

# The synergistic effect of molybdenum dopant content and pressure on the optoelectronic and mechanical performance of CeO<sub>2</sub>: DFT+U study

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## Abstract

This contribution investigates the structural, opto-electronic, and mechanical properties of cerium oxide (CeO<sub>2</sub>) and molybdenum-included cerium oxide (Ce<sub>0.75</sub>Mo<sub>0.25</sub>O<sub>2</sub>) 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 CeO<sub>2</sub> phase accounts to 5.438 Å. The electronic characteristics have been inspected by assessing the band gap of the pure CeO<sub>2</sub> 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 CeO<sub>2</sub> lattice declines the band gap to 2.045 eV of Ce<sub>0.75</sub>Mo<sub>0.25</sub>O<sub>2</sub>. 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 CeO<sub>2</sub> 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<sub>0.75</sub>Mo<sub>0.25</sub>O<sub>2</sub> 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 (CeO<sub>2</sub>); 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 (CeO<sub>2</sub>) 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 Ce<sup>3+</sup> and Ce<sup>4+</sup> [4–6]. CeO<sub>2</sub> is well-documented as an excellent costly effective contributor to potentially assist in lessening environmental contaminations and pollutions [7,8]. Experimentally, CeO<sub>2</sub> 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 CeO<sub>2</sub> 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 CeO<sub>2</sub> at various doping levels for reverse water gas shift (RWGS) reaction, showing promising results in CO<sub>2</sub> reduction [15]. The combined effect of oxygen vacancies and band gap contraction boost the performance of the dual-ion co-doped Ce<sub>0.8</sub>Sm<sub>2-x</sub>Ca<sub>x</sub>O<sub>2-δ</sub> where x= 0.04, 0.08, 0.12, 0.16 [16]. The integration of Mo into the host CeO<sub>2</sub> 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 CeO<sub>2</sub> catalysts via wet impregnation route. The catalyst demonstrated superior NO<sub>x</sub> removal efficiency at low temperatures, exhibited strong resistance to SO<sub>2</sub> poisoning and suppressed the formation of strongly adsorbed NO<sub>x</sub>, these findings highlight Mo surface modification as a promising route to enhance both the activity and durability of CeO<sub>2</sub>-based catalysts in environmental applications. C. Nan et al. [19] manufactured Mo-doped CeO<sub>2</sub> 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 CeO<sub>2</sub> nanorods. Li Wang et al. [20] facilitated the direct reduction of CO<sub>2</sub> to CO using Mo-modified CeO<sub>2</sub>. The catalyst's high efficiency was driven by the strong Mo–CeO<sub>2</sub> interfacial interactions. I. Diaz-Aburto et al. [21] synthesized Mo-doped CeO<sub>2</sub> 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 CH<sub>4</sub> non-oxidative coupling reaction over Mo-doped CeO<sub>2</sub>, inferring high catalytic activities in this reaction [23]. A recently published research has reported the green synthesis of CeO<sub>2</sub> 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 CeO<sub>2</sub>. A. Bouhlala et al. [25] investigated the fundamental properties of mono and co-dopant with tungsten (W) and (Mo-W) co-doped cubic CeO<sub>2</sub> by means of WIEN2k code. The band structure calculations indicated that the pure and co-doped CeO<sub>2</sub> exhibit semiconductor characteristics.

Ultimately, the lack of pressure-dependent studies that focuses on Mo-doped CeO<sub>2</sub> 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 CeO<sub>2</sub>.

## 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  $\text{CeO}_2$  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  $\text{CeO}_2$  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  $\text{CeO}_2$  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  $\text{CeO}_2$  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  $\text{Ce}^{4+}$  ion (ionic radius: 0.97 Å) with smaller  $\text{Mo}^{4+}$  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 O<sub>2</sub> bulks, respectively. These values were considered to be the chemical potentials Ce, Mo, and O<sub>2</sub> atoms. It is worth mentioning that to accomplish the calculations, the most stable phases of Ce and O<sub>2</sub> 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 CeO<sub>2</sub> 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.

