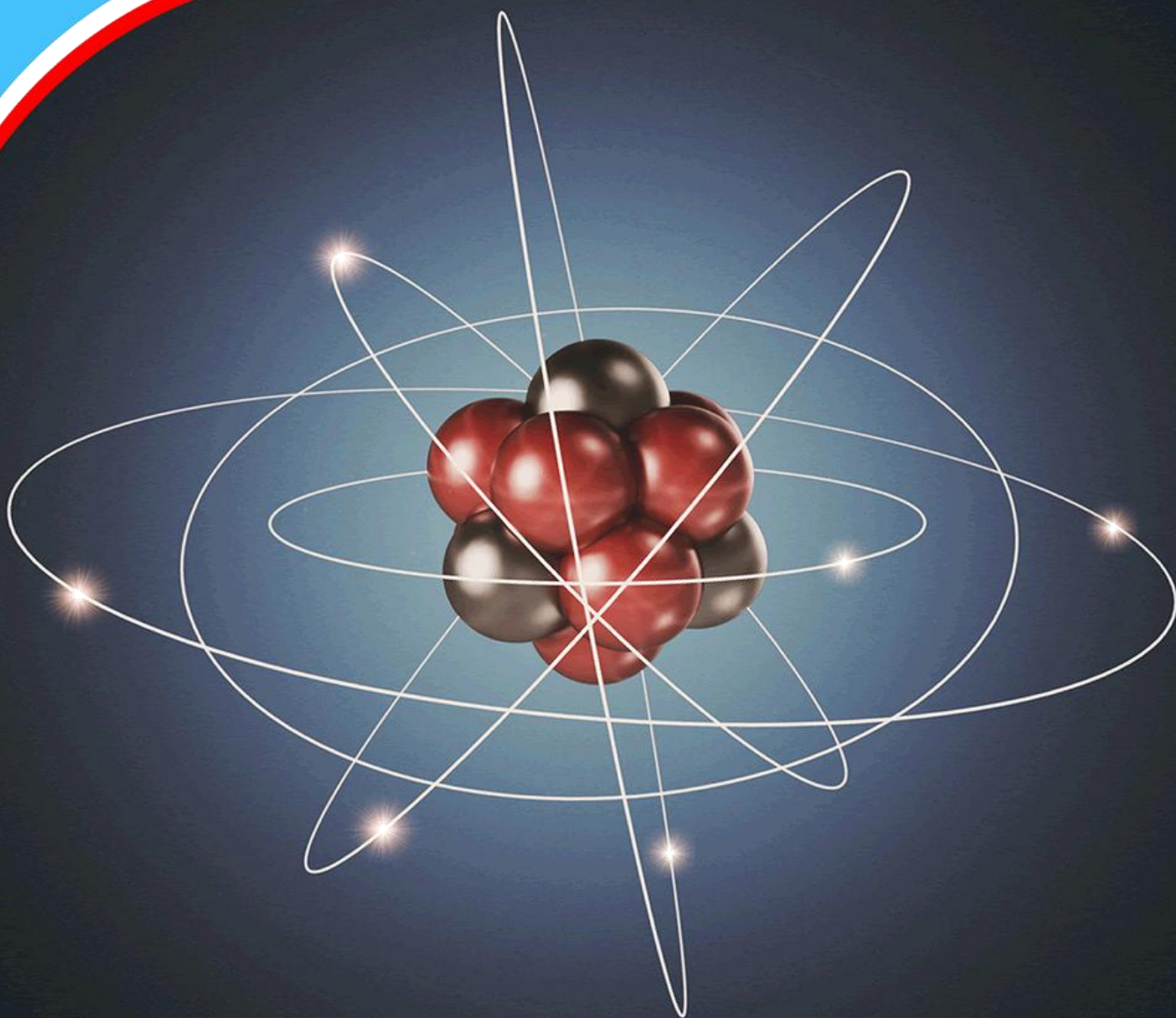


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Abstract

Purpose: This study used the density functional theory (DFT) to investigate the characteristics of Hf-doped ZnO in a hexagonal structural phase.

Methodology: First-principles calculations were employed in studying the structural, electronic, and optical properties of Hf-doped ZnO at the Zn site. The progression of the physical properties of the daughter nuclei in the Zn_{0.5}Hf_{0.5}O alloy was also comprehensively examined using the full-potential linearized augmented-plane-wave (FP-LAPW) method within DFT.

Findings: Variations in the lattice parameters of the ZnO and Zn_{0.5}Hf_{0.5}O alloy as well as the calculated 84.3 % difference in Bulk moduli values for these materials are indications of local structural distortions in the ZnO lattice and the production of secondary Hf phases. A 50 % doping of ZnO with Hf shifted the system's equilibrium volume to about 425 [a.u.]³ indicating that the Hf-doped system has lower resistance to volume

deformation. The Density of States (DOS) values and contributions from individual orbitals indicate that ZnO is a material of bandgap value 0.61 eV and behaves as a semiconductor, whereas the alloy [(Zn)_{0.5}Hf_{0.5}O] is a conductor with a high DOS(3.18 states/eV) and strong electronic activity likely to display high electrical conductivity due to electronic transitions.

Recommendation: The obtained values of the refractive index *n* and extinction coefficient *k* indicate that Hf doping significantly modifies the optical properties of ZnO, alters its dielectric response, refractive index, extinction coefficient, and optical absorption, and that incorporating Hf into the ZnO lattice can impact on its electronic structure and electronic transitions for possible optoelectronics applications.

Keywords: *Density-Functional Theory (DFT), First Principal Calculations, Alloys, Electronic structure, DOS Band Structure*

INTRODUCTION

The most common crystal structure of ZnO is the hexagonal Wurtzite structure. It is stable at ambient conditions and under normal conditions [1,2] with each zinc ion (Zn^{2+}) tetrahedrally coordinated by four oxygen ions (O^{2-}), and each oxygen ion is tetrahedrally coordinated by four zinc ions [3,4]. Zinc oxide (ZnO), famously known for its hexagonal wurtzite structure with the space group $P6_3mc$, exists in a triclinic structure [5] [6], specifically the space group $P1$ and as tetragonal zinc oxide $P4_2/mm$. The triclinic form of zinc oxide is less common than the hexagonal Wurtzite structure [7], and the tetragonal crystal is associated with a specific arrangement of atoms within the crystal [8] [9] [10] [11] [12].

Hafnium, a shiny-silvery metal, is a super alloy and can absorb neutrons, and while it is reported to be useful in semiconductor fabrication, it is resistant to corrosion even at high temperatures [13][14].

The process of co-doping ZnO films with Hafnium could produce materials suitable for optoelectronics applications, mitigate dielectric loss of ZnO, and modify its bandgap, thus enhancing its capacity to absorb visible light and facilitate the degradation of organic pollutants and contaminants [15].

This present study will dwell on establishing the relationship between the Hafnium concentration, the lattice parameter and unit cell volume of ZnO. It will also show the relationship between structural stability and equilibrium geometry. The electronic band structure, and atomic arrangements of materials formed will also be examined. Furthermore, the band gap energy of the resulting materials and how they change with Hafnium concentration, as well as the Density of states (DOS) and the contributions of the Hf states will be discussed. Finally, the implications of all these results for potential optoelectronic applications will be presented.

