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A DFT study of the structural, electronic and optical properties of transition metal doped fluorite oxides: $\text{Ce}_{0.75}\text{M}_{0.25}\text{O}_2$ (M=Fe, Co, Ni)

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ABSTRACT

The structural, electronic and optical properties of $\text{Ce}_{1-x}\text{M}_x\text{O}_2$ (M=Fe, Co, Ni; $x=0, 0.25$) fluorite type oxides are studied by using the method of density functional theory (DFT) + U method. The calculated equilibrium lattice parameter, cell volume, bulk modulus and optical properties for CeO_2 are in good agreement with the available experimental data and other theoretical results. The lattice parameter, cell volume, bulk modulus and bond length of Ce–O decreased after substituting Ce atom with Fe (or Co, Ni). Meanwhile, the band-gap (E_g) reduction is observed. It is interesting to find that doping of Fe (or Co, Ni) in CeO_2 obviously decreases the O 2p–Ce 4f transition intensity and the covalent character of the Ce–O bond. On the contrary, the static dielectric constant ϵ_0 and refractive index n_0 for the doped system increased. Compared with the undoped CeO_2 , the doped system has steep absorption peaks ranging from 1.0 eV to 2.0 eV at lower energy, and it can be used for visible light absorption applications. The $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$ has a high refractive index and reflectivity, therefore it is suitable as a high-refractive index film material in single and multilayered optical coatings.

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1. Introduction

Ceria (CeO_2) is of great interest in the modern catalytic industry [1–3] due to a wide variety of applications in three-way catalysts (TWCs), high oxygen storage capacity (OSC) and solid oxide fuel cells (SOFCs) [4–6]. The facility of formation and transportation of oxygen vacancies in CeO_2 is responsible for these technological applications [7].

Although CeO_2 has long been utilized as a material for oxygen storage [4–7], it is also found that CeO_2 is of potential interest as optical component materials and laser hosts [8]. CeO_2 has been considered as a useful high-refractive index film material in single and multilayered optical coatings [9,10]. It can absorb UV efficiently, and it is also used as an additive for glass (2–4% CeO_2) to protect light-sensitive materials [11]. It is reported that cubic CeO_2 has been proposed as a potential substitute for TiO_2 [12–14]. Veszelei et al. [15] thought that CeO_2 had a high absorption, when the wavelength was $\lambda < 400$ nm, it was more superior to TiO_2 .

Miyauchi et al. [16] thought that ceria exhibited a much lower photocatalytic activity, hence limited the formation of reactive oxygen species, thus reducing the degradation of the medium containing the UV absorber particles, in contrast to rutile TiO_2 .

Over the past few years, the optical properties of CeO_2 have been the focus of intensive research [13,17–21]. Goubin et al. [13] mentioned that ceria has a band gap of 3.2 eV, a high UV absorption and a refractive index of 2.35. Niwano et al. [21] have measured the optical reflectance spectra of CeO_2 in the photon energy ranging from 2.5 to 40 eV, and obtained the dielectric and the related functions. It is interesting to find that transition metal has a characteristic lower ionic radius and strong valence. Meanwhile, transition metal has a d electronic structure that is similar to the noble metal. So the transition metal is the ideal modified element which is widely used in the modern catalytic industry to improve the performance of metal oxide [22–34]. For example, Park et al. [23] have studied that substitutional doping of Fe (or Co, Ni, Mn) in TiO_2 , which has a profound effect on the electronic and magnetic properties. They got the conclusion that doping of Fe (or Co, Ni) in TiO_2 led to the band gap reduction, Ni-doped TiO_2 has the paramagnetic ground state, and Co-doped TiO_2 has the anti-ferromagnetic ground state. Whereas, Fe-doped system has the magnetic ground states with local magnetic moments. Anghel

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et al. [24] have investigated transition metal ($M = \text{Cr, Mn, Fe, Co, or Ni}$) doped ZnO and compared the effects that doping with different transition metal ions had on the structural and optical properties, and got profound effect on electronic and optical properties. Kim et al. [25] calculated the optical absorption of transition metal Pr-doped Ceria, and got the conclusion that the formation of the Pr impurity band within the optical band gap of ceria induced broad absorption at 2.0–3.3 eV in the visible spectrum, resulting in a red/orange coloration. There are some experiments showing that the transition metal (Fe, Co or Ni etc) doped CeO_2 has changed or improved the properties of material, and both the electronic structure and optical properties of CeO_2 and $\text{CeO}_2\text{-M}$ have attracted the attention of researchers [26–34]. For instance, Li and Wang et al. [27–30] have used the coprecipitation method to prepare a series of $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ ($x = 0, 0.2, 0.4, 0.6, 0.8$, and 1) complex oxide catalysts in an experiment, and found that cerium iron complex oxide ($\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$) had a high oxygen storage capacity, high redox stability and strong interaction between Ce and Fe species. Ranjith et al. [31] have investigated the optical properties of Co-doped CeO_2 in an experiment, and found that doping of Co ions in ceria increased the absorption edge towards higher wavelength, this made the absorption shift in the visible region. Wen et al. [32] have studied the effect of Fe doping CeO_2 on the dielectric constant, and the result showed that the doped system had a relatively large dielectric constant (ϵ_0). Bi et al. [33] have studied the structural, magnetic, and optical properties of $\text{Ce}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ ($x = 0, 0.02, 0.06, 0.15$, and 0.25) films in an experiment, and found that their refractive indices and extinction coefficients increased with Co concentration. Kumar et al. [34] have investigated the structural and magnetic properties of Ni doped CeO_2 nanoparticles in

an experiment, showing that the lattice parameters calculated by using Powder-X software, decreased from 5.41 to 5.40 Å with Ni doping. However, the structure and optical properties of transition metal (Fe, Co or Ni) doped CeO_2 have been less studied theoretically. These systems may induce a different electronic structure and optical properties which may lead to new applications, so it is time to investigate the structure and optical properties of these systems. In order to provide more insights into the relationship between the transition metal doping CeO_2 structure and the related properties, we carried out first-principles calculations to investigate the structural, electronic and optical properties of CeO_2 and transition metal Fe (or Co, Ni) doped CeO_2 in this paper, based on density functional theory (DFT) + U method within the generalized gradient approximation (GGA).

