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A Theoretical Insight into the Electronic and Optical Behavior of $ZnCo_2O_4$

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ABSTRACT

Density functional theory (DFT) uniquely predicts diverse materials phenomena by seamlessly connecting electron interactions at the atomic scale to tangible structure and property evolution for revolutionary materials design. Through DFT, materials behavior can be predicted without expansive experimentation. This work imparts a fundamental evaluation on the electronic and optical behavior of optimized zinc cobaltite ($ZnCo_2O_4$), computed via Density Functional Theory (DFT), within the Cambridge Serial Total Energy Package (CASTEP) framework. By employing two generalized gradient approximation (GGA-PBE and GGA-PBESOL) and a local density approximation (LDA-CAPZ) at the optimized cut-off energy of 630 eV and 4×4×4 k-points, the electronic and optical properties analysis was successfully deduced. The direct band gap and conductive behavior of $ZnCo_2O_4$ have been evaluated by means of band structure and Density of States (DOS) calculation. The dielectric constant, refractive index, and absorption spectrum also reveals the viability of $ZnCo_2O_4$ in electronic device application.

1. Introduction

Zinc cobaltite with the structural formula of $ZnCo_2O_4$ has been applauded for its remarkable contribution in the energy storage domain, owing to their suitable spinel structure and the availability of several oxidation states [1]. Furthermore, excellent electronic and optical behavior of $ZnCo_2O_4$ is also the reason behind the demanding needs. One of the vital contributions of $ZnCo_2O_4$ is in the field of supercapacitor application, with the reported specific capacitance can reach up to 1841 Fg^{-1} at 1 Ag^{-1} current density [2]. As of 2024, there were more than 150 available publications in Scopus that are associated with $ZnCo_2O_4$ supercapacitor, showing the relevancy of $ZnCo_2O_4$ in the realm of supercapacitors. On the other hand, a limited number of publications that relate $ZnCo_2O_4$ with DFT,

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first principles study, and CASTEP that can be attained as a result of the Scopus search. Hence, more research on the first principles study of $ZnCo_2O_4$ is needed.

The progression of cobalt-based material for supercapacitor electrode studies have shown impressive feedback from the energy storage research communities [3]. It is mainly due to its excellent establishment in the electrochemistry discipline. Electrochemical properties such as excellent rate capability and good capacitance are the duo that is compulsory for a supercapacitor material. Binary metal oxide system which combined two types of metals have shown an improved reversible capacity and conductivity in comparison to single metal oxide constituent. The synergistic effects of each metal in a binary metal oxide system are believed to be the cause of the upgraded performance. For instance, $ZnCo_2O_4$ with a normal spinel structure is recognized as one of the materials that meets the performance benchmark of a supercapacitor electrode [2]. It is also proven that the electrical conductivity of $ZnCo_2O_4$ is better compared to its single metal constituents: ZnO and Co_3O_4 [4]. Experimentally, $ZnCo_2O_4$ can be prepared via various synthesis routes such as solvothermal/hydrothermal [5,6], ionothermal, [7] and sol-gel combustion method [8]. Solvothermal/hydrothermal method, also known to be a wet chemical synthesis process is the most common synthesis route used for binary metal oxides production. In a typical wet chemical synthesis process, it is customary to mix a proper precursor with solvent in a closed system until the reaction temperature of the mixed material exceeds the boiling point of the system. At the elevated temperature and pressure with induced catalysts, reaction then occurred in the system thus producing 2D metal oxide structure [9].

In a typical material design process, potential materials were discovered through trial-and-error basis. Therefore, a platform to prove the hypothesis, and expedite the material selection process are of great demand. For this purpose, this work will highlight the first principles calculation with the ability to produce more precise prediction and rapid calculations without physical experiment. Through DFT, an important insight into the $ZnCo_2O_4$ at the elemental extent can be explored, and further compared with its experimental results. Various computational methods such as CASTEP [10], VASP [11], Quantum Espresso [12], and WIEN2k [1] are already known for their effectiveness and convenience. For instance, a number of theoretical studies have been done to investigate the structural [13], electronic [14], optical [15,16], and magnetic [17] properties of metal oxides material. The integration of theoretical and experimental approaches has been shown to be crucial for optimizing the performance of materials and devices [18]. Simulation tools facilitate the efficient tuning of material properties, thus reducing the complexity of the optimization process. More importantly, excessive expenditure on chemicals can be averted.