Research Questions

Possible research questions which this work will address include:

- How does Hf- doping impact on the structural properties of ZnO especially its lattice parameter or unit cells?
- How does increasing the Hf concentration change the electronic band structure, structural stability, or energy band gap of the ZnO?
- Can Hf doping of the zinc oxide create a material whose electronic properties make it a potential material for Optoelectronic applications?

Problem Statement

ZnO, is widely studied because of its wide bandgap, good optical transparency, and chemical stability, but its intrinsic properties can limit its performance in certain optoelectronic applications. Alloying ZnO with a material like hafnium offers a pathway to modify its structural, electronic, and optical properties. However, the extent to which a high concentration of Hf impacts the properties of ZnO is not fully understood. Consequently, there is a need to investigate the changes that occur when the Hf concentration is introduced at 50 % and 100% relative to the ZnO host composition and not as conventionally doped ZnO to see how the incorporation of these high concentrations of Hf may affect the lattice parameters, electronic band structure, density of states, dielectric response, and optical properties of ZnO. The relationship between this alloy series at high Hf concentrations (50% and 100%) and its properties, as well as the extent to which the resulting material retains or

deviates from the characteristic properties of ZnO needs to be further investigated using DFT simulations.

LITERATURE REVIEW

Hafnium-doped ZnO has been reported to show improved electrical characteristics with increased and low sub-threshold swing, and improved V_{ON} shift attributed to the high binding energy of Hafnium ions at 4% and 8 % hafnium, respectively [16]. Hafnium-doped ZnO inhibits the formation of oxygen vacancies owing to its large binding energy and hafnium is reported to improve the crystallinity of ZnO thin films and enhance the conductivity of zinc oxide thereby reducing trap densities [17]. Optically, hafnium-doped ZnO at 10 % hafnium exhibits better transparency and shows a blue or red shift in the UV-emission band, and could have its bandgap significantly widened [15].

Furthermore, combining Hafnium with ZnO forms Hafnium oxide, a material with a high dielectric constant that could be useful for fabricating capacitors and gate dielectrics required in Field Effect Transistors (FETs). This process could also yield a material with improved chemical properties and thermal stability suitable for fabricating high-temperature sensors, and for studying and monitoring environmental degradation. [18] [19] [20]. When Hafnium is used to dope ZnO, the Hf^{4+} ions will substitute for the Zn^{2+} ions and shift the Fermi energy level in the ZnO lattice towards the conduction band, resulting in n-type conductivity [21]. Furthermore, Hafnium's high dielectric constant can enhance the dielectric properties of ZnO and increase its suitability as a potential material for gas sensors or transistor applications. The substitution of hafnium also affects the ZnO surface roughness and its lattice constants [22], as hafnium is a highly transparent material exhibiting optical losses. While alloying ZnO with higher concentrations of Hafnium could produce other phases, such as HfO_2 , doping ZnO with a low concentration of Hafnium can improve its crystallinity [15]. Furthermore, substituting Hf^{4+} ions with Zn^{2+} ions provide excess positive charge, which results in higher carrier concentration with fewer oxygen vacancies and the process is suitable for producing a material with lower resistivity and enhanced electrical conductivity [15].

Research Gap

In spite of extensive studies of the doping of ZnO with various elements, the structural and electronics consequences of Hafnium incorporation and more importantly the relationship between Hafnium concentration, structural modification and bandgap variation remain insufficiently established hence the need for a systematic DFT investigation to know how Hf doping modifies equilibrium, structure, Stability, electronic band structure and bandgap energy of Zinc oxide. This present study is interested in correlating the structural changes induced by Hf substitution with the resulting electronic properties of the material.

Computational Framework

Density Functional Theory (DFT) simulations are used to study alloyed materials and provide a cost-effective, fast method that enables multiple co-dopant combinations to be derived before the laboratory synthesis of the real thin film [23]. DFT simulations provide more insight into band structure and density of states, and highlight defect sites in a created material, thereby guiding the experimental synthesis of real materials. The DFT approach deals with electron density, which in turn depends on three spatial variables x , y , and z , and models' systems to predict the electronic structure of atoms, molecules, and solids. A review of DFT methods compared to those that use complex wave functions shows it to be simpler because it is based on electron density [24].

This current study examined the structural, electrical, and optical properties of the simulated materials using the DFT approach, and the findings were subsequently utilized to elucidate the observed behaviors and attributes of the developed materials.

Method of Study

In this work, the physical properties of Wurtzite and alloy materials were studied using a full-potential linearized augmented-plane-wave approach within Density Functional Theory [25][26], as implemented in the Quantum Espresso code [27]. The lattice parameters are calculated using first-principles computations, and the exchange energy is evaluated within the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [28].

A $14 \times 14 \times 14$ Monkhorst-Pack k-point mesh was implemented for the Brillouin zone sampling to have an accurate description of the structural properties of the solids [29]. A 500 Ry cutoff charge density and a 50Ry cut off wave function was selected to define the number of plane waves in the expansion within the irreducible Brillouin zone for self-consistent convergence. The cut-off kinetic energy (ecutwfc) and the cut-off charge density (ecutrho) were obtained through separate convergence tests. Based on the convergence results, the ecutrho of 500 Ry was set while a cut-off energy was set to 50Ry. The ecutrho selected from the converted values is ten (10) times the cut-off kinetic energy. These converged results were used as part of the inputs in the plane-wave calculations. The convergence criterion was set to a total energy of 0.00001 Ry and optical parameters were calculated using the thermos-pw code [30], while employing standard exchange-correlation of the energy functionals [31].

The structural properties of ZnO and $\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$ were evaluated using structural convergence of the cut-off charge density, k points, and optimization tests, respectively and the total equilibrium energy was calculated using Equation (1).

To determine the minimal volume and energy of the material (ZnO and $\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$), a computation of the total equilibrium energy was utilized in equation (1). Additionally, the Birch-Murnaghan third-order equation of state was fitted to the computed data, using equation (2) [32][33].

$$E = \sum_i f_i \epsilon_i - E_H[n] + E_{XC}[n(\mathbf{r})] - \int n(\mathbf{r}) V_{XC}[n(\mathbf{r}')] d\mathbf{r} + E_{ion-ion} \quad (1)$$

$$E_v = E_0 + \frac{9V_0 B_0}{16} \left\{ \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right]^3 B'_0 + \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right]^2 \left[6 - 4 \left(\frac{V_0}{V} \right)^{2/3} \right] \right\} \quad (2)$$

where E_0 ; V_0 ; B_0 and B'_0 are the equilibrium energy, volume, bulk modulus, and derivative of modulus, respectively.

RESULTS AND DISCUSSIONS

Structural Properties

The studied crystal structures of ZnO and $\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$ alloy are as shown in Figures 1(a) and (b). The Hafnium doped ZnO seems to maintain the wurtzite structure of pristine ZnO with the Hf^{4+} ions replacing the Zn^{2+} ions at the Zn lattice sites.

