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THEORETICAL INVESTIGATIONS OF β-TRICALCIUM PHOSPHATE BIOMATERIALS: DFT INSIGHT

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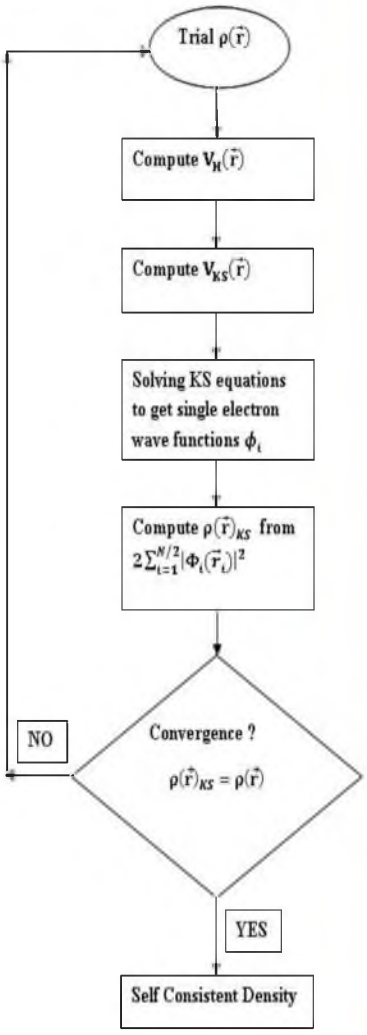
Graphical abstract



Abstract

Beta-tri-calcium phosphate (β-TCP) materials have gained a great deal of research considerations in biomaterial area due to their excellent biocompatibility and identical chemical compositions to the natural teeth and bones. Therefore, the β-TCP compound can be used as coatings, cement and composites as well as biocompatible ceramics for medical and dental applications. Electronic and optical properties for β-TCP compound have been investigated using density functional theory (DFT). For the calculations, we used full potential linear augmented plane wave method (FPLAPW), within three types of approximations along with local density approximations (LDA), generalized gradient approximations (GGA) and Modified Becke-Johnson (mBJ) to get the effect of the exchange and correlation in our calculations to get an accurate results. The computed band gap values for (β-TCP) compound using LDA, GGA, and mBJ-GGA approximations are 5.5 eV, 5.9 eV and 6.8 eV respectively. This is also predicted that the chemical bonding in this compound is a kind of combination of covalent and ionic character that is in a line with the experimental findings. The optical parameter, static dielectric constant $\varepsilon_1(0)$ reaches the values of 3.23681 (eV) at 0 GPa for the β-TCP compound. The obtained results are of vital nature for rising the quality of the electronic and optical properties of this material, and provide more evidence to fabricate novel Beta-Tri-calcium phosphate biomaterials for medical and dental applications.

Keywords: Density functional theory; tri-calcium phosphate; biomaterial, electronic properties; optical properties.

Abstrak

Bahan Beta-tri-kalsium fosfat (β-TCP) telah mendapat banyak pertimbangan penyelidikan dalam bidang biobahan kerana keserasian bio yang cemerlang dan komposisi kimia yang serupa kepada gigi dan tulang secara semula jadi. Oleh itu, sebatian β-TCP boleh digunakan sebagai salutan, simen dan komposit serta seramik keserasian bio untuk kegunaan perubatan dan pergigian. Sifat elektronik dan optik sebatian β-TCP telah dikaji menggunakan teori fungsional ketumpatan (DFT). Untuk pengiraan, kita menggunakan potensi penuh kaedah gelombang satah linear diperkukuhkan (FP LAPW), dalam tiga jenis anggaran bersama-sama dengan anggaran ketumpatan setempat (LDA), anggaran kecerunan umum (GGA) dan Ubahsuai Becke-Johnson (MBJ) untuk mendapatkan kesan pertukaran dan korelasi dalam pengiraan kami untuk mendapatkan keputusan yang tepat. Nilai jurang jalur dikira untuk sebatian (β-TCP) menggunakan LDA, GGA dan MBJ-GGA anggaran adalah 5.5 eV, 5.9 eV dan 6.8 eV masing-masing. Ini juga meramalkan bahawa ikatan kimia dalam sebatian ini adalah sejenis gabungan kovalen dan sifat ionik yang selaras dengan dapatan eksperimen. Parameter optik, pemalar dielektrik statik $\varepsilon_1(0)$ mencapai nilai-nilai 3.23681 (eV) pada 0

GPa untuk sebatian β-TCP. Keputusan yang diperolehi adalah sifat penting untuk meningkat kualiti sifat elektronik dan optik bahan ini, dan menyediakan lebih banyak bukti untuk merekabentuk Beta-Tri-kalsium fosfat biobahan yang baru untuk aplikasi perubatan dan pergigian.

