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DENSITY FUNCTIONAL THEORY STUDY OF THE ELECTRONIC AND OPTICAL PROPERTIES OF PURE AND MAGNESIUM DOPED B-TRICALCIUM PHOSPHATE COMPOUND

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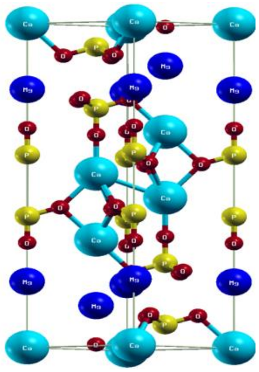
Graphical abstract



Abstract

β-Tri-calcium phosphate material (β-TCP), have attract a wide interest in the material science and medical science applications, due to its excellent biocompatibility and its identical chemical compositions to the natural teeth and bones. For that reason, (β-TCP) compound is widely used as biocompatible ceramics in medical and dental science applications. However, research shows that, pure β-TCP material has lower ability to stimulate the growth of natural bone and teeth as needed. Therefore, in order to address this deficiency magnesium impurity is used to replace calcium in the matrix of pure β-TCP to enhance its electronic and optical properties which are not present in the pure one. Thereby, its biological performance becomes improved. By changing the chemical composition of β-TCP to be similar to the mineral compositions of the natural teeth and bones. This will give more insight in fabrication of biomaterial devices for replacing, repairing and rebuilding the broken or damaged human teeth and bones. Here, we present the study of compound β-TCP using density functional theory (DFT). For the calculations, we used full potential linear augmented plane wave method (FPL-APW), along with generalized gradient approximations (GGA) potential. The band gap values of 5.2 eV and 3.4 eV are obtained for the pure and Mg-doped β-TCP, respectively. These results are in good agreement with the experimental values. Our results show peaks which correspond to the refractive index, complex dielectric function, optical conductivity, optical reflectivity, extinction coefficient, absorption efficient, and electron energy loss. These peaks are shifted towards the higher energy values for the pure and Mg-doped β-TCP material. The obtained results have more significance for increasing the quality of electronic and optical properties of this material and offer more evidences to synthesize enhanced β-TCP material for dental and medical applications.

Keywords: Density Functional Theory, β_Tri-Calcium Phosphate, Electronic Properties, Biomaterial, Optical Properties

Abstrak

Bahan β-Tri-Kalsium Fosfat, (β-TCP), telah mencapai kegunaan yang meluas dalam bidang sains bahan dan sains perubatan disebabkan oleh bio-keserasiannya yang baik dan kesamaan kandungan kimianya dengan gigi dan tulang semulajadi. Oleh sebab itu sebatian (β-TCP) digunakan sebagai seramik biokeserasian bagi kegunaan dalam sains perubatan dan pergigian. Walau bagaimanapun, para penyelidik mendapati bahawa bahan β-TCP tulin mempunyai kebolehan yang rendah untuk merangsang pertumbuhan tulang dan gigi semulajadi seperti yang dikehendaki. Jadi, β-TCP tulin telah didopkan dengan unsur Magnesium (Mg) untuk memantapkan sifat-sifat elektronik dan optic yang tidak terdapat dalam bahan bahan tersebut. Langkah ini telah memantapkan prestasi biologi bahan tersebut selepas pendopanan, yang telah menukar sebatian kimia β-TCP untuk menjadikannya serupa dengan sebatian galian bagi tulang dan gigi semulajadi. INi baik untuk membina peranti biobahan bagi menukar, membaiki dan membina semula gigi dan tulang manusia yang pecah atau rosak. Untuk mencapai matlamat ini, sifat-sifat elektronik dan optik bagi bahan β-TCP tulin dan yang didopankan telah dikaji dengan menggunakan Teori Kefungsian Ketumpatan (density functional theory, DFT). Bagi pengiraan tersebut kaedah gelombang satah keupayaan penuh teragumen linear (full potential linear augmented plane wave method (FPL-APW)) telah digunakan, beserta dengan kira-hampir cerun umum (generalized gradient approximations (GGA)). Nilai-nilai jurang jalur (5.2 eV dan 3.4 eV) telah diperolehi bagi β-TCP tulin dan β-TCP terdop Mg. Keputusan–keputusan ini bersesuaian dengan nilai-nilai eksperimen. Dalam geraf parameter optikal, puncak-puncak yang berkaitan dengan indeks pembiasan, fungsi dielektrik kompleks, kekonduksian optik, kepantulan optik, pekali kehilangan, pekali serapan dan kehilangan tenaga electron didapati teranjak kea rah nilai tenaga lebih tinggi bagi bahan β-TCP tulin dan β-TCP terdop Mg. Keputusan yang diperolehi mempunyai lebih kebaikan bagi penambahan kualiti sifat-sifat elektronik dan optic bahan ini dan mendedahkan lebih banyak bukti kepada bahan β-TCPtermantap sintisis bagi kegunaan perubatan dan pergigian.