It appears the presence of the Hf^{4+} ions produced local structural distortions attributable to the difference in ionic radius and valence between Hf^{4+} and Zn^{2+} and produced secondary phases of Hafnium, resulting in some variations in the lattice parameters. The calculated lattice constants for ZnO were found to be $a = 3.282 \text{ \AA}$; $c = 7.753 \text{ \AA}$, while that for $\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$ was $a = 3.443 \text{ \AA}$; $c = 7.584 \text{ \AA}$. Notably, the lattice constant a for the alloy

material($\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$) increased while its c value decreased. These results are consistent with the enhanced photocatalytic activity of Hf-doped ZnO and cubic Zn_2TiO_4 as corroborated by some available online sources [34] [35].

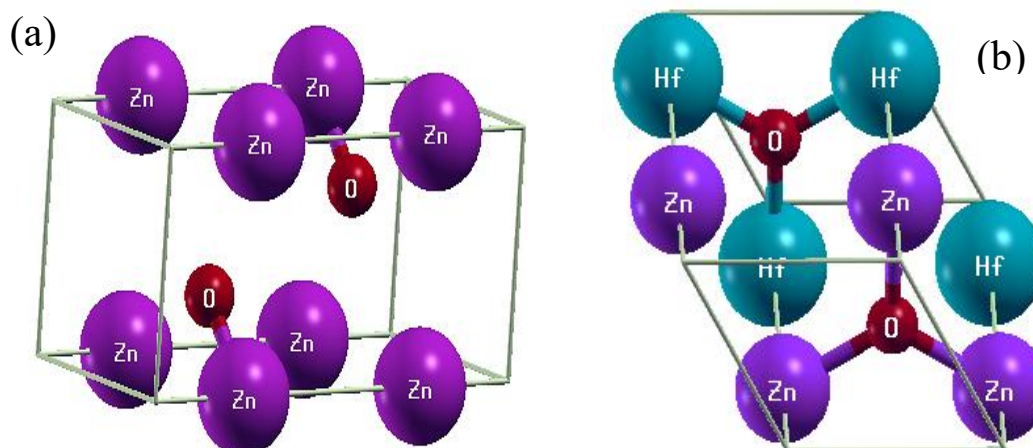


Figure 1: Studied Crystal Structures of (a) ZnO and (b) $\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$ alloy

Electronic Properties

The optimization plots are as presented in Figure 2 (a) to (d). The ground state volume of ZnO was found to be $66.31 \text{ \AA}^3$ with a corresponding total energy of -361.57 Ry . Upon Hafnium substitution, the daughter nuclei $\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$ system exhibited $\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$ a reduced equilibrium volume of $62.58 \text{ \AA}^3$, and an optimized equilibrium configuration with total energy of -657.80 Ry . The resulting 5.6 % reduction in equilibrium volume suggests that Hf incorporation into the ZnO lattice induces structural contraction, causes anisotropic lattice distortion with an attendant reduction in the equilibrium unit-cell volume.

The bulk moduli, and pressure derivative of bulk moduli for the ZnO and $\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$ were also evaluated and the obtained results are as presented in Table 1.

The decrease in bulk moduli for the ZnO and $\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$ was approximately 84.3 %. Thus, the ZnO with $B_0 = 92.9 \text{ GPa}$ is relatively stiff and resists compression while $\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$ with $B_0 = 14.6 \text{ GPa}$ is much more compressible indicating a softer hydrostatic compression. The doping of the ZnO with Hf results in a material with a lower bulk modulus indicating that the ZnO lattice is more compressible because of distortion defects and changes in bonding and crystal structure. The pressure derivative of the bulk modulus B_0' for ZnO is 3.99 while that of the $\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$ was 0.00 showing that the ZnO becomes much more difficult to compress under increasing pressure. The observed B_0' value for $\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$ of 0.00 raised a concern and was further investigated. Obtained data were fitted to the Birch–Murnaghan third–order equation of state (Equation (2)), resulting in the results shown in Figures 2 and 3.

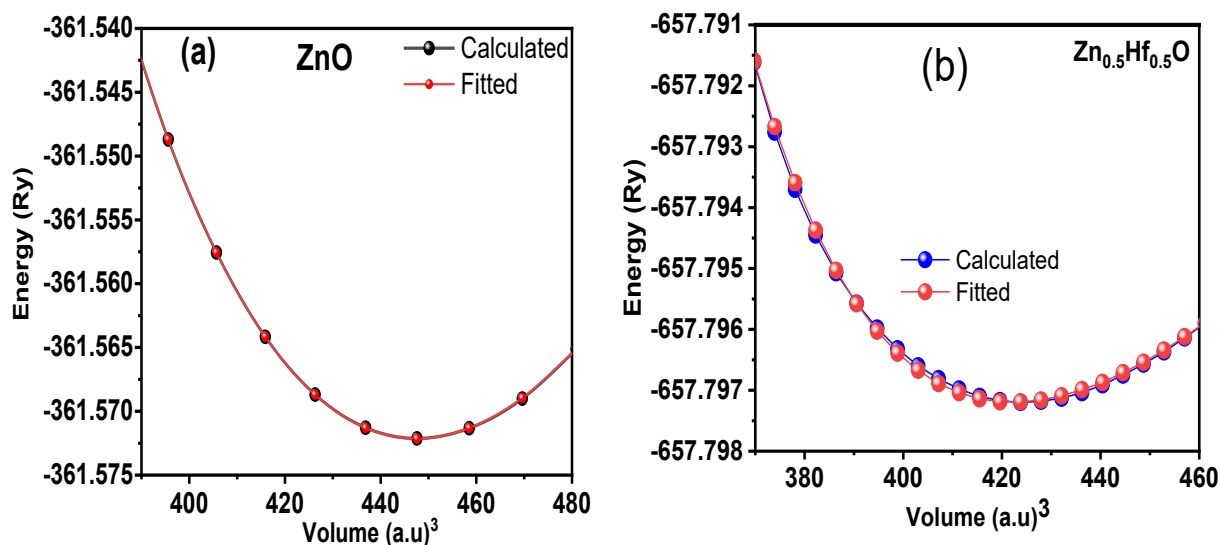


Figure 2: Fitted Equilibrium Energy-Volume Curves for (a) ZnO and (b) Zn_{0.5}Hf_{0.5}O alloy

The parabolic curve (a) is typical of ZnO and shows that as the volume increases from 390 a.u.³, and the energy decreases, getting to a minimum (the equilibrium volume) under zero pressure at approximately 445-450 a.u.³. Beyond this point, further expansion leads to an increase in energy. The steep curvature around the minimum indicates that ZnO strongly resists changes in its volume, and this observation is consistent with the calculated bulk modulus of about 92.9 GPa, thus confirming it to be a comparatively stiff material.

