

RESEARCH ARTICLE

Structural and elastic properties of Ce_2O_3 under pressure from LDA+ U method

Yuan-Yuan Qi, Zhen-Wei Niu, Cai Cheng, Yan Cheng[†]

Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China

E-mail: [†]ycheng@scu.edu.cn

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We investigate the structural and elastic properties of hexagonal Ce_2O_3 under pressure using LDA+ U scheme in the frame of density functional theory (DFT). The obtained lattice constants and bulk modulus agree well with the available experimental and other theoretical data. The pressure dependences of normalized lattice parameters a/a_0 and c/c_0 , ratio c/a , and normalized primitive volume V/V_0 of Ce_2O_3 are obtained. Moreover, the pressure dependences of elastic properties and three anisotropies of elastic waves of Ce_2O_3 are investigated for the first time. We find that the negative value of C_{44} is indicative of the structural instability of the hexagonal structure Ce_2O_3 at zero temperature and 30 GPa. Finally, the density of states (DOS) of Ce_2O_3 under pressure is investigated.

Keywords elastic properties, high pressure, density functional theory, Ce_2O_3

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1 Introduction

Cerium oxides are important materials with remarkable properties applied in a number of technological products [1, 2]. They are not only high-yield fission products but also substitutes of plutonium in nuclear fuels research [3]. Because of the ability to store, release and transport oxygen ions, ceria is not only the support but also one of the active participants in some reactions, such as low-temperature CO and volatile organic compounds (VOC) oxidation catalysts [4]. In addition, ceria is also an available material of microelectronics applications [5]. Thus, it is necessary to obtain an accurate description of ceria materials in theory for understanding the nature and the effective applications, especially the elastic constants of cerium oxides are of primary interest in its future applications.

It is known that the elastic constants provide valuable information about the bonding characteristic between adjacent atomic planes and the anisotropic character of the bonding and structural stability. They are directly linked to the various fundamental solid-state quantities,

such as the bulk, shear, and Young's moduli, and so on. It is also an easy method to estimate the Debye temperature by using the average sound velocities, which can be calculated from the elastic constants [6]. However, to our knowledge, there are few theoretical reports about the elastic properties of Ce_2O_3 owing to the fact that the standard local density approximation (LDA) and generalized gradient approximation (GGA) approaches would be unable to yield a certain description for the localized $4f$ states in Ce_2O_3 .

In principle, the Ce^{3+} still remains a $4f$ valence electron, which results in inaccurate prediction of many properties of the related material with the conventional LDA and GGA approaches. For example, such approaches predict a metallic ground state of Ce_2O_3 compared to the experimental, an insulating ground state with a band gap about 2.4 eV [7, 8]. Hence, several corrections have been added to band theory to solve the problem, such as the density functional theory (DFT) plus Hubbard corrections (DFT+ U) method [9–12], dynamical mean-field theory (DMFT) [13, 14], GW quasiparticle method [15], and hybrid density-functional theory (HSE) [4, 16–18]. By using these methods, one can

obtain correct prediction for the ground state of Ce_2O_3 , which makes it possible to continue a further theoretical study of the structural and electronic properties of Ce_2O_3 under high pressure. This is meaningful for geodynamics, astrophysics, and related sciences.

Since the elastic constants provide valuable information about the bonding characteristic between adjacent atomic planes and the anisotropic character of the bonding and structural stability of Ce_2O_3 under high pressure, in this work we perform a systematic study of the elastic properties of Ce_2O_3 under pressure within the LDA+ U method through the Cambridge Serial Total Energy Package (CASTEP) program [19, 20]. This paper is organized as follows: the details of the methods used to perform the calculations are discussed in Section 2. The results and some discussion are presented in Section 3. A conclusion of our main findings is given in Section 4.