2. Model and computational details

CeO_2 has a face-centered cubic structure of space group $Fm-3m$ (number 225 in the international tables) [35], it is a rare earth oxide with a fluorite-type compound, wherein the Ce atoms are at the corner of the cube and are coordinated by eight equivalent nearest-neighbor oxygen atoms, while the O atoms are tetrahedrally coordinated by four Ce atoms [36,37] (Fig. 1(a)). For the doped systems ($\text{Ce}_{1-x}\text{M}_x\text{O}_2$ ($M = \text{Fe, Co, Ni}$)), the Fe (or Co, Ni) concentration is 25%, which results from substituting one Ce atom with one Fe (or Co, Ni) atom in a 12-atoms supercell. There is only one cation site in CeO_2 , and the symmetrical structure of CeO_2 itself, so substituting Ce atom with Fe (or Co, Ni) need not consider the site preference. This is in accordance with the report [31], and

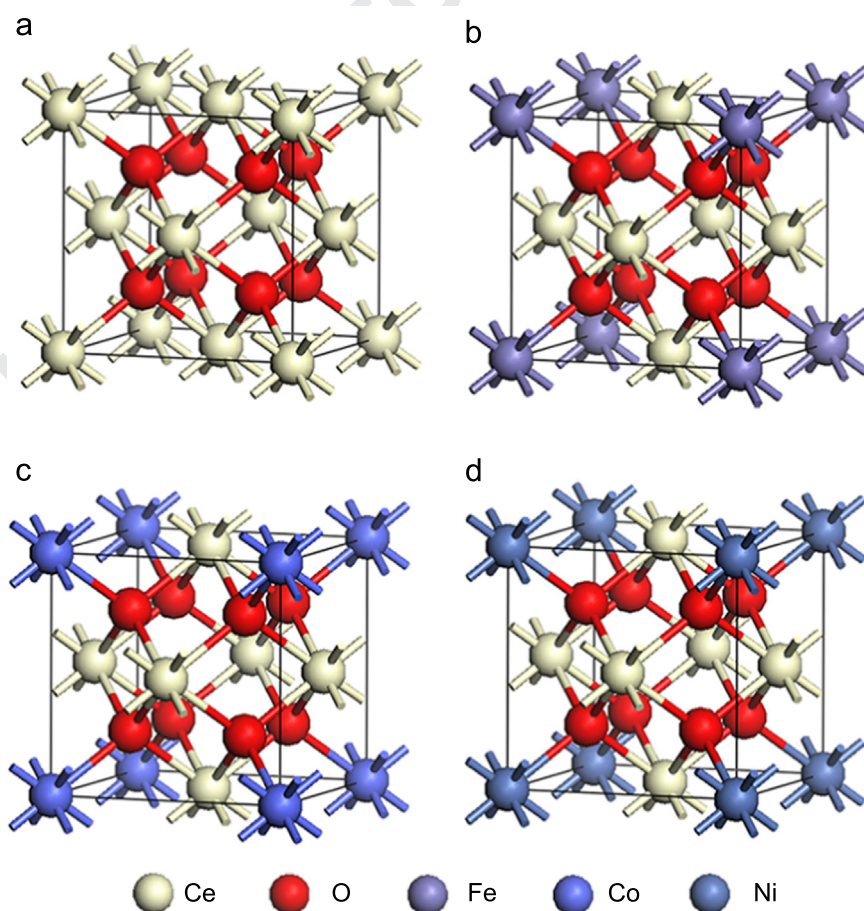


Fig. 1. (Color online) $\text{Ce}_{1-x}\text{M}_x\text{O}_2$ ($M = \text{Fe, Co, Ni}$; $x = 0, 0.25$) crystal structure: (a) CeO_2 structure, (b) $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_2$ structure, (c) $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$ structure, and (d) $\text{Ce}_{0.75}\text{Ni}_{0.25}\text{O}_2$ structure, respectively.

it shows that the Co-doped CeO₂ NPs are monodispersed with face centered cubic structure in an experiment. To study the lattice parameter, band structure, optical properties of Ce_{1-x}M_xO₂ (M=Fe, Co, Ni; x=0, 0.25), the 1 × 1 × 1 supercell with 12 atoms as an initial model (Fig. 1(b)–(d) represents Fe, Co, Ni doped ceria, respectively.) is adopted. We substituted Ce atom by Fe (or Co, Ni) atom to model substitutional Fe, Co or Ni neutral impurity in CeO₂, the resulting supercells are Ce_{0.75}Fe_{0.25}O₂ (Fig. 1(b)), Ce_{0.75}Co_{0.25}O₂ (Fig. 1(c)) and Ce_{0.75}Ni_{0.25}O₂ (Fig. 1(d)). The first-principles calculations are implemented in the Cambridge Serial Total Energy Package (CASTEP) program, based on the spin-polarized DFT (density functional theory) + U method [38], the GGA [39] is used along with ultrasoft pseudopotentials to represent the atoms. Specifically, for geometric optimization, the Perdew–Burke–Ernzerhof potential for solids (PBEsol) is used [40]. The PBEsol method combines the flexibility of the pseudo potential approach with the accuracy of all-electron methods, reproducing the exact valence wave function with all nodes in the core region. Here the cerium 5s, 5p, 5d, 4f, and 6s, iron 4s and 3d, cobalt 4s and 3d, nickel 4s and 3d and the oxygen 2s and 2p electrons are treated as valence electrons [41]. The gradient-corrected exchange and correlation functionals of the Perdew–Burke–Ernzerhof potential for solids (PBEsol) [40] with the Ce 4f and Fe, Co, Ni 3d states treated with on-site correction for Coulomb interaction (DFT+U) are also used in the calculations based on generalized gradient approximation (GGA) [39,42,43]. Here, we choose 5.0 eV [42,44] and 4.0 eV [45,46] for the U term to describe Ce 4f and Fe, Co, Ni 3d states, respectively. The plane-wave basis set cutoff energy is 500 eV [47]. The convergence tolerance of energy charge, maximum force and stress are 5 × 10⁻⁶ eV, 0.01 eV/nm and 0.02 GPa, respectively [48,49]. Geometry optimization of the initial model in each case is optimized to minimize the total energy using the Broyden, Fletcher, Goldfarb, Shanno (BFGS) method [50]. The Brillouin zones integration is performed by using 4 × 4 × 4 Monkst-Pack grid [47] for the geometry optimization, electronic structure and optical property calculation of the Ce_{1-x}M_xO₂ (M=Fe, Co, Ni; x=0, 0.25).

3. Results and discussion

3.1. Structure stability, population analysis and electronic properties

To obtain the stable structure of Ce_{1-x}M_xO₂ (M=Fe, Co, Ni; x=0, 0.25), the internal coordinates and the lattice parameters are relaxed during geometry optimization process. The calculated lattice constants, cell volume, bulk modulus, charge and bond order are listed in Tables 1 and 2. From Table 1, the calculated results for bulk CeO₂ show that the method from model and computational details (Part two) gives a good description of the bulk CeO₂. The calculated equilibrium lattice parameter, cell volume and bulk modulus are 5.366 Å, 154.546 (Å³), and 213.7 GPa in LDA, 5.423 Å, 159.520 (Å³), 193.5 GPa in GGA, respectively. They are all in agreement with the experimental values of the lattice constant [51], cell volume and bulk modulus [52,53], and also in good agreement with other calculations [3,54–56]. Compared with the experimental data and values from other calculations in Table 1, the lattice constant *a*₀ of CeO₂ is larger than the experimental and other calculated values with less than 2% deviation in GGA. Simultaneously, from Table 1, we can obviously know that the lattice constant *a*₀ decreases when Fe, Co or Ni doped ceria for the structure of Ce_{1-x}M_xO₂ (M=Fe, Co, Ni; x=0.25), as asserted by the experiments [30–33]. This is due to the difference in covalent radii of Fe³⁺, Co³⁺ and Ni³⁺ in comparison with Ce⁴⁺: *R*_{Fe³⁺} = 0.645 Å [32], *R*_{Co³⁺} = 0.545 Å, *R*_{Ni³⁺} = 0.56 Å and *R*_{Ce⁴⁺} = 0.97 Å

Table 1

Calculation of the structure parameters, cell volume and bulk modulus for four structures, experimental measurement and other available theoretical data.

