

The synergistic effect of molybdenum dopant content and pressure on the optoelectronic and mechanical performance of CeO₂: DFT+U study

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Abstract

This contribution investigates the structural, opto-electronic, and mechanical properties of cerium oxide (CeO₂) and molybdenum-included cerium oxide (Ce_{0.75}Mo_{0.25}O₂) under applied hydrostatic pressures of 0, 25, 50, 75, and 100 GPa. The calculations were performed using the state of the art density functional theory (DFT+U). The generalized gradient approximation (GGA) supported by the PBE functional has been utilized. Initially, the lattice dimensions of the cubic CeO₂ phase accounts to 5.438 Å. The electronic characteristics have been inspected by assessing the band gap of the pure CeO₂ unit cell, which amounts to 3.134 eV. The computed results of lattice dimensions and band gap energy are in line with the precedent experimental work. Incorporating Mo element into the host CeO₂ lattice declines the band gap to 2.045 eV of Ce_{0.75}Mo_{0.25}O₂. This value is more dropped when applying hydrostatic pressure till reaching 1.808 eV at 100 GPa. The projected and total density of states (PDOS) findings reveal hybridization between CeO₂ and Mo with key contributions of Ce-4*f*, O-2*p*, and Mo-3*d* states. Furthermore, the assessed negative formation energy magnitudes of Ce_{0.75}Mo_{0.25}O₂ under zero and applied hydrostatic stress evidence the thermodynamic stability, proposing the possible experimental fabrication of such system. Under applied pressures, absorption curves examinations reveal blue shift for the inspected structures. In addition, an enhancement in the absorption spectra has been observed by shifting toward the ultraviolet (UV) wavelength region, indicating the potential applications in optoelectronic devices. The simulated findings of the mechanically elastic properties manifest ductile behavior, with an enhancement by doping introduction. Consequently, this material would be a promising candidate in high-ductility applications, including protective coatings, solid oxide fuel cells, and microelectronic devices.

Keywords: Cerium dioxide (CeO₂); Charge distribution; Dielectric response; DFT+U; Anisotropy

1. Introduction

Globally, solid material oxides receive growing attention owing to their unique characteristics rendering them to be involved in photovoltaic, optoelectronic, and biological applications [1–3]. Particularly, cerium oxide (CeO₂) has occupied a great area in literature because of its brilliant physical and chemical properties. These distinguished properties are motivated by the partially filled 4*f* orbital in Ce as well as swinging between two oxidation states of Ce³⁺ and Ce⁴⁺ [4–6]. CeO₂ is well-documented as an excellent costly effective contributor to potentially assist in lessening environmental contaminations and pollutions [7,8]. Experimentally, CeO₂ exhibits a semiconductor character with band gap energy spanning from 2.2-3.5 eV, good absorption trend in the Ultra violet area of the solar spectra with a very limited absorbance in the visible region [9,10]. Transition metals doping effect on the physico-

chemical characteristics of the host CeO₂ crystal has been reported extensively. Particularly, Molybdenum (Mo) inclusion can optimize the catalytic activities in various reactions [11–13]. An experimental study has carried out to synthesize cerium telluride (CeTe) and Mo-CeTe films at doping levels ranged between 0.1–0.3 mol%. The results proposed that the insertion of Mo dopant into CeTe motivates band gap stretching from 1.20–1.60 eV [14]. Transition elements including Fe, Co, Ni and Cu have been inserted into CeO₂ at various doping levels for reverse water gas shift (RWGS) reaction, showing promising results in CO₂ reduction [15]. The combined effect of oxygen vacancies and band gap contraction boost the performance of the dual-ion co-doped Ce_{0.8}Sm_{2-x}Ca_xO_{2-δ} where x= 0.04, 0.08, 0.12, 0.16 [16]. The integration of Mo into the host CeO₂ supported Ni catalyst (Ni/MoCe) lattice would play a vital role in improving the surface oxygen vacancies, decreasing the particle size of Ni species and develop the metal-support interaction [17].

L. Li et al. [18] have developed Mo-doped CeO₂ catalysts via wet impregnation route. The catalyst demonstrated superior NO_x removal efficiency at low temperatures, exhibited strong resistance to SO₂ poisoning and suppressed the formation of strongly adsorbed NO_x, these findings highlight Mo surface modification as a promising route to enhance both the activity and durability of CeO₂-based catalysts in environmental applications. C. Nan et al. [19] manufactured Mo-doped CeO₂ nanorods by means of a hydrothermal route under calcination. The catalyst with 5% Mo doping revealed high efficiency for electrocatalytic nitrogen reduction reaction (NRR). This represents a four-fold improvement over pristine CeO₂ nanorods. Li Wang et al. [20] facilitated the direct reduction of CO₂ to CO using Mo-modified CeO₂. The catalyst's high efficiency was driven by the strong Mo–CeO₂ interfacial interactions. I. Diaz-Aburto et al. [21] synthesized Mo-doped CeO₂ via combustion process at different Mo contents of 5 wt.%, 7 wt.%, and 10 wt.%. The reported Young's modulus upsurge with the Mo compositions, suggesting the highest value of 289.4 GPa at 10 wt.% Mo. In addition, Vickers microhardness displays that Mo incorporation yields a decrease in the microhardness. H. Zhang et al. [22] employed flame spray pyrolysis to examine CH₄ non-oxidative coupling reaction over Mo-doped CeO₂, inferring high catalytic activities in this reaction [23]. A recently published research has reported the green synthesis of CeO₂ nanoparticles coated with silver (Ag) and doped with cadmium (Cd) exhibit improved photocatalytic and antibacterial activities [24]. On the other hand, density functional theory (DFT) based studies revealed that Mo incorporation would induce modulation of the electronic properties of CeO₂. A. Bouhlala et al. [25] investigated the fundamental properties of mono and co-dopant with tungsten (W) and (Mo-W) co-doped cubic CeO₂ by means of WIEN2k code. The band structure calculations indicated that the pure and co-doped CeO₂ exhibit semiconductor characteristics.

Ultimately, the lack of pressure-dependent studies that focuses on Mo-doped CeO₂ motivates us to examine the synergistic effect of 25% Mo dopant under applied hydrostatic pressures (0, 25, 50, 75, 100 GPa) on the physical properties of CeO₂.

2. Computational methods

In the current investigation, Cambridge Serial Total Energy Package (CASTEP) based on density functional theory (DFT) was used to perform the calculations [26] in order to investigate the structural, electronic, optical, and mechanical properties of $\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$ at varying hydrostatic pressures of 0, 25, 50, 75, and 100 GPa. Generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional have utilized [27]. DFT+U is adopted to improve the accuracy of the band gap calculations, as pure DFT tends to underestimate the band gap of the studied compounds [9,28]. Herein, U represents the Hubbard parameter, which describes the coulomb interaction of the outer electrons of the highly correlated system [29]. Within the CASTEP program, Hubbard parameter values of $U = 4.0$ eV for Ce (*f*-orbital), $U = 4.0$ eV for Mo (*d*-orbital) and $U = 4.3$ eV for O (*p*-orbital) were applied. Furthermore, the calculations were performed on a conventional unit cell consisting of 4 Ce atoms and 8 O atoms. Therefore, the least concentration of Mo doping is achieved by replacing one atom of Ce which corresponds to 25 at%. It is worth mentioning that literature has not yet reported any result on solubility limit of Mo in CeO_2 crystal. For the strongly correlated systems, pure DFT undervalues the electronic properties (i.e. the experimental band gap energy cannot be reproduced). Literature has indicated that the hole states located at the O *2p* state in CeO_2 is unstable [30]. As a result, U value of 4.3 eV was employed for O *2p* state [31]. The Brillouin zone was sampled using a $4 \times 4 \times 4$ Monkhorst-Pack k-point mesh [32] with cut-off energy set at 600 eV. Moreover, for precise calculations, Norm-conserving pseudo potential has been implemented in the current investigation. Finally, using the "stress-strain method" within the CASTEP package, the elastic constants were calculated. The self-consistent field (SCF) tolerance is set to 10^{-6} eV/atom and smearing value corresponds to 0.1 eV.