This work aims to provide a fundamental insight on the electronic and optical properties of $ZnCo_2O_4$ originated from Co_3O_4 parent metal oxide via first principles calculation. Once the initial stable structure is obtained, the material functional can be predicted. Herein, we also highlight the importance of the theoretical approach in predicting the synergy of various materials when they are combined, thus providing guidance for future work without having to conduct a series of laboratory experiments first-hand.

2. Methodology

The atomic characteristic of a material can be explored by optimizing the first principles calculation without having to conduct experimental observations. This fast calculation allows a precise prediction of material's behavior by implementing the CASTEP code [19], in accordance with DFT. The $ZnCo_2O_4$ crystal structure was built by replacing Zn atoms onto the tetrahedral sites of Co_3O_4 matrices. Specifically, in a typical spinel Co_3O_4 spinel composition, the tetrahedral sites are inhabited

by Co^{2+} ions whilst octahedral sites contain Co^{3+} ions. To build $ZnCo_2O_4$ crystal structure, Zn^{2+} ions will substitute the lattice sites that are originally occupied by Co^{2+} ions [20]. The Co_3O_4 structure was optimized beforehand, prior to Zn substitution. Co_3O_4 has a space group of Fd3m (227) with cobalt positioned at Wyckoff coordinates of 8a and 16d, while Oxygen occupies Wyckoff equipoint 32e [21]. The geometrical optimization of both Co_3O_4 and $ZnCo_2O_4$ was performed using three different exchange-correlation functionals: the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE), the PBE for solids (PBESOL), and the local density approximation (LDA) as introduced by Ceperley and Alder and parameterized by Perdew and Zunger (CAPZ). Convergence test was carried out to obtain the optimized cut off energy value and the k-points of the material's Brillouin zone. Subsequently, all calculations were performed at 630 eV cut-off energy and 4×4×4 k-points of $ZnCo_2O_4$. On that account, the impetus of this work is to attain an appropriate description of $ZnCo_2O_4$ now it can be used for further research in various field.

3. Results

3.1 Geometry Optimization

To grasp the fundamental properties of $ZnCo_2O_4$ matrices, it must undergo geometrical optimization first to ensure valid DFT calculations. Figure 1 features the optimized $ZnCo_2O_4$ with Co_3O_4 as the parent metal oxide. On the other hand, Table 1 depicts the calculated lattice constant of $ZnCo_2O_4$ obtained in this work and the comparable lattice constant values adapted from previous studies. The consistency of the parameter obtained in this work is portrayed in Figure 2, in which the calculated lattice constants does not deviate much from the reported experimental values. GGA-PBE overestimates the reported value whilst LDA-CAPZ underestimates it. GGA-PBESOL established the closest agreement to [22-24] with less than 0.5 % deviation.

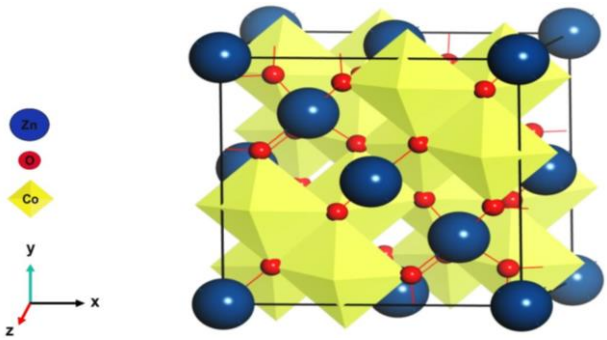


Fig. 1. Crystal structure of $ZnCo_2O_4$

Table 1
Details on lattice parameter of $ZnCo_2O_4$

Software	XC	Lattice constant, a = *b* = *c*, (Å)	References
CASTEP	GGA-PBE	8.156	This work
CASTEP	GGA-PBESOL	8.067	This work
CASTEP	LDA-CAPZ	7.956	This work
Experimental	-	8.095	[22]
Experimental	-	8.091	[23]
Experimental	-	8.10	[24]

