	464.5

The Debye temperature is largest for solids with high melting points, for many solids, θ_D is roughly proportional to the melting point T_m. It is given by Lindeman relation [24]

$$\theta_D \propto \left(\frac{T_m}{MV^{2/3}}\right)^{1/2} \qquad \textbf{IV-6}$$

Where V is the molar volume in cm3/mol, M is the molar mass in g/mol, and T_m the melting point in K

IV.6. Optical properties

IV.6.1. Introduction

The dielectric function ε describes the behavior of light in the solid which means the response of the solid to the perturbation or electric field E of light. The real part Re (ε) is directly related to the refractive properties (square root of Re (ε). At 0eV gives the static refractive index). Moreover, the imaginary part Im (ε) determines the absorption spectrum.

The CASTEP module can calculate the imaginary part ε_2, using the following relation III 7

$$\varepsilon_2 = \frac{2e^2\pi}{\Omega\varepsilon_0}\sum_{k,v,c}\left|\langle\Psi_k^c\left|\vec{u}\bullet\vec{r}\right|\Psi_k^v\rangle\right|^2\delta\left(E_k^c - E_k^v - E\right) \qquad \textbf{IV-7}$$

Where,

- $\vec{u}$ is the vector defining the polarization of the incident electric field
- $\vec{r}$ is the position operator
- $\Psi_k^c\ \Psi_k^v$ represent the valence band and the conduction band states in which the direct transitions are possible
- $E_k^c - E_k^v = \hbar\omega$ is the transition energy
- ε_0 is the dielectric constant of free space
- e is the electronic charge
- Ω is the volume of unit cell

The physical meaning of this relation is, the possibility or the probability of an electronic transition for a photon energy value, from the valence band to the conduction band. In addition, the ε_2 obtained by CASTEP Module describes the electronic transition only (inter band) FigIII_12.

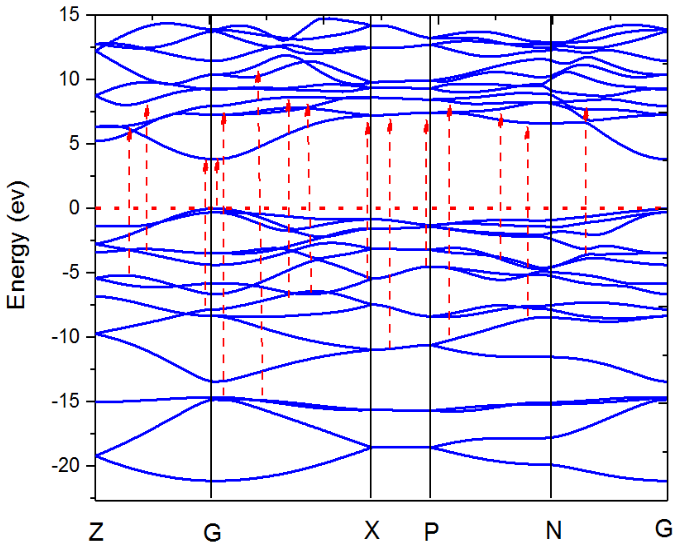


Figure IV-12: Electronic transition: a_ from the band structure b_ from density of state.

The real part ε_1 of the dielectric function is related to ε_2 by the Kramers-Kronig relation III 8

$$\varepsilon_1 = 1 + \frac{2}{\pi}\int_0^{\infty} \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega' \qquad \textbf{IV-8}$$

The refractive properties and the absorption spectrum calculated by eqIII 9

$$\varepsilon_1(\omega) = n^2(\omega) - k^2(\omega), \quad \varepsilon_2(\omega) = 2n(\omega) \bullet k(\omega) \qquad \textbf{IV-9}$$

We are looking for a good material for nonlinear optic application. Therefore, it is essential to study the anisotropy of the dielectric function and the anisotropy of the refractive index.

IV.6.2. Calculated dielectric function:

For calculate the optical properties we used 0.03 1/A separation and a cut off energy equal to 700eV .Figures IV-13 and IV-14 shows the calculated Re (ε) and Im (ε) for all six studied compounds, with different polarizations for both orthorhombic and tetragonal phases, we interested to transparency region. Therefor we discus in this part only for the anisotropic of our compounds in this region.

Only two tensor-components (parallel to the a-axis **or** b-axis and c-axis corresponding to the electric field) are required to describe the optical properties of tetragonal phase.