3. Results and discussion

3.1. Structural characteristics and stability

Figure 1 presents the optimized unit cells of both pure and Mo-doped CeO_2 structure, displaying fluorite crystal structure within the Fm-3m (#225) space group [33]. The unit cell contains four formula units, comprising four Ce and eight O atoms. In the current investigation, 25% of cerium (Ce) atoms in the unit cell are replaced with molybdenum (Mo) and the novel $\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$ model adopts a primitive cubic symmetry, belonging to the Pm-3m (No. 221) space group. The optimized pristine unit cell exhibit a lattice constant of 5.438 Å, as reported in Table 1. Previous studies have reported the lattice parameters of the optimized bulk CeO_2 as 5.44 Å [16] and 5.423 Å [35]. The integration of Mo content induces a reduction in the lattice constant of $\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$ system and attains a value of 4.894 Å under 100 GPa. This contraction arises from the substitution of larger Ce^{4+} ion (ionic radius: 0.97 Å) with smaller Mo^{4+} ion (0.71 Å), which shortens the interatomic distances within the crystal lattice. The reported lattice compression of the investigated structures reveals that the incorporation of dopant would lessen the unit cell volume and band gap, which is affecting the materials functioning. Table 1 summarizes the charge transfer values, signifying that Ce atoms undergo charge depletion from +1.53 to +1.60 electrons while the inclusion of Mo shows lower charge loss of +1.27 to +1.34 electrons. Oxygen atoms gain substantial negative charge, ranging from -0.73 to -0.78 electrons. These charge distribution patterns reveal distinct bonding characteristics the Ce-O bonds exhibit strongly ionic behavior due to pronounced charge transfer from Ce to O, whereas the Mo-O bonds display a mixed covalent-ionic nature with predominant covalent character, evidenced by the relatively smaller charge transfer from Mo. The negative

formation energy values presented in Table 1 further confirm the thermodynamic stability of the doped material under both doping and high-pressure conditions, validating its potential for practical synthesis. The formation energies of the investigated systems were computed using the following relations [36];

$$E_{f(\text{CeO}_2)} = \frac{1}{k+m} (E_{\text{CeO}_2}^{\text{total}} - (kE_{\text{Ce}}^{\text{Bulk}} + mE_{\text{O}}^{\text{Bulk}})) \quad (1)$$

$$E_{f(\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2)} = \frac{1}{k+l+m} (E_{\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2}^{\text{total}} - (kE_{\text{Ce}}^{\text{Bulk}} + lE_{\text{Mo}}^{\text{Bulk}} + mE_{\text{O}}^{\text{Bulk}})) \quad (2)$$

Here $E_{f(\text{CeO}_2)}$ and $E_{f(\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2)}$ correspond to the formation energy of the intrinsic and doped systems, while $E_{\text{CeO}_2}^{\text{total}}$ and $E_{\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2}^{\text{total}}$ represent the total energies of the intrinsic and Mo-doped structures. $E_{\text{Ce}}^{\text{Bulk}}$, $E_{\text{Mo}}^{\text{Bulk}}$, $E_{\text{O}}^{\text{Bulk}}$ refer to the total energies of the most stable solid phases Ce, Mo, and O₂ bulks, respectively. These values were considered to be the chemical potentials Ce, Mo, and O₂ atoms. It is worth mentioning that to accomplish the calculations, the most stable phases of Ce and O₂ are considered as body-centered cubic (bcc) structure with space groups correspond to Im-3m-229 and Fd-3m-227, in that order. While for Mo phase, a hexagonal structure of P63/mmc-194 was adopted. The full counts of Ce, Mo, and O atoms in the modeled unit cell is represented by $k=3$, $l=1$, and $m=8$, correspondingly. It follows that the evaluated formation energy of CeO₂ is -5.209 eV, indicating the thermodynamic stability of the modeled configurations as reported in Table1. Interestingly, the computed formation energies of the simulated compounds suggest exothermicity reactions reflecting their feasibility to be fabricated experimentally. While incorporating Mo dopant resulted in lessening the exothermicity. Applying hydrostatic pressures have affected the exothermicity occurring process positively as reported in Table 1.

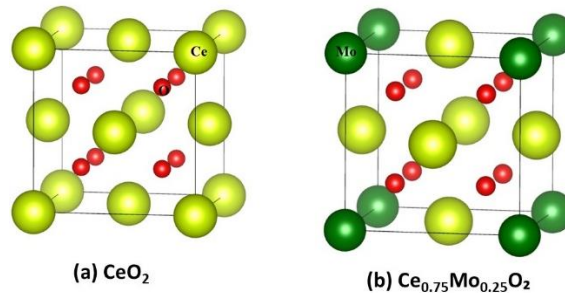


Figure1: The relaxed unit cells of CeO₂ and Ce_{0.75}Mo_{0.25}O₂ configurations. Neon yellow, dark green and red spheres signify Ce, Mo and O atoms, correspondingly.

Table 1. The evaluated lattice constants (Å), formation energies (eV), electronic band gaps (eV), and charge transfer (*e*) analysis of the pristine and Mo-doped CeO₂.

Configurations	lattice constants (Å) a=b=c	Formation energy (eV)	Band gap (eV)	Charge Transfer (e)		
				Ce	Mo	O
CeO ₂ (0 GPa)	5.438	-5.209 -8.83 [37]	3.134	1.56	-	-0.78
	5.481 [37]		3.23 [38]			
	5.39 [38]		3.15 [39]			
Ce _{0.75} Mo _{0.25} O ₂ (0 GPa)	5.353	-4.831	2.045	1.6	1.33	-0.77
Ce _{0.75} Mo _{0.25} O ₂ (25 GPa)	5.188	-5.168	2.058	1.58	1.34	-0.76
Ce _{0.75} Mo _{0.25} O ₂ (50 GPa)	5.067	-5.304	1.985	1.56	1.33	-0.75
Ce _{0.75} Mo _{0.25} O ₂ (75 GPa)	4.972	-5.415	1.910	1.54	1.3	-0.74
Ce _{0.75} Mo _{0.25} O ₂ (100 GPa)	4.894	-5.575	1.808	1.53	1.27	-0.73

3.2 Electronic properties analysis

Figure 2 presents the projected and total density of states and band structure for the CeO₂ system covering an energy range from -20 eV – 10 eV. Within the 0 eV – 3.13 eV range, the conduction band (CB) is primarily formed by Ce-4*f* states, along with minor contributions of s and p orbitals. In contrast, the valence band (VB) expanded from -4 eV – 0 eV displays dominant p-orbital character, accompanied by small contributions of d and f orbitals. Even under increasing hydrostatic pressure, Ce_{0.75}Mo_{0.25}O₂ continues to behave like a semiconductor, exhibiting an energy gap between 3.134 eV and 1.808 eV, as illustrated in Figure 3. At 0 GPa, the introduction of dopant would lower the energy gap from 3.134 eV (pristine CeO₂) to 2.045 eV (Ce_{0.75}Mo_{0.25}O₂). The projected and total density of states and band structure along the high symmetry points X-R in the Brillouin zone are presented in Figures 3 and 4 confirming the material's semiconductor characteristics across varying pressures.

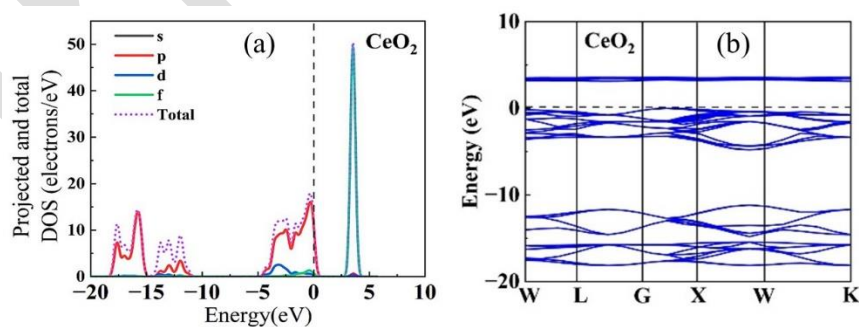


Figure 2: (a): The projected and total density of states (DOSs). (b): The band structure of the pristine CeO₂ at 0 GPa.