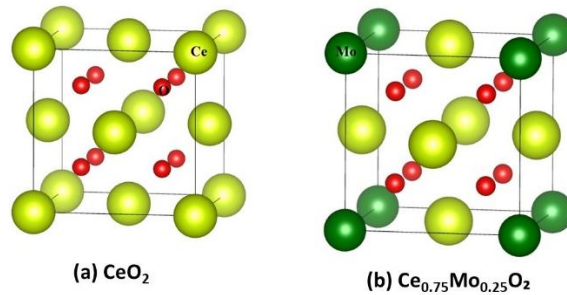


Figure1: The relaxed unit cells of CeO<sub>2</sub> and Ce<sub>0.75</sub>Mo<sub>0.25</sub>O<sub>2</sub> configurations. Neon yellow, dark green and red spheres signify Ce, Mo and O atoms, correspondingly.

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 CeO<sub>2</sub>.

Configurations	lattice constants (Å) a=b=c	Formation energy (eV)	Band gap (eV)	Charge Transfer (e)		
				Ce	Mo	O
CeO <sub>2</sub> (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 <sub>0.75</sub> Mo <sub>0.25</sub> O <sub>2</sub> (0 GPa)	5.353	-4.831	2.045	1.6	1.33	-0.77
Ce <sub>0.75</sub> Mo <sub>0.25</sub> O <sub>2</sub> (25 GPa)	5.188	-5.168	2.058	1.58	1.34	-0.76
Ce <sub>0.75</sub> Mo <sub>0.25</sub> O <sub>2</sub> (50 GPa)	5.067	-5.304	1.985	1.56	1.33	-0.75
Ce <sub>0.75</sub> Mo <sub>0.25</sub> O <sub>2</sub> (75 GPa)	4.972	-5.415	1.910	1.54	1.3	-0.74
Ce <sub>0.75</sub> Mo <sub>0.25</sub> O <sub>2</sub> (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 CeO<sub>2</sub> 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<sub>0.75</sub>Mo<sub>0.25</sub>O<sub>2</sub> 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 CeO<sub>2</sub>) to 2.045 eV (Ce<sub>0.75</sub>Mo<sub>0.25</sub>O<sub>2</sub>). 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.

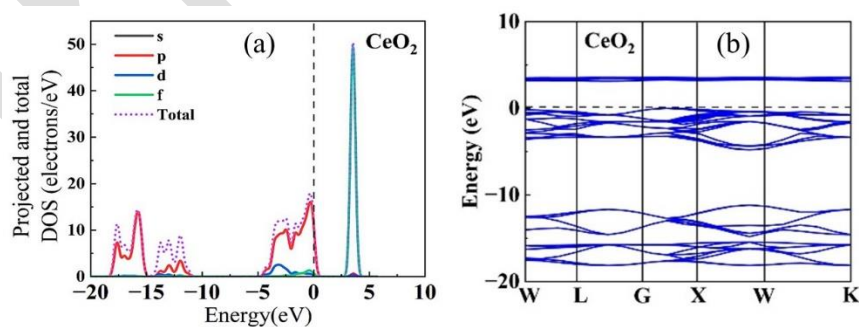


Figure 2: (a): The projected and total density of states (DOSs). (b): The band structure of the pristine CeO<sub>2</sub> at 0 GPa.