For the hafnium –doped material (Zn_{0.5}Hf_{0.5}O), (b) the energy decreases from 370 a.u.³, as the volume increases, and at a value between 420 -430 a.u.³, (approximately 425 a.u.³), an increase in energy occurs. This curve is broader and flatter, showing that this alloy material is more compressible and succumbs easily to volume deformation. Thus, a 50 % alloying of this ZnO with Hafnium changes the bonding and lattice arrangement of ZnO.

The calculated energy-volume curves for pristine ZnO and Zn_{0.5}Hf_{0.5}O show well-defined minima confirming the existence of stable equilibrium configurations. While the equilibrium volume of ZnO is approximately 445-450 a.u.³, the 50 % alloying of ZnO with hafnium shifts the equilibrium volume of Zn_{0.5}Hf_{0.5}O to approximately 425 a.u.³. The Hf-doped system curve indicates a lower resistance to volume deformation and agrees with the calculated bulk modulus, which decreases from 92.9 GPa for ZnO to 14.6 GPa for Zn_{0.5}Hf_{0.5}O and shows that Hf doping substantially raises the compressibility of the ZnO lattice.

Table 1: Calculated Lattice Parameters A(Å), C(Å), V(Å³), Ratio C/A, Bulk Modulus and Derivative B'_0 And Energy E_{min} (Ry) for ZnO and Zn_{0.5}Hf_{0.5}O Alloy

Phase	a (Å)	c (Å)	c/a	V (Å ³)	B_0 (GPa)	B'_0	E_{min} (Ry)	Reference
ZnO	3.282	7.753	2.362	66.31	92.9	3.99	-361.57	This work
Zn _{0.5} Hf _{0.5} O	3.443	7.584	2.023	62.58	14.6	0.00	-657.80	This work
Hf. ZnO	3.22	5.18	1.61	46.51	-	-	-	(Ahmad et al., 2013)
ZnTiO ₃	3.79	-	-	-	205.7308	5.00	-	(Ali et al., 2013)

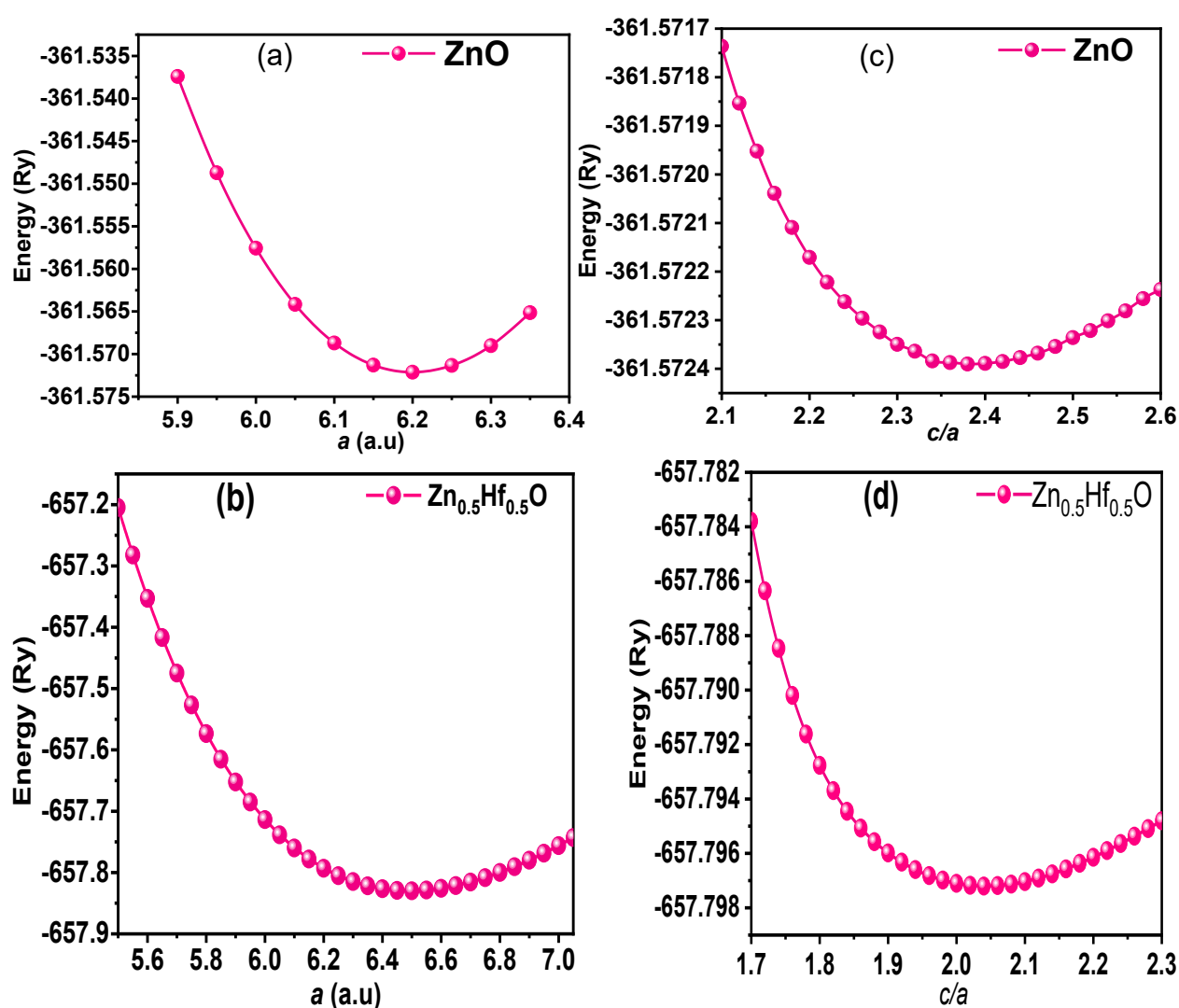


Figure 3: Calculated Lattice Parameters of (a) ZnO, (b) Zn_{0.5}Hf_{0.5}O, (c) ZnO, (d) Zn_{0.5}Hf_{0.5}O