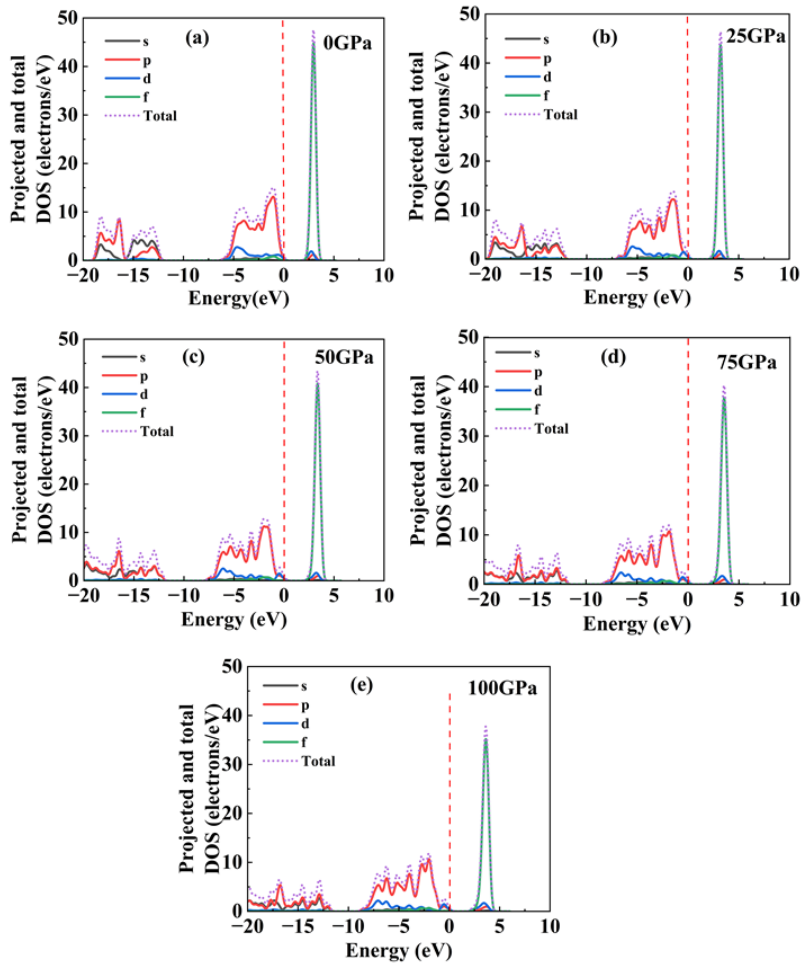


Figure 3: The Projected and total density of states (DOSs) of $\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$ under the selected pressures.

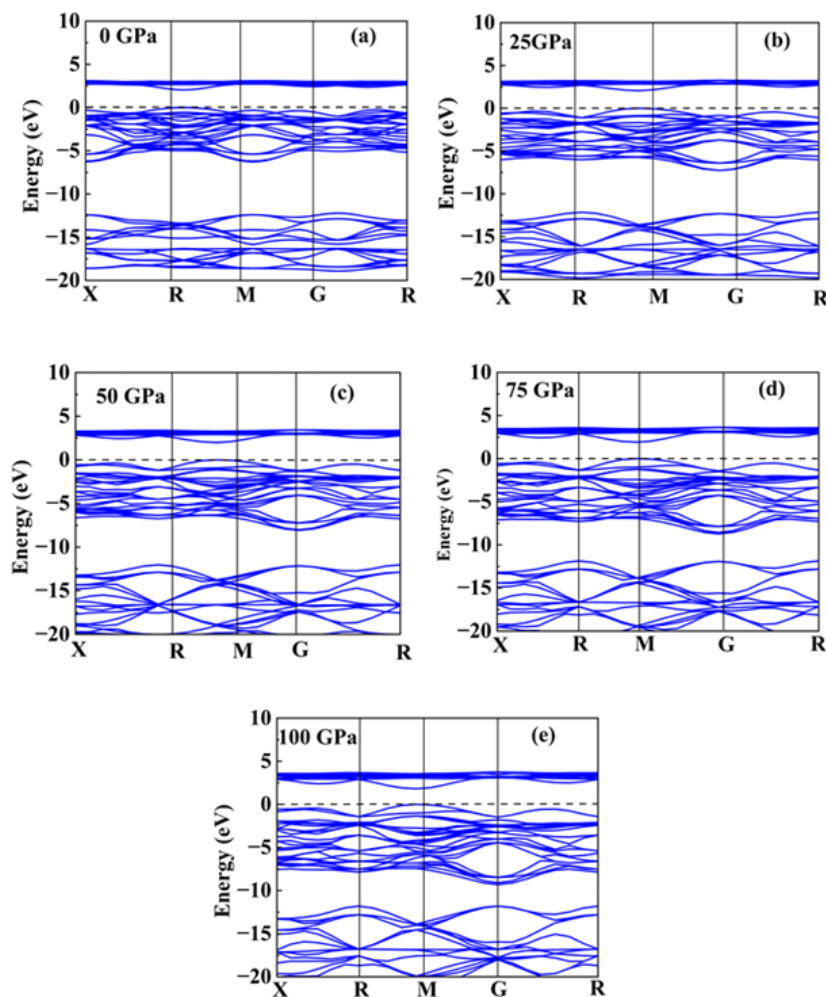


Figure 4: The band structure of $\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$ under the applied pressures.

3.3 Optical characteristics analysis

This investigation confirms fundamental optical performance parameters such as light absorption, surface reflectance, optical conductivity, refraction index, dielectric performance, and energy loss are demonstrated according to these findings.

3.3.1 Absorption coefficient and Reflectance

As shown in Figure 5, pure CeO_2 displays high UV absorption with negligible absorption in the visible light region, implying high transmittance in the visible region that motivates its use in various optical applications. Moreover, for $\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$ configuration under applying pressures would induce blue shift (moving toward shorter wavelengths) in the absorption edge as displayed in Figure 5. It has demonstrated that the insertion of Mo dopant into CeO_2 host lattice tends to reduce the band gap energy owing to the contribution of new localized electronic states (d-orbitals) in the forbidden band and thereafter absorbing photons in the visible region of the electromagnetic spectrum.

It can be evidently seen that the simulated electronic and optical results are confidently correlated by initiating the absorption coefficients values from the non-zero values which confirming the semiconducting character for the entire inspected systems [40]. All the plotted absorption coefficients proceed from non-zero values emphasizing semiconducting tendency of the chosen materials as depicted in Figure 5.

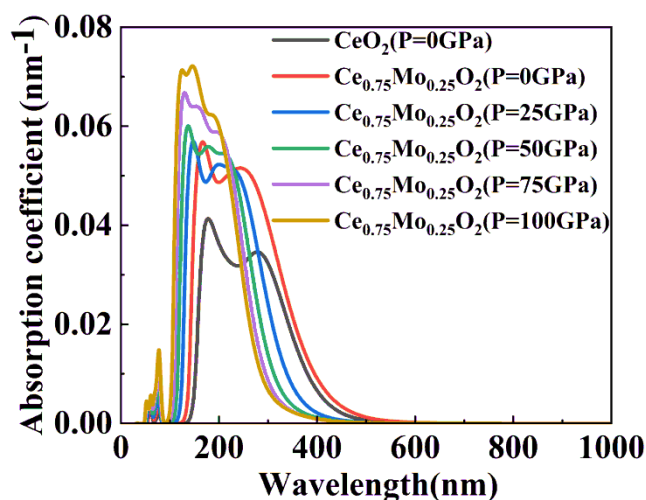


Figure 5: Pressure-dependent absorption coefficient spectra

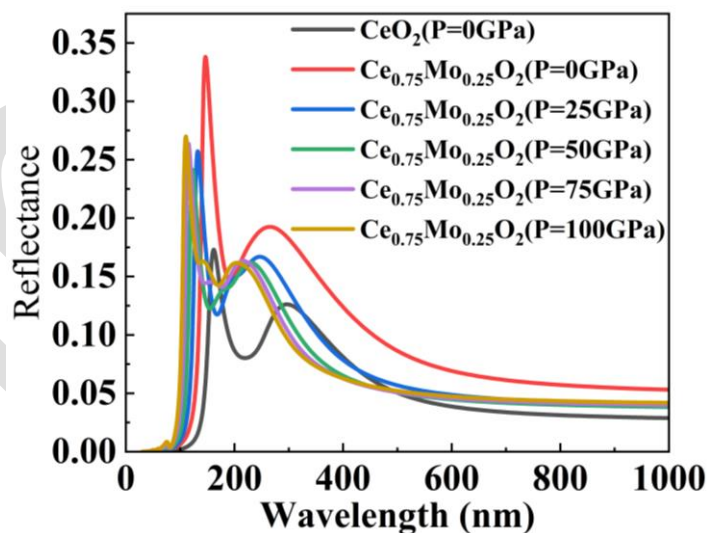


Figure 6: Pressure-dependent reflectance spectra.