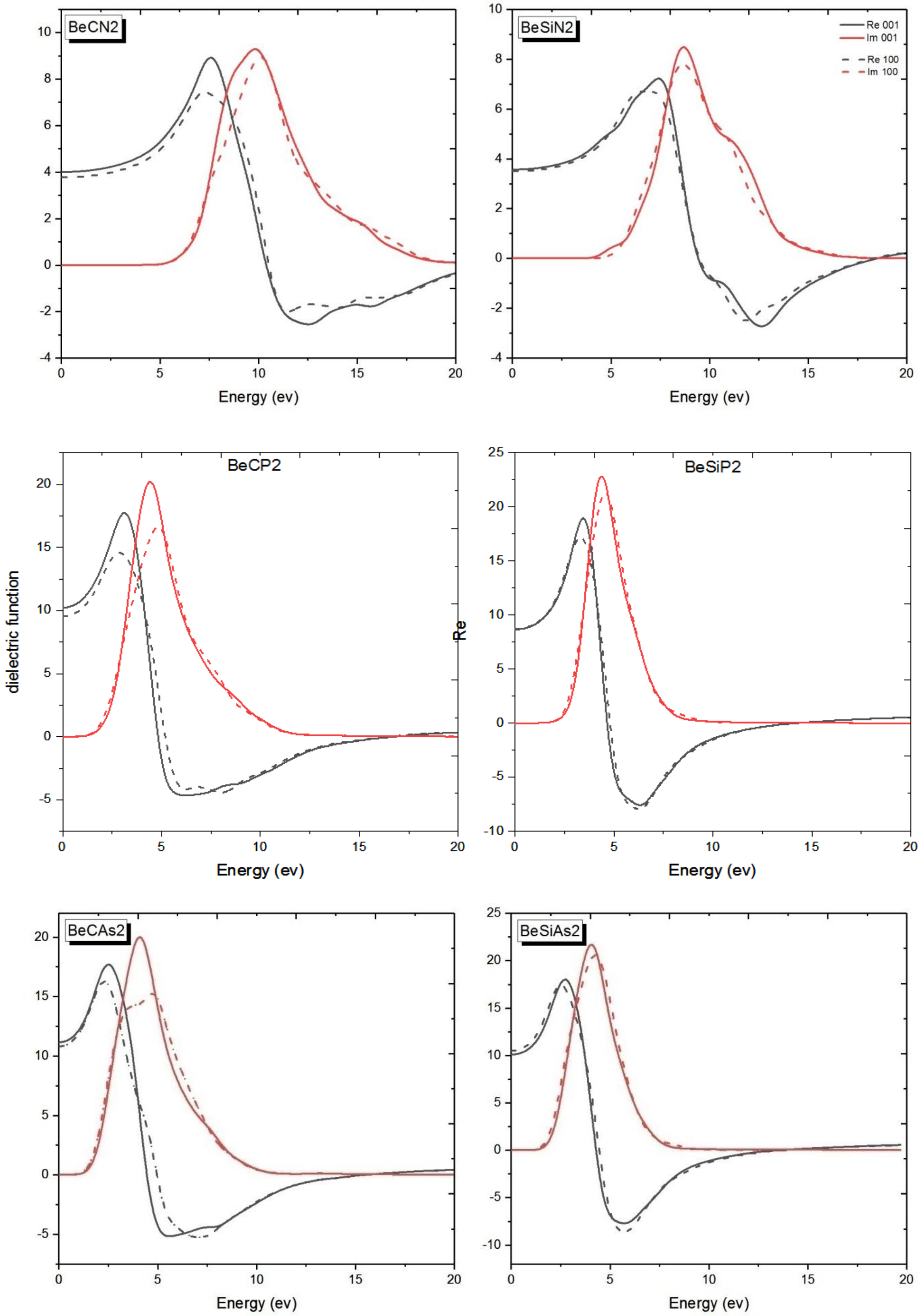


Figure IV-13: Calculated dielectric function of $BeCN_2$, $BeCP_2$, $BeCAs_2$, $BeSiN_2$, $BeSiP_2$ and $BeSiAs_2$in tetragonal phase.