Kata kunci: Teori Kefungsian ketumpatan, tri-kalsium posfat, sifat elektronik dan sifat optik bio-bahan

1.0 INTRODUCTION

During the last fifty years, a great progress has been made in material and medical sciences areas to improve the calcium phosphate ceramic properties to use it for repairing and rebuilding the damaged part (s) of the skeletal bones [1]. Therefore, the development of calcium phosphate bio-ceramic has been recognized as a major addition to the medical science applications [2]. Calcium phosphate biomaterials have been regarded as a potential bone replacement due to their mineral composition similar to the natural bones and teeth [3, 4]. Therefore, calcium phosphate biomaterials are extensively used in bone replacement, bone augmentation, as well as in bone repairing and reformation [5]. The crystal structure of β-TCP is rhombohedral with a space group of (R3c, Z = 21), which is shown in Fig. 1. β-TCP is formed at low temperature, and it is stable under 1120 C^0 [6], which makes it as essential constituent elements for living teeth and bones [7].

Beta-tri-calcium phosphate has important applications when it is used as the synthetic material in bone replacement for surgical therapy, in order to fix the bone injury using maxillofacial surgeons and orthopedic surgeons [8]. However, some researchers reported that, doping β-TCP compound with Zinc (Zn) element has a high solubility for the bone cells when it is used as bone substitution [9]. Another experimental study reported that, a doping β-TCP compound with Zn element changed the β-TCP structure; thereby the electronic and optical properties are changed as well. This means, the substitution of Zn decreases the crystallinity and destabilizes the structure of β-TCP compound [10], which has a negative effect on β-TCP properties when it is used as bone and teeth replacement. Therefore, in this study we have used theoretical investigations, to calculate electronic and optical properties of the pure β-TCP compound in the R3c crystal structure of the experimental lattice constants at ground state energy. This study will provide more understanding and a clear picture of this compound, and supports researchers to design a compatible β-TCP biomaterial that can be used in several clinical applications.

For the electronic and optical properties calculations, we used full potential linear augmented plane wave method (FPLAPW), within (LDA), (GGA) and (mBJ-GGA) approximations as implemented into WIEN2k Package [11].

The materials that are used for implants purposes should possess special characteristics such as, high biocompatibility, good solidity and adequate resistance to the corrosion defects [7]. In this regards, β-TCP compound is considered as essential constituent elements for living teeth and bones. Indeed, it plays an important role in graft issues, which is made it as uniquely biocompatible ceramics in medical and dental applications [12].

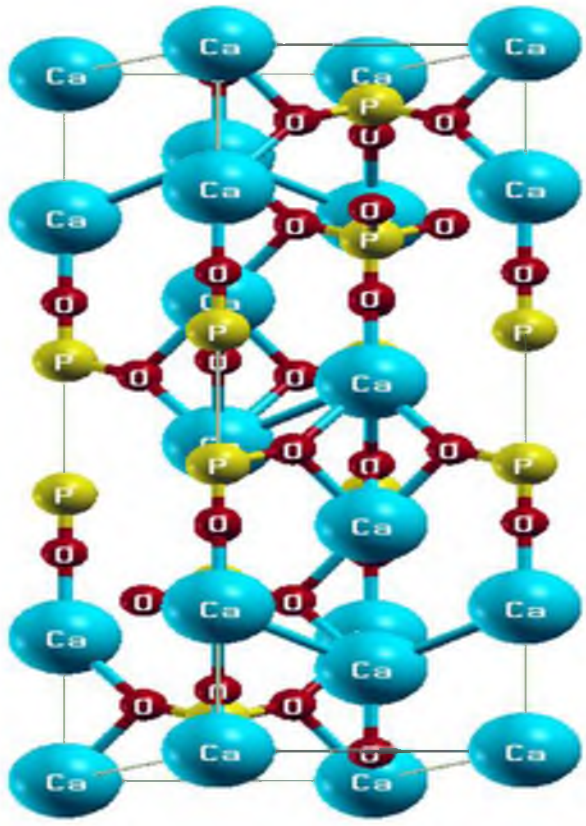


Figure 1 Crystal structure of pure Beta-Tri-calcium phosphate (β-TCP) compound.