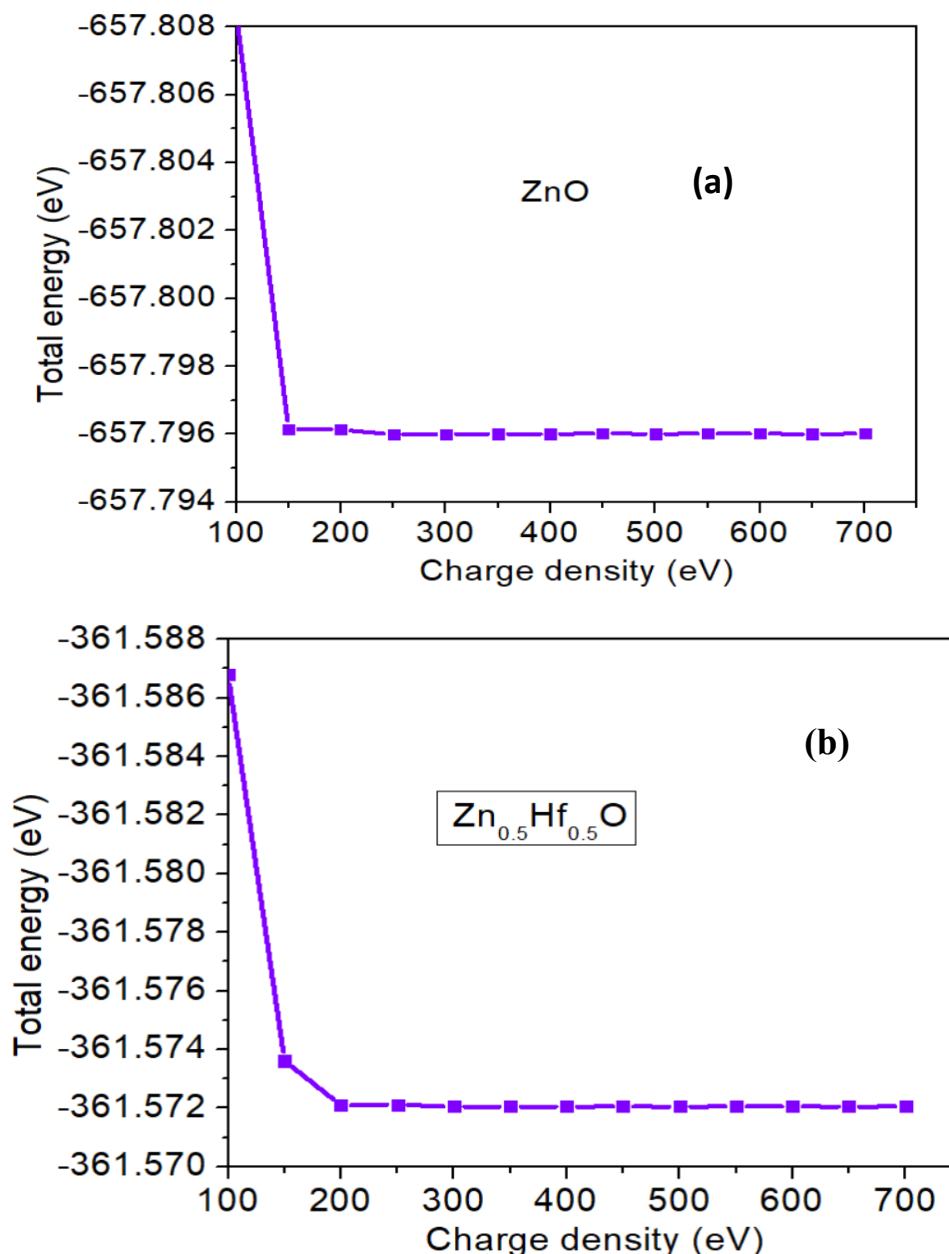


Figure 4: Convergence Curves for (a) ZnO and (b) Zn_{0.5}Hf_{0.5}O Alloy

For the ZnO, (Figure 4 a) there is a sharp change in total energy between 100 eV and 150 eV from -657.808 Ry to -657.796 Ry. Beyond 150 eV, the curve becomes horizontal, and between 150 eV and 200 eV the total energy is relatively stable and converged.

For the Hf-doped ZnO (Zn_{0.5}Hf_{0.5}O), (Figure 4 b), there is a considerable change in energy between 100 eV and 200 eV before the curve flattens, showing that a higher cutoff is needed before its energy becomes stable, and between 200 eV and 300 eV the calculation approaches convergence. Increases in the cutoff beyond this range only produce minimal changes in total energy.

Diagrams of the electronic band structures of ZnO and Zn_{0.5}Hf_{0.5}O alloy, respectively, along high- symmetry paths in the first Brillouin zone are as presented in Figures 5 (a) and Figure 6 (a), while the DOS and PDOS for ZnO and Zn_{0.5}Hf_{0.5}O are depicted in Figures 5(b) and Figure 6(b), respectively.

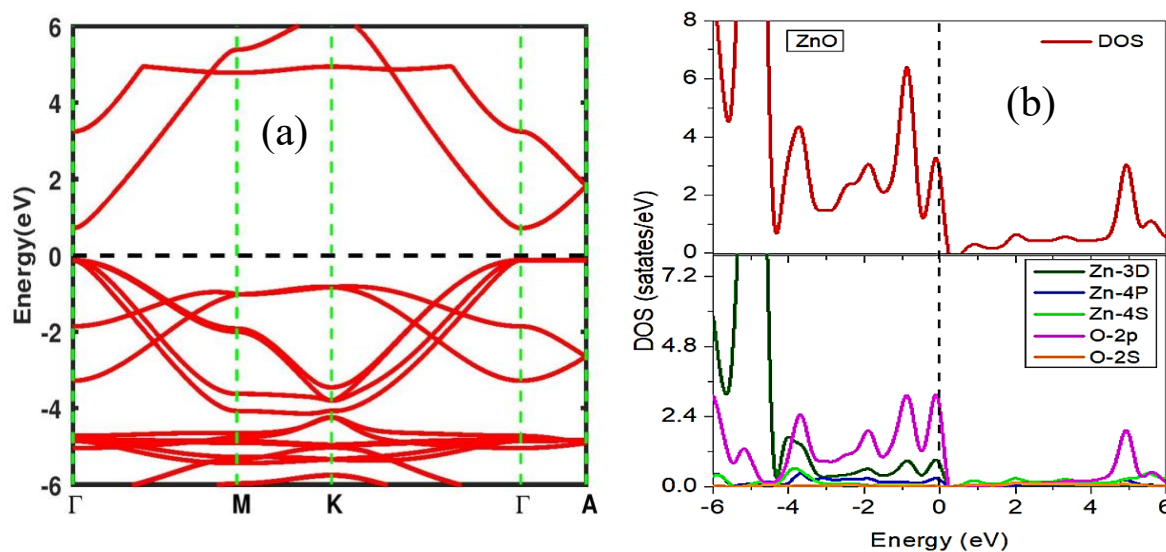


Figure 5: (a) Energy Bands of ZnO and (b) DOS of ZnO

The DOS and contributions from individual orbitals for ZnO and $\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$ alloy show that the ZnO is a material whose bandgap value is 0.61 eV which behaves like a semiconductor, while its alloy the daughter nuclei $\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$ is a conductor of high DOS (3.18 states/eV) and has no bandgap because its valence and conduction bands overlap [36]. That means that its conduction properties are mostly due to the Hf-5d (1.85 states/eV), Hf-5s (0.25 states/eV), O-2p (0.25 states/eV), Zn-4s (0.17 states/eV), and O-2s (0.11 states/eV) energy states, respectively.

This daughter nuclei $\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$ with its high density of states (DOS) has strong electronic activity and could display high electrical conduction due to electronic transitions.

