Effect of Creating Oxygen Deficiency on the Optical Characteristics of CdO: A DFT based theoretical study

Sumbal Tahir[1], Malik Sajjad Mehmood[1],*

[1]Department of Basic Sciences, University of Engineering and Technology, 47050, Taxila, Pakistan

Corresponding Author's email: sajjadmehmood76@gmail.com

Abstract

This study presents detailed computational research using density functional theory (DFT) with the PBE-GGA functional and Material Studio software to investigate the optical characteristics of pure CdO and oxygen-deficient CdO at the supercellular level. The study optimizes the structures of both CdO configurations with convergence tests which are confirmed result with structural deviations of 4.1% for simple CdO and 4.2% for oxygen-deficient CdO, respectively. The optical characteristics are afterwards examined, including the conductivity, loss function, dielectric function, and refractive index. The dielectric function for both structures exhibits distinct features, with significant absorption peaks in the region of 2.9-10 eV for oxygen-deficient CdO and a band gap at 2.58 eV for simple CdO, according to the research. The refractive index remains constant at lower energies while the conductivity curves show excitonic behavior on inducing oxygen deficiency at the super cellular level. In addition to this, the loss function exhibits peaks indicating various excitations and absorption activities. It is worth to mention here that understanding these properties contributes to the development of optical devices, and the computational approach offers a powerful tool for atomic-level investigations.

Keywords: CdO, oxygen-deficient CdO, density functional theory (DFT), structural properties, optical properties, dielectric function, refractive index, conductivity.

Introduction

Cadmium oxide, with the chemical formula CdO and a molecular mass of 128.4112 g/mol, is an inorganic substance that is commonly used as an elementary block other cadmium composites[1]. This can be taken in various forms such as tablets, pellets, bits, powder, sputtering targets, and nano powder, and can be produced commercially by oxidizing cadmium vapor. CdO is an amorphous crystalline solid that occurs naturally as a mineral[2]. It is an n-type semiconductor transparent metal oxide with a direct band gap of 0.25 at energy 3.16 eV at ambient temperature, and the crystal structure of the material is characterized by a cubic rock salt lattice, wherein the cation and anion centers are arranged in an octahedral manner, similar to sodium chloride[3]. The melting and boiling points for sublimation of CdO are 1,559 °C and 900–1,000 °C for the amorphous form, respectively. Its preferred crystal direction is [2x1x1], with a cubical structure[4]. Two most Working areas of

CdO are as transparent conductor and cadmium plating.

➢ Transparent Conductor

CdO, a transparent conductor material that Karl Baedeker discovered in 1907, has been widely employed in a variety of applications, including as photodiodes, phototransistors, photovoltaic cells, transparent electrodes, liquid crystal displays, infrared detectors, and more [8]. Some applications specifically use CdO thin films[5].

➢ Cadmium plating

The predominant method for commercial cadmium electroplating involves the use of cyanide baths, which facilitate the deposition of electrons. To generate these baths, CdO and sodium cyanide are mixed in water, resulting in the formation of cadmium sodium hydroxide and cadmium cyanide. The formula for this mixture includes 32 g/L of CdO and 75 g/L of sodium cyanide, though the amount of cadmium present in the environment may vary by up to 50%. To enhance the plating process, brighteners are often introduced into the bath, and the plating is carried out using high purity cadmium anodes at room temperature [6].

Applications of CdO

The following fields are where CdO has applications:

- Electrodes for storage batteries
- In Ceramic glazes
- Use in Electroplating baths
- Applicant as Pigments
- Special optical glass and plasma display panels
- As additives, catalysts, and dopants

CdO is an inorganic substance. Its crystal structure is a cubic lattice similar to sodium chloride, with octahedral cation and anion centers where Cd^{2+} is bonded to six equivalent O^{2-} atoms. In this figure, red ball represents Cd and golden ball represents O atoms respectively.
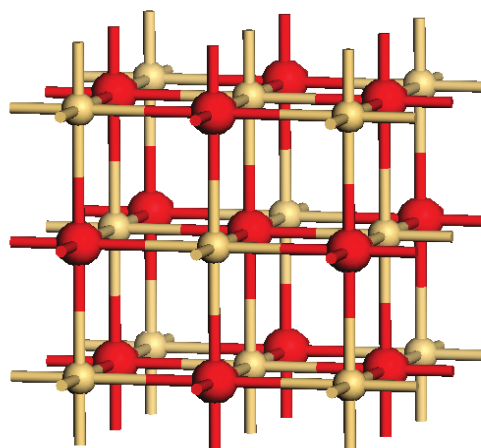