2 Theoretical method and computation details

2.1 Total energy electronic structure calculations

We employ on-the-fly (OTF) pseudopotential for the interactions of the electrons with the ion cores, together with the local density approximation (LDA) proposed by Vosko *et al.* [21] for the exchange-correlation potential. The LDA have been used in the LDA+ U variant, in which the orbital-dependent LDA+ U functional form is given as

$$E_{\text{LDA}+U} = E_{\text{LDA}} + \frac{U - J}{2} \sum_{\sigma} [\text{Tr}(\rho^{\sigma}) - \text{Tr}(\rho^{\sigma} \rho^{\sigma})] \quad (1)$$

where ρ^{σ} is the density matrix of f states, U is the Coulomb energy, and J is the exchange energy. In this approach, the Coulomb parameter, U , and exchange parameter, J , do not enter separately, but combine into a single meaningful parameter $U(U_{\text{eff}} = U - J)$. In this work, we also use the $U = 6$ eV for Ce in Ce_2O_3 , which is reasonable value taken from Refs. [10, 14].

The electronic wave functions are expanded in a plane wave basis set with energy cut-off of 620 eV. The atomic levels $4f^{15}5s^25p^65d^16s^2$ of Ce atom, and $2s^22p^4$ of O atom were treated as valence electron states. For the Brillouin-zone sampling, we use the $4 \times 4 \times 2$ Monkhorst-Pack mesh [22]. The self-consistent convergence of the total energy is 1.0×10^{-6} eV/Atom, the maximum ionic Hellmann-Feynman force within 0.01 eV/Å, the maximum ionic displacement within 1.0×10^{-4} Å, and the maximum stress within 0.02 GPa. These parameters are carefully tested. It is found that these parameters are sufficient to lead to a well-converged total energy.

2.2 Elastic properties

To calculate the elastic constants, we use the symmetry-dependent strains that are non-volume conserving. The elastic constants, C_{ijkl} , with respect to the finite strain variables is defined as [23]

$$C_{ijkl} = \left(\frac{\partial \sigma_{ij}(x)}{\partial e_{kl}} \right)_X \quad (2)$$

where σ_{ij} and e_{kl} are the applied stress and Eulerian strain tensors, X and x are the coordinates before and after deformation, respectively. For the hexagonal structure Ce_2O_3 (with space group $P\bar{3}m1$), there are five independent elastic constants, i.e., C_{11} , C_{12} , C_{13} , C_{33} , and C_{44} .

The theoretical polycrystalline elastic modulus can be determined from the independent elastic constants above. There are two approximation methods to calculate the polycrystalline modulus, namely the Voigt method [24] and the Reuss method [25]. For the hexagonal structure Ce_2O_3 , the Voigt (B_V) and Reuss (B_R) bulk moduli and shear moduli are given by

$$B_V = \frac{1}{9} [2(C_{11} + C_{12}) + C_{33} + 4C_{13}] \quad (3)$$

$$B_R = \frac{(C_{11} + C_{12})C_{33} - 2C_{13}^2}{C_{11} + C_{12} + 2C_{33} - 4C_{13}} \quad (4)$$

$$G_V = \frac{1}{30} (C_{11} + C_{12} + 2C_{33} - 4C_{13} + 12C_{44} + 12C_{66}) \quad (5)$$

$$G_R = \frac{5}{2} \frac{C^2 C_{44} C_{66}}{3B_V C_{44} C_{66} + C^2 (C_{44} + C_{66})} \quad (6)$$

where $C_{66} = (C_{11} - C_{12})/2$, and $C^2 = (C_{11} + C_{12})C_{33} - 2C_{13}^2$. The arithmetic average of the Voigt and the Reuss bounds is called the Voigt-Reuss-Hill (VRH) average and is commonly used to estimate elastic modulus of polycrystals. The VRH averages for shear modulus (G) and bulk modulus (B) are: $G = (G_R + G_V)/2$, $B = (B_R + B_V)/2$. The polycrystalline Young's modulus (E) and the Poisson's ratio (ν) are then calculated from these elastic constants using the following relations

$$E = \frac{9BG}{3B + G}, \quad \nu = \frac{3B - 2G}{2(3B + G)} \quad (7)$$

From the elastic constants, one can obtain the elastic Debye temperature (Θ), which may be estimated from the average sound velocity V_m by the following equation