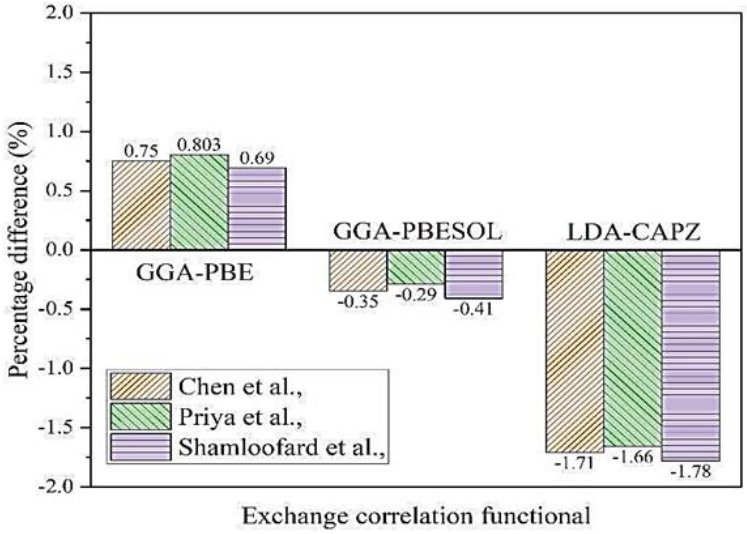


Fig. 2. $ZnCo_2O_4$ lattice parameter percentage difference using local functionals with respect to the previously reported work [22-24]

3.2 Electronic Properties

After optimization, the energy band gap at three different XC functionals, and DOS of $ZnCo_2O_4$ were acquired to apprehend its electronic properties. The band structure in Figure 3 shows an apparent direct band gap (E_g) of $ZnCo_2O_4$ at G point in which the valence band maximum (VBM) and conduction band minimum (CBM) crossed at an equivalent k-point of Brillouin zone. A non-flat and wavy energy band near fermi energy (E_f) level stipulates a good electron mobility behavior along with appropriate electron conductivity [25]. Also depicted in the band structure, the E_g value of $ZnCo_2O_4$ is in the range of 0.77 eV to 0.81 eV, varying upon different functionals. In a DFT work conducted by Silambarasan *et al.*, a comparable E_g value of 0.91 eV was obtained, indicating the validity of this work [26].

