PHYSICAL PROPERTIES OF MAGNESIUM NITRIDOPHOSPHATE (Mg$_2$PN$_3$) COMPOUND

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In this work, we investigated structural, electronic and optical properties of orthorhombic Mg$_2$PN$_3$ compound. The calculations were performed with full-potential linearized augmented plane-wave (FP-LAPW) method based on Density Functional Theory by using Wien2k packet. PBE-GGA (Perdew, Burke and Ernzerhof) were selected as exchange-correlation functional. We calculated cell dimensions, bulk modulus and cohesive energy of this compound. The calculated structural parameters have a good agreement with experimental works. We have also calculate DOS curve, electronic band structure, dielectric function, absorption coefficient and optical conductivity parameters. The DOS and electronic band calculations show that Mg$_2$PN$_3$ has indirect band gap with 5.2 eV value.

1. Introduction

Phosphates are very important for laser materials [1]. Intensive research in the last few decades has been proven that carbites and especially nitrides are prominent because of the desirable physical properties make the early transition metal nitrides important materials for various technological applications [1-3]. The high-temperature reaction calorimetry was effective to understand the formation of ternary oxides [1,4]. The novel nitridophosphate was obtained at high-pressure and high-temperature synthesis utilizing the multianvil technique (8 GPa, 1400∘C) [2]. Hence, the parameter pressure appears to be necessary for the P / O / N chemistry [2,3].

Marchand et al. had already reported that Mg$_2$PN$_3$ crystallized in a wurtzite-like structure, but the structural data reported was contradictory and was not allowing a reasonable inference to the nature of the P-N substructure [5]. For the first time, Mg$_2$PN$_3$ (1070 K, 140 MPa) and Zn$_2$PN$_3$(800 K, 200 MPa) phosphorus nitrides which have a wide application potential in optoelectronic or photovoltaic batteries were synthesized as ammonothermally at high temperature and high pressure starting from P$_3$N$_5$ and the corresponding metals (Mg or Zn) [5,6]. Mg$_2$PN$_3$ and Ca$_2$PN$_3$ were synthesized by reacting the corresponding metal nitrides with P$_3$N$_5$ at 800°C [7]. The band gaps of the nitrides were estimated as 5.0 eV for Mg$_2$PN$_3$ and 3.7 eV for Zn$_2$PN$_3$ by using diffuse reflection spectroscopy. First principle calculations of compounds, Ba$_2$ZnN$_2$, Ca$_2$ZnN$_2$, CaZn$_2$N$_2$ and CuPN$_2$ were predicted as 1.3 eV, 1.7eV, 1.83 eV, 1.67 eV, respectively. DFT calculations were performed to confirm the experimental values [5,6,8]. The absorption coefficient of CaZn$_2$N$_2$, Ca$_2$ZnN$_2$ and Ba$_2$ZnN$_2$ compounds reaches as high as 5×10^4cm^{-1}[8]. As it can be seen, theoretical studies can be very valuable to understand material and device properties. For these reasons, an increasing number of first principle calculations have been performed for these materials and most of these calculations are based on density-functional theory [2,9]. From previous studies it has been observed that the properties of this compound are not examined theoretically in detail and the synthesis method especially has been emphasized [6].

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In this study, we investigated the structural, electronic and optical properties of the Mg_2PN_3 compound. DFT calculations will be important to learn more about the nature of these materials and verify the experimental values.

2. Computational method

We searched structural, electronic and optical properties of orthorhombic Mg_2PN_3 within a self-consistent scheme by solving the Kohn–Sham equation based on Density Functional Theory (DFT). The calculations were performed using the self-consistent full potential linearized augmented plane wave (FPLAPW) method [10] with the ab-initio simulation package WIEN2k [11]. We selected the modified Becke-Jonhson potential (mBJ) for the exchange and correlation potential implemented in WIEN2K packet. In the LAPW method the unit cell space is divided into non-overlapping muffin-tin (MT) spheres separated by an interstitial region. The basis functions are enlarged into spherical harmonic functions inside the muffin-tin sphere and Fourier series in the interstitial region. The muffin-tin (MT) sphere radii were selected as 1.84, 1.44, 1.52 a.u. for Mg, P and N, respectively. The energy of separating the valence and core states (E_{cut}) was selected as -7 Ry. The convergence of the basis set was checked by a cut off parameter $R_{mt}K_{max}$ was chosen as 8. The magnitude of the largest vector in charge density Fourier expansion (G_{max}) was selected 12. The highest orbital momentum for the wave function expansion inside atomic spheres (L_{max}) is equal to 10.