$$\Theta = \frac{h}{k} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{1/3} V_m \quad (8)$$

where h is Planck's constant, k is Boltzmann's constant, N_A is Avogadro's number, n is the number of atoms in the molecule, M is the molecular weight, and ρ is the

density. The average wave velocity V_m is approximately calculated from

$$V_m = \left[\frac{1}{3} \left(\frac{2}{V_S^3} + \frac{1}{V_P^3} \right) \right]^{-1/3} \quad (9)$$

where V_P and V_S are the compressional and shear wave velocities, respectively, which are obtained from Navier's equation [26]

$$V_P = \sqrt{\left(B + \frac{4}{3}G \right) / \rho}, \quad V_S = \sqrt{G/\rho} \quad (10)$$

Through the method described above, one has investigated successfully the elastic properties of some materials [27–32].

3 Results and discussion

3.1 Structural properties

At ambient conditions, Ce_2O_3 stabilizes in the hexagonal phase (space group: $P\bar{3}m1$) with the lattice parameters $a=3.89$ Å and $c=6.06$ Å [33]. In Fig. 1, we illustrate the primitive unit cell crystal structure of the hexagonal Ce_2O_3 . In the unit cell, two Ce atoms are set at positions (0.3333, 0.6667, 0.2458; 0.6667, 0.3333, 0.7542), and three O atoms at positions (0, 0, 0; 0.3333, 0.6667, 0.6457; 0.6667, 0.3333, 0.3543). To obtain the most stable structure of Ce_2O_3 in the ground state, we performed the following procedures: firstly, for a fixed axial ratio c/a , we take a series of different values of a and c to calculate the total energies E and the corresponding primitive cell volumes V , and then obtain the lowest energy E_{min} for the given ratio c/a . This procedure is repeated over a wide range of c/a . Finally, by fitting the calculated energy–volume (E – V) data to the third-order Birch-Murnaghan equation of state (EOS) [34]

$$\Delta E(V) = E - E_0 = \frac{9V_0B_0}{16} \left\{ \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^3 B'_0 + \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^2 \left[6 - 4 \left(\frac{V_0}{V} \right)^{\frac{2}{3}} \right] \right\} \quad (11)$$

where E_0 is the equilibrium energy, V_0 is the equilibrium cell volume of Ce_2O_3 at 0 GPa and 0 K, and V is the cell volume corresponding to the applied pressure P at 0 K, we obtained the equilibrium parameters $a, c, c/a$, the bulk modulus B_0 and its pressure derivative B'_0 of Ce_2O_3 . In Table 1, we list our calculated lattice parameters a and c , bulk modulus B_0 and its pressure derivative B'_0 , and the insulating energy gap E_{Gap} of the hexagonal Ce_2O_3 at 0 GPa and 0 K, together with other theoretical results [10, 14, 15, 18] and the available experimental data [7, 8, 33].

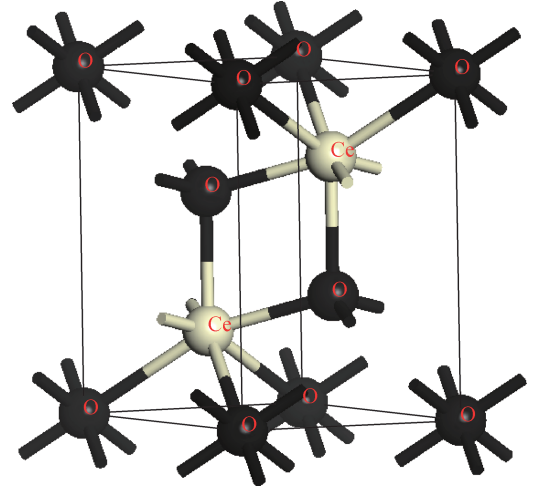


Fig. 1 The primitive unit cell of the hexagonal structure of Ce_2O_3 . Black and grey balls represent O and Ce atoms, respectively.