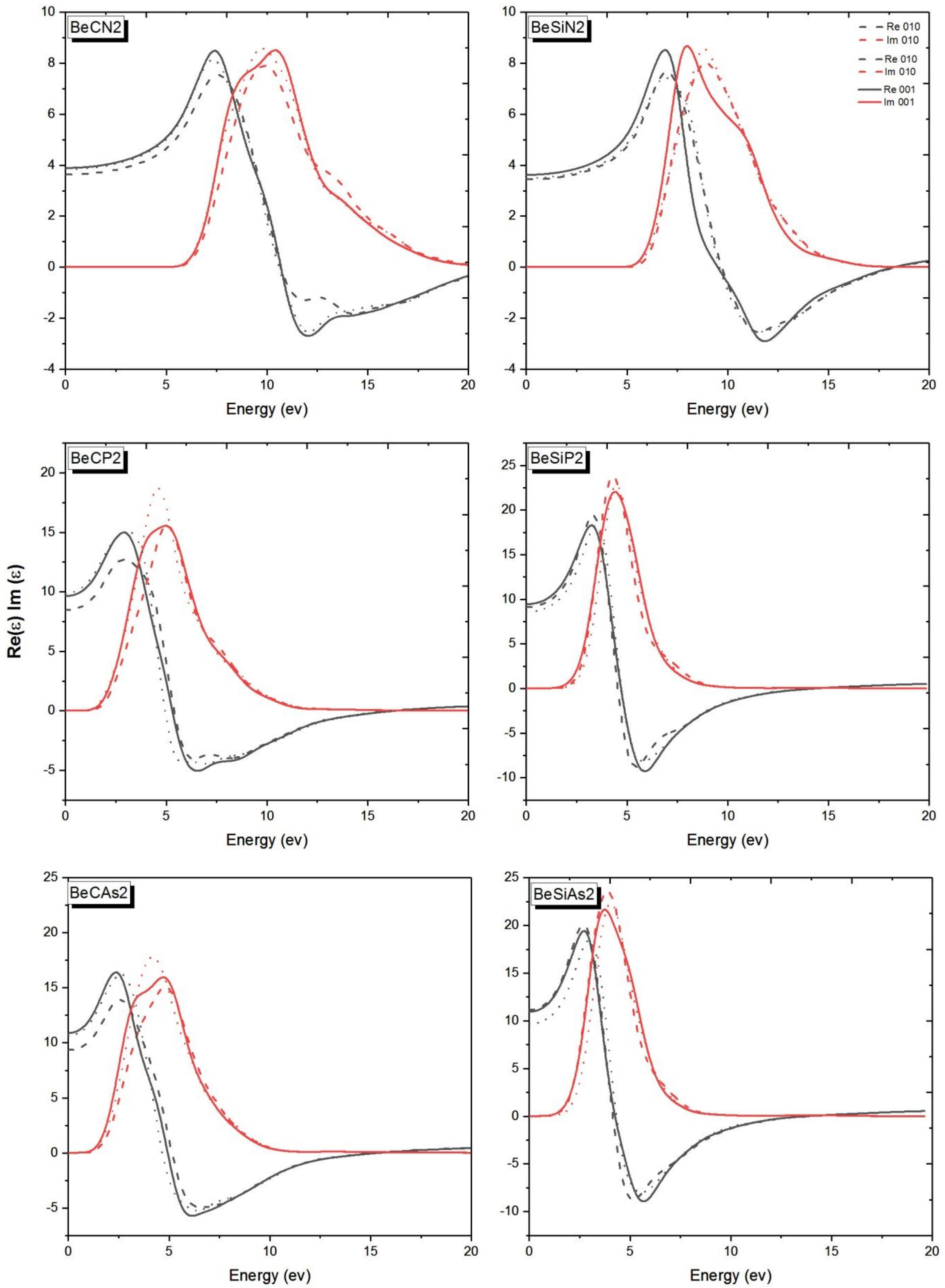


Figure IV-14: Calculated dielectric function of $BeCN_2$, $BeSiN_2$, $BeCP_2$, $BeCAs_2$, $BeSiP_2$ and $BeSiAs_2$ for orthorhombic structure.

Both $BeCN_2$ and $BeSiN_2$ compounds have a larger domain of transparency than other compounds Infrared, Visible and ultraviolet (Deep UV).