Kata kunci: Teori Kefungsian Ketumpatan, β-TCP kalsium posfat, sifat elektronik dan sifat optik bio-bahan

1.0 INTRODUCTION

A great progress has been made in the material and medical science areas to enhance the properties of calcium phosphate biomaterial to use for rebuilding and replacing damaged parts of the living skeletal bones [1]. Therefore, much of the current research has been dedicated to improving the properties of β-TCP to synthesize and fabricate novel β-TCP biomaterial for medical and dental applications [2].

The early use of calcium phosphate material in medical scince area has been discovered by Albee in 1920 [3]Albee, defined this calcium phosphate compound as Tri-calcium phosphate, which was the first successful application of β-TCP compound for human bones recovery. In the early of 1970s, another study reported that, calcium phosphate materials can be used in dental applications[4].Calcium phosphate biomaterials have been regarded as a potential bone replacement due to their similar mineral composition of the living natural bones and teeth [5, 6]. Therefore, calcium phosphate biomaterials are usually used in bone replacement, bone augmentation, as well as in bone repairing and reformation [7]. The importance of doping β-TCP with Mg in this study, because Mg element is highly needed for connective tissues, healthy bone and in increasing the biological activity of β-TCP biomaterial when it is used inside the human body [8]. β-TCP compound is considered as essential constituent elements for living teeth and bones [9].

The idea of using β-TCP biomaterial for treatments or substitution of some part (s) of unhealthy or damaged bones is to assist bone repair when its lost are too big like in case of accidents when it cannot fix or repair themselves [10, 11]

The crystal structure of β-Tri-calcium phosphate is rhombohedral with a space group of (R3c, Z = 21). Figure 1 shows the crystal structure of the β-TCP material. In this study, we used theoretical investigations for pure and Mg-doped β-TCP material, to provide more understanding and a clear picture of the electronic and optical properties of this compound. This will provide insight into a clinical design for a compatible and novel β-TCP. A number of theoretical and experimental investigations' have been carried out focused on the electronic properties of calcium phosphate material, and the results are quite promising [12-17]. This motivates us to carry out the present work, to get more understanding and a clear picture of the electronic and optical properties of the pure and Mg-doped β-Tricalcium Phosphate compound.

In addition, we studied the electronic and optical properties of pure and Mg-doped β-TCP compound in the R3c crystal structure of the experimental lattice constants in static condition. Using density functional theory a long with Full-Potential Linearized Augmented Plane Wave (FP-LAPW) method [18, 19].