Figure 6 shows the reflectance spectra of the studied systems. The results indicate prominent peaks for the pure and Mo-included CeO₂ are positioned in the UV region reflecting the higher reflectance magnitudes than that of other studied wavelength regions (i.e. visible and near IR). Among the samples, pure cerium oxide (CeO₂) exhibits the

lowest reflectance, while the doped samples show slightly higher reflectance, particularly in visible and near IR ranges. This is can be attributed to the tightening of the electronic band gap energy as Mo is introduced and hence making the material to act such as a metal [41]. Obviously, Mo dopant results in raising the free carriers (i.e. electrons and holes) that vibrates when absorbing visible and near IR incident photons and as a consequence the emitting process increases. Furthermore, the reflectance decreases with increasing pressure, with the highest reflectance observed at 0 GPa. Lastly, it can reach a conclusion that all the studies spectra have a trivial reflectance values in the visible and near IR.

3.3.1. Conductivity and Insulating Activities

The absorption of photons by a material leads to the emission of photoelectrons, a phenomenon known as the photoelectric effect. This phenomenon produces detectable optical conductivity, which can be theoretically modeled. Optical conductivity represents a key indicator for analyzing charge transfer mechanisms in photoactive materials. It provides a quantitative measure of electron transport dynamics in materials under optical stimulation [42]. The optical conductivity, which depends on frequency, can be represented as a complex function [43];

$$\delta(\omega) = \delta'(\omega) + i\delta''(\omega) = -i \frac{\omega}{4\pi} [\varepsilon'(\omega) + i\varepsilon''(\omega) - 1] \quad (3)$$

The real and imaginary components of conductivity are given by $\delta'(\omega)$ and $i\delta''(\omega)$, whereas the dielectric function is expressed in terms of its real part $\varepsilon'(\omega)$ and imaginary part $\varepsilon''(\omega)$. As demonstrated in Figure 7, the optical conductivity of pure CeO₂ exhibits measurable values in the visible light spectrum, with the imaginary component reflecting transparency behavior that aligns with the observed absorption characteristics. Figure 8 illustrates that doping and applying pressure (0-100 GPa) can induce transparency in pure CeO₂ within the visible light spectrum. This effect occurs when molybdenum (Mo) atoms replace cerium (Ce) atoms at a doping ratio of 25% in the system.

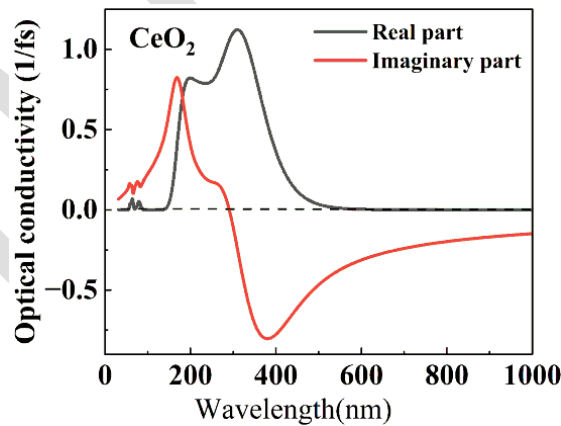


Figure 7: The optical conductivity of CeO₂ at 0 GPa.

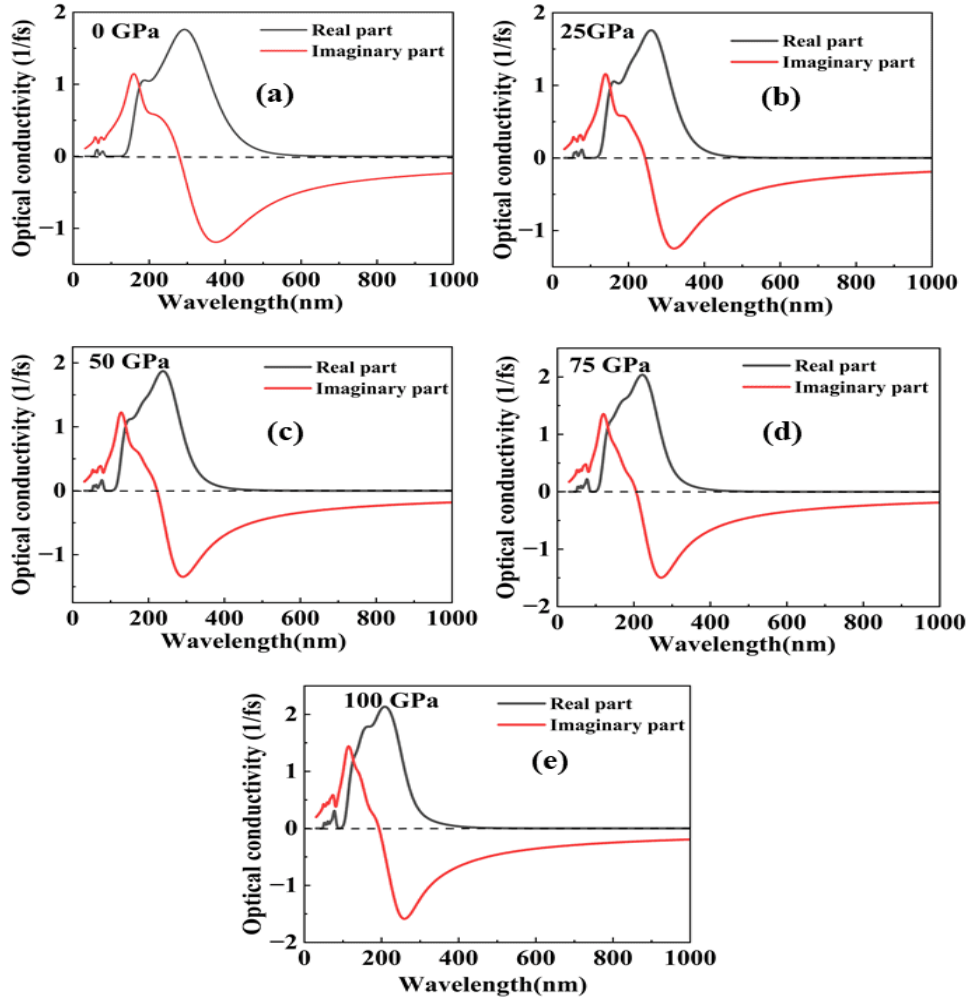


Figure 8: The pressure-dependent optical conductivity of $\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$.

As revealed in Figure 9, the energy loss spectra of the pristine CeO_2 at zero pressure shows a predominant peak at about 175 nm before sharply declining to zero at higher wavelengths. For $\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$, applying pressures shift the loss energy spectra toward shorter wavelengths. Concisely, these remarkable findings propose negligible energy loss in the visible region of electromagnetic radiation.

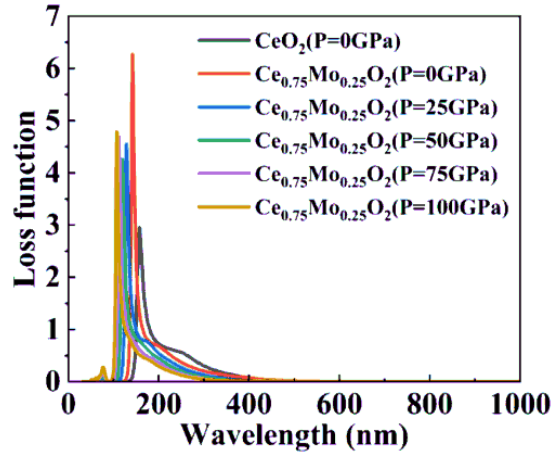


Figure 9: Pressure-dependent energy loss function of CeO_2 and $\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$.

3.3.3 Dielectric Function

In materials science, the dielectric response of a substance plays a considerable role in predicting its capability toward storing electrical energy, which is crucial for applications such as capacitors. Consisting of real $\epsilon_1(\omega)$ and imaginary $\epsilon_2(\omega)$ components, the dielectric function $\epsilon(\omega)$ captures electronic polarization and photon absorption coefficient, respectively according to the expression below [37];

$$\epsilon(\omega) = \epsilon_1 + i\epsilon_2(\omega) \quad (4)$$

Figure 10 depicts the dielectric responses of CeO_2 . The real and imaginary dielectric components spectra suggest sharp peaks at around 425 nm and 325 nm, correspondingly. However, these peaks are shifted toward shorter wavelengths of $\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$ under the selected pressures as illustrated in Figure 11 [44].

