Pressure dependent electronic properties of $\alpha$-Be$_3$P$_2$

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Abstract. The first-principles linear combination of atomic orbitals method implemented in the CRYSTAL code has been applied to compute equilibrium lattice constant and bulk modulus of $\alpha$-Be$_3$P$_2$. The electronic band structure calculations are also performed to report bandgap. The properties are computed at the level of density functional theory and hybrid calculation. The effect of pressure on the bandgap is studied and the pressure coefficient and volume deformation potential are computed. The computed lattice parameters are well in agreement with the experimentally reported data. Band structure calculation at the level of density functional theory reveals that $\alpha$-Be$_3$P$_2$ is a direct bandgap semiconductor with $E_g=2.39$ eV. The pressure dependent calculations show that the bandgap decreases almost linearly with pressure giving negative value of pressure coefficient.

1. Introduction

The phosphides and nitrides of II group elements are mostly found in the II$_3$-V$_2$ unit. In the bulk form, these have technological applications in optoelectronics, detectors, IR sensors, solar cells ultrasonic multipliers and Hall generators. The larger excitonic radii and narrow bandgap in these materials offer promising applications at nanoscale. Compared to II-VI and III-V semiconductors, the II$_3$-V$_2$ type phosphides and nitrides are studied less both in the bulk and nanophase [1-4]. It has mostly been attributed to the complex crystal structures and large number of atoms. Major studies are directed to the Cd$_3$P$_2$, Zn$_3$P$_2$, Mg$_3$N$_2$, Mg$_3$P$_2$, Be$_3$N$_2$ etc. [1-7]. In this work we compute lattice constant and bulk modulus of $\alpha$-Be$_3$P$_2$. The pressure dependent isothermal band structure calculations are performed to report volume deformation potentials and the pressure coefficient of bandgap. The calculations are performed using the first-principles linear combination of atomic orbitals methods (LCAO) at the level of density functional theory (DFT) and hybrid scheme implemented in the CRYSTAL code [8].

It is known that DFT under local density approximation gives incorrect estimate of fundamental bandgap in semiconductors [9,10]. The GGA shows only some improvement in predicting bandgap. HF theory, gives good results in systems where screening is unimportant but overestimates bandgap in general. Quasi particle (QP) shift and GW calculations performed on ZnO, CdO and InN revealed improvement in the computed bandgaps. These calculations suggest a correction term to be included in the bandgap computed form the DFT. According to the $\frac{1}{4}$ recipe of Fuchs et al [11] the correction in Kohn-Sham eigenvalues due to QP shift is negligibly small when hybrid functional mixing 25% of

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HF exchange with the 75% DFT exchange is taken to compute band structure [9,10]. Therefore, in this work we report electronic band structure calculations using hybrid scheme. The calculations at the level of DFT taking Perdew-Burke-Ernzerhof (PBE) exchange and correlation functionals are also reported.

2. Computational detail

Beryllium phosphide (Be$_3$P$_2$) may be found in the bcc anti-bixbyite and tetragonal structures. The α-Be$_3$P$_2$ crystallises in cubic anti-bixbyite type structure belonging to the space group 206. The lattice constant of α-Be$_3$P$_2$ is $a=10.15$ Å [12,13] and the unit cell contains 80 atoms, 48 (Be) and 32(P). Each beryllium atom is tetrahedrally coordinated with phosphorous and each phosphorous atom is coordinated by six beryllium atoms [12,13]. The beryllium atom situated at ($x_1, y_1, z_1$) occupies 48e Wyckoff position while crystallographically different phosphorous atoms P1 at ($x_2, 0.0, 0.25$) and P2 at ($0.25, 0.25, 0.25$) occupy 24d and the 8b Wyckoff positions, respectively [13,14].

The first-principles periodic LCAO method implemented in the CRYSTAL code [8,15] is applied considering the density functional theory (DFT) and the hybrid scheme. In the current non-cellular method, each crystalline orbital $\psi(r,k)$ is a linear combination of Bloch functions $\varphi(r,k)$ defined in terms of local functions $\varphi(r)$, normally referred as atomic orbitals. The local functions are expressed as linear combination of certain number of individually normalized Gaussian type functions. The 5-111G [16] and 85-21d1G [17] Gaussian basis sets were taken for Be and P, respectively. The gradient corrected PBE exchange and correlation functionals [18] were taken. Additionally, hybrid calculation adopting hybrid functional which is very similar to the B3LYP scheme is also performed. However, total exchange is taken care of by mixing 75% PBE exchange with the 25% Fock exchange. The LYP correlation functional is replaced by the PBE correlation functional and all other non-local parameters were same as in the B3LYP scheme. The self-consistent calculations were performed considering Monkhorst and Pack [8] net of 11×11×11 points. The self consistency was achieved within 14 cycles.

To perform geometry optimization, force calculations were performed which enables to find the atomic positions of Be and P atoms. To begin with experimental atomic positions available for α-Be$_3$N$_2$ [7] were taken for geometrical optimization. The positions were optimized by performing force calculations (OPTGEOM option). The total energy curve i.e. E(V) was generated to obtain the lattice constant (say, $a_1$). The atomic coordinates were optimized at $a_1$. Considering these optimized coordinates, the E(V) curve is generated to obtain refined lattice constant (say, $a_2$). Thereafter, the atomic coordinates were optimized at $a_2$. Finally the total energy curve for α-Be$_3$P$_2$ was obtained and coupled with the Murnaghan equation of state [19] to propose equilibrium lattice constant and the bulk modulus for α-Be$_3$P$_2$ computationally.