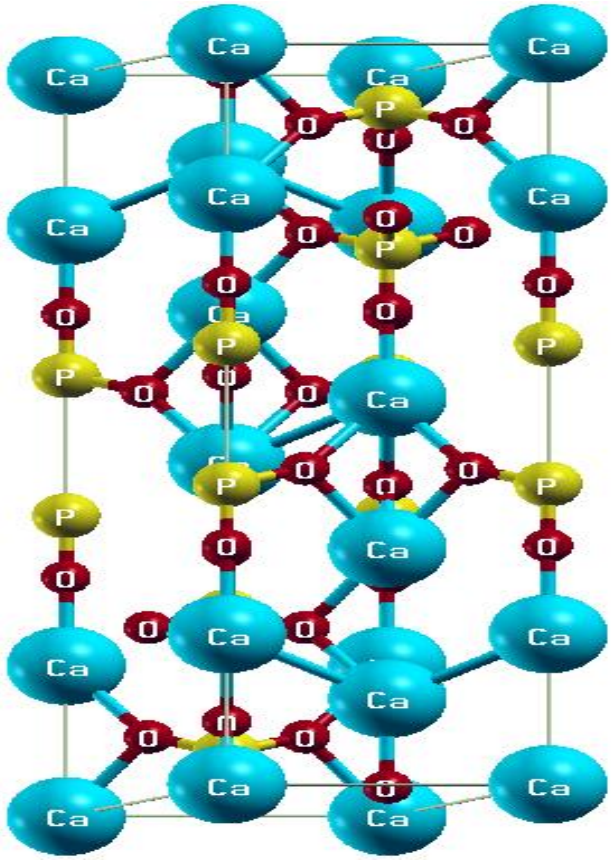


Figure 1 Crystal structure of pure Beta-Tri-calcium phosphate compound

2.0 METHODOLOGY

To study different chemical and physical properties of the solid materials at the atomic level using theoretical and computational studies are considered as an effective way and the best choice for predicting materials with desired properties when experimental methods became difficult [20].

In this regards, we calculated the electronic and optical properties of pure and Mg-doped β-TCP material. Using self-consistent scheme by solving the Kohn–Sham equations with generalized gradient approximations (GGA) [21]. Together with potential linearized augmented plane wave (FP-LAPW) method and implemented into the WIEN2k code [22].

In FP-LAPW method, the unit cell is divided into two regions, one is the interstitial region (*IR*) and the second is the non-overlapping muffin-tin (*MT*) spheres centered at the atomic sites.

In this work, we used plane wave cutoff (defined by the product of the magnitude of the largest reciprocal lattice vector $\mathrm{K_{max}}$ in the plane wave expansion times the smallest atomic radius of the sphere $\mathrm{R_{MT}}$), with value of $\mathrm{R_{MT}K_{max}} = 3$, to achieve self-consistence field (SCF) convergence for our calculations. The number of 1000 k-points was used as input parameter for the self-consistent charge density determination, in the irreducible symmetry wedge of the Brillion Zone (BZ) [23]. The value of $-6\ \mathrm{Ry}$ was chosen for the cut-off energy (which is the required energy to separate the valance and core states).

The values of the muffin-tin radii for Ca, P, and O are 2.3, 1.8, and 0.97 a.u. (atomic units), respectively for a pure compound. While for the doped one, the values of muffin-tin radii for Ca, P, O, and Mg are 2.2, 1.75, 1.62 and 0.96 a.u (atomic units), respectively.

The present calculations were performed with the above mentioned computational parameters for our considered compound in two steps:

Firstly, we performed our calculations by using the values of experimental lattice constant (taken from reference) [24], which were used as input parameters to obtain the initial structure of the pure β-TCP to calculate its electronic and optical properties.

Secondly, we construct a super cell of 1x1x2 for the initial structure of the pure β-TCP material which was obtained in the first step, with 0.16**%** of Mg element in the pure β-TCP structure.