We find that our lattice parameters a and c from LDA+ U method are in better agreement with the experimental values [33] than those from LDA method, with the errors less than 0.26% and 0.5% for LDA+ U , respectively. It is seen that the LDA method cannot correctly describe the energy band gap of Ce_2O_3 . In addition, our calculations are somewhat better than the LDA+ U calculations of Andersson *et al.* [10] and Amadon [14]. The results of Da Silva *et al.* [18] showed that the hybrid density-functional theory (HSE) has nearly the same precision as LDA+ U and is better than the local density approximation plus dynamical mean-field theory

Table 1 The lattice parameters (a, c) (Å), bulk modulus B_0 (GPa) and its pressure derivative B'_0 , and the insulating gap E_{Gap} (eV) of Ce_2O_3 , together with the experimental data and other calculation results.

Methods	a	c	B_0	B'_0	E_{Gap}	References
LDA	3.77	5.83	162	4.56	0	Present work
LDA+ U (6 eV)	3.88	6.03	135	4.96	2.7	Present work
LDA+ U (6 eV)	3.87	5.98	130		2.6	Andersson <i>et al.</i> [10]
LDA+ U (6 eV)	3.85	6.01	150			Amadon [14]
HSE	3.87	6.08			2.5	Da Silva <i>et al.</i> [18]
LDA+DMFT	3.83		160			Amadon [14]
G_0W_0 @LDA+ U (5.4 eV)					1.8	Jiang <i>et al.</i> [15]
Exp.	3.89	6.06	111		2.4	[7, 8, 33]

(LDA+DMFT) method. The zero pressure bulk modulus B_0 obtained from our LDA+ U calculation has a higher value 135 GPa compared with the experimental value 111 GPa, but is consistent with the values of Andersson *et al.* [10] and Amadon [14]. In addition, the obtained insulating energy gap (2.7 eV) agrees with the experimental value (2.4 eV) [7, 8] and those of Andersson *et al.* (2.6 eV) [10] and Da Silva *et al.* (2.5 eV) [18]. The values are larger than that of Jiang *et al.* (about 1.8 eV) [15] with the GW approach, in which the GW calculations are based on LDA ground state calculations including a Hubbard U correction (denoted as $G_0W_0@LDA + U$).

In Fig. 2, we illustrate the pressure dependences of the normalized lattice parameters a/a_0 and c/c_0 , the lattice ratio c/a , and the normalized primitive cell volume V/V_0 of Ce_2O_3 , where a_0 , c_0 and V_0 are the zero pressure equilibrium structure parameters. As the applied pressure increases from 0 to 25 GPa, the ratio c/a changes from 1.554 to 1.418, and the normalized volume V/V_0 changes from 1.000 at zero pressure to 0.860 at 25 GPa. Also, it is noted that as the applied pressure increases from 0 to 25 GPa, the ratio c/c_0 decreases linearly and the change is about 10.5%, while the change of a/a_0 is not more than 1.9%, indicating that the compression along c -axis is larger. The compression of V of Ce_2O_3 under pressure is mainly owing to the compression along the c -axis.

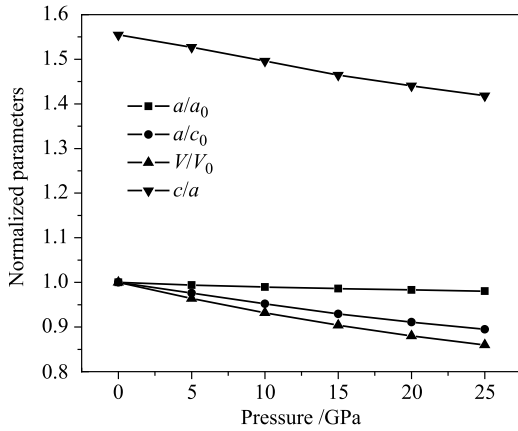


Fig. 2 The normalized parameters a/a_0 , c/c_0 , c/a and V/V_0 of Ce_2O_3 at $T=0$ K as a function of pressure P .