2.0 COMPUTATIONAL METHODOLOGY

Theoretical calculations that employ periodic boundary conditions are an effective way to model the physical properties of solid materials at the atomic level as a complement to the experimental studies [13]. In this respects, we performed our calculations using a self-consistent scheme by solving the Kohn–Sham equations using density functional theory (DFT) along with local density approximations (LDA), generalized gradient approximations (GGA) [14] and Modified Becke-Johnson method (mBJ-GGA) as implemented into WIEN2k package [11].

The value of $R_{MT}K_{max} = 3$, is adopted to achieve self-consistence field (scf) convergence for the electronic and optical calculations, where R_{MT} is the smallest atomic radius in a unit cell, and K_{max} is the magnitude of the maximum value of k-vector in the plane wave expansion. The number of 1500 k-points is used as input parameter for the self-consistent charge density determination, in the irreducible symmetry wedge of the Brillion Zone (BZ) [15]. The energy convergence of 10-6 Ryd is chosen for the cut-off energy. In addition, we have used the values of muffin-tin radii of 2.2, 1.8, and 1.07 atomic units (a.u) for Ca, P, and O elements, respectively.

The electronic and optical properties calculations are investigated with the above mentioned computational parameters, using experimental lattice constants of the pure β-TCP compound, which are taken from reference [16], and our above-mentioned computation details to get the relaxed structure of the β-TCP compound. Then, we have used it to perform our electronic and optical properties calculations using LDA, GGA, and mBJ-GGA approximations.

3.0 RESULTS AND DISCUSSION

3.1 Electronic Properties

We have investigated the electronic band structure calculations for β-TCP compound, and the results are displayed in Fig. 2. It is clear from Fig. 2 that, the Fermi level is set at 0 eV on energy scale, conduction band minima (CBM) and valence band maxima (VBM) are located at the central symmetry (C) line of the Brillion zone, which shows the direct band gap nature for the full range of concentration.

The calculated band gap values using mBJ-GGA method has high value compared to those using LDA and GGA approximations. The obtained band gap value with GGA method is quite closer to that one computed by mBJ-GGA method. Fig. 2 shows the calculated band gap plot for a β-TCP compound with values of 5.2 eV, 5.9 eV and 6.8 eV using LDA, GGA, mBJ-GGA approximations, respectively.

We reported the results of calculated band gap values for the β-TCP compound of other studies to make a comparison with our current work. Xilin and Lazaro calculated the band gap value (2.4eV) for a β-TCP compound using density functional theory calculations along with Perdew-Wang (PWC) exchange-correlation [10]. Whereas L. Liange, P. Rulis and W.Y. Ching in 2010, performed DFT study to calculate the band gap value (5.25 eV) for β-TCP compound [17], this result is closer to our calculated band value using GGA approximation.

In order to get more understanding of the nature of electronic band structure, we have also calculated the projected density of states (PDOS) and total density of states (TDOS) for a β-TCP compound using LDA, GGA and mBJ-GGA approximations. The results of calculated TDOS and PDOS for β-TCP compound are presented in Fig. 3, 4 and 5 using LDA, GGA, and mBJ-GGA methods, respectively. In Fig. 3, 4 and 5, the total density of states of β-TCP compound are shown between -23.6 eV and 15 eV. For the projected density of states, the p-state of Ca_1 and Ca_2 atoms are participated into the total Dos of pure β-TCP, in the energy range of -18 eV to -20 eV. While for P atom, the S and P states are contributed into the total DOS started at -21eV (LDA), -17eV (GGA), and 23eV (mBJ-GGA), and ended at 15.0 eV. The S state of O_1 is participated into TDOS from -20 eV to 12.5 eV, from -20 eV to -18.0 eV and from -25 eV to 13.5 eV for the LDA, GGA, mBJ-GGA approximations, respectively.