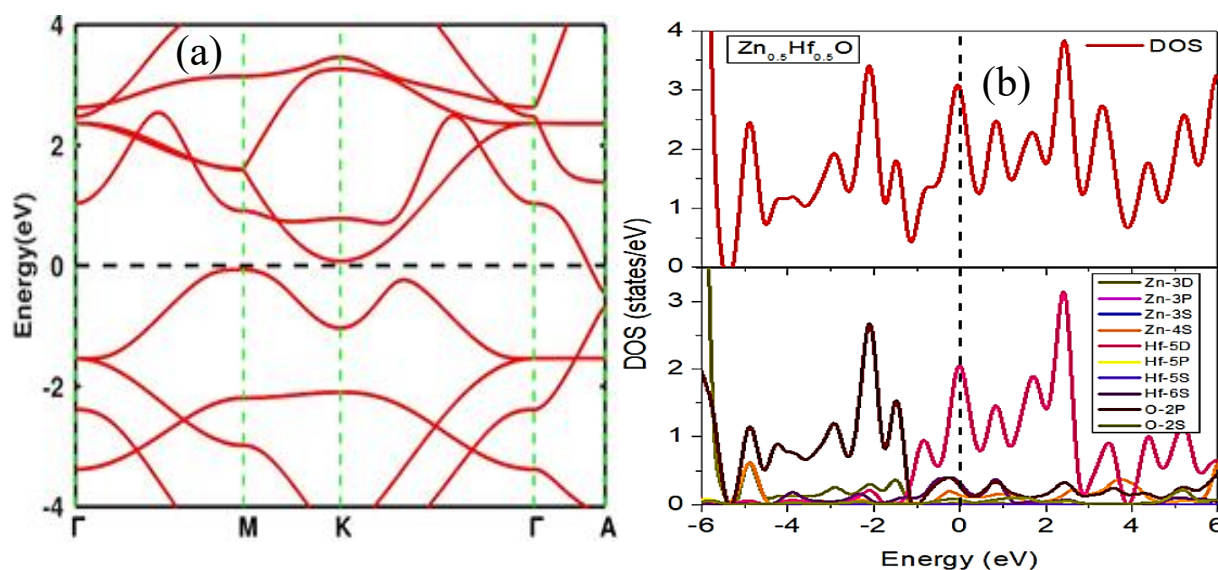


Figure 6: (a) Energy Band and (b) DOS of $\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$

Optical properties

The electronic band structure and density of states of a material play a fundamental role in understanding its optical behaviour [37][38]. Furthermore, important features of optoelectronic materials, such as their linear response and the behaviour of radiation transmitted by them, can also be explained.

The complex dielectric function is also an important parameter that defines a material's optical properties, as is given in equation (3).

$$\varepsilon(\omega) = \varepsilon_1(\omega) + \varepsilon_2 \dots\dots\dots(3)$$

Thus, the real part of equation 3 $\varepsilon_1(\omega)$ was evaluated using the Kramers-Kronig relations.

Equations (4) and (5) deal with the complex dielectric function $\varepsilon(\omega)$ and enables the optical response of the materials at all photon energies to be evaluated. While the real part $\varepsilon_1(\omega)$ of the dielectric function gives the energy stored in the material, the imaginary part $\varepsilon_2(\omega)$ enables the absorption behaviour of the medium and its electronic band structure to be evaluated.

As shown in equation 4, the imaginary part $\varepsilon_2(\omega)$ of the complex dielectric function is obtained by summing transitions from valence (occupied) to conduction (unoccupied) states (with a fixed k value) over the Brillouin Zone, as shown in equation (5), while P the Cauchy principal value, and C_k and V_k represent the Bloch functions for the unoccupied and occupied states.

While the frequency of incident radiation and the momentum operator respectively are given by ω and k , the total energy is given by an integral part of equation (5). In equation 6, the refractive index is given by $n(\omega)$ while the extinction coefficient $k(\omega)$ is given by equation (7).

$$\varepsilon_1(\omega) = 1 + \left(\frac{2}{\pi}\right) P \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{(\omega'^2 - \omega^2)} d\omega' \dots\dots\dots(4)$$

$$\varepsilon_2(\omega) = \frac{4e^2\pi}{\omega^2 m^2} \left(\sum_{C,V} \int_k C_k |P| V_k^2 \delta(\epsilon_{Ck} - \epsilon_{Vk} - \hbar\omega) dk \right) \dots\dots\dots(5)$$

$$n(\omega) = \left(\frac{1}{2}\right)^{1/2} \sqrt{(\varepsilon_1(\omega) + (\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega))^{1/2})} \dots\dots\dots(6)$$

$$k(\omega) = \left(\frac{1}{2}\right)^{1/2} \sqrt{(-\varepsilon_1(\omega) + (\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega))^{1/2})} \dots\dots\dots(7)$$

Other factors that can be calculated using the equations (8) – (11) are: conductivity, $(\sigma(\omega))$, reflectivity index $(R(\omega))$, absorption coefficient $(\alpha(\omega))$, and electron loss function $(L(\omega))$, respectively [39- 41]

$$\sigma(\omega) = \frac{1}{4\pi} (\omega \varepsilon_2(\omega)) \quad (8)$$

$$R(\omega) = \left(\frac{\sqrt{i\varepsilon_2(\omega) + \varepsilon_1(\omega) - 1}}{\sqrt{i\varepsilon_2(\omega) + \varepsilon_1(\omega) + 1}} \right)^2 \quad (9)$$

$$\alpha(\omega) = \left(\frac{\omega}{c} \right) (2(\varepsilon_2^2(\omega) + (\varepsilon_1^2(\omega))^{1/2} - (\varepsilon_1^2(\omega))^{1/2}) \quad (10)$$

$$L(\omega) = \left(\frac{\varepsilon_2(\omega)}{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} \right) (2(\varepsilon_2^2(\omega) + (\varepsilon_1^2(\omega))^{1/2} - (\varepsilon_1^2(\omega))^{1/2}) \quad (11)$$

Figure 6 (a- d) and Figure (a-d) show how $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ of the complex dielectric function for ZnO and Zn_{0.5}Hf_{0.5}O varied with energy ω (eV).

In Figure 6 (a), the corresponding value $\varepsilon_1(0)$ at $\omega = 0$ for ZnO material is 3.6. Beyond $\omega = 0$, the magnitude of $\varepsilon_1(\omega)$ starts to increase gradually and thereafter begins to fluctuate decreasingly until it reaches 0.5 within the energy range of 0.65 eV to 1.63 eV for ZnO. Conversely, in Figure 6(b), the $\varepsilon_2(\omega)$ peak corresponds to an energy of 0.45 eV with sharp falls on either side of the energy.

Similarly, for the Zn_{0.5}Hf_{0.5}O alloy, $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ have negative spectra within the energy range of 0.1 to 0.3 eV, as presented in Figure 7 (a) and (b), respectively, corroborating that the daughter nuclei behave like a metal and agree with their energy bands and density of states, as shown in Figure 5 (a) and (b). This clearly shows that the electronic band structure and density of states of a material play a fundamental role in understanding its optical behaviour [40][41]. Furthermore, important features of optoelectronic materials such as their linear response and the behaviour of radiation transmitted by them can also be explained.