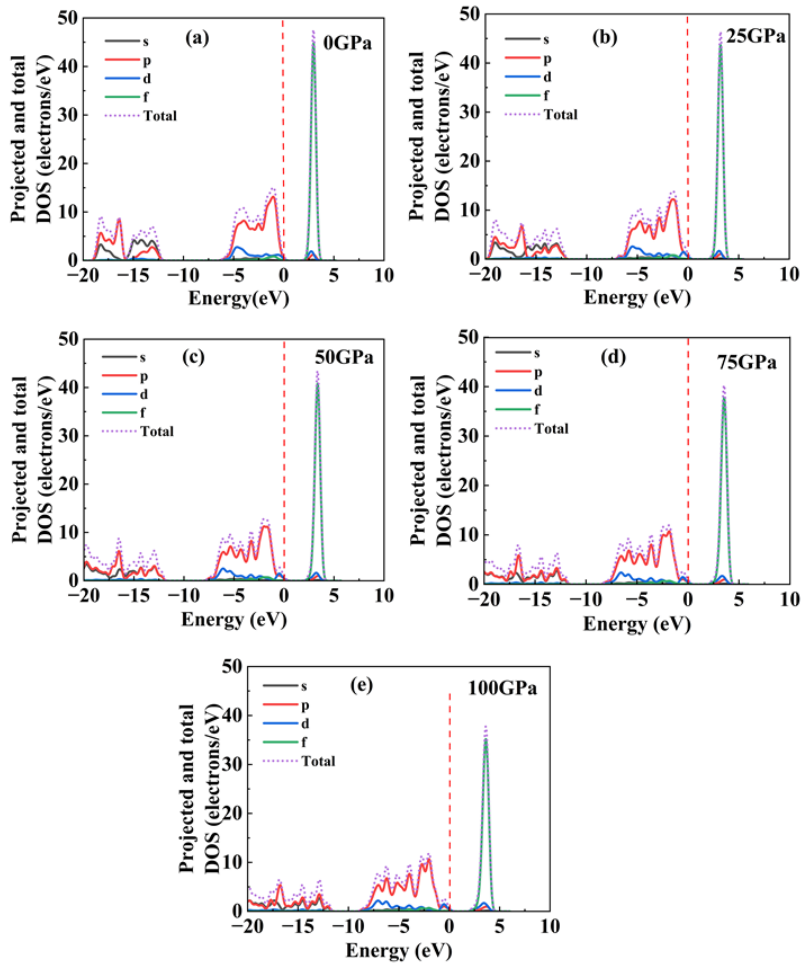


Figure 3: The Projected and total density of states (DOSs) of  $\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$  under the selected pressures.

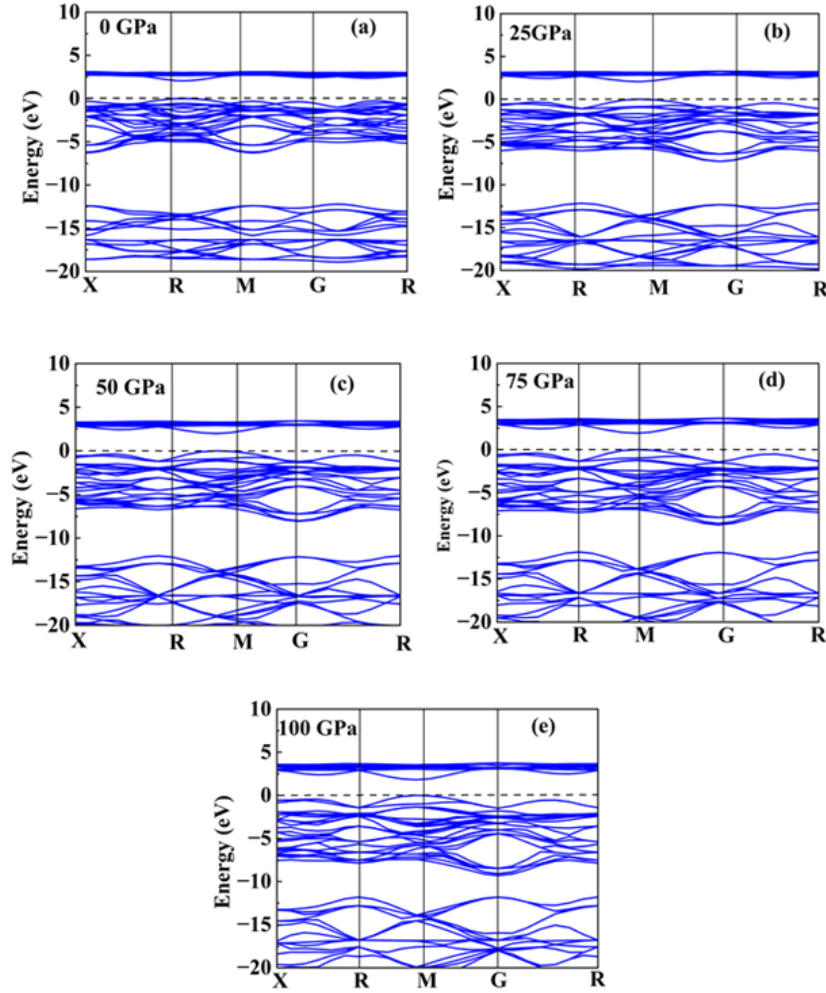


Figure 4: The band structure of  $\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$  under the applied pressures.