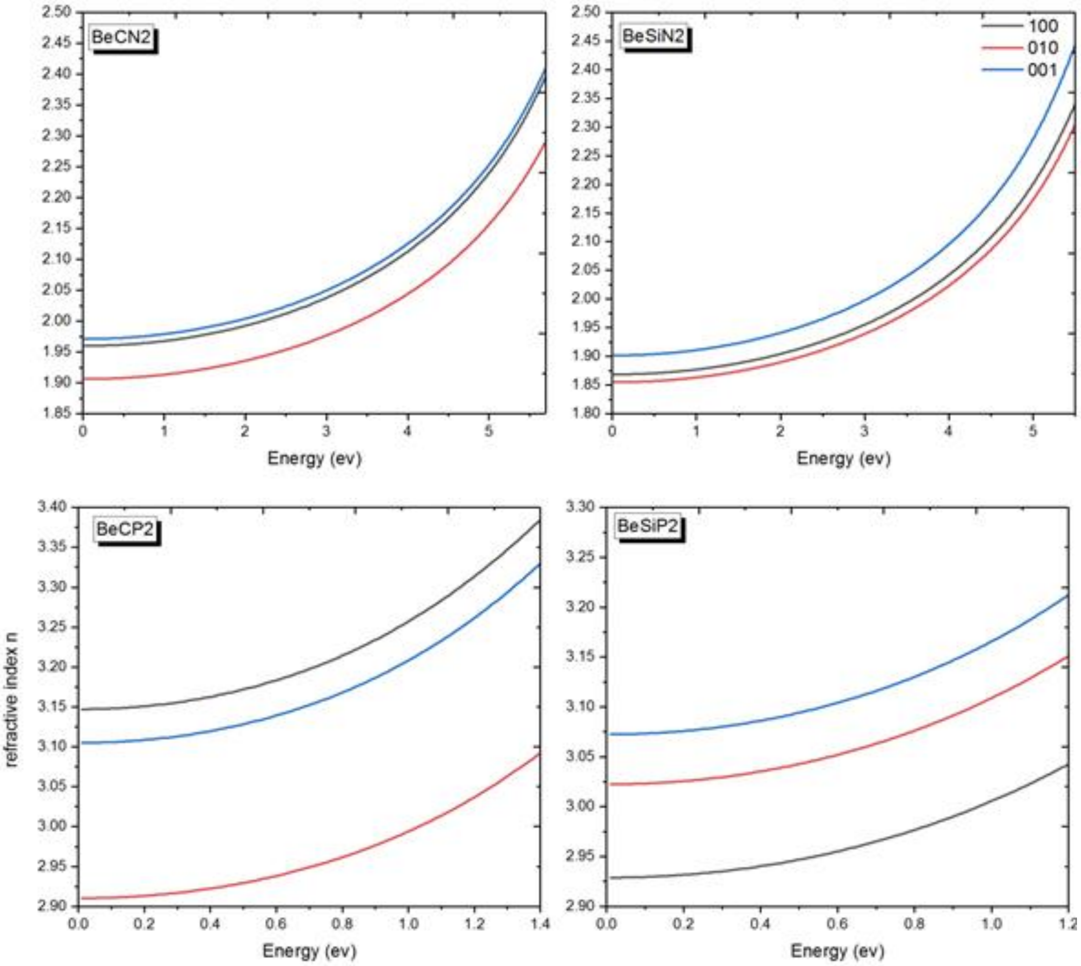
The domain of transparency of the last four compounds is smaller than $BeCN_2$ and $BeSiN_2$, this result can be explained by the larger band gap, However the orthorhombic symmetry, two tensor-components (parallel to the a-axis **and** b-axis) are different so for describe the optical properties we need all tenser-components.

IV.6.3. Refractive index

From the analysis of dielectric function, CASTEP module calculate the refractive index from eqIII 9, we know, photon energies lower than the gap, there is no absorption (transparent) so we need just a real part. We calculated the values of the refractive indexes, for these compounds in tow crystals phases $n_x$and $n_y$are known as an ordinary beam or o-beam and $n_z$is called an extraordinary beam or an e-beam.

The difference between the refractive indices of the ordinary and extraordinary beams is known as birefringence Δn

Figure IV-15 shows the calculated refractive index *n* for all six studied orthorhombic crystals for different polarizations.