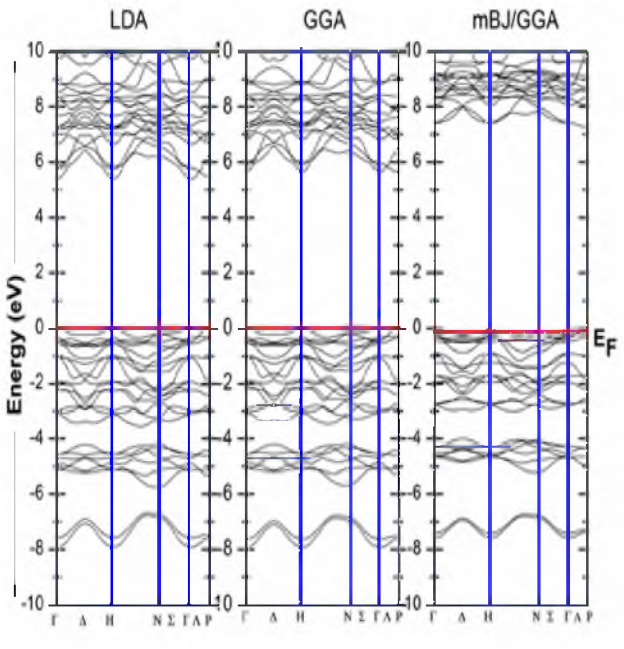


Figure 2 Structures of the β-TCP compound with LDA, GGA, and mBJ-GGA calculations.

The s and p-states of O_2 element are participated into the TDOS from -21 eV to 12 eV (LDA), from -21.5 eV to 13.0 eV (GGA), and from -23 eV to 14.0 eV (mBJ-GGA) approximations. The p-state of Ca_1 and Ca_2 has high

contribution into the TDOS, which is shown in Fig. 3 and Fig. 4, while in Fig. 5, both s &p-states of $Ca_1$and Ca_2 have high contribution into the TDOS.

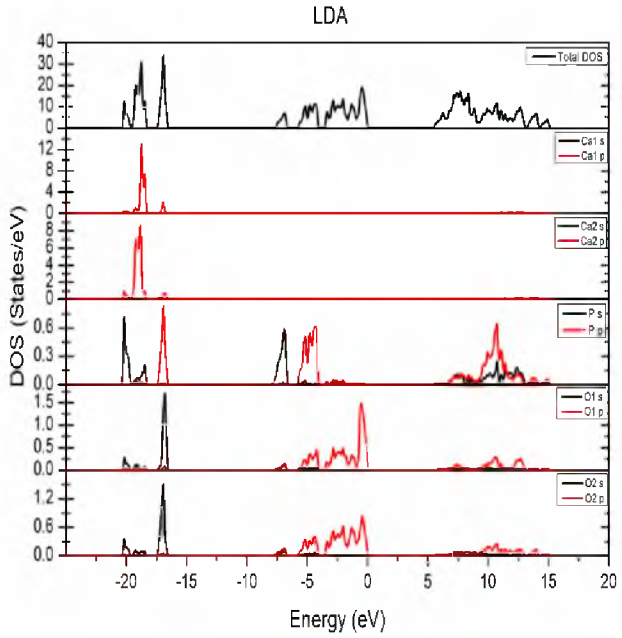


Figure 3 Density of States (DOS) of the β-TCP compound with LDA calculations.

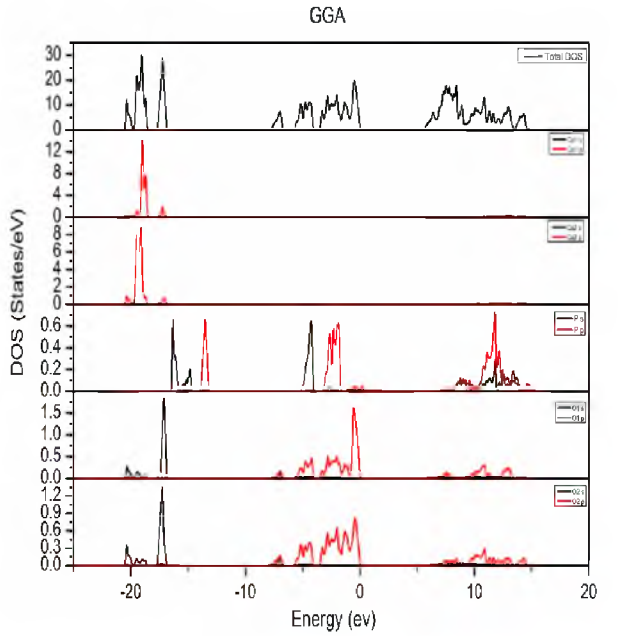


Figure 4 Density of States (DOS) of the β-TCP compound with GGA calculations.