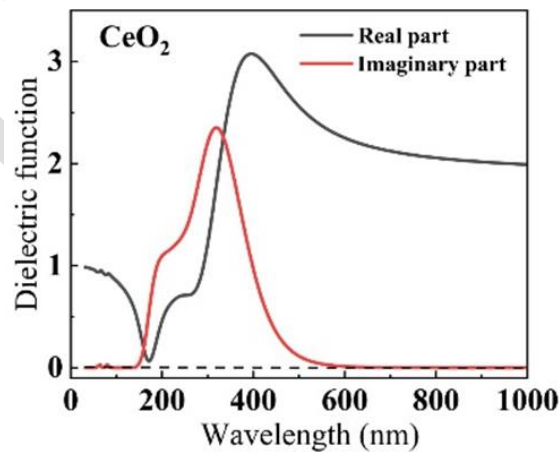


Figure 10: The calculated dielectric function of CeO_2 at 0 GPa.

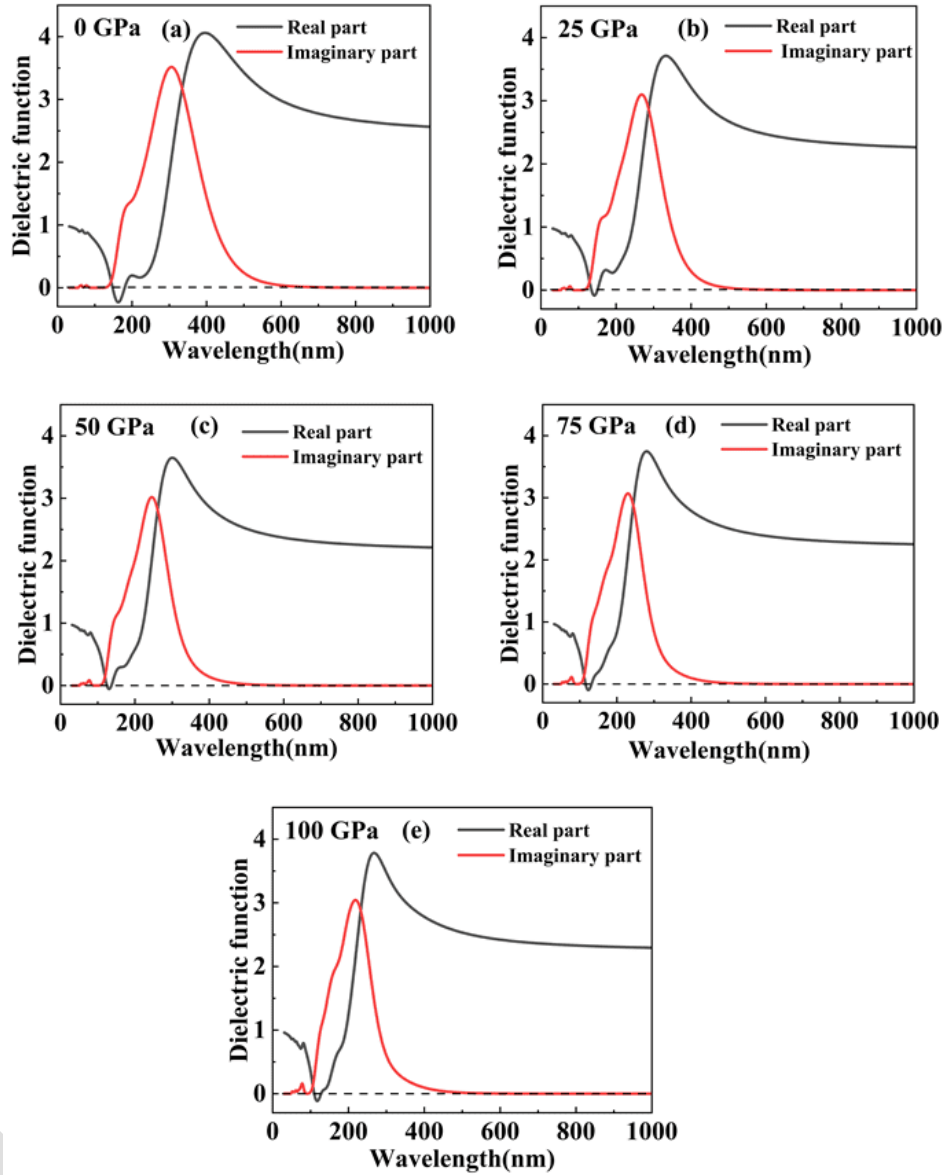


Figure 11: The calculated dielectric function of $\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$ at varying pressures.

3.4 Complex refractive Index

It has been reported that CeO_2 thin films display high refractive index (n) of 2.33 at 632.8 nm [45]. Nonetheless, the simulated refractive index value at the ground state energy level corresponds to approximately 1.5 at the same wavelength. In view of that, the imaginary component of refractive index is typically represented by extinction coefficients (k) that is given by the relation;

$$k = \frac{\epsilon_2}{2n} \quad (5)$$

Figure 12 displays the evaluated refractive index (n) and imaginary part (k) of CeO_2 crystal at 0 GPa. It is obviously identified from the figure that the maximum k value discloses 0.73 at 325 nm, however; this value is dropped at higher wavelengths. Figure 13 displays the combined effect of Mo insertion and applied pressures on the host CeO_2 crystal lattice. The n and k spectra of $\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$ configurations demonstrate gradual shift toward shorter wavelengths under applied pressures, suggesting reduced transparency. This finding strongly indicates its potential utilization in optoelectronic applications.

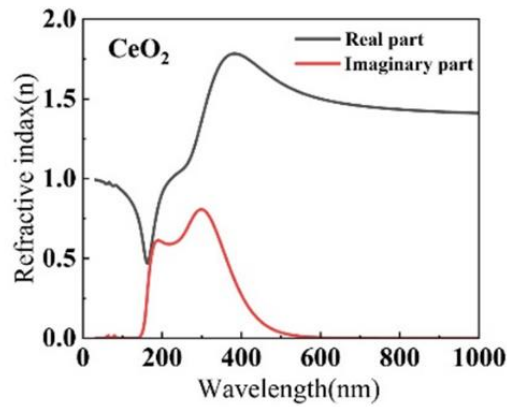


Figure 12: Complex refractive index of CeO_2 at 0 GPa.