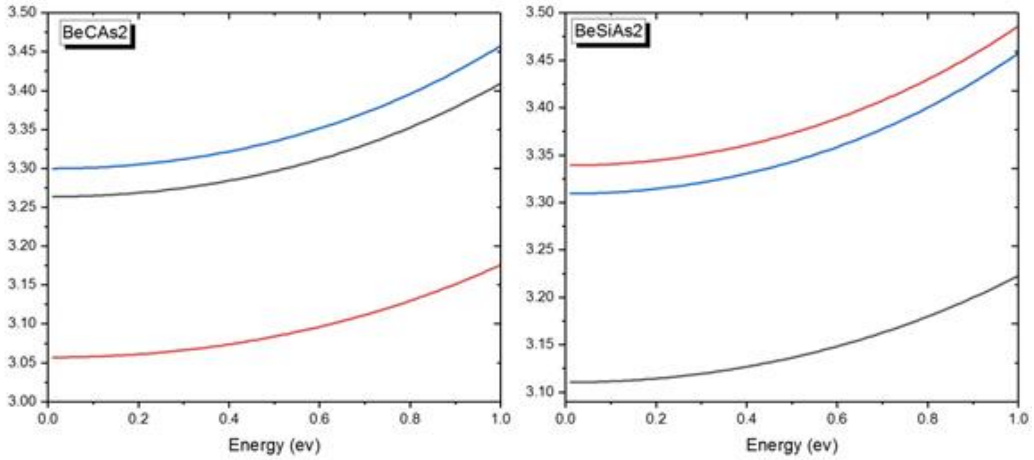
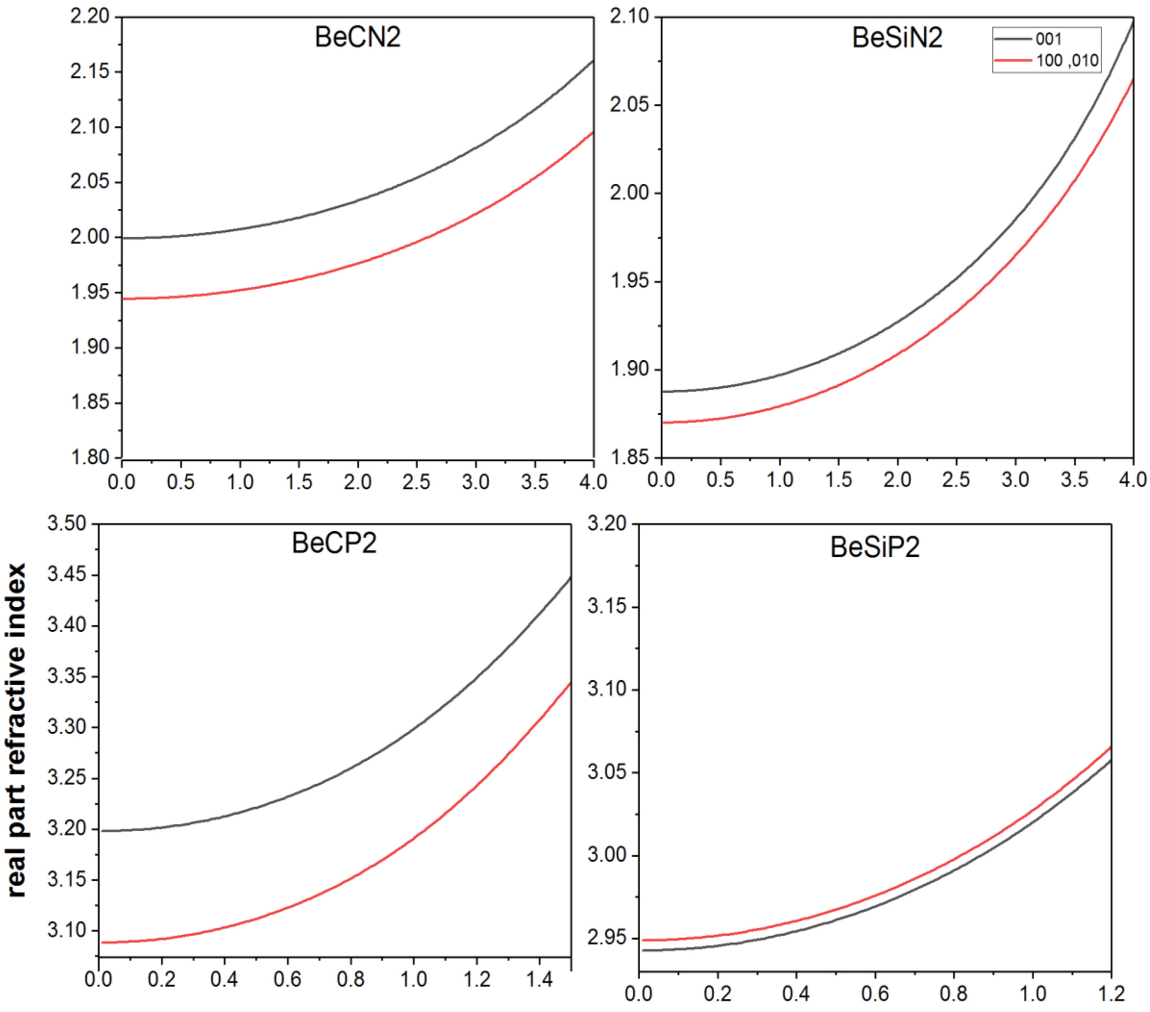


Figure IV-15: Calculated refractive index of BeCN$_2$, BeCP$_2$, BeCAs$_2$, BeSiN$_2$, BeSiP$_2$ and BeSiAs2 for orthorhombic structures.

All orthorhombic compounds are biaxial crystals. Figure IV-16: Shows the calculated n for all six studied tetragonal crystals with different polarizations.