Structure	<i>a</i> ₀ (Å)	Cell volume (Å ³)	B (GPa)
CeO ₂	5.423 ^a , 5.480 ^b , 5.410 ^c , 5.366 ^d , 5.390 ^h , 5.370 ⁱ	159.520 ^a , 158.340 ^b 154.546 ^e	193.500 ^a , 187.700 ^b 213.700 ^c , 214.700 ^g , 201.000 ⁱ
Ce _{0.75} Fe _{0.25} O ₂	5.250	144.774	174.154
Ce _{0.75} Co _{0.25} O ₂	5.278	147.118	165.703
Ce _{0.75} Ni _{0.25} O ₂	5.304	149.215	149.767

^a Present work in GGA.

^b From Ref. [54] in GGA.

^c From Ref. [51].

^d Present work in LDA.

^e Present work in LDA.

^f Present work in LDA.

^g From Ref. [54] in LDA.

^h From Ref. [54] in LDA.

ⁱ From Ref. [55] in LDA.

[32]. The bond distances of *d*_{Ce–O} decreased after substituting Ce atom with Fe (or Co or Ni). For the structure of Ce_{1-x}M_xO₂ (M=Fe, Co, Ni; x=0, 0.25), the Ce_{0.75}Ni_{0.25}O₂ has the maximum bond distance of *d*_{Ce–O}, it is 2.323 Å, which is smaller than that of the experimental values of CeO₂, listed in Table 2. This reflects that the strength of chemical bond for CeO₂ is stronger than the structure of Ce_{1-x}M_xO₂ (M=Fe, Co, Ni; x=0.25). From Table 1, we can also know that the cell volume and bulk modulus decreased after Fe (or Co or Ni) doped ceria for the structure of Ce_{1-x}M_xO₂ (M=Fe, Co, Ni; x=0.25). This is probably the reason for the differences in covalent radii of Fe³⁺, Co³⁺ and Ni³⁺ in comparison with Ce⁴⁺, which leads to the lattice distortion of Fe (or Co or Ni) doped CeO₂.

The results of population analysis (Table 2) shows the charge density redistributions after substituting Ce atom with Fe (or Co, Ni) atom in CeO₂. This is due to the electron exchange. For example, it is clear to find that substitutional doping of Fe (or Co, Ni) has changed the Mulliken charge of O and Ce atoms, and the charge of O and the charge of Ce are increased for the structure of Ce_{1-x}M_xO₂ (M=Fe, Co, Ni; x=0.25). The bond order is a measure of the strength of the bond, which occurs between a pair of atoms. This can be calculated from the overlap integrals between the Bloch functions with an atomic basis expansion [14,57]. By multiplying the individual bond order by the number of bonds per molecular unit, we can calculate the total bond order for a crystal. In Table 2, it is interesting to find that doping of Fe (or Co, Ni) with CeO₂ has changed the Mulliken bond order of Ce–O same, and the bond lengths change little, because doping of Fe (or Co, Ni) with CeO₂ does not change its fluorite-type structure. On the contrary, for Fe–O, the Mulliken bond order is ~0.22 (bond length = 2.141 Å), which is slightly higher than Ce–O ~0.21 (2.321 Å). For Co–O and Ni–O, the Mulliken bond order are ~0.20 (2.182 Å) and ~0.18 (2.200 Å), which obviously decrease than Ce–O ~0.21 (2.321 Å). Compared with undoped system (6.30), the total bond order for Fe-doped (6.16), Co-doped (6.0) and Ni-doped CeO₂ (5.84) obviously decrease. For all of these three doped systems, the total 30 Ce–O bond order decreased obviously. Above all, we can conclude that the covalent of Ce–O bond in CeO₂ is much more stronger than that of Fe (or Co, Ni) doping of CeO₂.

It is known that the band gap is usually underestimated in the calculation of GGA and LDA with the CASTEP, WIEN2K, VASP and other packages of the first principles calculations [58–60], due to the defect in inherent DFT calculation [61–63]. To overcome the discrepancy effectively, it has been reported that the “scissors operator (0.9 eV)” was introduced, which can produce a simple rigid shift of the unoccupied conduction band with respect to the valence band [13,14,64], and we set the instrumental smearing at

Table 2
Calculation of the results of population analysis of four structures and other available theoretical data.

Structure	Charge (e)	Bond order (bond length in Å)
CeO ₂	Ce: 1.230, O: -0.62; Ce ^a : 1.30, O ^a : -0.65	(Ce–O): 0.21(2.348) in total: 6.30 in total of 30 Ce–O: 6.30 (Ce–O) ^a : 0.21(2.366) in total ^a : 6.72 in total of 30 Ce–O ^a : 6.30
Ce _{0.75} Fe _{0.25} O ₂	Ce: 1.240, O: -0.580, Fe: 0.960	(Ce–O): 0.20 (2.321) (Fe–O): 0.22 (2.141); in total: 6.16 in total of 30 Ce–O: 6.0
Ce _{0.75} Co _{0.25} O ₂	Ce: 1.250, O: -0.580, Co: 0.870	(Ce–O): 0.20 (2.322) (Co–O): 0.20 (2.182); in total: 6.0 in total of 30 Ce–O: 6.0
Ce _{0.75} Ni _{0.25} O ₂	Ce: 1.250, O: -0.560, Ni: 0.700	(Ce–O): 0.20 (2.323) (Ni–O): 0.18 (2.200); in total: 5.84 in total of 30 Ce–O: 6.0

^a From Ref. [14].