For the Brillouin zone (BZ) integration, the tetrahedron method [12] with 125 special k points in the irreducible wedge (1000 k-points in the full BZ; 9 x 9 x 10 k-point mesh) was used to construct the charge density in each self-consistency cycles (SCF). The energy convergence criteria was chosen as 0.0001 Ry during SCF calculations.

3. Results and discussion

3.1. Structural properties

Mg_2PN_3 compound is orthorhombic with *Cmc*21 (no. 36) space group (Fig. 1). The calculation was started with experimental data derived from ref.[5]. We calculated total energy of compound for various volumes around experimental data to find ground state properties. The calculated total energy depending on unit cell volume is given in Fig. 2.
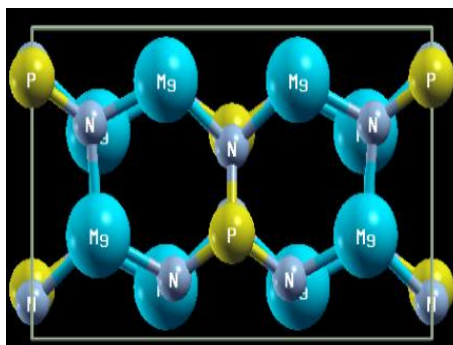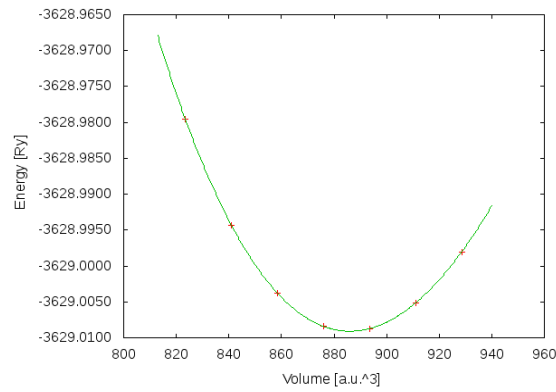

Fig. 1. Unit cell of Mg₂PN₃.

Fig. 2. Calculated total energy versus unit cell volume of Mg$_2$PN$_3$ compound.

According to Murnaghan's equation, the calculated volume (V$_0$), bulk modulus (B$_0$), minimum energy (E) and derivative pressure (B') values are listed in Table 1. Deviation value of optimized unit cell volume from experimental value is % 1.14.

Table 1. Calculated structural parameters of Mg$_2$PN$_3$.

V$_0$ (a.u^3)	B$_0$(GPa)	E(Ry)	B'(GPa)
885.9956[a]	172.6432	-3629.00909	4.2967
876.03485[b]			
873.707[c]			

3.2. Electronic properties

DOS (Fig. 3) and electronic band plot (Fig. 4) were calculated to determine electronic properties of compound.

(a)