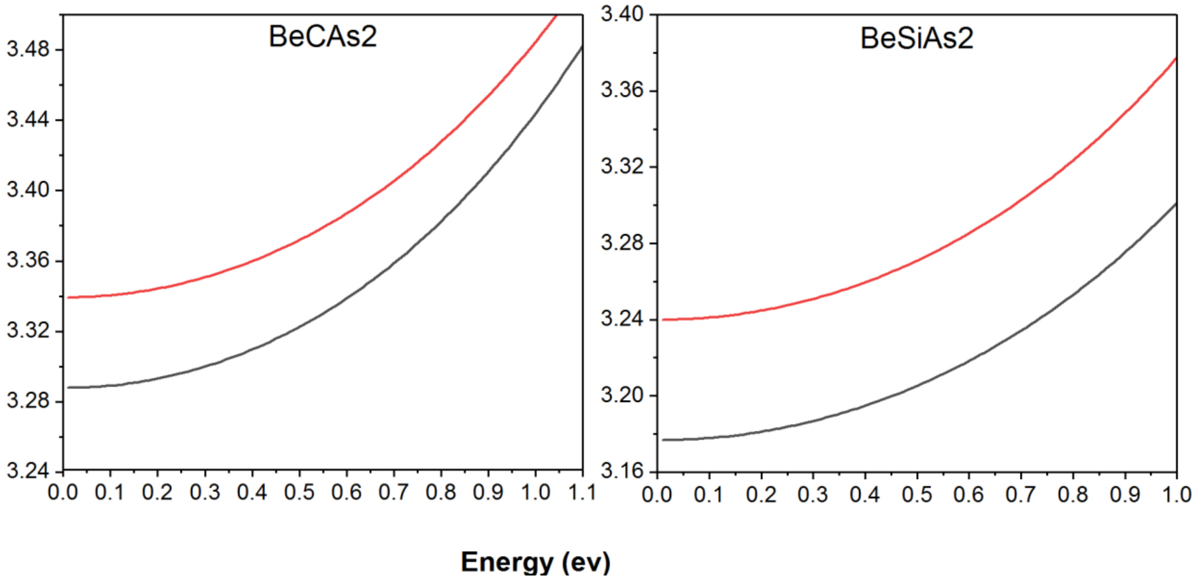
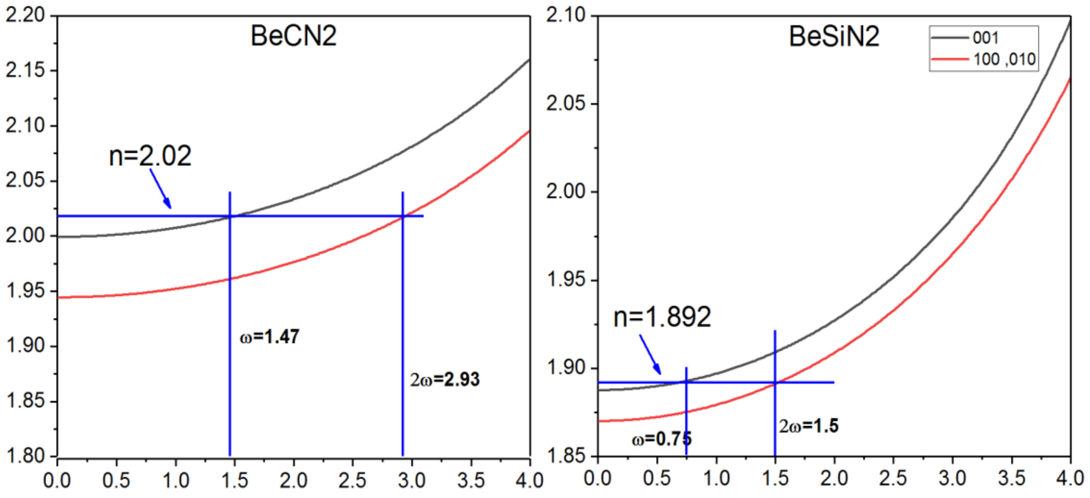


Figure IV-16: Calculated refractive index of $BeCN_2$, $BeSiN_2$, $BeCP_2$, $BeCAs_2$, $BeSiP_2$ and $BeSiAs_2$ for tetragonal structure.

The tetragonal crystals are uniaxial crystal. Moreover, $BeCN_2$, $BeSiN_2$ and $BeCP_2$ are positive uniaxial crystals $n_e > n_o$, $BeSiP_2$, $BeCAs_2$ and $BeSiAs_2$ are Negative uniaxial crystals $n_o > n_e$ but the last compound has a smaller birefringence.

In the following, we are going to examine a number of phase matching conditions in our crystals, calculated phase matching condition for normal condition θ =90, of tetragonal crystals condition are shown in the Figure IV-17.