### 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  $\text{CeO}_2$  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  $\text{CeO}_2$  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.

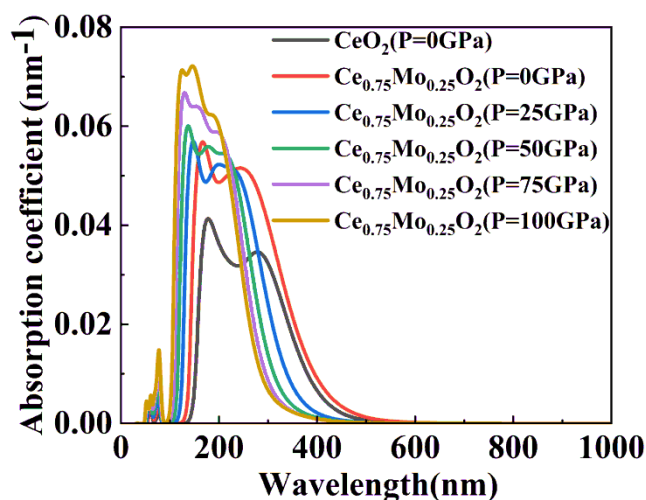


Figure 5: Pressure-dependent absorption coefficient spectra

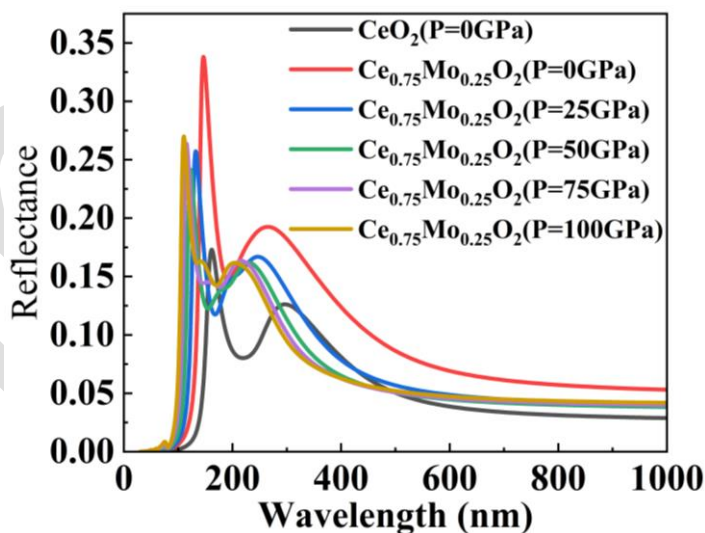


Figure 6: Pressure-dependent reflectance spectra.

Figure 6 shows the reflectance spectra of the studied systems. The results indicate prominent peaks for the pure and Mo-included CeO<sub>2</sub> 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 (CeO<sub>2</sub>) 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.

### 3.3.4. 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 CeO<sub>2</sub> 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 CeO<sub>2</sub> 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.

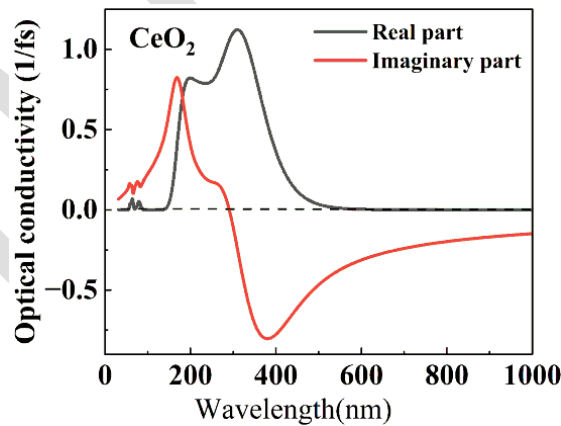


Figure 7: The optical conductivity of CeO<sub>2</sub> at 0 GPa.