Figure 1: Cubical Structure of Cadmium Oxide

The valence-electron configurations of CdO are 4d105s2 and 2s22p4. Supercell, a term often used in meteorology to describe a type of thunderstorm, is also used in materials science to describe a larger unit cell that contains multiple primitive unit cells of a material[7]. In this context, a supercell structure is used to study the properties of a material at larger scales, including the effects of defects, impurities, and other structural features. For example, a supercell structure can be taken to study the effects of ''oxygen'' vacancies on the both properties of CdO like electronic and optical, as demonstrated in a research study. A deficiency of atoms in a material can occur when there is an incomplete or missing atomic structure, resulting in changes to the material's physical and chemical properties. This can happen in several ways, such as the absence of atoms in a lattice site, the presence of vacancies, or the substitution of one atom with

another. Here, with the CdO, eliminating oxygen atoms from the composition creates oxygen-deficient CdO, which can alter the material's electronic structure and physical properties. Oxygen vacancies in CdO, for instance, can generate free electrons that increase the material's electrical conductivity[8].
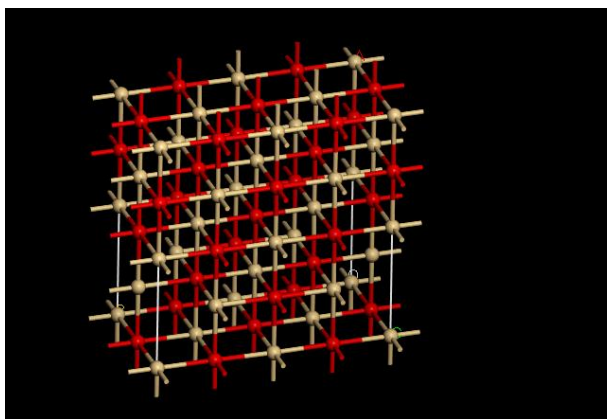

Figure 2: Oxygen Deficient Supercell of CdO of scale [2x2x1]

The oxygen vacancies can significantly alter the electronic and optical properties of CdO, which could have CdO's unique physical and chemical properties make it a strong contender among transparent conductive oxides for various applications such as energy, electroplating baths, optoelectronic devices, and pigments[9]. The band gaps, density of states, and other properties of transparent metal oxides can be adjusted by introducing charge deficits at the cellular level, which enhances their optical properties[10]. Over the past 20 years, a lot of theoretical and experimental research has been done to examine the characteristics of CdO. Here, in this study all computations were performed by utilizing the CASTEP code in the Materials Studio (MS) 6.1 software based on the Density Functional Theory (DFT) approach. DFT is employed to compute the optical characteristics of materials. For

general energy, the ultra-soft pseudopotential technique is utilized. Ion potential is substituted with ultra-soft pseudopotential when using plane wave basis groups, which unfold the electronic wave function. Ions and electrons are included in the technology for ultra-soft pseudopotentials. To accurately find the exchange correlation potential used two different approximations: the generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE) function and the local density approximation (LDA) [11, 12]. To the best of our knowledge, however, no study has yet been done on how charge deficiencies affect the electrical properties of CdO [13].

This paper presents a comprehensive investigation into the effect of creating oxygen deficiency on the optical characteristics of CdO using a DFT[7]. The simulation was carried out with CASTEP software package. While analyzing the results among oxygen vacancies and the optical properties, this study contributes to the fundamental understanding of CdO as a semiconductor material and opens new avenues for its application in various technological domains[14].

Computational Detail

a) Geometrical Optimization of Pure CdO & Oxygen Deficient Supercell of CdO:

PBE-GGA functional based on DFT and "Material Studio" were used to examine the structural and electronic characteristics of original CdO within the context of **the CASTEP simulation pack.** The **CdO cell of (27 atoms)** includes 14-Cd atoms and 13 O-atoms. The convergence test rely on k-points was conducted, and the good one meeting point was found at **k-points (3x3x3)** and with **600 eV Cutoff energy**. A **maximum force of 0.05 eV/Å** and a **stress of 0.1 Gpa** are used for convergence. Here,

a **maximum displacement of 0.002 Å** is taken into account. The CdO deviation computed using the following formula in accordance with observed calculations is:

Div % = [Final volume-Initial Volume/Initial Volume]x100

So, from calculated data for final and initial volume as,

Initial Volume=105.286808 A^3
Final Volume=109.700173 A^3
The value of Deviation we got is:

Div % = 4.1

The Calculations Calculated for ***Oxygen Deficient CdO at Super cellular level*** using PBE-GGA functional based on DFT using "**Material Studio**" in the framework of *CASTEP* simulation package. Supercell of CdO was made of **scale [2x2x1]**.Now, there were *74 atoms out of 75 atoms of CdO supercell with 1 Oxygen Deficiency.* Here, Cell optimizes at **600 eV cutoff Energy** and **k points (3x3x3)** for Supercell of CdO with deficiency of 1 Oxygen atom. Same as simple CdO structure, **Maximum Force** used for convergence is **0.05eV/Å** & the value of **stress** is **0.1 Gpa**.

Max-displacement having value of **0.002 Å** is considered. The value of ***Deviation*** calculated according to observed calculations by using formula as:

Div % = [Final volume-Initial Volume/Initial Volume]x100

So, from calculated data for final and initial volume as,

Initial Volume=421.14723 A^3
Final Volume=438.957976 A^3
The value of Deviation we got is:

Div % = 4.2

The value of ***Deviation*** calculated for CdO according to observed calculations is *4.2*.

Results and Discussion

In this Paper Optical Properties of simple & Oxygen Deficient CdO cell at Supercellular level are discussed.

b) Optical Properties of Simple & Oxygen Deficient CdO at Super-cellular Level:

Optical properties refer to the way a material interacts with light. These properties can be used to describe how light is transmitted, absorbed, reflected, or scattered by a material. Optical properties are influenced by the electronic structure of a material, as well as its composition, structure, and physical properties such as refractive index. In order to study the optical characteristics of materials, it is essential to compute the imaginary component of the dielectric function $\varepsilon''(\omega)$[15]. Typically, the optical characteristics are expressed in terms of the dielectric function (ω), refractive index (ω), extinction coefficient (ω), and absorption coefficient (ω). These properties shows play a crucial part to find out both the electronic and optical properties of the crystal. Understanding the optical properties of a material can provide insight into its composition, structure, and potential applications.

In this section, Results of optical properties for simple CdO cell & Oxygen Deficient CdO cell at Super-cellular Level are discussed.

➢ The Dielectric Function

Dielectric Function is denoted by **$\varepsilon(\omega)$**, is a mathematical function that describes that how a material give response to an outsider electric field at a given frequency ω. It can be explain as the ratio of the electric flux density in the material to the electric field strength of the applied field:

$$\varepsilon(\omega) = D(\omega)/E(\omega)$$

Where D(ω) is the electric flux density and E(ω) is the electric field strength at the given frequency ω.

The dielectric function is a complex function that can be shown in actual and unreal parts as:

$$\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$$

where **$\varepsilon'(\omega)$ is the real part**, also known as the relative permittivity, and **$\varepsilon''(\omega)$ is the imaginary part**, also known as the absorption coefficient or loss factor.

The imaginary part of the dielectric function **$\varepsilon''(\omega)$** is given by:

$$\epsilon_2(\omega) \propto \frac{1}{\omega^2} \sum_{nm} \int_{BZ} dk\, |P_{nm}(k)|^2\, \delta\,(\varepsilon_m(k$$

Understanding the imaginary portion of the dielectric function requires considering (DOS) and momentum matrix elements. For calculating the direct inter-band grant to $\varepsilon''(\omega)$, we have must look over all potential electron moved from occupied to unoccupied states. In contrast, the Kramers-Kronig relation can be used for getting the actual part of $\varepsilon'(\omega)$. In materials science, the electron energy-loss function is a functional appliance for examine optical properties of materials. It provides information on the energy that an electron loses during an inelastic collision with the material.

$$L\,(\omega) = \frac{\varepsilon_2(\omega)}{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}$$

The electron energy-loss function, which shows the energy loss of rapid electrons crossing the material, is one more useful tool for examining different aspects of materials. Plasma oscillations are what causes the sharp peaks of this function. The distribution of oscillator strengths for both intra-band and inter-band transitions can be estimated using the sum rule. The number of valence electrons that are effective in bonding is one quantitative quantity that can be determined using this rule.