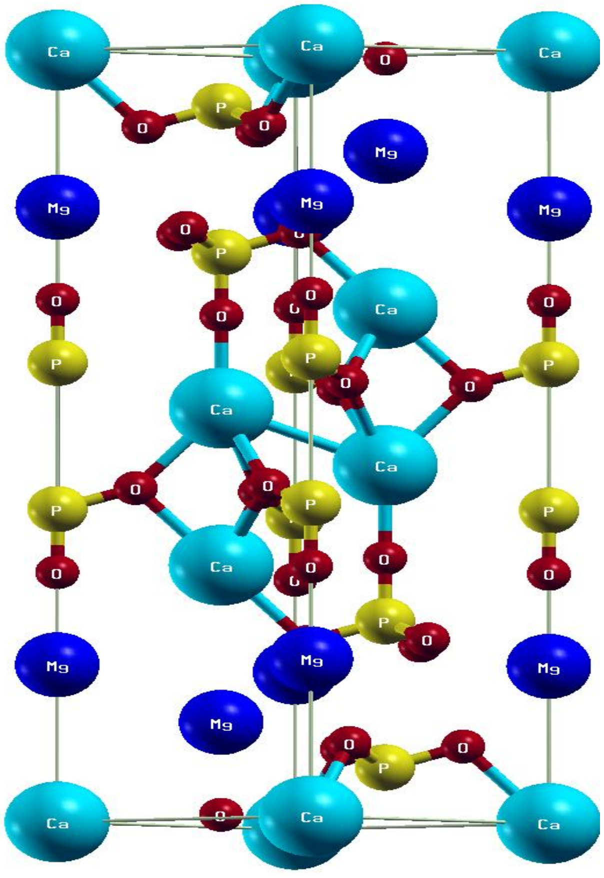


Figure 2 Crystal structures of Mg-doped Beta-Tri-calcium phosphate compound

3.0 RESULTS AND DISCUSSION

3.1 Electronic Properties

We have studied the electronic band structure for our considered material, to know its band gap values, which gives more insight about the optical behavior of the materials [25].

The results of calculated band gap values for pure and Mg-β-TCP are plotted in Figure 3 and Figure 4, respectively. It is clear from Figure 3, the Fermi level is fixed at 0 eV on energy scale. The conduction band minima (CBM) and valence band maxima (VBM) are separated by the energy gap in each case of the corresponding material. While in Figure 4 shows less value of the band gap for Mg-β-TCP compound.

As shown in Figure 3 and Figure 4, the obtained band gap values are 5.2 eV and 3.4 eV, for pure and Mg-β-TCP material, respectively. In these two Figures, we started from the lower energy part, in which the two deep electronic structures are located around -7.5 eV for pure β-TCP and -8.0 eV for Mg doped β-TCP below the Fermi level.

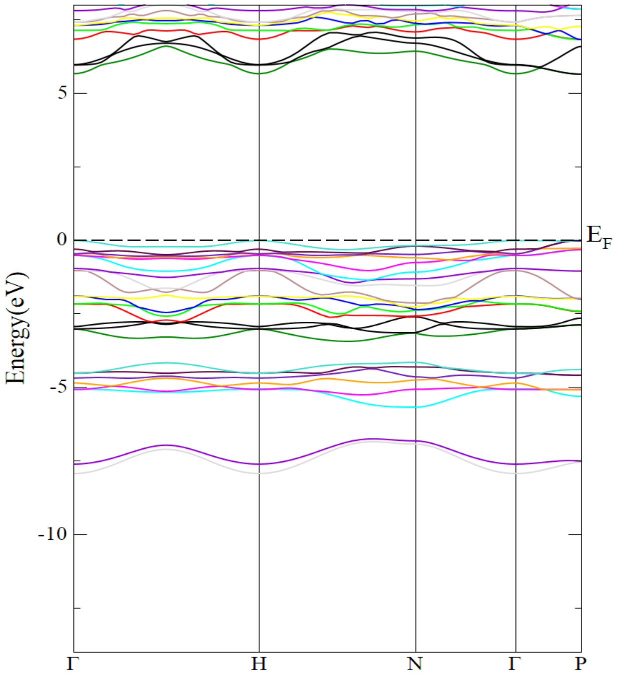


Figure 3 Band gap structure for pure β-TCP material

The second structure is located at -5.0 eV of SS states for pure β-TCP and -6.0 eV for Mg-doped β-TC.