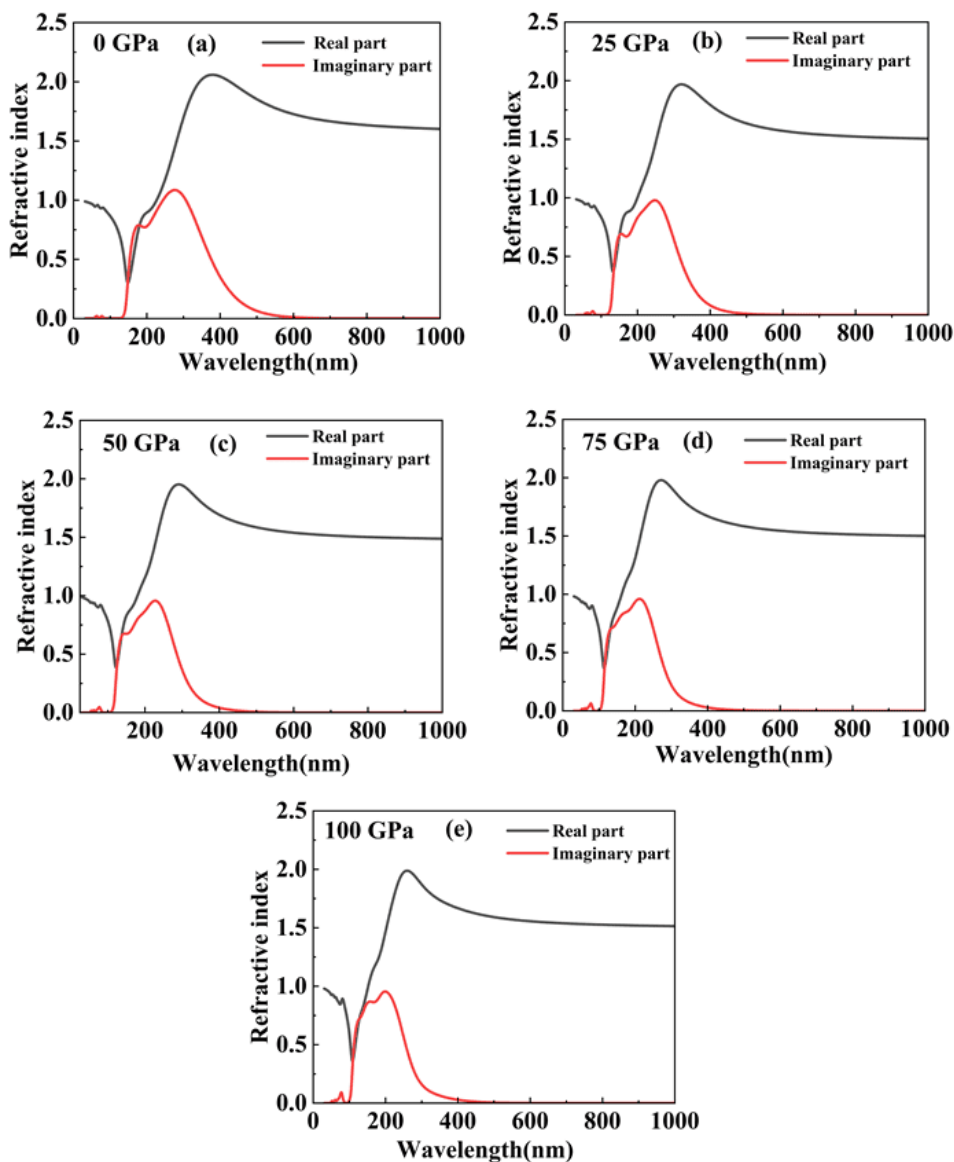


Figure 13: Complex refractive index of $\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$ at different pressures.

3.4 Mechanical properties analysis

Each crystal system is characterized by a specific number of elastic constants (C_{ij}). For instance, the cubic crystal system has only three independent elastic constants which are C_{11} , C_{12} , and C_{44} . This reduction in the number of constants arises from the high degree of symmetry in cubic crystals, the more symmetric the structure; the fewer independent elastic constants are needed to describe its mechanical behavior. These constants are vital for analyzing the mechanical properties of materials, which is crucial to evaluating their suitability for industrial applications, especially under extreme environmental conditions. By calculating these constants in CASTEP of CeO_2 and $\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$ under applied pressures, key parameters can be determined. These parameters offer valuable insights

for predicting material properties such as hardness, deformation resistance, and brittleness versus ductility. For the cubic system, to ensure mechanical stability, the following standard criteria must be accomplished [46];

$$(C_{11} + 2C_{12}) > 0; C_{44} > 0; (C_{11} - C_{12}) > 0; C_{11} > 0$$

As evidenced by the data in Table 2, the results meet the necessary conditions for mechanical stability. This is reinforced by the behavior of C_{11} , which quantifies the material's resistance to compressive or tensile stresses along the principal crystallographic directions. The value of C_{11} serves as a measure of the material's stiffness. We observed a systematic rise in C_{11} with both doping concentration and applied pressure, demonstrating improved resistance to deformation. This enhancement stems from the replacement of relatively weaker Ce–O bonds with more robust Ce–Mo bonds. The increase in C_{44} indicates stronger shear deformation resistance. This trend parallels the enhancement in bulk modulus (B), which quantifies the material's resistance to volume change under pressure, as detailed in previous study [47];

$$B = \frac{C_{11} + 2C_{12}}{3} \quad (6)$$

Doping and hydrostatic pressure both lead to elevated bulk modulus values, confirming improved bulk stiffness in the modified materials. The observed behavior indicates strong interatomic bonding. Shear modulus (G) can be calculated using the following equation [46];

$$G_V = \frac{1}{5}(C_{11} - C_{12} + (3C_{44})) \quad (7)$$

$$G_R = \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})} \quad (8)$$

$$G = \frac{G_V + G_R}{2} \quad (9)$$

For pure CeO₂ at 0 GPa, the measured shear modulus reached 75.024 GPa, demonstrating significant inherent hardness. However, introducing 0.25 content of Mo enhances this value to 85.905 GPa under identical conditions. Interestingly, when pressure is elevated while maintaining a fixed doping concentration, the material's hardness shows a substantial improvement, reaching 143.215 GPa at 100 GPa. These results highlight the synergistic effects of doping and pressure on mechanical properties. To assess a material's ductile versus brittle behavior, the Pugh ratio (B/G) must be evaluated. The Pugh ratio (B/G) serves as a key indicator of a material's ductile or brittle nature. A ratio exceeding 1.75 signifies ductile behavior, while values below this threshold indicate brittleness [48]. The findings indicate that the material exhibits ductile behavior, with its ductility further enhanced by doping. As a result, this material holds potential for use in high-ductility applications, including protective coatings, solid oxide fuel cells, nuclear industries, and microelectronic devices [29]. Another key parameter that differentiates ductile from brittle materials is Poisson's ratio (ν). Typically, a value greater than 0.3 confirms ductile behavior, suggesting the material's ductility. This ratio can be calculated using the following expression [46];

$$\nu = \frac{3B - 2G}{6B + 2G} \quad (10)$$

The Cauchy pressure ($C_{12} - C_{44}$) was calculated for all samples. The positive values listed in Table 3 confirm the material's ductile behavior and metallic bonding nature. The drastic increments in elastic stiffness coefficient values (C_{12}) with increasing pressure validate the significant increase in Cauchy pressure of $Ce_{0.75}Mo_{0.25}O_2$ structure. Furthermore, the reduction in lattice parameters when applying pressures, as shown in Table 1, leads to lessening the interatomic distances and thereafter, enhancing the ductility trend of the material being strongly correlated with enhancing the Cauchy pressure. Additionally, the low compressibility values ($1/B$), where B is the bulk modulus, further indicate the material's hardness and ductility. Similarly, Zener's anisotropy ratio (A) reflects mechanical anisotropy when its value is less than one. These values provide insight into the material's stiffness characteristics, with the results presented in Table 3 based on the following relation [37];

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \quad (11)$$

The high Young's modulus (E) values presented in Table 2 serve as key indicators of the material's enhanced hardness. These results clearly demonstrate how doping contributes to improved hardness under increasing pressure. Young's modulus was determined using the following equation [46];

$$E = \frac{9BG}{3B+G} \quad (12)$$

Prior to applying pressures, the bulk modulus B increased with introducing 25% Mo content, signifying that Mo dopants results in a strong resistance to volume change for CeO_2 . Moreover, shear modulus G and Young's modulus E augmented inferring that Mo dopants motivate the resistance against elastic and shear deformations of CeO_2 host lattice. Table 2 indicates that Young's modulus is increased with introducing 10 wt.% Mo content and its experimentally measured value by Díaz -Aburto et al. [21] was 289.4 GPa.

The formability ratio (μ_m), with values exceeding 1.75 (Table 2), confirms the material's excellent workability and shaping potential. This property exhibits a positive correlation with applied pressure, making the material particularly suitable for industrial applications demanding high formability, such as solar cell manufacturing. The formability ratio was determined via the following equation;

$$\mu_m = \frac{B}{C_{44}} \quad (13)$$

The calculated Vickers hardness (H_V) values demonstrate the material's significant hardness, indicating strong resistance to penetration. This property makes it particularly valuable for applications requiring durable surfaces. The hardness values were derived theoretically using the following relation [46];

$$H_V = 2\left(\frac{G^3}{B^2}\right)^{0.583} \quad (14)$$

Table 2: The predicted elastic properties of CeO₂ and Ce_{0.75}Mo_{0.25}O₂. Elastic stiffness constants C_{ij} (GPa), Bulk modulus B (GPa), Shear modulus G (GPa), Young's modulus E (GPa), Poisson's ratio ν , machinability index μ_m , and Vicker's hardness H_v.