Actual component of the dielectric function $\varepsilon'(\omega)$ in a **Simple CdO Structure** describes how the material disperses incoming photons, whereas the imaginary component $\varepsilon''(\omega)$ is crucial for identifying the various transitions that occur during photon absorption from filled to unfilled states. In Fig 3(a) the constant valued dielectric function $\varepsilon'(0)$ at 0 Energy for pure CdO was calculated to be 13. The peak of the real DF observed at 2.58 eV having the band gap

value, which signifies the transition from taken valence band to unoccupied states in conduction band. The higher energy peaks that are observed are caused by transitions from occupied states to unoccupied states, which occur between the valence and conduction bands.

In an **Oxygen Deficient CdO Structure**, the real component $\varepsilon'(\omega)$ also describes how the material disperses incoming photons, while the imaginary component $\varepsilon''(\omega)$ is crucial for identifying the various transitions that occur during photon absorption from occupied to unoccupied states. In Fig 3 (b), the static dielectric function $\varepsilon'(0)$ at 21 Energy for this structure was calculated to be 0. A peak of high magnitude is detected in the low-energy region of the actual portion of the dielectric function near 1.5 eV for Oxygen Deficient CdO. The other peaks observed at higher energies result from the movement of electrons from valance band of O to conduction band of Cd. The figure in part b also shows a significant increase in the unreal area $\varepsilon''(\omega)$ of the dielectric function under oxygen deficiency. In the $\varepsilon''(\omega)$ curve, there is an intense absorption peak in the energy range of 2.9–10eV, with the first peaks appearing from 2.9 to 5eV. The lowest peaks appear at 22eV, and the other one at 34eV are can be access by the transition between orbitals.
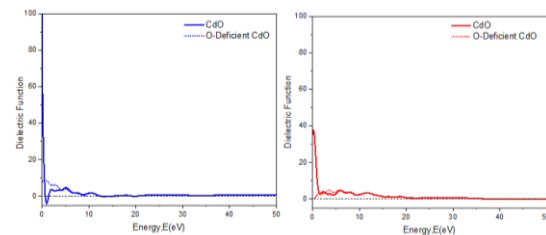

Figure 3 (a,b): Real & Imaginary Parts of Dielectric Function For Simple CdO cell & Oxygen Deficient Supercell of CdO

➢ Refractive Index

The measurement of **refractive index** is a crucial physical parameter that has a

valuable part in the microscopic atomic interactions, as well as in the development and examination of hetero structure lasers and various semiconductor devices that rely on wave guiding. In terms of conductivity, permeability, and the dielectric constant, the index of refraction *n* and the extinction coefficient *k* may be expressed.

$$\hat{n}^2 = \frac{\mu_1}{2}\left\{\left[\varepsilon_1^2 + \left(\frac{4\pi\sigma_1}{\omega}\right)^2\right]^{\frac{1}{2}} + \varepsilon_1\right\}$$

$$\hat{k}^2 = \frac{\mu_1}{2}\left\{\left[\varepsilon_1^2 + \left(\frac{4\pi\sigma_1}{\omega}\right)^2\right]^{\frac{1}{2}} - \varepsilon_1\right\}$$

Figure 4(a), shows the refractive index for a *simple CdO cell*, which remains same at small energy values and reaches higher numbers before becoming less for greater values of E. The constant refractive index n (0) has a value of 8, while the extinction coefficient k (ω) has a static value of 1.9. In the transparent region, k (ω) increases with energy and reaches a maximum at 3.4 eV.

For an *Oxygen Deficient Supercell of CdO,* Figure 4(b), shows that refractive index remains same at smaller values of energies and reaches at peak before lowering for greater values of energies. The fixed refractive index n (0) has a value of 2.75, while the extinction coefficient k (ω) has a static value of 0. In the transparent region, k (ω) rise with energy and get maxima at 2 eV. Like in simple CdO cell, the refractive index very much relates to bonding, but any process that increases electron density in a material also increases the refractive index.
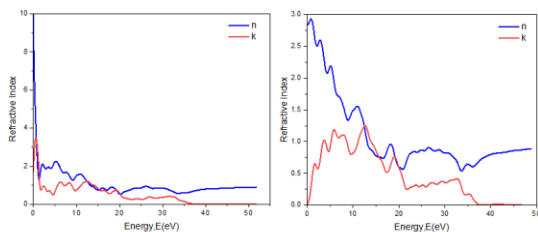
➢ Conductivity

Another optical property that we have is **Conductivity**. In physics it refers to the measure the conducting property of a material. It is the opposite of electrical resistivity that is a measure the property of a material of stopping the passage of electric current through it. Figure 5(a) displays the *cadmium oxide's* conductivity regarding the energy. Graph indicates the presence of excitons, which are bound states of an electron and pair of electron hole that move within crystal's periodic structure, resulting in energy transport but not charge transport.