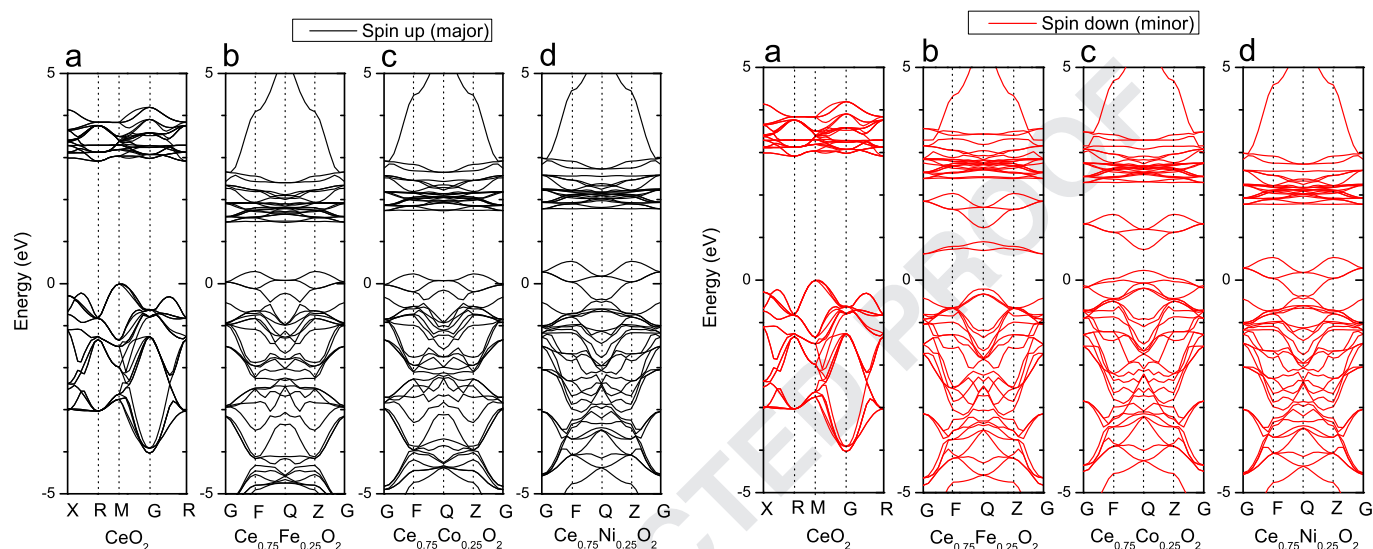


Fig. 2. (Color online) GGA results on the electronic band structure of $\text{Ce}_{1-x}\text{M}_x\text{O}_2$ ($\text{M}=\text{Fe}, \text{Co}, \text{Ni}, x=0, 0.25$). The major (spin up) and minor spin (spin down) bands are plotted with black and red lines, respectively. The Fermi energy level was set at zero. X, R, M, G and R represent (0.5, 0.0, 0.0), (0.5, 0.5, 0.5), (0.5, 0.5, 0.0), and (0.0, 0.0, 0.0) k-point in the first Brillouin zone for the band structure of (a) CeO₂, G, F, Q, Z, and G represent (0.0, 0.0, 0.0), (0.0, 0.5, 0.0), (0.0, 0.5, 0.5), and (0.0, 0.0, 0.5) k-point in the first Brillouin zone for the band structure of (b) Ce_{0.75}Fe_{0.25}O₂, (c) Ce_{0.75}Co_{0.25}O₂, and (d) Ce_{0.75}Ni_{0.25}O₂, respectively.

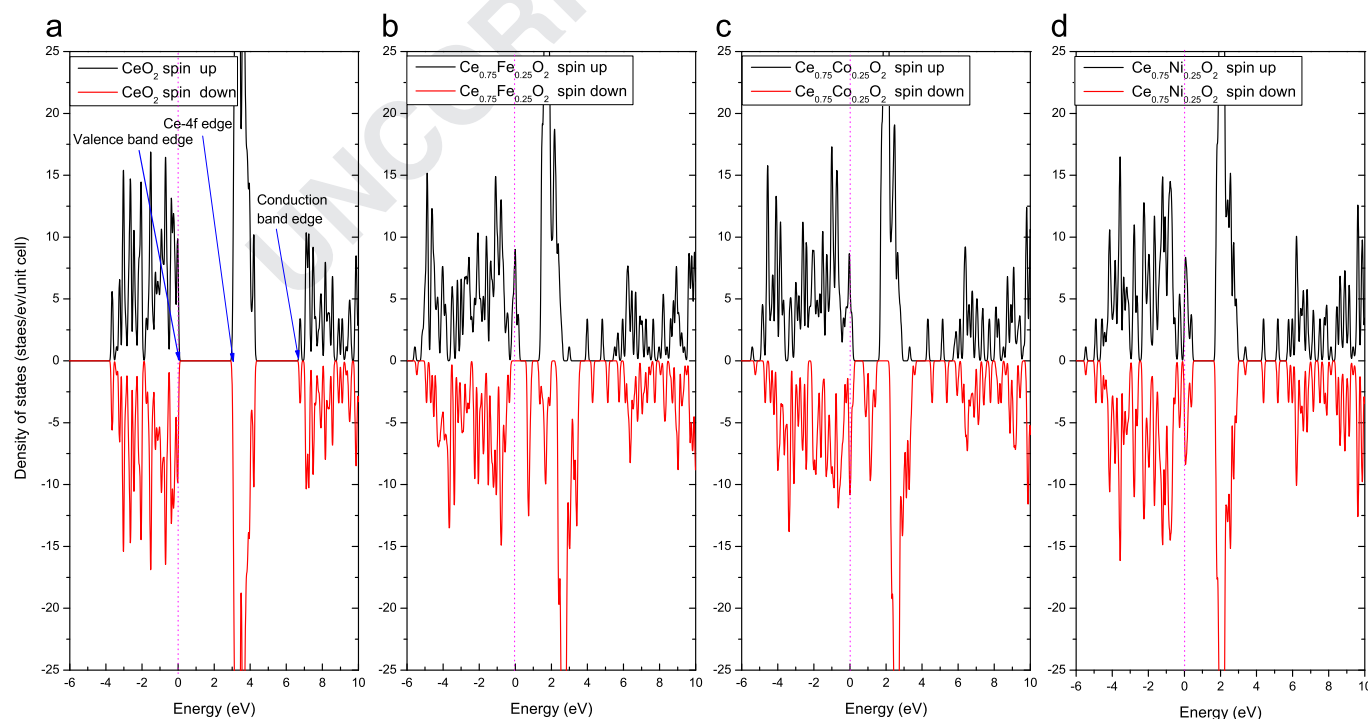


Fig. 3. (Color online) The DOS (total density of states) for the structure of (a) CeO₂, (b) Ce_{0.75}Fe_{0.25}O₂, (c) Ce_{0.75}Co_{0.25}O₂, and (d) Ce_{0.75}Ni_{0.25}O₂, respectively.

0.04 eV to simulate the Gaussian broadening effects that has been presented in previous reports [43,55]. The calculated electronic band structures of $\text{Ce}_{1-x}\text{M}_x\text{O}_2$ ($\text{M}=\text{Fe}, \text{Co}, \text{Ni}; x=0, 0.25$) are all plotted with spin-polarized method in Fig. 2. It is shown that CeO_2 is an insulator, and has an indirect band gap (both valence band maximum (VBM) and conduction band minimum (CBM)) value of 3.151 eV occurred at $M-R$ point, which is consistent with the previous report [13,14] and experimental values [19,65,66]. For the doped systems, when Ce is replaced by Fe (or Co, Ni), a band gap (E_g) reduction is observed, and it reflects that the conductivity of $\text{Ce}_{1-x}\text{M}_x\text{O}_2$ ($\text{M}=\text{Fe}, \text{Co}, \text{Ni}; x=0.25$) is increased. This may be due to the strong correlation effects happening between the d electronic state of transition metals (Fe, Co, Ni) and the f electronic state of rare earth (Ce), which caused the electronic structure of the material appear to have abnormal physical properties. For further explanation, doping with Fe (or Co, Ni) atom in CeO_2 leads to the lattice distortion, and creates oxygen vacancies, which favors the formation of Ce^{+3} from Ce^{+4} . This increases the amount of Ce^{+3} states, resulting in the formation of localized energy states that are closer to the conduction band, so that the band gap is decreased, as asserted in [67]. Meanwhile, for the doped system, the conduction band becomes wider than pure CeO_2 , predicting that metallic features of doped system increases. For $\text{Ce}_{1-x}\text{M}_x\text{O}_2$ ($\text{M}=\text{Fe}, \text{Co}, \text{Ni}; x=0.25$) (Fig. 2(b)–(d)), an impurity band is clearly found in the band gap, and an obvious increase at the top of valence band makes the width of valence band broaden.