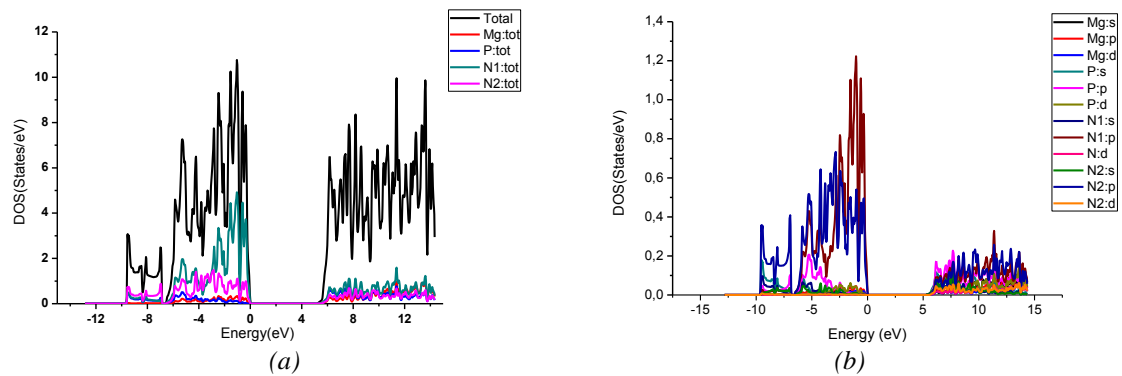*(b)*

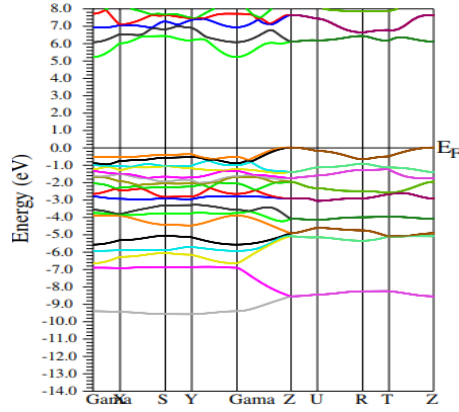*Fig. 3. Calculated total (a) and partial (b) DOS of Mg$_2$PN$_3$.*

Fig. 4. Electronic band plot of Mg_2PN_3.

At the valence band near the Fermi level, the most contribution comes from N1 and N2 atoms. At the intermediate valence band N2 atom gives the most contribution to DOS. At the conduction band most contribution comes from N1 atom but considerably contribution comes from N2, Mg and P atoms (Fig. 3(a)). The valence band maximum (VBM) is at the N1:p and the conduction band minimum is at the P:p states (Fig. 3(b)). Calculated band plot of Mg_2PN_3 with highly symmetric point in the Brillouin zone shows that the VBM is at Z and the CBM is at Gama point and the bandgap is indirect with 5.2 eV value.

3.3. Optical properties

It can be possible to suggest potentially new optoelectronic applications by studying optical properties of materials [13]. Thus, we calculated dielectric function, optical conductivity, absorption and reflection of Mg_2PN_3 to contribute to this area. One of the best approaches to investigate the optical properties of materials can be considered as calculation of the complex dielectric function [14]. The optical response of a medium at all photon energies is described by the dielectric function: $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$.