When a crystal occupy a photon, an electron can be elevated from the valence band to the conduction band, leading to exciton formation. In insulators, these bound electron-hole pairs are referred to as excitonic insulators. In Fig 5(a), the optical conductivity curve exhibits excitonic behavior at 6 and 10.3 eV for the real part and 5 and 11 eV for the imaginary part, which corresponds to electron movement from O empty bands to Cd filled bands.

Similarly, for *Oxygen Deficient CdO structure* shown in Fig 5(b), the optical conductivity curve displays excitonic behavior at 6 and 13 eV for the real part and 6 and 12 eV for the imaginary part. These peaks also result from electron transitions from O valence bands to Cd conduction bands.
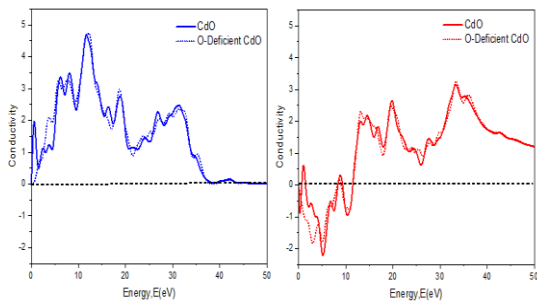

Figure 4 (a,b): The Graph Of Refractive Index For Simple CdO cell & Oxygen Deficient Supercell of CdO

Figure 5(a,b):Real & Imaginary Conductivity Graph For Simple CdO cell & Oxygen Deficient Supercell of CdO.

➢ Loss Function

Here now, the last one optical property is the **loss function** that is an optical property that can be define as the electromagnetic radiations absorbed by the substance. It is a measure of the unreal area of the refractive index for the material that shows the material's ability to dissipate energy through absorption. The loss function is used to describe how much of the incoming radiation is absorbed by the material at a given frequency or wavelength, and it show a vital role in making and optimizing optical and electronic equipment such as solar cells, photodetectors, and lasers.

Fig 6 shows that, the electron energy-loss is draw for both Simple CdO & Oxygen Deficient CdO of cubical structure. There are different values for peaks having different origin points, such as inter-band excitation & intra-band activity. In Fig 6(a); the first top is presented at 4eV begin from Oxygen to cadmium orbitals. For Simple CdO, The max peak located at 21 & 34eV.Two highest peaks of same magnitude are occur at 21 & 33eV.In this area, there occur maximum loss function.

Now here, figure 6(b); for Oxygen Deficient Supercell of CdO, the 1st peak occur at 2eV starting from Oxygen to cadmium orbitals. Here, the max peak located at 34eV.Another peaks of less magnitude occur at 23 & 18eV.After

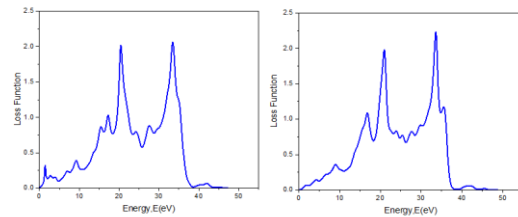Deficiency, we get greater value of Loss Function then the simple CdO cell.

Figure 6 (a,b):Loss Function Graph For Simple CdO cell & Oxygen Deficient Supercell of CdO.

In summary, this computational investigation comprehensively examined the optical properties of pure CdO and oxygen-deficient CdO at the supercellular level using density functional theory (DFT). After optimization of both structure, the analysis focused on the optical properties, revealing significant findings in the dielectric function, refractive index, conductivity, and loss function which are:

- The dielectric function analysis identified a peak at 2.58 eV in the simple CdO cell, corresponding to the band gap, while the oxygen-deficient CdO supercell displayed intense absorption peaks ranging from 2.9 to 10 eV.
- The refractive index remained constant at lower energy values before peaking and decreasing for both structures.
- The conductivity curves exhibited excitonic behavior with peaks resulting from electron transitions, and the loss function showed distinct peaks indicating inter-band excitations and intra-band activities.

The approach used in this study offers a powerful tool for exploring and predicting material properties at the atomic level thus providing an insight for the advancement of

optical and electronic devices, such as solar cells, photodetectors, and lasers.

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