To further elucidate the nature of the electronic band structure, we calculate the total density of states (DOS) and partial density of states (PDOS) of the optimized $\text{Ce}_{1-x}\text{M}_x\text{O}_2$ ($\text{M}=\text{Fe}, \text{Co}, \text{Ni}; x=0.25$), which are all plotted with the spin-polarized DFT+ U method. As shown in Figs. 3–5, the Fermi level is set to zero, which is mainly created by Ce- p , Ce- d , Ce- f , O- s , O- p states, as well as small contributions of Ce- s , the features of O- $2s$ states are localized between -19.0 and -11.2 eV below the Fermi level for pure CeO_2

(far below the energy window, and is not shown in Figs. 3(a) and 4). From Figs. 3(a) and 4, we know that the density of states and partial density of states clearly show that CeO_2 is an insulator. This is in consistency with the previous band structure analysis. The highest occupied valence band exhibits significant O $2p$ character mixing with small contribution from Ce $4f$ state and Ce $5d$ state, while the narrow band situated above the Fermi level is mainly due to Ce $4f$ states. The states situated above the empty Ce $4f$ states are due to $5d$ and $6s$ of Ce (far below the energy window, and is not shown in Figs. 3(a) and 4). The Ce $5s$ state is located at about -33 eV below the Fermi level (far below the energy window, and is not shown in Figs. 3(a) and 4). The calculated energy gap $E_{\text{O}2p-\text{Ce}4f}$ (between O $2p$ and Ce $4f$ states, i.e., between the valence band edge and Ce- $4f$ edge) is 3.0 eV, and the other energy gap $E_{\text{O}2p-\text{Ce}5d}$ (between O $2p$ and Ce $5d$ states, i.e., between the valence band edge and conduction band edge) is 6.3 eV, in excellent agreement with the previous experimental measurements [3,21,68] and calculations [43,55,63,69,70], which is listed in Table 3. The results show that our method can give a good description of the electronic structure for the bulk CeO_2 .

From Figs. 3(b)–(d), 4, and 5, it is found that the valence band mainly consisted of O $2p$ states and Fe (or Co, Ni) $3d$ states. The conduction band mainly resulted from the contribution of Ce $5d$ states, and these states are located at about 0.4, 0.5, 1.2 eV above the valence band for Fe-doped, Co-doped and Ni-doped CeO_2 , respectively. Between the valence band and the conduction band, there are the Ce $4f$ states located at 0.9, 1.3 and 1.0 eV, above the top of the O $2p$ states for Fe-doped, Co-doped and Ni-doped CeO_2 , respectively. These energies are also the energy gap $E_{\text{O}2p-\text{Ce}4f}$ (between O $2p$ and Ce $4f$ states) for $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_2$, $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$ and $\text{Ce}_{0.75}\text{Ni}_{0.25}\text{O}_2$, respectively. Obviously, the energy gap $E_{\text{O}2p-\text{Ce}4f}$ (between O $2p$ and Ce $4f$ states) for CeO_2 is higher than Fe (or Co, Ni) doped CeO_2 . By comparing the Ce $4f$ surrounding environment, the observations can be elucidated. In the cubic CeO_2 , wherein the Ce atoms are at the corner of the cube and are

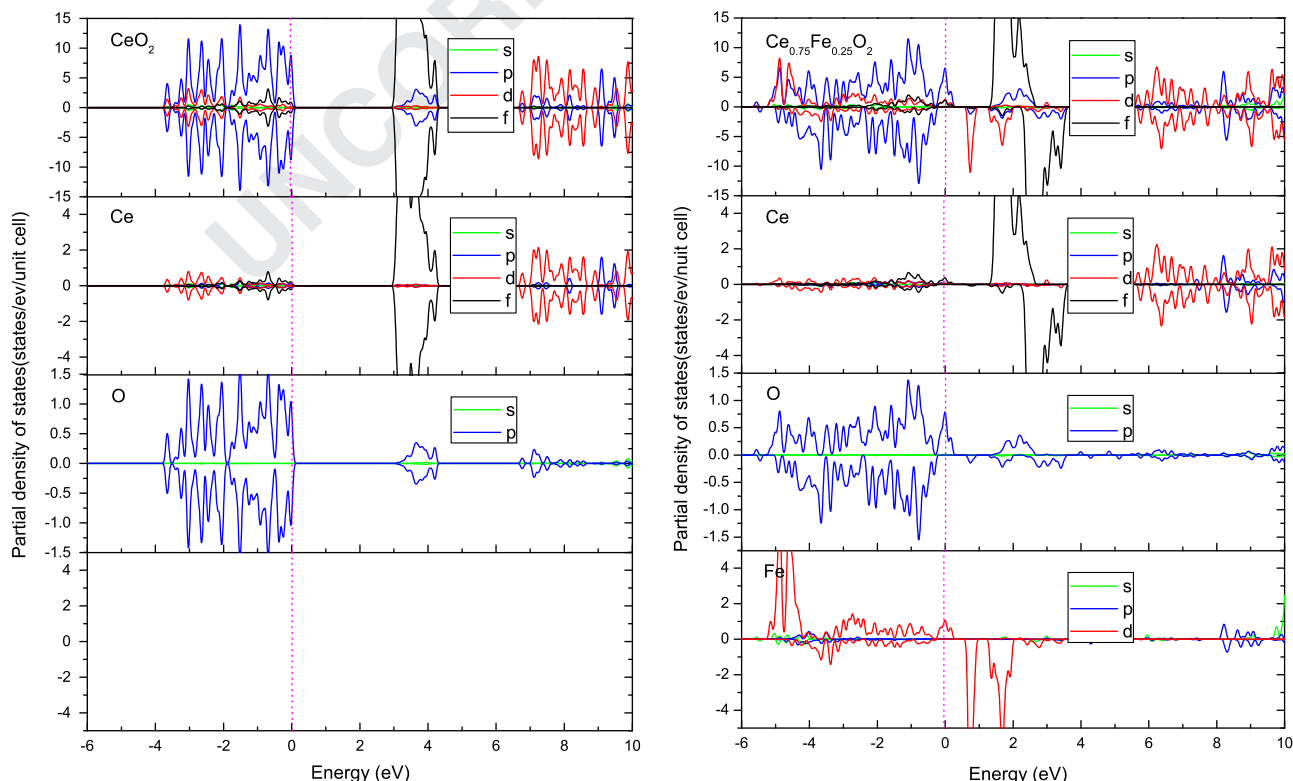


Fig. 4. (Color online) The PDOS (partial density of states) for the structure of CeO_2 (the left) and $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_2$ (the right), respectively. Upper and lower panels represent spin up and spin down, respectively.