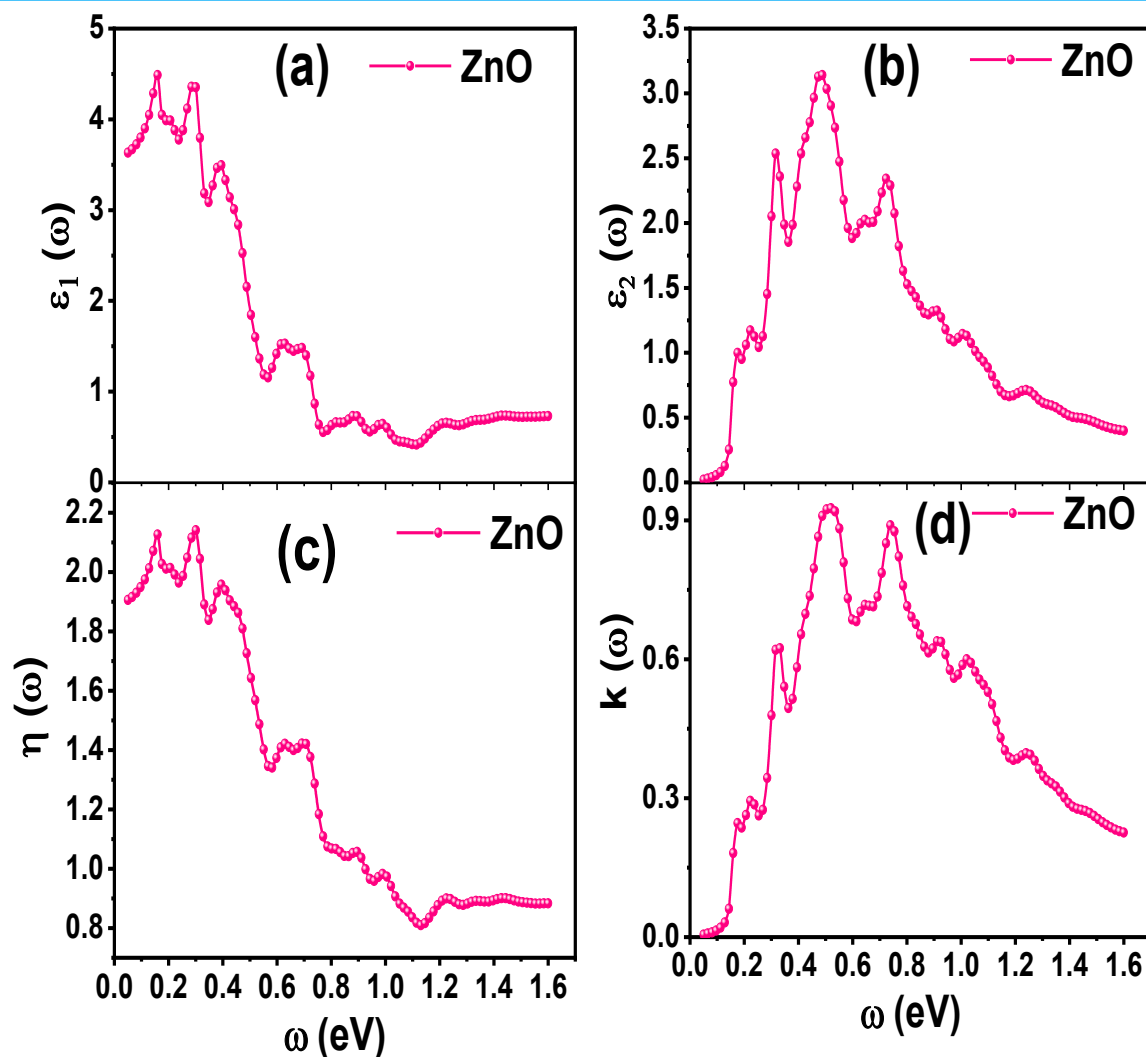


Figure 7: Calculated Complex Dielectric Plots of the (A) Real Part, (B) Imaginary Part, (C) Refractive Index, and (D) the Extinction Coefficient of ZnO.

At zero frequency, the static dielectric constant $\varepsilon(\omega)$ was found to be 3.62 and 20.65, respectively, for the ZnO Wurtzite and $\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$ alloy, see figures 6(a) and 7(a),

The value $\varepsilon(\omega) = 3.62$ is close to the values 3.869 and 4.0 reported for doped and undoped ZnO, respectively, and exhibits a signal (≥ 0) similar to the behavior of a semiconductor [41]. Figure. 6(c-d) and Figure. 7(c-d), show the plots of the refractive index $n(\omega)$ and the $k(\omega)$ extinction coefficient and the index of refraction $n(\omega)$ to the y-axis and indicate important results for the materials.

Utilizing equation 3: $\varepsilon(\omega) = \varepsilon_1(\omega) + \varepsilon_2(\omega)$, the refractive index $n(\omega)$ and the extinction coefficient $k(\omega)$ are found to clarify the other observed optical properties, and the process entails a normalization procedure on the Kramers-Kronig relations.

The dielectric constant value is 1.91 for ZnO and approximately 5.00 for $\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$, meaning that the introduction of Hf into the ZnO lattice modifies the polarizability and dielectric response of ZnO. The increased dielectric constant may be beneficial for

applications requiring greater electrical polarization, such as dielectric coatings, capacitive components, and selected electronic devices.

As seen in Figure 8, there are peaks which represent regions with strong electronic transitions, and increases in photon energy produce smaller peaks and consequently reduced optical absorption. Strong peaks exist between 22 and 23 eV at low photon energies, and other peaks also occur at 0.3, 0.5, and at 0.7 -1.0 eV. This suggests that the Hf-doping introduces electronic states that affect the optical transitions of ZnO.