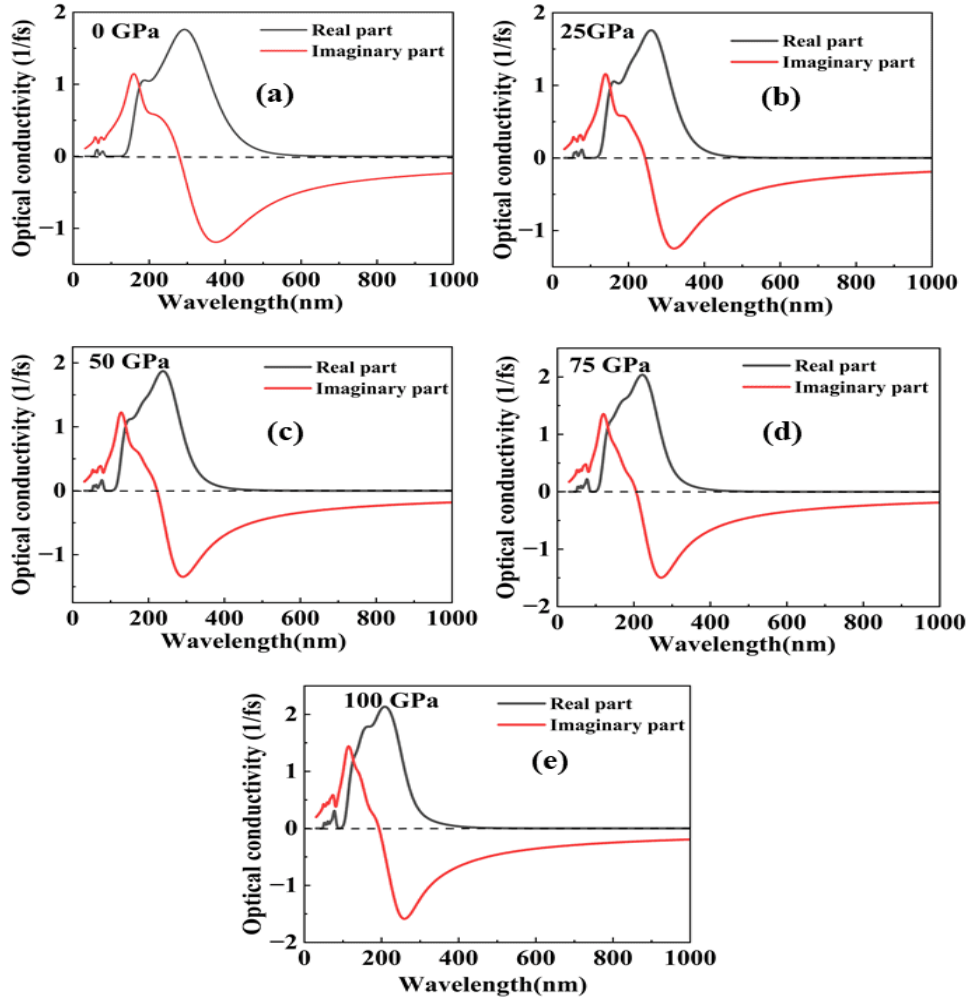


Figure 8: The pressure-dependent optical conductivity of  $\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$ .

As revealed in Figure 9, the energy loss spectra of the pristine  $\text{CeO}_2$  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.

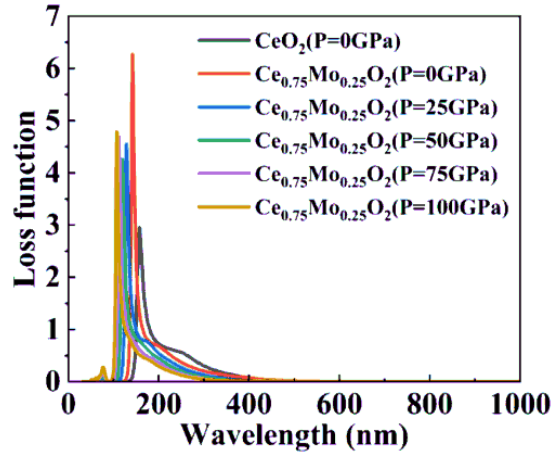


Figure 9: Pressure-dependent energy loss function of  $\text{CeO}_2$  and  $\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$ .