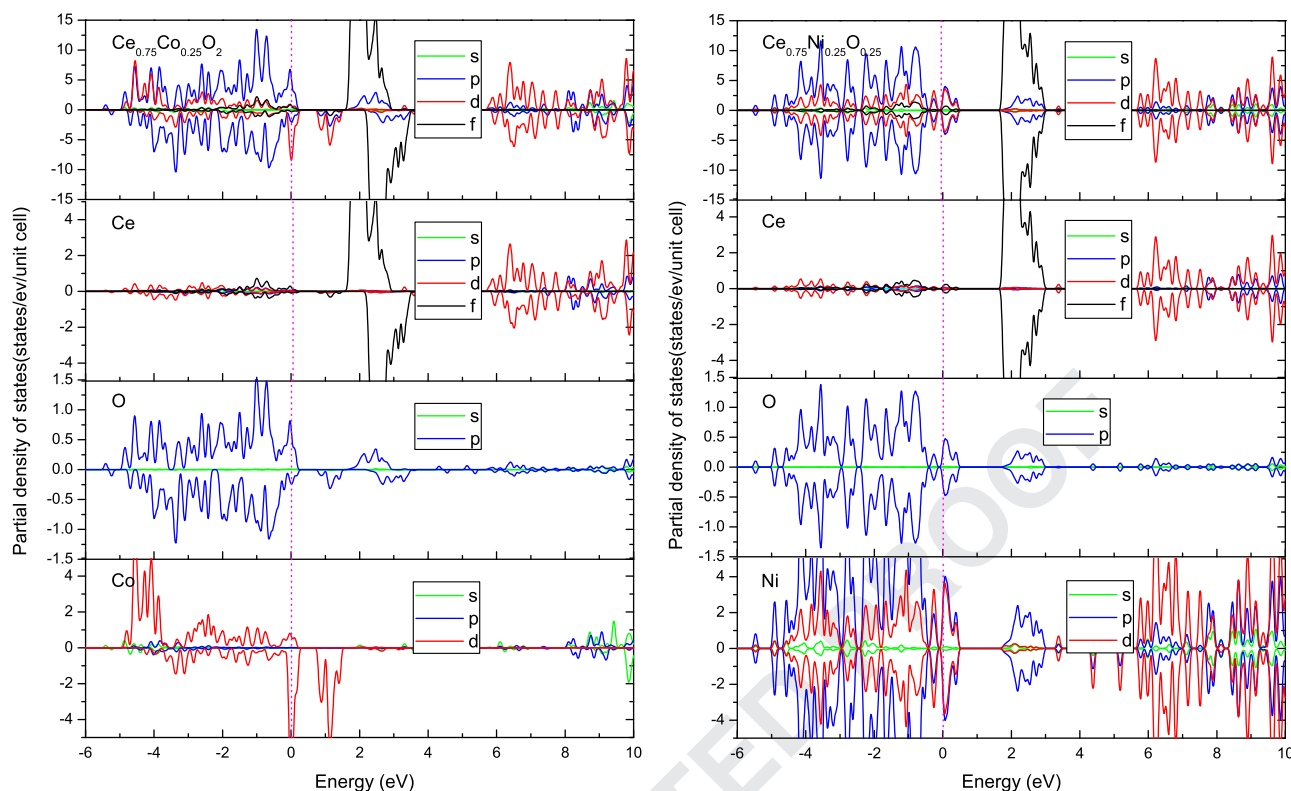


Fig. 5. (Color online) The PDOS (partial density of states) for the structure of $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$ (the left) and $\text{Ce}_{0.75}\text{Ni}_{0.25}\text{O}_2$ (the right), respectively. Upper and lower panels represent spin up and spin down, respectively.

Table 3

Calculation of the energy gap for CeO_2 , including other experimental measurements and available theoretical data. Here we define the energy gap between O 2p and Ce 4f (i.e., between the valence band edge and Ce-4f edge) as $E_{\text{O}2p-\text{Ce}4f}$ (i.e., between the valence band edge and conduction band edge), similarly, define the energy gap between O 2p and Ce 4f as $E_{\text{O}2p-\text{Ce}5d}$.

CeO_2	Present work	Exp ^a	Exp ^b	Exp ^c	Calc ^d	Calc ^e	Calc ^f	Calc ^g	Calc ^h
$E_{\text{O}2p-\text{Ce}4f}$ (eV)	3.0	1.8		3.0	2.8	2.5	2.3	1.9	2.5
$E_{\text{O}2p-\text{Ce}5d}$ (eV)	6.3	5.7	5.7	6.0	5.5	5.5		5.5	6.0

^a From Ref. [3].

^b From Ref. [21].

^c From Ref. [68].

^d From Ref. [63].

^e From Ref. [69].

^f From Ref. [70].

^g From Ref. [43].

^h From Ref. [55].

coordinated by eight equivalent nearest-neighbor oxygen atoms. The O 2p-Ce 4f transition corresponded to the electron excitation from the 2p states of eight Ce-connected O atoms to the Ce 4f states [14]. Due to the decreasing donating electrons ability on going from O, Fe, Co and Ni atoms, these electrons come from the 2p states of O atoms and Fe (or Co, Ni) 3d states of Fe (or Co, Ni) atoms to the 4f states of their adjacent Ce atoms. Therefore, the O 2p-Ce 4f transition intensity decrease on going from undoped, Co-doped, Fe-doped and Ni-doped systems. This can be explained by the decreasing covalent character of the Ce-O bond on going from undoped and Fe (or Co, Ni)-doped CeO_2 with decreasing total bond order (presented in Table 2). For the doped system (Figs. 4 and 5), the impurity band in the band gap originates from the hybridization between Fe (or Co, Ni) 3d states and O 2p states, which are the states mainly located at the impurity band. In Fig. 3(b)-(d), the DOS increase at the top of valence band for $\text{Ce}_{1-x}\text{M}_x\text{O}_2$ (M=Fe, Co,

Ni) that mainly due to the Fe (or Co, Ni) are introduced into CeO_2 , because the Fe (or Co, Ni) 3d states are the mainly states located at the valence band maximum. The widths of the valence band are 6.0 eV, 5.8 eV and 6.2 eV for Fe-doped, Co-doped and Ni-doped CeO_2 , respectively. The valence bands for Fe (or Co, Ni) doped CeO_2 are all wider than undoped CeO_2 (3.8 eV), this mainly resulted from the hybridization between Fe (or Co, Ni) 3d states and O 2p states. The bottom of conduction band in energy for Fe-doped, Co-doped and Ni-doped CeO_2 is lower than undoped CeO_2 . The widths of the Ce 4f states for Fe (or Co, Ni) doped CeO_2 are all 1.2 eV, and they are lower than pure CeO_2 (1.4 eV) in Fig. 3 (spin up). On the contrary, for Fig. 3 (spin down), the widths of the Ce 4f states for Fe-doped and Co-doped CeO_2 are 1.5 and 1.7 eV, which are higher than pure CeO_2 (1.4 eV). For Ni-doped CeO_2 , the widths of the Ce 4f states is 1.2 eV, which is lower than pure CeO_2 (1.4 eV) Fig. 3 (spin down). Due to the magnetism of Fe (or Co, Ni) and the hybridization between Fe (or Co, Ni) 3d states and Ce 4f states, the width of the Ce 4f states between spin up and down for Fe (or Co, Ni) doped CeO_2 and undoped CeO_2 is different. Compared with undoped CeO_2 , the Ce 4f states obviously shift to lower energy for Fe (or Co, Ni) doped CeO_2 (Fig. 3(b)-(d)) spin up and down). These reflect the stronger mixing between Ce 4f-Fe (or Co, Ni) 3d than Ce 4f-O 2p states, which can also elucidate the reduction of the energy gap $E_{\text{O}2p-\text{Ce}4f}$ and the band gap for Fe (or Co, Ni) doped CeO_2 . Figs. 3-5 clearly show a substantial obvious mixing between Ce 4f and anion 2p orbital. This may also be one reason for the density of states asymmetric when Fe (or Co) dope CeO_2 (Fig. 3 (b) and (c)).