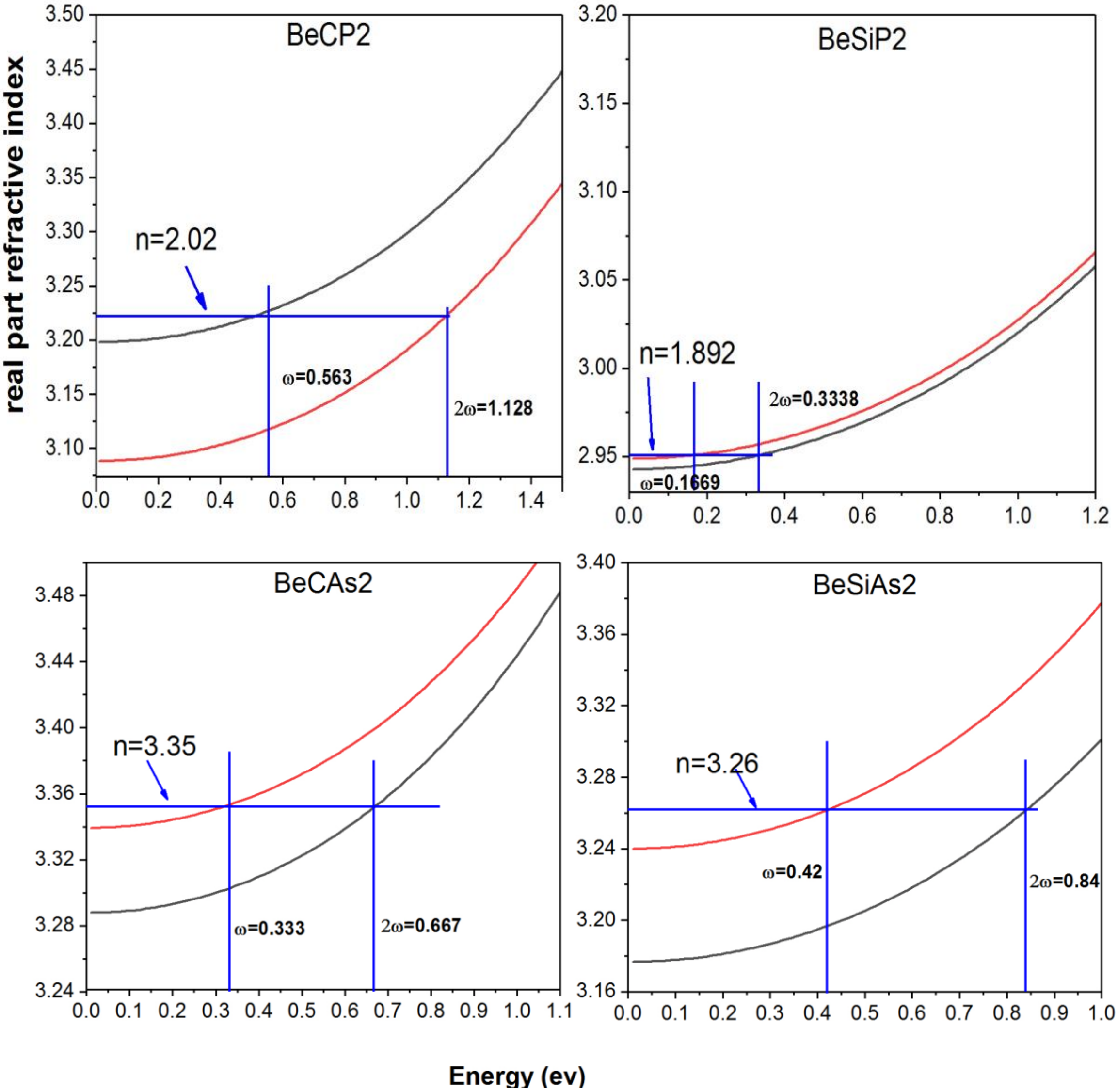


Figure IV-17: Second harmonic generation for normal condition

All our compounds can will use to generate frequency for normal condition. Moreover, Matching phase angle for positive uniaxial crystal calculated using the flowing relation:

$$\theta_{ph} = \arctan\left(\frac{n_e(\omega)}{n_o(\omega)} \sqrt{\frac{n_o^2(2\omega) - n_o^2(\omega)}{n_e^2(\omega) - n_o^2(\omega)}} \right)$$

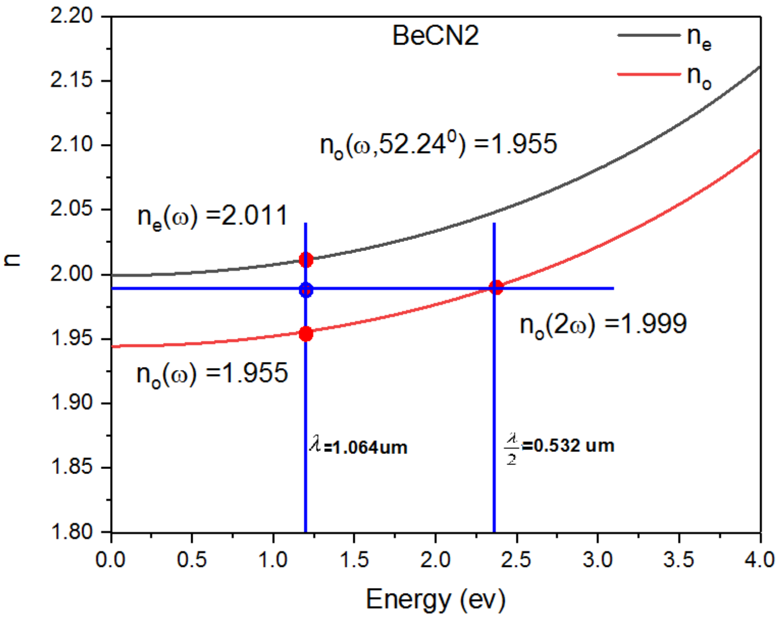


Figure IV-18: The condition for make green 532 nm lasers from a 1064 n m source by tetragonal $BeCN_2$.