3.2 Elastic properties

The calculated pressure dependences of the elastic constants of Ce_2O_3 at 0 K are presented in Table 2. Unfortunately, no experimental and other theoretical data of elastic constants are available for our comparison. It is shown that the five elastic constants increase with the applied pressure. As the elastic constants C_{11} and C_{33} are related to the deformation behavior and atomic bonding characteristics of Ce_2O_3 , they can be used to judge the

atomic bond strength in different plane. In our calculations, the elastic constant C_{11} is greater than the elastic constant C_{33} at the applied pressure, implying that the atomic bonds along the $\{100\}$ planes between nearest neighbors are stronger than those along the $\{001\}$ plane. It is noted that when the applied pressure equals to 30 GPa, the elastic constant C_{44} is lower than zero and other elastic constants have big discrepancies compared to the elastic constants at 25 GPa. According to the mechanical stability conditions of a hexagonal crystal [35]

$$\begin{aligned} C_{44} - P > 0, \quad C_{11} - P > |C_{12} + P| \\ (C_{11} + C_{12})(C_{33} - P) > 2(C_{13} + P)^2 \end{aligned} \quad (12)$$

where P is the applied pressure. We can judge that Ce_2O_3 is unstable at the pressure of 25–30 GPa.

Table 2 The calculated elastic modulus (GPa), bulk modulus B (GPa), shear modulus G (GPa), B/G , Young's modulus E (GPa), Poisson's ratio ν , and Debye temperature θ (K) of Ce_2O_3 under pressure (GPa) at 0 K.

P	0	5	10	15	20	25	30
C_{11}	198.5	230.9	247.8	272.5	293.5	316.5	462.0
C_{33}	119.0	140.1	143.9	160.2	172.5	180.5	198.0
C_{44}	62.7	74.3	82.9	89.6	95.7	101.7	-163.8
C_{12}	99.4	130.9	135.8	152.2	176.5	187.5	120.8
C_{13}	78.0	90.8	114.8	123.8	133.4	166.2	302.7
B	109.0	129.5	144.1	158.4	172.3	192.2	289.3
G	50.8	57.0	58.6	64.4	67.1	65.9	-99.5
B/G	2.15	2.27	2.46	2.46	2.57	2.92	-2.91
E	131.9	149.2	154.9	170.2	178.1	177.4	-337.2
ν	0.30	0.31	0.32	0.32	0.33	0.35	0.69
θ	359.2	364.2	396.4	404.8	402.5	456.1	-

From the elastic constants, we can obtain the bulk modulus B and shear modulus G according to the Voigt–Reuss–Hill (VRH) average scheme. The aggregate elastic modulus B , shear modulus G , B/G , Young's modulus E , and Poisson's ratio ν are also presented in Table 2. Pugh [36] indicated that a material is brittle if the B/G ratio is less than 1.75. From Table 2, it is shown that the obtained B/G ratio of Ce_2O_3 increases from 2.15 to 2.92 as the applied pressure is added from 0 to 25 GPa, and then changes to -2.91 when the pressure is up to 30 GPa, which implies the structure of Ce_2O_3 becomes more and more ductile with the increase of pressure and unstable at 30 GPa. It can also be seen that the obtained Young's modulus E and Poisson's Ratio ν have small but continuous increase with the increasing pressure from 0 to 25 GPa. Strangely, there have some abnormal phenomena when the pressure increases to 30 GPa (E becomes a negative value and ν has an abrupt big increase). These suggest that the pressure has a small effect on the Poisson's ratio and Young's modulus from 0 to 25 GPa but a remarkable impact during 25 and 30 GPa.

The Debye temperature Θ is an important parameter related to many physical properties of solids, such as specific heat, elastic constants, and melting temperature. From the calculated Debye temperature in Table 2, we can clearly see that the Debye temperatures increase with the increasing pressure, and especially, the variation is more than 90 K in the pressure range of 10 to 25 GPa, which means the pressure is the main factor to Debye temperature in the pressure range of 10 to 25 GPa. We can not obtain the Debye temperature at 30 GPa because of the negative value of the yielded G at 30 GPa. In addition, the obtained Debye temperature of Ce_2O_3 at 0 GPa is 359.2 K.