3. Results and discussion

The total energy curves, E(V) generated considering DFT and the hybrid scheme, show that energy is lower in the entire range of volume for the hybrid scheme. The equilibrium lattice constants, bulk moduli and pressure derivative of bulk moduli deduced by coupling E(V) curves with Murnaghan equation of state for the two calculations are given in Table 1. The optimized atomic positions are also listed in the table. It is obvious that the exchange and correlation schemes affect atomic positions upto 1 part in $10^3$. Also, the current calculations and published results on atomic positions agree upto 1 part in $10^2$. The lattice constant obtained from the hybrid scheme is closer to the experiment than the PBE-GGA. The lattice constant predicted by PBE-GGA scheme is merely 0.36% higher than the experiment compared to the 0.42% predicted by the FP-LAPW method. For hybrid scheme difference is smaller. Naturally, the bulk modulus proposed by PBE-GGA is larger than the FP-LAPW method. The difference is, however, very small (~14 GPa). Moreover, the density 2.24 gm/cm$^3$ given by current calculations is in very good agreement with 2.25 gm/cm$^3$ reported experimentally.
Table 1. Optimized atomic positions, lattice constants ($a$), bulk modulus ($B_0$) and its pressure derivative ($B'$) and density ($\rho$) of Be$_3$P$_2$.

|          | Atomic positions | $a$ (Å) | $B_0$ (GPa) | $B'$ | $\rho$ (g/cm$^3$) |
|----------|------------------|---------|-------------|------|-----------------|
| PBE-GGA  | $x_1$ 0.3824 | $y_1$ 0.1333 | $z_1$ 0.3735 | $x_2$ 0.9926 | 10.1862 | 114.23 | 2.716 | 2.24 |
| Hybrid   | $x_1$ 0.3837 | $y_1$ 0.1344 | $z_1$ 0.3732 | $x_2$ 0.9920 | 10.1741 | 115.97 | 2.742 | 2.24 |
| FP-LAPW* | $x_1$ 0.3790 | $y_1$ 0.1300 | $z_1$ 0.3740 | $x_2$ 0.9940 | 10.1929 | 99.087 | 3.600 | --  |
| Expt.    | --- | --- | --- | --- | 10.1500 | -- | -- | 2.25$^c$ |

$^a$Ref. [14], $^b$Ref [13], $^c$Ref [20]

The electronic band structure computed from density functional PBE-GGA is shown in figure 1. The upper valence bands are predominantly of the phosphorous 3$p$ type states. The lower valence bands are the phosphorous 3$s$ states with a minor contribution from Be 2$s$ states. The lower conduction bands are dominated by the beryllium 2$s$ and 2$p$ states. Other bands arising from the 1$s$, 2$s$, and 2$p$ states of phosphorous and 1$s$ of beryllium are deep below the lowest band visible in figure 1. The band structure exhibits direct bandgap of 2.39 eV. Bandwidth of the upper valence bands is 6.79 eV and lower bands are extended within 2.86 eV. As discussed earlier, hybrid scheme has also been adopted to compute band structure. The overall topology of the band structure obtained from hybrid functional, not shown here, is similar to the band structure shown in figure 1. However, the direct bandgap predicted by the hybrid calculation is 3.75 eV. Bandwidth of the upper and valence bands is 7.61 eV and 3.82 eV, respectively. Notably, the bandgap 1.6 eV, proposed by FP-LAPW method is lower than the current results.

The application of hydrostatic pressure causes shift of conduction band edge relative to the valence band edge owing to change in volume. The change allows direct estimation of the effective hydrostatic deformation potentials for the bandgap. As the pressure derivatives of band energy differences tend to be correctly calculated without resorting to GW or QP calculations, band structure calculations combined with structural study from first-principles methods enable computation of deformation potentials and pressure dependent bandgaps [9,21]. In order to examine pressure dependence of the bandgap, calculations were performed up to 50 GPa and no change in the nature of the bandgap was observed.
seen. To know the pressure dependence a quadratic equation was fitted to the computed bandgaps [22]:

\[ E_g(P) = E_g(0) + \alpha_p P + \beta_p P^2, \]

where \( E_g \) is the fundamental gap (eV), \( P \) is pressure (GPa) while \( \alpha_p \) and \( \beta_p \) are the pressure coefficients. The \( \alpha_p \) obtained after fitting Eq. 1 to the fundamental gap is -0.89 (meV kbar\(^{-1}\)) while \( \beta_p \) is \( \sim 10^{-4} \) (meV kbar\(^{-2}\)). It suggests almost linear change in bandgap as shown in figure 2. The \( \alpha_p \) helps to obtain volume deformation potentials \( (a_v=-\alpha_p B_0) \) useful in thin films applications of semiconductors [22]. The volume deformation potential \( a_v \) suggested for \( \alpha \)-Be\(_3\)P\(_2\) by the current study is 1.016 eV.

### 4. Conclusions

Structural and electronic properties of \( \alpha \)-Be\(_3\)P\(_2\) are studied applying the first-principles method considering the PBE-GGA and hybrid functional. The optimized atomic positions, lattice constant and the bulk modulus are presented. The proposed lattice constant and bulk modulus follow general trend and in very good agreement with experiment. The band structure calculations show that the \( \alpha \)-Be\(_3\)P\(_2\) is a direct bandgap semiconductors. The PBE-GGA calculations predict bandgap of 2.39 eV while hybrid calculation gives 3.75 eV. The band structure calculations performed at various pressures, considering the low pressure limit, show that the bandgap decreases linearly with pressure. The computed pressure coefficient \( \alpha_p \) is -0.89 (meV kbar\(^{-1}\)) while the volume deformation potential \( a_v \) suggested by the current study is 1.016 eV.

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