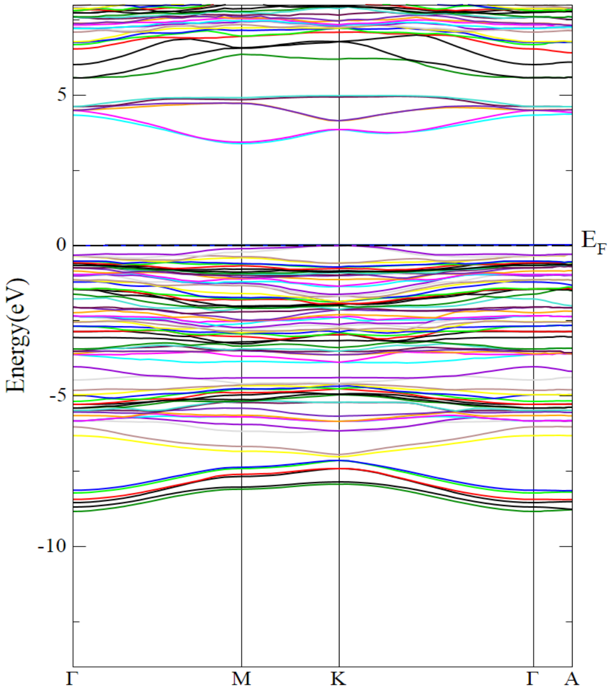


Figure 4 Band-gap structure for Mg-doped β-TCP material.

The band gap character for both materials gives more evidence to select appropriate material to design a suitable biomaterial for the clinical use.

3.2 Optical Properties

The importance of calculating the optical properties of our considered materials is to get more information and a clear understanding of the electronic band structure, collective excitations, and the internal structure of this material. In addition, optical parameters and band gap values provide more clarification about the analysis and fabricating materials.

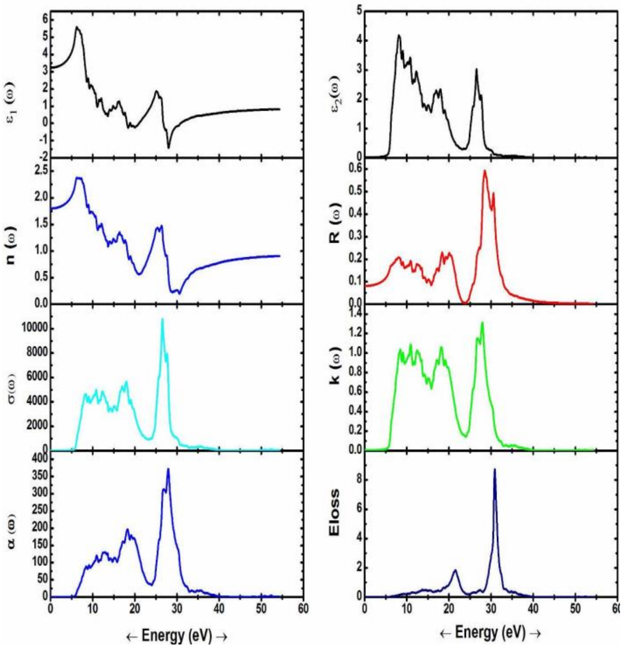


Figure 5 Calculated real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of the dielectric function, refractive index $n(\omega)$, extinction coefficient $k(\omega)$, reflectivity $R(\omega)$, absorption coefficient $\alpha(\omega)$, optical conductivity $\sigma(\omega)$ and energy loss function $L(\omega)$ of the pure β-TCP compound

Figure 5 and Figure 6 show the plotted curves of the static dielectric constant ε1(0), static refractive index n(0), the magnitude of the coefficient of reflectivity at zero frequency *R*(0), absorption coefficient $\alpha(\omega)$, optical conductivity $\sigma(\omega)$ and energy loss function $L(\omega)$ for pure and Mg doped β-TCP material, respectively.

As shown in Figure 5 and Figure 6, the static dielectric function $\varepsilon_1(\omega)$ has lower values at higher energy for both materials, which is corresponding to the higher values of the optical reflectivity R(0) for the pure and Mg doped β-TCP material.