### 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  $\text{CeO}_2$ . 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].

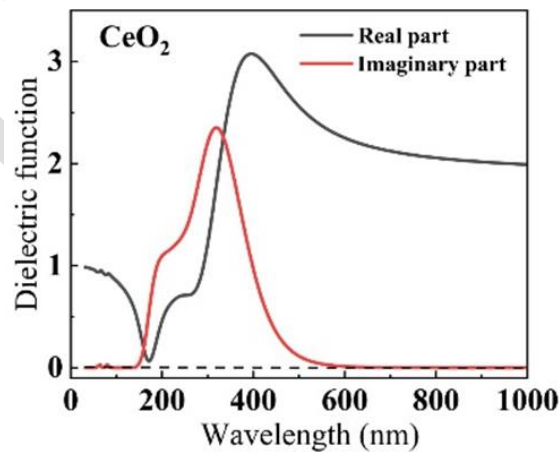


Figure 10: The calculated dielectric function of  $\text{CeO}_2$  at 0 GPa.

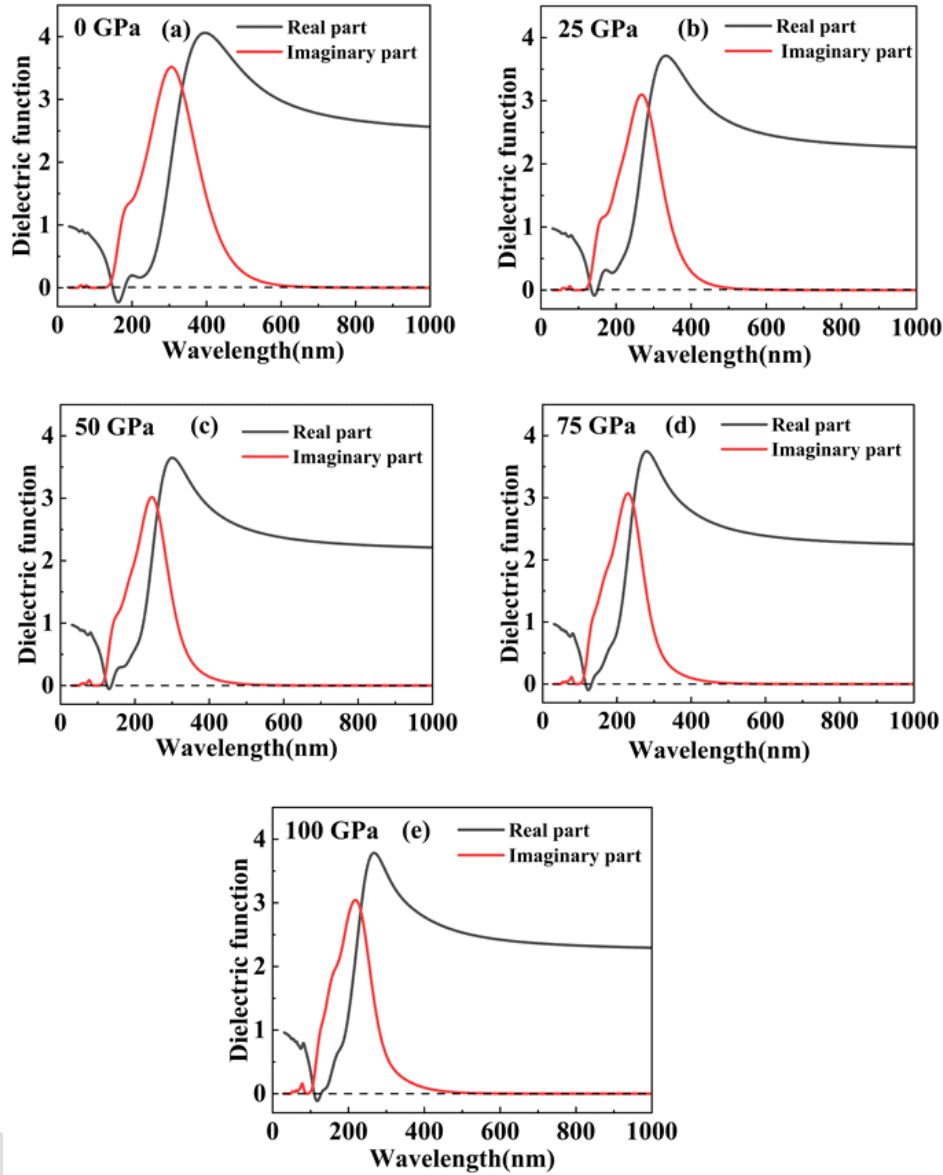


Figure 11: The calculated dielectric function of  $\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$  at varying pressures.

### 3.4 Complex refractive Index

It has been reported that  $\text{CeO}_2$  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  $\text{CeO}_2$  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  $\text{CeO}_2$  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.

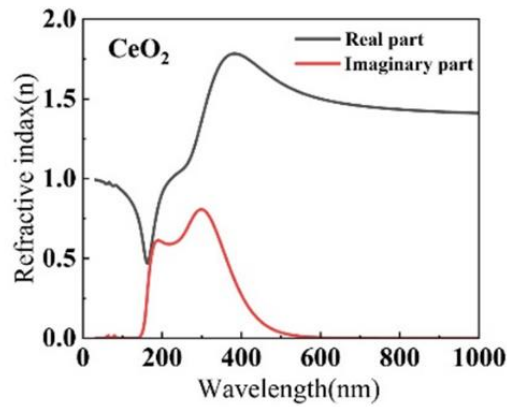


Figure 12: Complex refractive index of  $\text{CeO}_2$  at 0 GPa.