The real part $\varepsilon_1(\omega)$ is related to the dispersive conduct and the imaginary part $\varepsilon_2(\omega)$ corresponds to the absorptive conduct of the material. The other optical properties can be directly calculated from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ [15]. Therefore, we calculated real and imaginary part of epsilon, absorption coefficient, reflection index, optical conductivity and extinct coefficient with xx, yy and zz directions (Fig. 5). Imaginary part of epsilon start at 5.5 eV for xx and zz direction and at nearly 6 eV for yy direction (Fig. 5(b)). Absorption edge is 5.5 eV for xx and zz direction approximately 6 eV for yy direction (Fig. 5(d)). Optical conductivity edge is approximately 8 eV. The optical conductivity value increases until 11.5 eV energy and decreases for higher energy value than 11.5 eV (Fig. 5(c)).
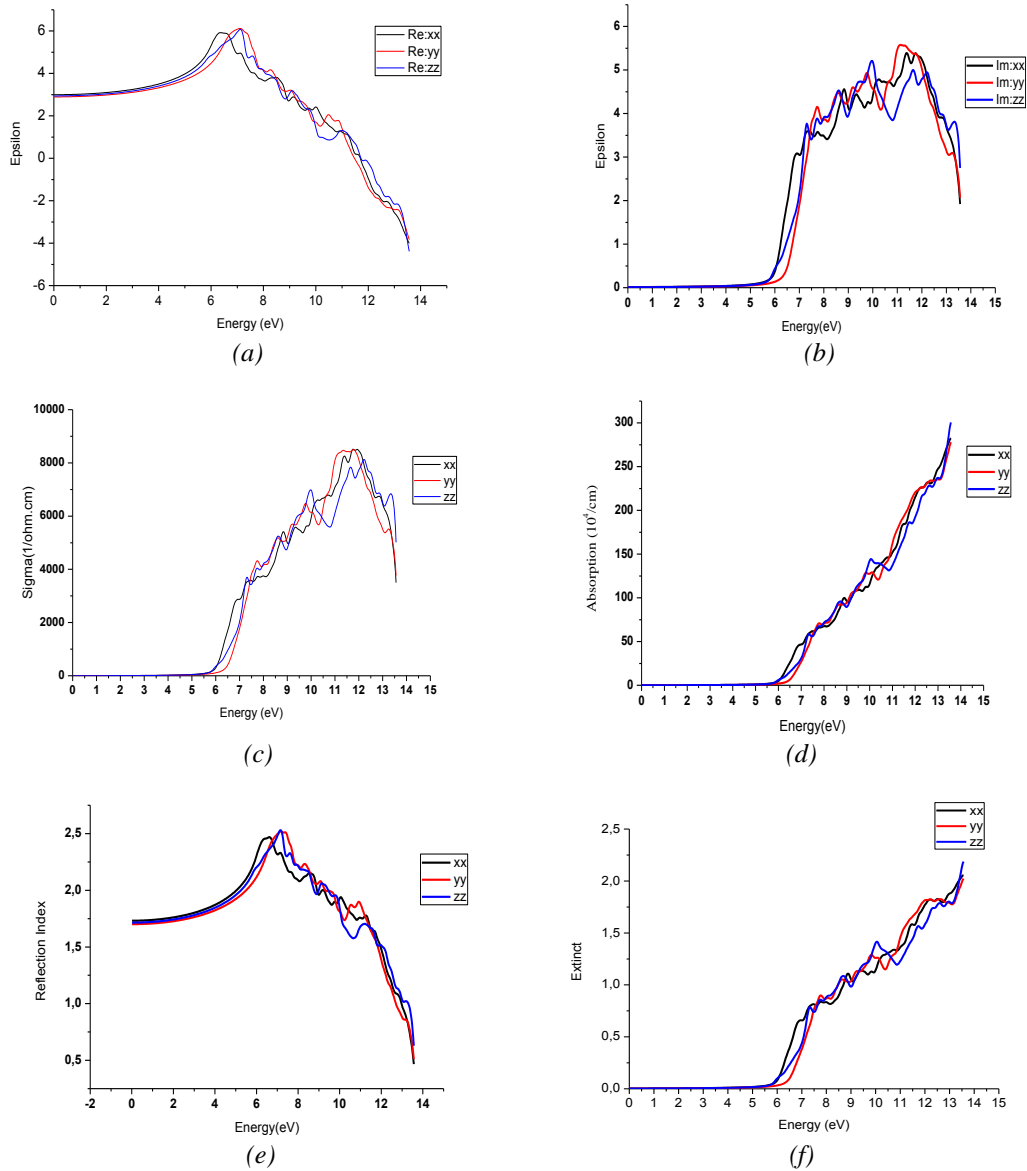
*Fig. 5. a) Real part of epsilon b) imaginary part of epsilon c) optical conductivity
d) Absorption coefficient e) reflective index and f) extinct coefficient.*

4. Conclusions

We have investigated structural, electronic and optical properties of Mg_2PN_3 employing all electrons full potential linearized augmented plane wave (FP-LAPW) method based on DFT within modified Becke-Jonhson potential (mBJ). The calculated structural parameters are compatible with experimental and other theoretical works.

The DOS and electronic band plots show that the Mg_2PN_3 is has indirect band gap with 5.2 eV value. And this result is very close to experimental band gap value that is 5 eV [6]. Optical nature of Mg_2PN_3 is explored with the help of calculating optical parameters such as absorption coefficient, dielectric function, and optical conductivity for photon energy up to 14.0 eV. The results show that the compound is transparent with visible light and good absorber in ultaviolet region.

Acknowledgments

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