The real part of the dielectric function $\varepsilon_1(\omega)$ spectrum, reaches the stability stage at higher energy values greater than 50 eV and 13 eV for pure and Mg doped β-TCP, respectively, which is demonstrating that, when the incident photons fall into these materials can pass safely without causing any major interaction inside the target material. While, the imaginary part of the dielectric functions $\varepsilon_2(\omega)$, reaches higher values at higher energy values for both compounds.

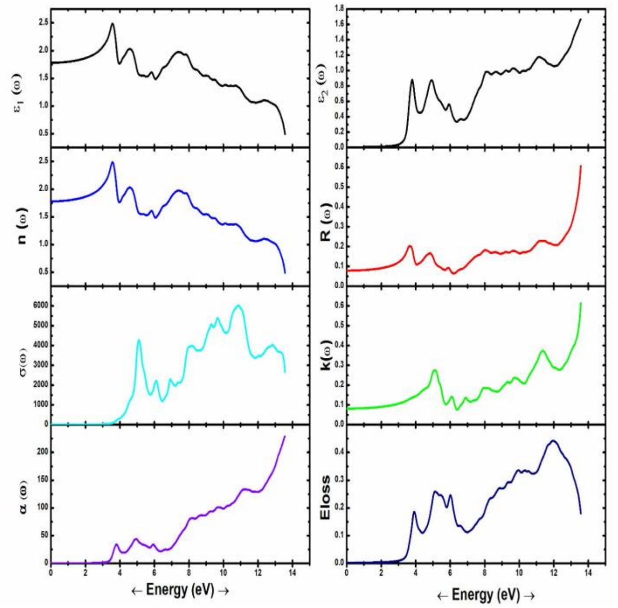


Figure 6 Calculated real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of the dielectric function, refractive index $n(\omega)$, extinction coefficient $k(\omega)$, reflectivity $R(\omega)$, absorption coefficient $\alpha(\omega)$, optical conductivity $\sigma(\omega)$ and energy loss function $L(\omega)$ of Mg doped β-TCP compound

The refractive index n(ω) curve shows acceptable values for both compounds and remains with values less than one after energy range of 19.50 (eV) and 12.04 (eV) for pure and Mg doped β-TCP, respectively.

For both materials, the extinction coefficient $k(\omega)$ curve is similar to the curve of the dielectric function $\varepsilon_2(\omega)$, which is verifying the established theory of the materials [26].

The values of optical conductivity spectra $\sigma(\omega)$, are increasing as energy increases for both materials.

Electron energy loss studies (EELS) provide more information of the energy range of the fast moving electrons, when it falls into the material and interacts with it. In this case, these electrons will lose their energy per unit length as shown in Figure 5 and Figure 6. The obtained values for EELS, the moving electrons have the maximum values at plasmon energy $\hbar\omega_p$ region. This refers to the different electronic configuration of both materials.

4.0 CONCLUSION

Density functional theory calculations were carried out using (FPL-APW) method along with GGA approximations for the exchange and correlation potential as implemented in WIEN2K code. To study the electronic and optical properties of pure and Mg doped β-TCP compound. The results show the calculating band gap values of 5.2 eV and 3.4 eV for pure and Mg doped β-TCP respectively. Optical parameter such as, real ε_1 and imaginary $\varepsilon_2(\omega)$ parts of the dielectric function, refractive index $n(\omega)$, extinction coefficient $k(\omega)$, reflectivity $R(\omega)$, absorption coefficient $\alpha(\omega)$, optical conductivity $\sigma(\omega)$ and energy loss function $L(\omega)$ which are depend on the band gap are also presented and discussed.

The refractive index has values less than 1.0 at higher energy values for both materials. The real dielectric function reaches the stability stage at higher energies above 50 eV. Which is indicating that, when the incident photons falls into the target material can pass safely without causing any major interaction inside the material.

Theoretical investigations for pure and Mg doped β-TCP have been done, to provide more understanding and improvement to design an excellent β-TCP biomaterial which can be used in bones and teeth replacements.

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