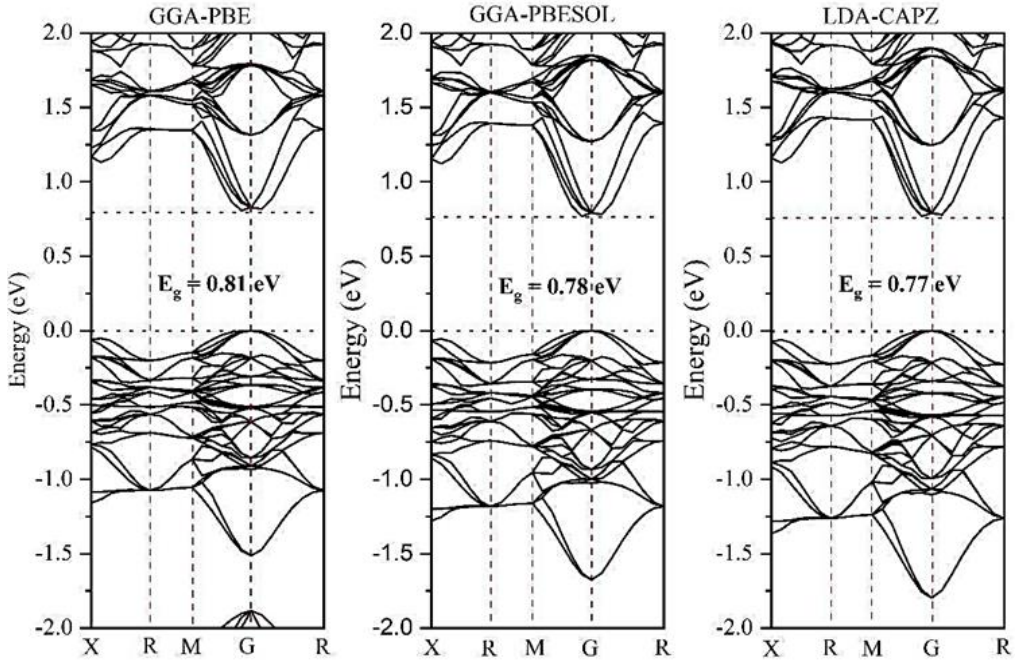
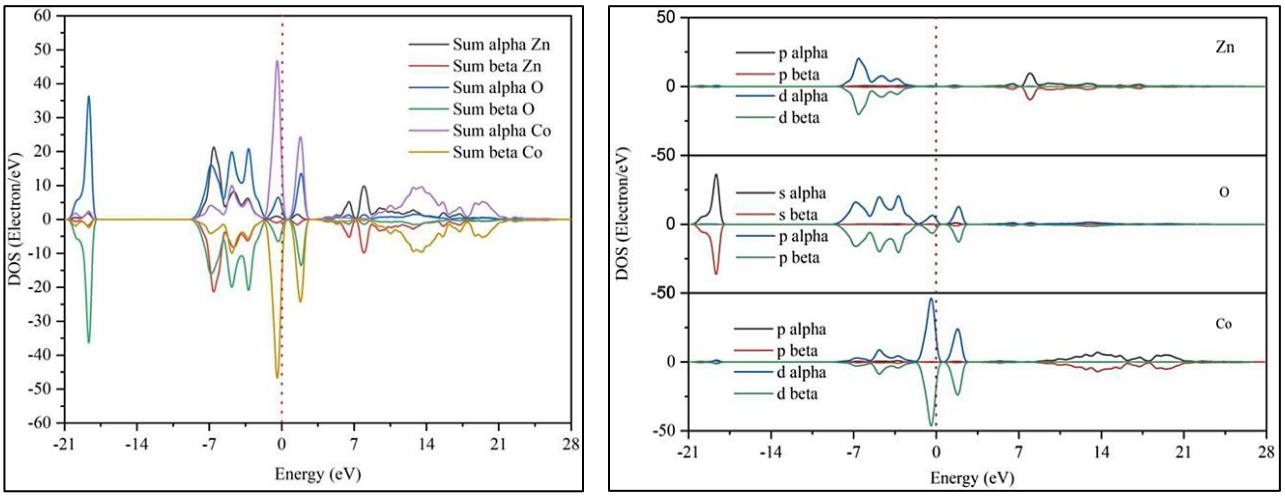


Fig. 3. Band structure of $ZnCo_2O_4$ at three different exchange correlation functionals

The DOS feature at the band edge provides a perception into the electronic properties of a specified material [27]. In general DOS can be termed as the available electronic states over a unit volume for a specified energy range [28]. Figure 4 portrays the calculated DOS of $ZnCo_2O_4$ structure by GGA-PBESOL XC functional where Figure 4(a) indicates the total density of states (TDOS) whereas Figure 4(b) shows the partial density of states (PDOS) of Zn, O, and Co. In a typical PDOS graph, alpha (α) and beta (β) for orbitals typically indicate spin states, where α indicates the spin-up states whilst β for spin-down. The symmetrical and identical α and β states indicates no net magnetic moment. Near the fermi level, the distribution of α and β states signifies the material's electrical properties. Based on quantum theory, the electrons that are located close to the E_f can contribute to conductivity [25]. It appears that the DOS of $ZnCo_2O_4$ is predominantly contributed by the 3d states of Zn and Co, and the 2p orbital of O, which is well conceded with the principle of valence electrons [29]. It is also revealed from the PDOS that the electron accepting ability of Co^{3+} is more prominent compared to Zn^{2+}, as Co shows an intense peak near E_f.