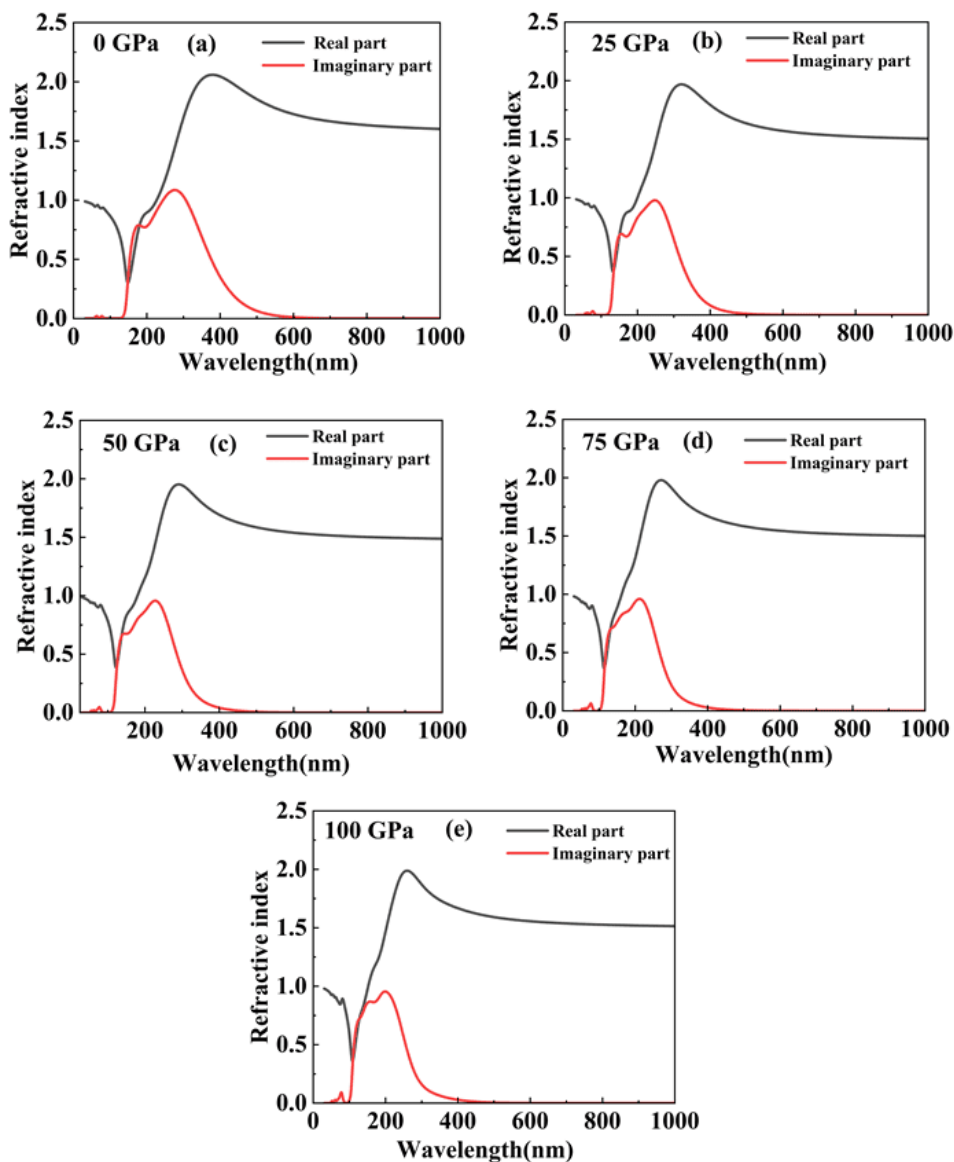


Figure 13: Complex refractive index of  $\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$  at different pressures.

### 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  $\text{CeO}_2$  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 CeO<sub>2</sub> 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 ( $\nu$ ). 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 ( $\mu_m$ ), 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  $\text{CeO}_2$  and  $\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$ . Elastic stiffness constants  $C_{ij}$  (GPa), Bulk modulus  $B$  (GPa), Shear modulus  $G$  (GPa), Young's modulus  $E$  (GPa), Poisson's ratio  $\nu$ , machinability index  $\mu_m$ , and Vicker's hardness  $H_v$ .

Crystal structures	$C_{11}$	$C_{12}$	$C_{44}$	$B$	$G$	$E$	$\nu$	$\mu_m$	$H_v$
$\text{CeO}_2$ (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]
$\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$ (0GPa)	363.233	106.972	65.394	192.392	85.905	224.327	0.305	3.433	9.378
$\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$ (25GPa)	472.759	186.429	92.552	281.872	110.296	292.711	0.326	2.942	9.256
$\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$ (50GPa)	595.386	268.671	93.660	377.576	117.236	318.722	0.359	3.045	8.711