3.2. Optical properties

Due to the electronic transitions, the optical properties of solid can be calculated in CASTEP. We take the ionic and electronic polarization into consideration, as they affect the optical

properties of material, though electronic polarization is only considered to affect the dielectric function. As the local field effects are neglected, we have not taken the phonon into account. It is common to use the complex dielectric function to express other optical properties because complex dielectric function can derive other optical parameters, for instance, refraction index, absorption coefficient, loss function and reflectivity. The complex dielectric function $\varepsilon(\omega)$ is given as

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \quad (1)$$

Here $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are real and imaginary parts of the dielectric function, respectively. The relationship between the complex dielectric function and the complex refractive index ($N = n + ik$) is given by the relationships [13]:

$$\varepsilon_1(\omega) = n^2 - k^2 \quad (2)$$

where $n = \varepsilon_2(\omega)/2k$, the imaginary part of the dielectric function can be given by formula (3) [13,71,72]. In formula (3), we define the vertical transition from a filled initial state $|i_k\rangle$ of energy as $E_{\text{initial}}(k)$, similarly, define the empty final state $|f_k\rangle$ of energy as $E_{\text{final}}(k)$. Here, Δ_c is the shift value of the scissors operator, m is the free electron mass, e is the electron charge, ν is the frequency, and p_α is the Cartesian component of the momentum operator. From the above description, formula (3) is given in the following:

$$\varepsilon_2(\omega) = \frac{4e^2\pi^2}{m^2\left(\omega - \frac{\Delta_c}{\hbar}\right)^2} \sum_{if} \int_{BZ} \frac{2dk}{(2\pi)^3} | \langle i_k | p_\beta | f_k \rangle | \cdot | \langle f_k | p_\alpha | i_k \rangle | \cdot \delta(E_{\text{final}}(k) + \Delta_c - E_{\text{initial}}(k) - \hbar\nu) \quad (3)$$

$$\varepsilon_1(\omega) = 1 + \frac{2p}{\pi} \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (4)$$

The real and imaginary parts of the dielectric function are linked by a Kramers–Kronig transform [formula (4), where p denotes the principal value of the integral], this relationship is similar to Fermi Golden rule [73], which is used to get the real part of the dielectric function. Meanwhile, the imaginary part $\varepsilon_2(\omega)$ of the dielectric function can be thought as describing the real transitions between the occupied and unoccupied electronic states. The scissors of 0.9 eV [13,14] and smearing of 0.3 eV are used to simulate the broaden effects, which raise the bands locating above the valence band position in energy prior to the interband transition strength calculation to correspond to the general features of the measured $\varepsilon_2(\omega)$ (the imaginary part of dielectric function) [58,59]. According to the energy of photon and transitions, we analyze the

imaginary parts of dielectric function $\varepsilon_2(\omega)$ in order to decide which type of electronic transitions would occur. Owing to the close relationship between the interband transitions and imaginary part of dielectric function, and relying on the electronic transition energy of conduction and valence band, the singularity (the imaginary part of dielectric function) is in line with electronic transitions from valence to conduction bands.

Based on the calculated electronic structure and above theory, the real and imaginary parts of the dielectric function for Fe (or Co, Ni) doped CeO_2 and pure CeO_2 are calculated in CASTEP. The real and imaginary parts of the dielectric function for CeO_2 are shown in Fig. 6. For comparison, the experimental data [19–21] and other results [54] are presented in Fig. 6. The calculated $\varepsilon_2(\omega)$ curve in Fig. 6(b) shows a sharp increase at about 3.5 eV at the first onset of the optical transitions. The second main peak is situated at about 10.4 eV and the third one at 20.6 eV, which are in good agreement with experimental [19–21] and theoretical values [74], listed in Table 4. In Fig. 6(b), the peaks of $\varepsilon_2(\omega)$ originated from interband transitions that form the valence band states to the conduction band states. As discussed above, the dipolar selection rule, only transitions that change the angular momentum quantum number l by unity ($\Delta l = \pm 1$) are permitted. The DOS (Density of states) and PDOS (Partial density of states) of CeO_2 in Figs. 3 and 4 show that the first peak in $\varepsilon_2(\omega)$ at about 3 eV can elucidate the transition from Ce 5d $\rightarrow$ Ce 4f states, while the second peak corresponds to the Ce 5p $\rightarrow$ Ce 5d transition, as asserted in Ref. [19]. According to Kramers–Kronig transformation, the real part of the dielectric function for CeO_2 is shown in Fig. 6(a). The results are compared to the experimental data and other calculations (the inset shows experimental and calculated values taken from [54] in Fig. 6(a)) with the same way as for $\varepsilon_2(\omega)$. The calculated shape of $\varepsilon_1(\omega)$ curve exhibits the same main features as the experimental results [21]. The peak at about 3.0 eV corresponds to the experiment at 3.0 eV [21] (the inset shows experiment in Fig. 6(a)), and the second quite broad peak of $\varepsilon_1(\omega)$ is situated at about 9.1 eV, corresponding to the experimental peak at 7.3 eV (the inset shows experiment in Fig. 6(a)). Third, the peak at 19.2 eV corresponds to the experimental peak at 21.0 eV (the inset shows experiment in Fig. 6(a)). These are in good agreement with the other calculation (2.5 eV, 9.2 eV and 19.25 eV for the first, the second and the third peak of $\varepsilon_1(\omega)$ for CeO_2 , respectively) [54], and also in better agreement with other experiments [19,20].