Crystal structures	C ₁₁	C ₁₂	C ₄₄	B	G	E	ν	μ_m	H _v
CeO ₂ (0GPa)	347.378	96.73	52.513	180.279	75.024	197.675	0.317	3.433	8.919
	341 [37]	102 [37]	56 [37]	181 [37]	77 [37]	202 [37]	0.314 [37]	3.23 [37]	6.15 [37]
	353.6 [49]	101.4 [49]	52.9 [49]	185.5 [49]	75.6 [49]	199 [49]	0.321 [49]	3.51 [49]	5.75 [49]
Ce _{0.75} Mo _{0.25} O ₂ (0GPa)	363.233	106.972	65.394	192.392	85.905	224.327	0.305	3.433	9.378
Ce _{0.75} Mo _{0.25} O ₂ (25GPa)	472.759	186.429	92.552	281.872	110.296	292.711	0.326	2.942	9.256
Ce _{0.75} Mo _{0.25} O ₂ (50GPa)	595.386	268.671	93.660	377.576	117.236	318.722	0.359	3.045	8.711
Ce _{0.75} Mo _{0.25} O ₂ (75GPa)	642.058	352.159	113.108	448.792	124.924	342.952	0.372	4.031	8.295
Ce _{0.75} Mo _{0.25} O ₂ (100GPa)	742.341	437.137	137.279	538.872	143.215	394.683	0.377	3.967	7.597

Table 3: The estimated mechanical properties of the systems under consideration.

Crystal structures	Zener's anisotropy (A)	Compressibility (1/B)	Pugh ratio (B/G)	Cauchy pressure ($C_{12}-C_{44}$)
	0.419			44.217
CeO ₂ (0GPa)	0.467 [37]	0.005	2.402	46 [37]
Ce _{0.75} Mo _{0.25} O ₂ (0GPa)	0.510	0.0051	2.239	41.577
Ce _{0.75} Mo _{0.25} O ₂ (25GPa)	0.646	0.003	2.555	93.876
Ce _{0.75} Mo _{0.25} O ₂ (50GPa)	0.573	0.002	3.220	175.010
Ce _{0.75} Mo _{0.25} O ₂ (75GPa)	0.780	0.0022	3.592	239.051
Ce _{0.75} Mo _{0.25} O ₂ (100GPa)	0.899	0.001	3.762	299.858

4. Conclusion

This study aims at systematically investigating the electronic, structural stability, optical, and mechanical properties of CeO₂ and Ce_{0.75}Mo_{0.25}O₂ under pressures by means of Density Functional Theory (DFT). At 0 GPa, the band gap energy decreased from 3.134 eV of the pristine CeO₂ to 2.045 eV of Ce_{0.75}Mo_{0.25}O₂. With increasing hydrostatic pressures, the band gap of Ce_{0.75}Mo_{0.25}O₂ exhibited a gradual shrinkage until reaching 1.808 eV at 100 GPa. Overall, the synergistic effect of 25% Mo doping and applied pressure reduces the band gap by over 1.3 eV, enhances UV absorption, and motivates optoelectronic industries. Moreover, the analysis on the mechanical characteristics results improve the ductility while increasing stiffness of CeO₂, with an enhancement at Mo content insertion and hence nominating this material to be involved in high-ductility applications, such as protective coatings, solid oxide fuel cells, and microelectronic devices. Finally, for materials engineering, more systematic studies are promising toward investigating the effect of co-doping with multiple transition metals on CeO₂ crystal.

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References

- [1] G. Kumaravel, S. Kirthiga, M. M. H. Al Shekaili, and Q. H. S. A. AL Othmani, A Solar Photovoltaic Performance Monitoring and Statistical Forecasting Model Using a Multi-Layer Feed-Forward Neural Network and Artificial Intelligence, *Baghdad Sci. J.* **21**, 1868 (2024).
- [2] S. S. Al-Awadi, A. A. Ramadhan, F. T. Ibrahim, and A. K. Abbood, Optical and structural properties of titanium dioxide prepared by dc magneto-sputtering as a NO₂ gas sensor, *Iraqi J. Sci.* **61**, 2562 (2020).
- [3] D. S. Shaker, N. K. Abass, and R. A. U. Ulwali, Preparation and study of the Structural, Morphological and Optical properties of pure Tin Oxide Nanoparticle doped with Cu, *Baghdad Sci. J.* **19**, 24 (2022).
- [4] R. Kumar, V. K. Gupta, M. Khosya, S. Singh, and U. Kumar, Comparative computational and experimental insights into the structural, electrical, and biological properties of CeO₂ fluorite ceramics, *Sci. Rep.* **15**, 1 (2025).
- [5] J. Graciani, A. M. Marquez, J. J. Plata, Y. Ortega, N. C. Hernandez, A. Meyer, C. M. Zicovich-Wilson, and J. F. Sanz, Comparative study on the performance of hybrid DFT functionals in highly correlated oxides: The case of CeO₂ and Ce₂O₃, *J. Chem. Theory Comput.* **7**, 56 (2011).
- [6] H. A. Miran, Z. N. Jaf, I. H. Khaleel, and A. A. Alkhafaji, Photocatalytic and optical performances of CeO₂ by substitution of titanium, *Phys. Chem. Res.* **9**, 553 (2021).
- [7] S. S. Mahmood, B. A. Hasan, and A. F. Rauuf, Effect of Manganese Oxide Doping of Tin Oxide Thin Films on the Optical and Structural Properties, *Iraqi J. Sci.* **65**, 3754 (2024).
- [8] B. M. Reddy and A. Khan, Nanosized CeO₂-SiO₂, CeO₂-TiO₂, and CeO₂-ZrO₂ mixed oxides: influence of supporting oxide on thermal stability and oxygen storage properties of ceria, *Catal. Surv. from Asia* **9**, 155 (2005).
- [9] H. A. Miran, M. Altarawneh, Z. N. Jaf, M. M. Rahman, M. H. Almatarneh, and Z.-T. Jiang, Influence of the variation in the Hubbard parameter (U) on activation energies of CeO₂-catalysed reactions, *Can. J. Phys.* **98**, 385 (2020).
- [10] S. A. Ansari, M. M. Khan, M. O. Ansari, S. Kalathil, J. Lee, and M. H. Cho, Band gap engineering of CeO₂ nanostructure using an electrochemically active biofilm for visible light applications, *RSC Adv.* **4**, 16782 (2014).
- [11] Z. N. Jaf, M. Altarawneh, H. A. Miran, and Z. T. Jiang, Geometries, electronic properties and stability of molybdenum and tungsten nitrides low-index surfaces, *Mater. Res. Express* **5**, 126402 (2018).
- [12] Z. N. Jaf, H. A. Miran, I. H. Khaleel, and K. A. Jasim, Assessing the optoelectronic performance of d-orbital

doped cubic HfO₂: The case of W, Nb, and Mo, *Optik (Stuttg)*. **264**, (2022).