It is known that the acoustic velocities are related to the elastic constants by the Christoffel equation [37]

$$(C_{ijkl}n_jn_k - M\delta_{il})u_i = 0 \quad (13)$$

where C_{ijkl} is the fourth rank tensor description of elastic constants, n is the propagation direction, ρ is the density, u the polarization vector, $M = \rho v^2$ is the modulus of propagation and v the velocity. The acoustic anisotropy can be described as [38]

$$\Delta_i = \frac{M_i[n_x]}{M_i[100]} \quad (14)$$

where n_x is the extremal propagation direction other than [100] and i is the three types of elastic wave index (one longitudinal and two polarizations of the shear wave). By solving Eq. (13) for Ce_2O_3 , one can obtain the anisotropy of the compression wave (P)

$$\Delta_P = \frac{C_{33}}{C_{11}} \quad (15)$$

The anisotropies of the wave polarized perpendicular to the basal plane ($S1$) and the polarized one in the basal plane ($S2$) are written as

$$\Delta_{S1} = \frac{C_{11} + C_{33} - 2C_{13}}{4C_{44}}, \quad \Delta_{S2} = \frac{2C_{44}}{C_{11} - C_{12}} \quad (16)$$

While for $S2$ and P waves the extremum occurs along the c axis, for $S1$ it is at an angle of 45° from the c axis in the a - c plane. Depending on the values of the elastic constants, we note that an additional extremum may occur for the compression wave propagation at intermediate directions.

In Fig. 3, we illustrate the calculated pressure dependencies of the anisotropies of the elastic waves (Δ_P , Δ_{S1} , and Δ_{S2}). It is found that Δ_P almost equals to a constant 0.6 and Δ_{S1} descends slightly, while Δ_{S2} ascends in the range of the applied pressures. These results can be understood in comparison to a hexagonal crystal interacting with central nearest-neighbor forces (CNNF) [39]. For this model the elastic anisotropy is independent of

the interatomic potential to lowest order in P/C_{11} , hence the anisotropy is only dependent on the symmetry of the crystal. We also noted that the values of Δ_{S1} and Δ_{S2} go away from 1.0, which means that the anisotropies of the wave polarized perpendicular to the basal plane ($S1$) and the wave polarized in the basal plane ($S2$) become strong with the increasing pressure. These results indicate that the axial ratio c/a decreases with the increasing pressure, which agrees well with our foregoing work.

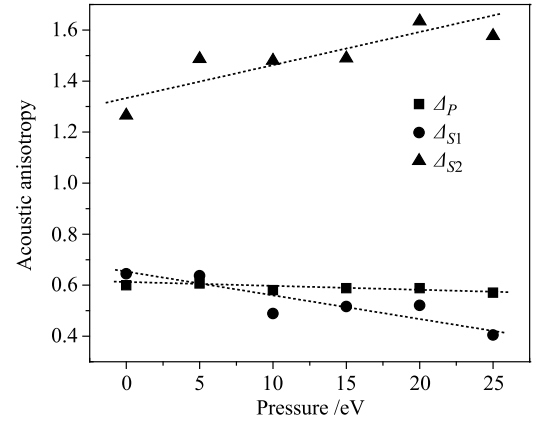


Fig. 3 Calculated anisotropies [Δ_P (compressional wave), Δ_{S1} and Δ_{S2} (shear waves)] of Ce_2O_3 as a function of pressure P .

3.3 The density of states of Ce_2O_3 under pressure

To understand the nature of the electronic structure of Ce_2O_3 under pressure, we have calculated the total density of states (TDOS) of Ce_2O_3 at 0, 20, and 30 GPa, which are shown in Fig. 4. At 0 GPa, an insulating gap of about 2.72 eV is obtained due to the splitting of $4f$ band, which is in good agreement with the experimental optical band gap of 2.4 eV [7, 8]. It is found from Fig. 4 that the unoccupied conduction bands of Ce- $4f$ and Ce- $5d$ and the valence band of O- $2p$ are pushed down to low energy region with the increase of pressure. However, the occupied valence band of Ce- $4f$ stays in the