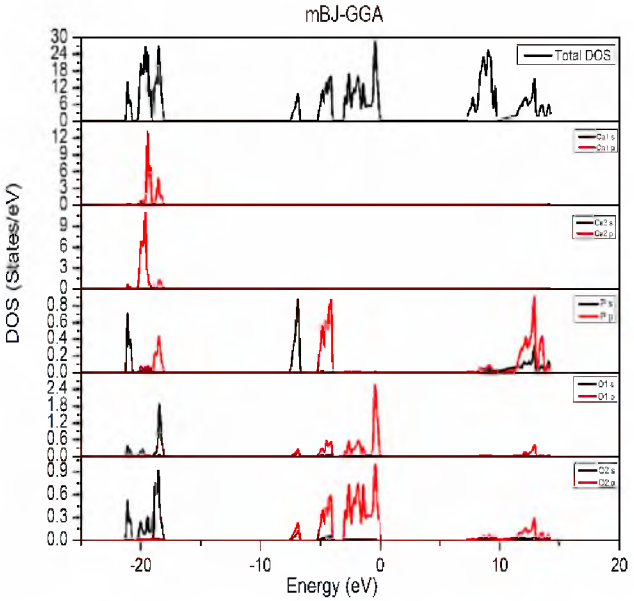


Figure 5 Density of States (DOS) of the β-TCP compound with mBJ-GGA calculations.

3.2 Optical Properties

Optical properties and band gap calculations provide more information about the analysis and designing materials. Therefore, we performed the optical properties calculations for β-TCP compound to get the optical parameters such as, static dielectric constant $\varepsilon_1(0)$, static refractive index n(0), magnitude of the coefficient of reflectivity at zero frequency R(0), number of effective electrons (N_{eff}) for each formula unit and plasmon energy $\hbar\omega_p$ (eV), and the results are shown in Table 1.

Table 1 Calculated static dielectric constant $\varepsilon_1(0)$, static refractive index n(0), magnitude of the coefficient of reflectivity at zero frequency R(0), number of effective electrons (N_{eff}) for each formula unit β-TCP and plasmon energy $\hbar\omega_p$.

Parameter	LDA	GGA	mBJ-GGA
$\varepsilon_1(0)$	3.3567	3.2368	2.4622
$\varepsilon_2(0)$	0.0000	0.0000	0.0000
n(0)	1.8321	1.7991	1.5691
R(0)	0.0863	0.0815	0.0490
N_{eff}	47.1050	46.645	42.872
$\hbar\omega_p$	8.1250	8.7354	6.9142

Table 2: Maximum attained values of refractive index n_{max}, reflectivity R_{max}, optical conductivity σ_{max}, absorptivity α_{max} with corresponding energies for the β-TCP compound.

Parameter	XC	Value at 0GPa Energy (eV)
n_{max}	LDA	2.41922
		6.13617
	GGA	2.37803
		6.27223
	mBJ-GGA	2.0558
		8.55798
R_{max}	LDA	0.568812
		28.20461
	GGA	0.593202
		28.53115
	mBJ-GGA	0.708052
		29.91893
σ_{max}	LDA	9995.63
		26.16376
	GGA	10812.3
		26.54472
	mBJ-GGA	15691.5
		28.1774
α_{max}	LDA	9995.63
		26.16376
	GGA	10758.9
		26.5175
	mBJ-GGA	15691.5
		28.1774

The maximum values of the refractive index n_{max}, reflectivity R_{max}, optical conductivity σ_{max}, absorptivity α_{max} for β-TCP compound with the corresponding energies are calculated, and the results are presented in Table 2. The obtained values of calculated refractive index, reflectivity, optical conductivity, and absorptivity using mBJ-GGA approximation are more accurate compared to the obtained ones from LDA and GGA approximations.

4.0 CONCLUSION

Density functional theory calculations are carried out using (FPL-APW) method along with three types of exchange-correlation potentials, LDA, GGA, and mBJ-GGA. The computed band gap values are 5.2 eV, 5.9 eV and 6.8 eV based on LDA, GGA, and mBJ-GGA techniques, respectively. The band gap results show that, β-TCP has direct band gap nature. The density of state calculation shows that the upper valence band energy is between -5eV and -6eV from mixture CaS and CaP states, but produced additional TDOS structure at -7.5eV in β-TCP compound. TDOS and PDOS calculation reveals a number of electronic density of states for mBJ-GGA technique compared to LDA and GGA. The optical parameter, static dielectric constant $\varepsilon_1(0)$ reaches the values of 3.23681 (eV) at 0 GPa for the β-TCP compound. The present results with mBJ-GGA approximation for the exchange correlation potential present very good agreements with the other theoretical and experimental findings. These investigations provide information about the electronic and optical properties of β-TCP compound, which can be used to fabricate useful and compatible β-TCP biomaterial for clinical applications.

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