- [13] Z. N. Jaf, M. Altarawneh, H. A. Miran, M. H. Almatarnah, Z. T. Jiang, and B. Z. Dlugogorski, Catalytic Hydrogenation of p-Chloronitrobenzene to p-Chloroaniline Mediated by γ -Mo₂N, *ACS Omega* **3**, 14380 (2018).
- [14] I. L. Ikhioya, S. O. Aisida, I. Ahmad, and F. I. Ezema, The effect of molybdenum dopant on rare earth metal chalcogenide material, *Chem. Phys. Impact* **7**, 100269 (2023).
- [15] Y. Yu, W. Xia, A. Yu, D. S. A. Simakov, and L. Ricardez-Sandoval, Transition-Metal-Doped CeO₂ for the Reverse Water-Gas Shift Reaction: An Experimental and Theoretical Study on CO₂ Adsorption and Surface Vacancy Effects, *ChemSusChem*. **18**, e202400681 (2025).
- [16] X. Hao, G. Wei, H. Zhang, S. Tan, and G. Ji, Defect chemistry-regulated design of doping CeO₂ with the enhanced high-temperature low infrared emissivity property, *Mater. Today Nano* **30**, 100614 (2025).
- [17] X. Zou et al., Molybdenum-doping promoted surface oxygen vacancy of CeO₂ for enhanced low-temperature CO₂ methanation over Ni-CeO₂ catalysts, *Appl. Surf. Sci.* **661**, 160087 (2024).
- [18] L. Li, C. Ge, J. Ji, W. Tan, X. Wang, X. Wei, K. Guo, C. Tang, and L. Dong, Effects of different methods of introducing Mo on denitration performance and anti-SO₂ poisoning performance of CeO₂, *Chinese J. Catal.* **42**, 1488 (2021).
- [19] C. Nan, H. Yang, F. Gao, N. Gao, W. Zhou, H. Du, and Z. Liang, Effects of Molybdenum Doping on the Enhanced Electrocatalytic Nitrogen Reduction Reaction Performance of CeO₂ Nanorods: Theoretical and Experimental Investigations, *ChemPlusChem*. **88**, e202300023 (2023).
- [20] L. Wang, X. Du, Y. Yi, H. Wang, M. Gul, Y. Zhu, and X. Tu, Plasma-enhanced direct conversion of CO₂ to CO over oxygen-deficient Mo-doped CeO₂, *Chem. Commun.* **56**, 14801 (2020).
- [21] I. Díaz-Aburto, F. Gracia, and M. Colet-Lagrange, Mo-doped CeO₂ Synthesized by the Combustion Method for Carbon-Air Solid Oxide Fuel Cell (CA-SOFC) Applications, *Fuel Cells* **19**, 147 (2019).
- [22] H. Zhang, Y. Su, N. Kosinov, and E. J. M. Hensen, Non-oxidative coupling of methane over Mo-doped CeO₂ catalysts: Understanding surface and gas-phase processes, *Chinese J. Catal.* **49**, 68 (2023).
- [23] Y. Yu, T. Wang, X. Jiang, K. Chen, Q. Wu, Y. Zhang, D. Shi, and H. Li, *Advances in the Preparation Strategies and Structural Regulation for CeO₂-Containing Electrocatalysts Applied to the Anodes of Direct Alcohol Fuel Cells: A Comprehensive Review*, *J. Mater. Chem. A*. **13**, 20143-20175 (2025).
- [24] P. S. Parab, A. A. Pawanaji, K. R. Jarhad, and A. S. Pawar, Harnessing the Effects of Cd-Doped and Ag-Coated CeO₂ (IV) Nanoparticles for Enhanced Nitrophenol Reduction, Photocatalytic Degradation, and

Other Potential Biological Applications, *BioNanoSci.* **15**, 1 (2025).

- [25] A. Bouhlala, M. Doghmane, W. T. Halais, and S. Chettibi, The impact of molybdenum and tungsten co-doping on the physical properties of CeO₂: First-principles calculations, *Mod. Phys. Lett. B* **38**, (2024).
- [26] R. Munirathnam, H. C. Manjunatha, Y. S. Vidya, L. Seenappa, K. N. Sridhar, T. C. S. Girisun, T. Sharmila, and S. V. R. Murugan, Optical limiting and two-photon absorption in transition metal and rare earth-doped CeO₂ nanoparticles, *Phys. B Condens. Matter* **711**, 417226 (2025).
- [27] J. P. Perdew, K. Burke, and M. Ernzerhof, *Generalized Gradient Approximation Made Simple*, 1996.
- [28] Z. N. Jaf, H. A. Miran, M. M. Rahman, A. Amri, and Z.-T. Jiang, DFT+ U investigation on high pressure properties of monoclinic CuO, *Can. J. Phys.* **102**, 316 (2024).
- [29] S. Lutfalla, V. Shapovalov, and A. T. Bell, Calibration of the DFT/GGA+ U method for determination of reduction energies for transition and rare earth metal oxides of Ti, V, Mo, and Ce, *J. Chem. Theory Comput.* **7**, 2218 (2011).
- [30] T. El-Achari, F. Goumrhar, L. B. Drissi, and R. A. Laamara, Structural, electronic and magnetic properties of Mn doped CeO₂: An ab-initio study, *Phys. B Condens. Matter* **601**, 412443 (2021).
- [31] B. Huang, R. Gillen, and J. Robertson, Study of CeO₂ and its native defects by density functional theory with repulsive potential, *J. Phys. Chem. C* **118**, 24248 (2014).
- [32] H. J. Monkhorst and J. D. Pack, Special points for Brillouin-zone integrations, *Phys. Rev. B* **13**, 5188 (1976).
- [33] J. L. Lu, H. J. Gao, S. Shaikhutdinov, and H. J. Freund, Morphology and defect structure of the CeO₂(1 1 1) films grown on Ru(0 0 0 1) as studied by scanning tunneling microscopy, *Surf. Sci.* **600**, 5004 (2006).
- [34] H. S. Batool, M. J. I. Khan, I. Taj, J. Ahmad, M. Yousaf, and M. Yousaf, DFT investigations of structural, electronic, magnetic, and optical properties of CeO₂-X (X= Mo/Cr) and Mo-Cr co-doped CeO₂ for optoelectronic applications, *Solid State Commun.* **385**, 115499 (2024).
- [35] Y. Xue, D. Tian, D. Zhang, C. Zeng, Y. Fu, K. Li, H. Wang, and Y. Tian, The mechanism of photocatalyst and the effects of co-doping CeO₂ on refractive index and reflectivity from DFT calculation, *Comput. Mater. Sci.* **158**, 197 (2019).
- [36] J. L. F. Da Silva, M. V. Ganduglia-Pirovano, J. Sauer, V. Bayer, and G. Kresse, Hybrid functionals applied to rare-earth oxides: The example of ceria, *Phys. Rev. B - Condens. Matter Mater. Phys.* **75**, 045121 (2007).
- [37] K. M. Hossain, S. Kumar Mitro, S. A. Moon, M. Mozahar Ali, S. Chandra, and M. A. Hossain, Influence of heavy Hf doping in CeO₂: Prediction on various physical properties, *Results Phys.* **37**, 105569 (2022).

- [38] Z. Liu, B. Wang, and C. Cazorla, Mechanical and electronic properties of CeO₂ under uniaxial tensile loading: A DFT study, *Materialia* **15**, 101050 (2021).
- [39] O. S. Polezhaeva, N. V. Yaroshinskaya, and V. K. Ivanov, Synthesis of nanosized ceria with controlled particle sizes and bandgap widths, *Russ. J. Inorg. Chem.* **52**, 1184 (2007).
- [40] M. Q. Saadon and H. A. Miran, Computational modeling study on the physical properties of Pd doped BaTiO₃ perovskite, *Comput. Condens. Matter* **39**, e00906 (2024).
- [41] F. T. Geldasa and F. B. Dejene, Effects of S Doping and Oxygen Vacancy on the Physical Properties of Rutile TiO₂ for Photocatalysis Applications Based on Density Functional Theory Study, *Materials (Basel)* **18**, 1688 (2025).
- [42] H. A. Miran, Z. N. Jaf, M. Al Tarawneh, M. M. Rahman, A. T. Al-Bayati, and E. M-T. Salman, First-Principles Analysis of Cr-Doped SrTiO₃ Perovskite as Optoelectronic Materials, *Iran. J. Mater. Sci. Eng.* **20**, 1 (2023).
- [43] B. Peng, H. Zhang, H. Shao, Y. Xu, R. Zhang, and H. Zhu, The electronic, optical, and thermodynamic properties of borophene from first-principles calculations, *J. Mater. Chem. C* **4**, 3592 (2016).
- [44] Z. N. Jaf, Z.-T. Jiang, H. A. Miran, and M. Altarawneh, Thermo-elastic and optical properties of molybdenum nitride, *Can. J. Phys.* **94**, 902 (2016).
- [45] F.-C. Chiu and C.-M. Lai, Optical and electrical characterizations of cerium oxide thin films, *J. Phys. D. Appl. Phys.* **43**, 075104 (2010).
- [46] H. A. Miran and Z. N. Jaf, A Systematic DFT Study on the Optoelectronic and Elastic Characteristics of H-Induced KMnF₃ Perovskite, *Brazilian J. Phys.* **55**, (2025).
- [47] H. A. Miran, M. Altarawneh, H. Widjaja, Z. N. Jaf, M. Mahbubur Rahman, J. P. Veder, B. Z. Dlugogorski, and Z. T. Jiang, Thermo-mechanical properties of cubic lanthanide oxides, *Thin Solid Films* **653**, 37 (2018).
- [48] R. J. Sabri and Z. N. Jaf, Optoelectronic characteristics of sulfur-doped LaAlO₃ at hydrostatic pressures: A computational study, *Comput. Condens. Matter* **44**, e01054 (2025).
- [49] H. Jia, M. Li, X. Li, B. Ren, X. Liu, and J. Zhao, Effects of nonmetal (F, Si, B, and P) doping on the electronic structure and elastic properties of CeO₂: A first-principles study, *J. Alloys Compd.* **666**, 419 (2016).