(a) (b)

Fig. 4. (a) TDOS of $ZnCo_2O_4$ (b) PDOS of Zn, O, and Co

3.3 Optical Properties

The optical properties computed in this work include dielectric constant, refractive index, and absorption spectrum which have been calculated at the cut-off energy of 630 eV. Figure 5 portrays the real (solid line) and imaginary (dashed line) dielectric functions for $ZnCo_2O_4$ plotted at the range of 0 to 45 eV photon energy. Theoretically, the dielectric function is mathematically expressed in Eq. (1).

$$\varepsilon\,(\omega) = \varepsilon'\,(\omega) + i\varepsilon''\,(\omega) \tag{1}$$

Herein, $\varepsilon'\,(\omega)$ represent the real part of dielectric constant which signify polarization whereas $i\varepsilon''\,(\omega)$ is correlated to absorption [19]. Besides, the real part also quantifies the energy stored whilst the imaginary part is parallel to the energy loss over the ion's movement in a continuously changing field. Based on the graph, the projected dielectric constant $\varepsilon'(\omega)$ without the presence of electromagnetic (EM) transmission $\varepsilon'\,(0)$ for $ZnCo_2O_4$ are 10.19, 10.22, and 11.23 for GGA-PBE, GGA-PBESOL, and LDA-CAPZ XC functionals, respectively. These values are matched closely to those reported by Wu *et al*., [30]. In the imaginary section, the apparent peaks represent the absorption transition from the valence band to the conduction band [31]. The peaks at the imaginary part are

located at several points inclusive of 1.97 eV, 5.01 eV, 12.3 eV, 15.9 eV,17.1 eV, 20.3 eV, 22.9 eV, and 25.5 eV. The real part of dielectric function and the real part of the index of refraction is inter-correlated by how the propagation of EM waves impedes as it enters a material, also denoted as a function of the material's ability to store and re-emits EM energy. Correspondingly, the imaginary part of both index of refraction and dielectric function is related by the slowing of EM propagation once it enters a different density medium, which is associated with the ability of the material to absorb energy.

Figure 6 represents the refractive index graph of $ZnCo_2O_4$ deduced at three different XC functional. Both refractive index, *n* (solid line) and extinction coefficient, *k* (dashed line) of $ZnCo_2O_4$ are well-plotted in the said graph. The value of *n* is affiliated to reflectivity whilst *k* value interprets the absorption factor of a specific material when interacted with electromagnetic rays [32]. Higher *n* values signify greater density and gradual speed of light when propagating through a material [30]. $ZnCo_2O_4$ was found to have a great *n* value of ~3.5 at perpendicular photon energy of ~1.1 eV. The interposing of *n* and *k* at five points which corresponds to ~5.6 eV, ~7.8 eV, ~20 eV, ~25 eV, and ~28 eV is correlated to the interception of the real part with the *x*-axis at zero reference line of dielectric constant, shown in Figure 5.

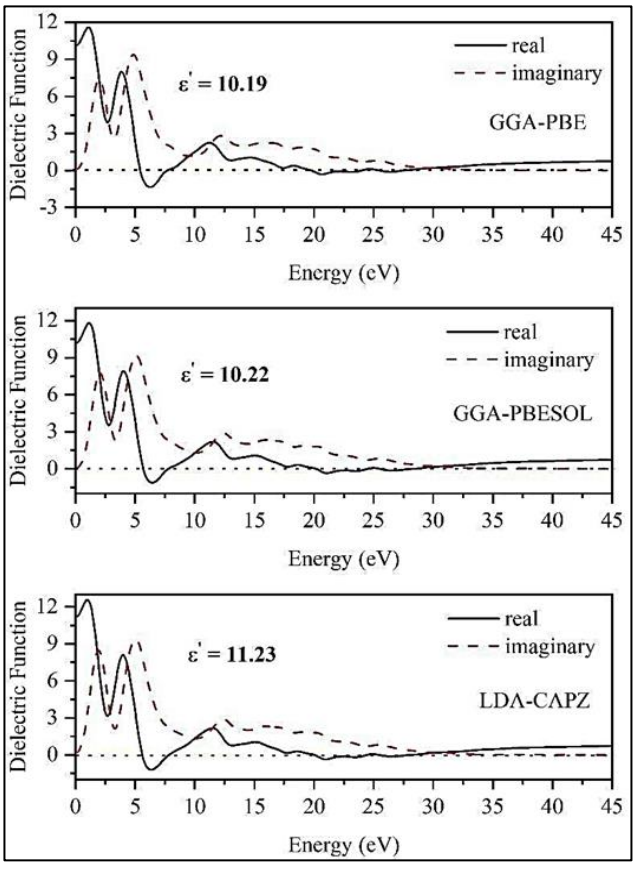


Fig. 5. Calculated dielectric function of $ZnCo_2O_4$ at three different exchange correlation functionals