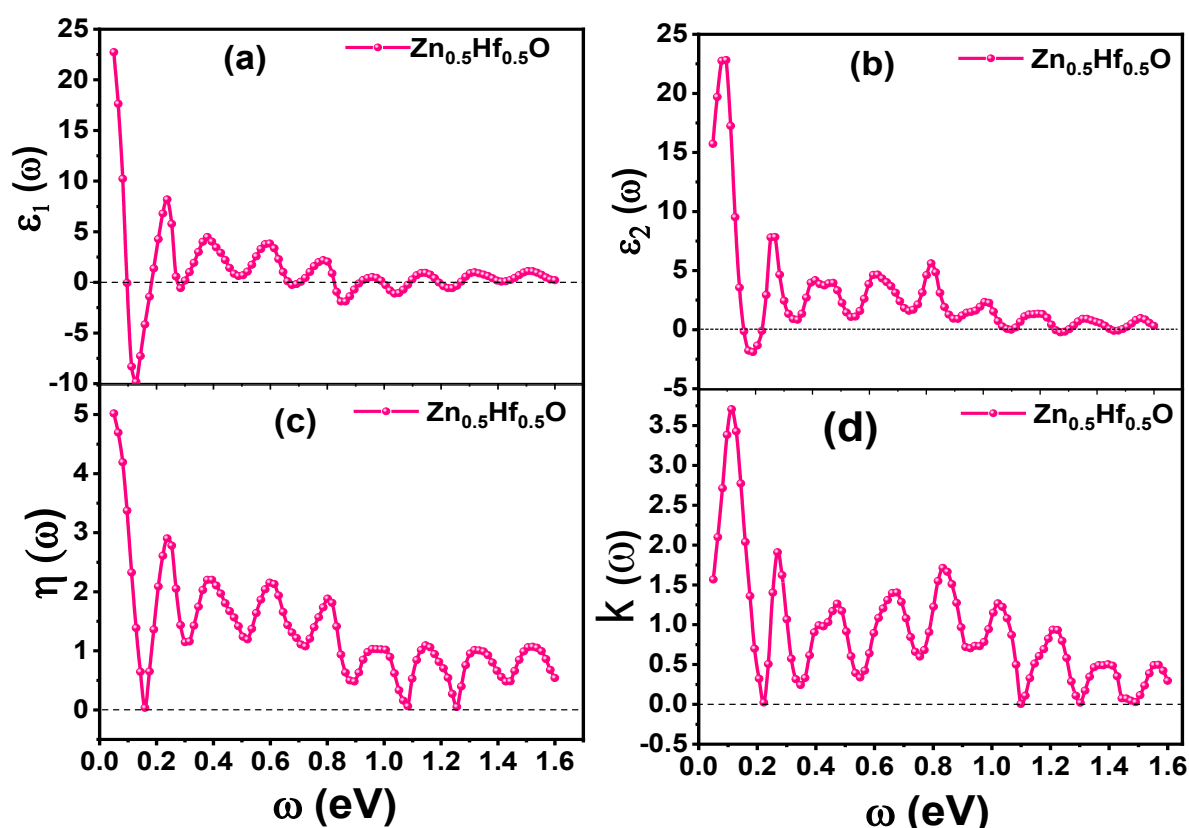


Figure 8: Calculated Complex Dielectric Plots of the (A) Real Part, (B) Imaginary Part, (C) Refractive Index And (D) the Extinction Coefficient of $\text{ZnO}_{0.5}\text{Hf}_{0.5}\text{O}$

The refractive index n of the material is high at low photon energy and gets as high as 5, though there are many other oscillations as the photon energy increases. At higher energies, values of refractive index range from 0.5 to 1.2, with repeated peaks indicating that Hf doping changes the refractive index of the ZnO. Changes in refractive index could be useful in optical coatings, photonic structures.

The extinction coefficient k is relatively high, with values ranging from 3.5 to 3.7. These values fall sharply and are composed of many oscillating peaks with maximum values occurring in the lower energy region and higher energies producing smaller extinction coefficients. This means that a large extinction coefficient implies stronger optical attenuation or absorption, while smaller extinction coefficients at particular energies imply that the material is more transparent at that energy value. Changes in the extinction coefficient may affect how strongly light is attenuated within the material and this can be beneficial for light absorption but undesirable in applications requiring optical transparency.

If Hf incorporation improves the absorption of useful wavelengths of light and promotes effective charge separation, it implies that the material may have potential in solar-driven environmental remediation.

Thus, we can infer that the Hf doping significantly modifies the optical properties of ZnO, alters its dielectric response, refractive index, extinction coefficient, and optical absorption, and the incorporation of the Hf into the ZnO lattice changes its electronic structure and electronic transitions.

Conclusion

In this study, the Structural, Electronic and Optical properties of hexagonal ZnO wurtzite and $\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$ alloy were investigated by using optimised lattice constants. The variation in the lattice parameters of the ZnO and $\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$ alloy as well as the calculated 84.3 % difference in Bulk moduli values for these materials are indications of local structural distortions in the ZnO lattice and the production of secondary phases of Hf.

The obtained energy-volume curves indicate stable equilibrium and the 50 % doping of the ZnO with Hf shifted the equilibrium volume of $\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$ to about $425 \text{ \AA}^3$ meaning that the Hf-doped system possesses a lower resistance to volume deformation. The modified electronic structure could be relevant to conductive functional materials, electronic interfaces, and selected optoelectronic devices.

The Density of States (DOS) values and contributions from individual orbitals show the ZnO to be a material of bandgap value 0.61 eV and therefore behaved as a semiconductor while the $\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$ alloy is a conductor of high DOS (3.18 states/eV) denoting it to be a material capable of strong electronic activity with high electrical conduction. Though the refractive index n of the doped material is high at low photon energy and gets as high as 5 though at high refractive index range from 0.5 to 1.2 with repeated peaks, the extinction coefficient k is relatively high with values ranging from 3.5 to 3.7. These results show that the Hf doping significantly modifies the optical properties of the ZnO, and alters its dielectric response, refractive index, extinction coefficient and optical absorption and the incorporation of the Hf into the ZnO lattice changes its electronic structure and electronic transitions. This study suggests that hafnium incorporation offers a possible approach for engineering the multifunctional properties of ZnO.

Potential Implications of Study

Introducing hafnium (Hf) into zinc oxide (ZnO) can significantly modify its structural, mechanical, electronic, and optical properties and broaden the potential applications of the material in photo catalysis, optoelectronics, dielectric devices, and other advanced technologies. Also, the substitution of Hf^{4+} for Zn^{2+} can change local bond lengths, bond angles, and lattice arrangement and ultimately affect the stability and properties of the resulting material.

The appearance of secondary hafnium-containing phases suggests that Hf incorporation may have a limit beyond which a single-phase solid solution becomes difficult to maintain and could influence the reproducibility and uniformity of the material. Furthermore, a knowledge of how Hf concentration affects lattice distortion and phase formation could help researchers optimize the composition and synthesis conditions to obtain materials with desirable properties. Thus, Hf doping provides a possible route for engineering the crystal structure of ZnO and tailoring its properties for specific technological applications.

The change in bulk modulus suggests that Hf incorporation modifies the effective bonding interactions and structural arrangement, potentially altering the response of the lattice to pressure. Furthermore, Hf incorporation may introduce or shift electronic states near the Fermi level thereby affecting the availability of states for electron transport.

Hf doping could also provide a means of tailoring the optical and dielectric properties of ZnO for applications in optical devices, dielectric materials, and light-responsive systems.

The photocatalytic activity of $\text{Zn}_{0.5}\text{Hf}_{0.5}\text{O}$ could be investigated experimentally and if confirmed the material could be investigated for the degradation of organic pollutants in wastewater and other contaminated environments.

The improved absorption of useful wavelengths of light by the Hf-doped ZnO could promote effective charge separation, thereby making the material useful in solar-driven environmental remediation. Also, changes in electronic states and optical constants may be useful for designing materials with tailored light absorption and electronic response.

Recommendations

The following are the recommendations from the outcome of this study:

- The doped material's response to pressure and temperature could be investigated to explore its potential to be used in Material engineering
- The effectiveness of Hf doped ZnO as a photo catalyst could be investigated.
- The observed increase in dielectric response may justify investigation for capacitive and other dielectric applications, although dielectric losses and frequency dependence must also be evaluated.
- The changes in bulk modulus and lattice dimensions suggests that studies of pressure-dependent structural stability and mechanical behaviour of the Hf-doped material can be done.

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