$\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$ (75GPa)	642.058	352.159	113.108	448.792	124.924	342.952	0.372	4.031	8.295
$\text{Ce}_{0.75}\text{Mo}_{0.25}\text{O}_2$ (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 <sub>2</sub> (0GPa)	0.467 [37]	0.005	2.402	46 [37]
Ce <sub>0.75</sub> Mo <sub>0.25</sub> O <sub>2</sub> (0GPa)	0.510	0.0051	2.239	41.577
Ce <sub>0.75</sub> Mo <sub>0.25</sub> O <sub>2</sub> (25GPa)	0.646	0.003	2.555	93.876
Ce <sub>0.75</sub> Mo <sub>0.25</sub> O <sub>2</sub> (50GPa)	0.573	0.002	3.220	175.010
Ce <sub>0.75</sub> Mo <sub>0.25</sub> O <sub>2</sub> (75GPa)	0.780	0.0022	3.592	239.051
Ce <sub>0.75</sub> Mo <sub>0.25</sub> O <sub>2</sub> (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 CeO<sub>2</sub> and Ce<sub>0.75</sub>Mo<sub>0.25</sub>O<sub>2</sub> under pressures by means of Density Functional Theory (DFT). At 0 GPa, the band gap energy decreased from 3.134 eV of the pristine CeO<sub>2</sub> to 2.045 eV of Ce<sub>0.75</sub>Mo<sub>0.25</sub>O<sub>2</sub>. With increasing hydrostatic pressures, the band gap of Ce<sub>0.75</sub>Mo<sub>0.25</sub>O<sub>2</sub> 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 CeO<sub>2</sub>, 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 CeO<sub>2</sub> crystal.

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