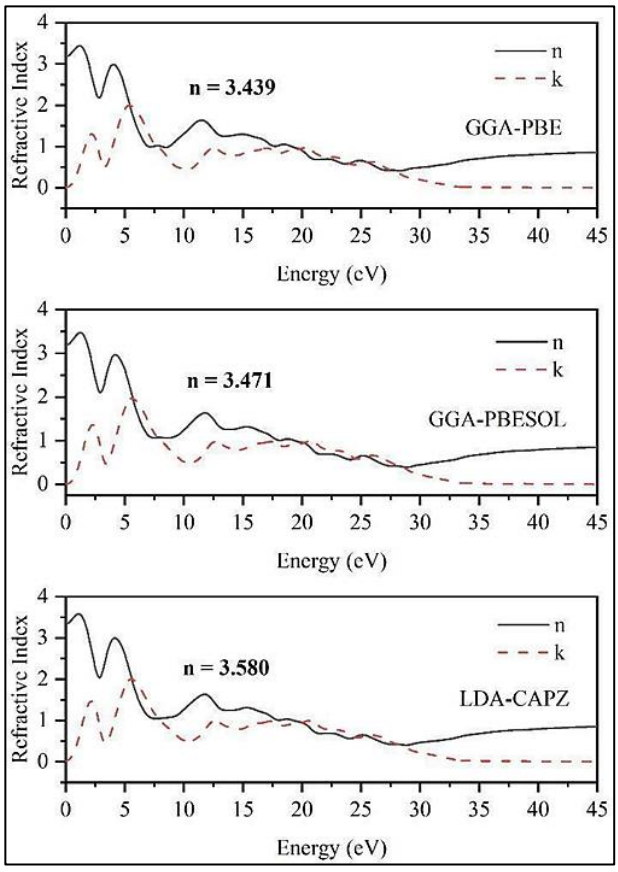
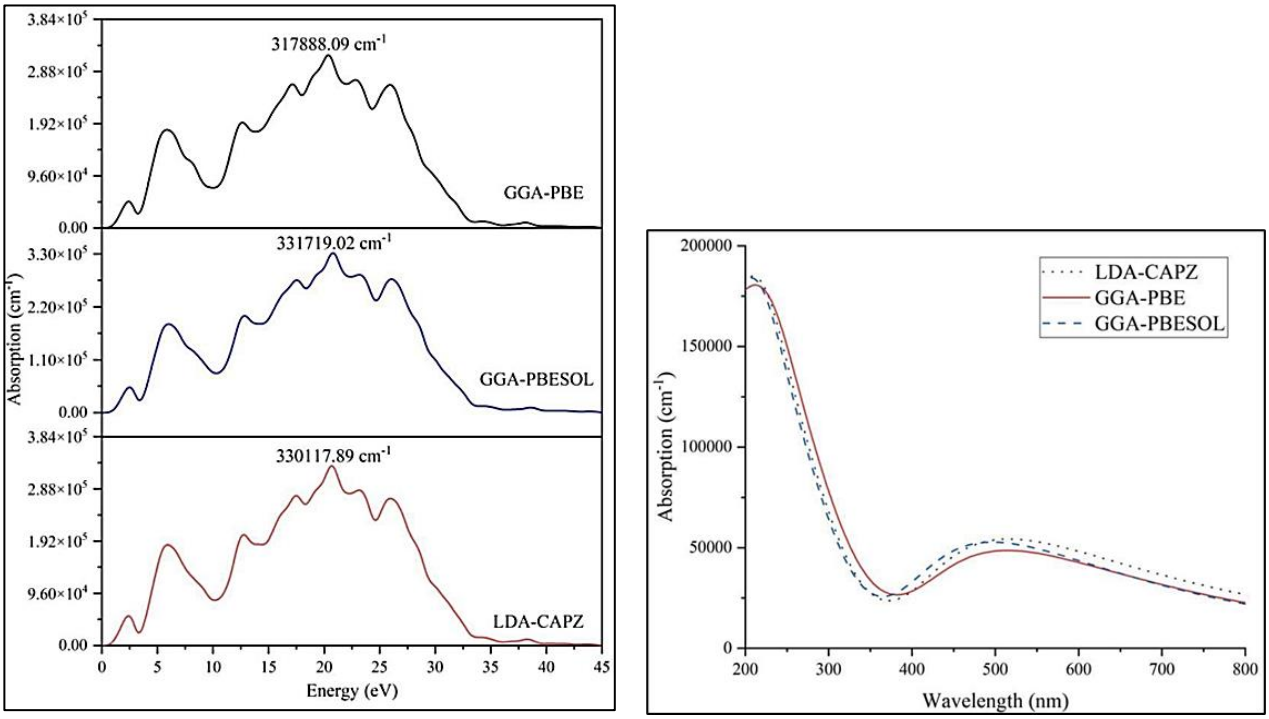