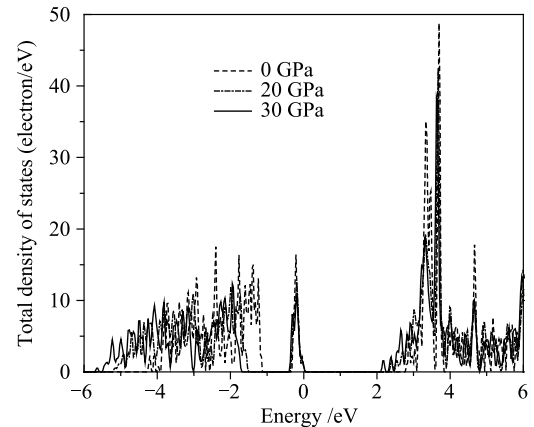


Fig. 4 Pressure dependencies of the total density of states (TDOS) of Ce_2O_3 at 0 K from LDA+ U method with $U=6$ eV.

highest occupied states and unchanged with the increase of pressure. Therefore, the insulating band gap decreases with the applied pressures, which means that Ce_2O_3 may transform into a metal phase.

In Fig. 5, we illustrate the partial density of states (PDOS) of Ce_2O_3 at 0, 20, and 30 GPa. It is found that the valence band mainly comes from the O-2p states, which will move to low energy region with the increase of pressure. The highest occupied valence band is mainly due to the occupied Ce-4f states. Then, the conduction band mainly comes from the Ce-4f and Ce-5d states and it will also move to low energy region with the increase of pressure. It is noted that, though the band decreases to low energy region, the intensities of them only suffer little impact from the pressure. All of these features agree well with our foregoing discussion about the total density of states (TDOS).

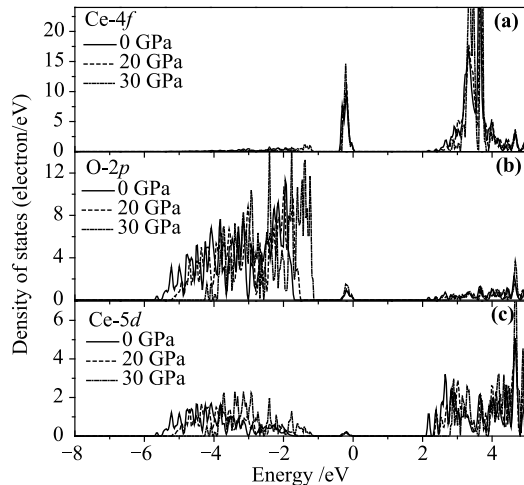


Fig. 5 The partial density of states (PDOS) of Ce_2O_3 under pressure from LDA+ U method with $U=6$ eV for: (a) Ce-4f, (b) O-2p, and (c) Ce-5d.

4 Conclusions

We have investigated the elastic properties of Ce_2O_3 under high pressure by using local-density approximation (LDA)+ U correction scheme in the frame of density functional theory (DFT) with on-the-fly (OTF) pseudopotential. The lattice constants, bulk modulus obtained here are in good agreement with the available experimental and other theoretical data. The pressure dependences of the normalized lattice parameters a/a_0 and c/c_0 , the ratio c/a , and the normalized primitive volume V/V_0 of Ce_2O_3 are obtained, which indicate that the compression of V is mainly due to the compression of c -axis. The pressure dependences of elastic properties of Ce_2O_3 are investigated for the first time. As pressure increases the elastic constants C_{11} , C_{33} , C_{12} and C_{13}

increase linearly, while the variation of elastic constant C_{44} is not obvious. At 30 GPa, the hexagonal structure Ce_2O_3 is instable at zero temperature due to the elastic constant C_{44} of less than zero. Moreover, the pressure dependences of three anisotropies of elastic waves are also predicted and the Debye temperature $\Theta=359.2$ K is obtained at 0 GPa. Finally, from the investigation of the density of states (DOS) of Ce_2O_3 under pressure, the insulating band gap decreases with the applied pressures and this means that Ce_2O_3 may transform into a metal phase with the increase of pressure.

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