We also calculated the second harmonic coefficient at this frequency for both $BeCN_2$ and $BeSiN_2$.

Table IV-17: Calculated second harmonic coefficient

Compound	$\chi^2(0)$ Pm/v		$\chi^2(1.064)$ Pm/v
	This work	Other work	This work
$BeCN_2$	10.38	12.49	13.16
$BeSiN_2$	3.4	6.45	58.5

IV.7. Conclusion

The tetragonal structure energetically is the most stable phase, the $BeAB_2$ compounds are a semiconductor, but $BeCN_2$ and $BeSiN_2$ have a wide band gap. Most of the chemical bonds in our compounds are near covalent character. The calculated elastic parameters show that our compounds are very hard materials. From the calculated high Debye temperatures, we can conclude that these compounds should have high melting temperatures. Moreover, most $BeAB_2$ compounds have clearly good optical birefringence, which makes them potential candidates for SHG.

V. General conclusion and perspective

Six compounds are investigated in this dissertation by density functional calculations in generalized gradient approximation; ExpensiveHSE06 functional is used to calculate the band gap of our compounds.

The calculated lattice parameters are in good agreement with available theoretical and experimental data value. In addition, the ground state energies show that tetragonal phases are energetically more stable and the calculated enthalpy indicate the possibility of synthesize these compounds.

The electronic properties show that all compounds are a semiconductor, $BeSiN_2$ and $BeCN_2$ have wide band gap. The bond character in the most compounds is near covalent.

All compounds have large elastic constants and all stability criteria are satisfied. On the basis of calculated Debye temperatures, we can say that our compound should have high melting temperatures. Furthermore, optical anisotropy, phase matching condition, the second harmonic generation susceptibility of some compounds have been studied.

The generation of the second harmonic in the $BeAB_2$ compounds could make these materials useful as nonlinear crystals for many applications.

My perspective is to complete my Ab initio calculation and understanding all theoretical details used in Ab initio method, and try to discover new nonlinearcrystals.

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ملخص

الهدف من أطروحة الماستر هذه حساب الخصائص البنيوية، الالكترونية، الميكانيكية، والضوئية لبعض مركبات البريليوم الثلاثية، اجري هذا الحساب في إطار نظرية الكثافة الدالية باستعمال طريقة أشباه الكمون والامواج المستوية (PPPW)المضمنان في برنامجي CASTEP وABINIT.

قمنا باستعمال تقريب GGA في حساب مختلف الخصائص، لحساب عرض المنطقة الممنوعة Gapاستعملنا التقريب HSE06 الذي يعطي نتائج مقاربة جدا للقيم التجريبية و لكنه جد مكلف، المركبات التي قمنا بدراستها مركبات تتمتع بثوابت مرونة ودرجة انصهار عاليتين، المركبان $BeCN_2BeSiN_2$ يملكان مجال شفافية أوسع من بقية المركبات، جميع المركبات لها تباين في قيمة قرنية الانكسار مما يؤهلها للتطبيقات البصرية اللاخطية وفى الأخير قمنا بحساب المعامل الضوئي التربيعي χ^2 ل $BeCN_2BeSiN_2$.

Abstract

The aim of this dissertation is the ab initio calculation of the properties: structural, electronic, elastic and optic of a Beryllium based ternary compounds, The calculation is conducted in the frame work of the density functional theory (DFT) used pseudo potential plane wave method (PPPW) which is implanted in the CASTEP and ABINIT codes

The different physical properties calculated using the generalized gradient approximation of Perdew-Burke Ernzerhof (GGA-PBE), for calculate the band gap I used the hybrid functional HSE06 it gives a result with a high degree of reliability. All compound are a hard semiconductor with high melting temperature, $BeCN_2$ and $BeSiN_2$ have a large transparency domain all compounds have a good birefringence all this characteristics could make these materials useful as nonlinear crystals for many applications.

Résumé

Le but de cette mémoire de master est le calcul ab initio des propriétés : structurales, électroniques, élastique et optique des quelque composé ternaire a base de béryllium, Le calcul a été mené dans le cadre général de la théorie de la fonctionnelle de la densité (DFT) utilise la méthode pseudo potentiels onde plane (PPPW) qui sont implanter dans les code de calcul CASTEP et ABINIT.

Nous avons utilisé l'approximation GGA pour calculer les différentes propriétés physiques, la fonctionnelle hybride HSE06 pour la structure de band qui donne des valeurs très proche a l’expérimental, tous les matériaux étudier sont des semi-conducteur, $BeSiN_2$ et $BeCN_2$ possède un large domaine de transparents, les constantes élastiques, la température de fusion de notre composée sont très élevée avec une bon biréfringence suffisantes l’accord de phase, les coefficients de deuxième harmonique sont calculer pour quelque composes.