Fig. 6. Calculated refractive index of $ZnCo_2O_4$ at three different exchange correlation functionals

Contrast to dielectric function, absorption spectra as shown in Figure 7 quantifies the energy spectrum that allows the greatest photoexcitation process. The absorption curves of $ZnCo_2O_4$ calculated at three different XC functionals extend from 0 eV up to 45 eV with the most intense peak appearing at approximately 20 eV. The highest absorption at approximately 200 nm falls under the ultraviolet region which signifies the "barrier type", and lower absorption in the visible light region

(390 nm-780 nm) [33]. The extensive range of $ZnCo_2O_4$ absorption spectra is expected as the material has a narrow band gap. The profile shown in Figure 7(b) agrees with the UV-Visible (UV-Vis) results obtained in [34,35]. In both studies, the synthesized $ZnCo_2O_4$ disclosed an excellent light absorption ability at the range of 200 nm-800 nm, also revealing its potential in photocatalysis application.



(a) (b)

Fig. 7. Calculated absorption spectrum of $ZnCo_2O_4$ at three different exchange correlation functionals (a) Absorption versus energy (b) Absorption versus wavelength

4. Conclusions

By implementing CASTEP framework, the electronic and optical behavior of $ZnCo_2O_4$ have been computed in this work by three different XC functionals; GGA-PBE, GGA-PBESOL, and LDA-CAPZ. Through series of convergence test, the optimized cut-off energy and k-points were obtained at 630 eV and 4×4×4, respectively. All calculations for both electronic and optical properties elucidation was run at the same cut-off energy and k-points value. Out of the three XC functionals being used, GGA-PBESOL shows the lowest percentage difference in terms of lattice constant with respect to the previously reported data. The calculated E_g values are in the range of 0.77 eV to 0.81 eV, analogous to the value reported by Shamloofard *et al*., [24]. Moreover, it shows the lowest total energy in DFT, indicating the stability of the build crystal structure. CASTEP calculation also deduced that $ZnCo_2O_4$ has a direct band structure which lies at the G-point of VBM and CBM. As a result of DOS measurement, it was discovered that the electron accepting ability of Co^{3+} is more prominent compared to Zn^{2+}. It is also worth noting that replacing the Zn atom onto the octahedral sites of Co might give a different outcome. Contrast to the narrow E_g, the dielectric constants obtained at three different XC functionals are all of great value, specifying the suitability of $ZnCo_2O_4$ in electronic device applications such as supercapacitors. Moreover, $ZnCo_2O_4$ was found to have a great *n* value of ~3.5, which classifies the material as a dense material. The extensive range of absorption profiles calculated in this work not only reveal the potentiality of $ZnCo_2O_4$ in supercapacitor devices, but also

in photocatalysis application. In the future, the outcome of this study can be extended in order to predict and tune a more advanced behavior of $ZnCo_2O_4$.

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