The real and imaginary parts of the dielectric function for $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_2$, $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$ and $\text{Ce}_{0.75}\text{Ni}_{0.25}\text{O}_2$ are shown in Fig. 7(a)–

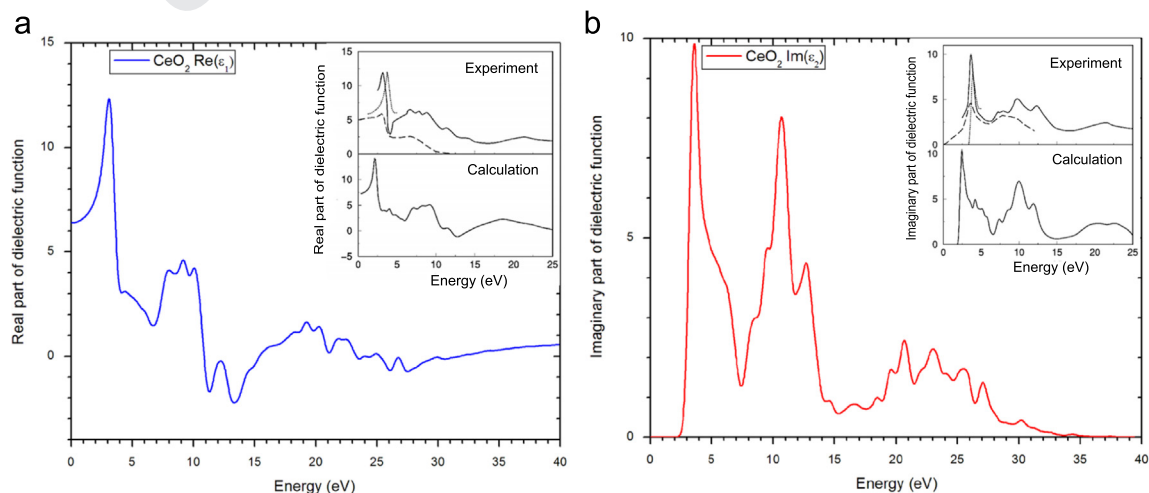


Fig. 6. (Color online) Calculated the dielectric of function for the structure of CeO_2 : (a) real part of the dielectric function, (b) imaginary part of the dielectric function. The inset shows experiment and calculation for (a) and (b) taken from Ref. [54]. In experimental for (a) and (b), the solid, dashed, and dotted lines represent the data from Refs. [21,19,20], respectively.

(c), respectively. The first critical point comes into being at 0.2, 0.1 and 0.16 eV for $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_2$, $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$ and $\text{Ce}_{0.75}\text{Ni}_{0.25}\text{O}_2$, respectively. This is known as the shoulder of optical absorption. Moreover, for $\varepsilon_2(\omega)$, the widths of nonzero can affect the widths of adsorption spectra. Other peak positions locate at 2.0, 3.5, 11.1, 20.0 and 25.0 eV for $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_2$, at 1.0, 3.9, 11.0, 21.0 and 24.5 eV for $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$, and at 2.0, 3.5, 11.0, 21.0 and 24.6 eV for $\text{Ce}_{0.75}\text{Ni}_{0.25}\text{O}_2$. On the basis of decomposing each spectrum to its individual pair contribution that come from each pair of valence to conduction bands, we analyze the imaginary parts of the dielectric function $\varepsilon_2(\omega)$ to determine the above peaks of origins and features [73,75]. Also, the differences in band structures lead to the differences in the structures of the optical spectra, due to the structures of the optical spectra originate from the transitions from the top valence bands to the bottom conduction bands. The real part of $\varepsilon_1(\omega)$ dielectric function in infinite wavelength (the static dielectric constant ε_0 is obtained as the zero frequency limit of the real part of the frequency-dependent dielectric function) locates at 11.75, 25.2 and 11.0 eV for $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_2$, $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$ and $\text{Ce}_{0.75}\text{Ni}_{0.25}\text{O}_2$, respectively. Compared with pure CeO_2 (the static dielectric constant ε_0 for CeO_2 is 6.4 eV, which is close to the experimental value 6.0 eV [20,76]) in Fig. 6, they are all larger than pure CeO_2 , and $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$ has the largest static dielectric constant ε_0 , it is in good agreement with the experiment [32]. In addition, it reflects that the static dielectric constant ε_0 has a square fit relationship with the refractive index n and the extinction coefficient k , as asserted by formula (2). The real part of dielectric function reaches maximum value of 12.9 about at 0.7 eV for $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_2$, 31.0 at 0.5 eV for $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$, 16.3 at 1.2 eV for $\text{Ce}_{0.75}\text{Ni}_{0.25}\text{O}_2$. Meanwhile, from Figs. 6(b) and 7 (a)–(c), the imaginary parts of the dielectric function for $\text{Ce}_{1-x}\text{M}_x\text{O}_2$ ($\text{M}=\text{Fe}, \text{Co}, \text{Ni}; x=0.25$), it can be noted that CeO_2 has a step absorption peak at the absorption edge at 3.4 eV, which is in good agreement with the experiment [13], and it can be used in UV absorption application. Compared with the undoped CeO_2 , the doped system has steep absorption peaks ranging from 1.0 eV to

2.0 eV at lower energy, and it can be used for visible light absorption applications.

The refractive index n and the extinction coefficient k are illustrated in Fig. 8. We know that the static refractive index n_0 is 2.54, 3.43, 5.02 and 3.33 for CeO_2 , $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_2$, $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$ and $\text{Ce}_{0.75}\text{Ni}_{0.25}\text{O}_2$, respectively, they correspond to the values derived from the real part $\varepsilon_1(\omega)$ of dielectric function. They reach a maximum value of 3.65 at 3.2 eV for CeO_2 , 3.62 at 0.6 eV for $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_2$, 5.7 at 0.8 eV for $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$, 4.15 at 1.5 eV for $\text{Ce}_{0.75}\text{Ni}_{0.25}\text{O}_2$, and other theoretical values for CeO_2 are listed in Table 5. We note that after Fe (or Co, Ni) doped CeO_2 , the refractive index n_0 increases, and the corresponding energy becomes low. It is likely to indicate that the refractive index n_0 is decided by the hybridization between Fe (or Co, Ni)-3d and O-2p, and it also elucidate the reason that the static dielectric constant ε_0 for doped ceria is bigger than undoped ceria. Previously experiments [9,10] certify that CeO_2 has high refractive index ($n_0=2.54$), it can be considered as a useful high-refractive index film material in single and multilayered optical coatings. From above discussion, we know that the doped system has higher refractive index than pure CeO_2 , especially for $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$ has the static refractive index n_0 is 5.02, which is larger than pure CeO_2 . This is in accordance with the experimental [33] report that the refractive index of CeO_2 increase with Co concentration. Thereby, compared with undoped CeO_2 , $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$ is more suitable as a useful high-refractive index film material in single and multilayered optical coatings. The calculated extinction coefficient k for CeO_2 is also in good agreement with the experimental data (the inset shows measured in Fig. 8(b) taken from Ref. [13]) and previous calculation (the inset shows calculated in Fig. 8(b) taken from Ref. [13]), and the shapes of the calculated curves exhibit the same characteristics as do the experimental curves [13]. From Fig. 8(b), the extinction coefficients k , and the spectrum of CeO_2 can be decomposed into three main absorption bands centered around 4.0, 11.0 and 26.0 eV, the first and second point peaks can be assigned to the $\text{O } 2p^6 \rightarrow \text{Ce } 4f^0$ and $\text{O } 2p^6 \rightarrow \text{Ce } 5d^0$ electronic transitions, respectively. The first band ranges from 2.5 to 7.5 eV and the second one from 8.0 to 16.0 eV. The second band range is wider than the first band range, suggesting that the width of Ce 5d state is wider than Ce 4f state, in line with Fig. 4 (the left). For the doped system, these three bands merge into one with four distinct contributions.

Furthermore, for the $\varepsilon_2(\omega)$ spectrum, if we take the excitonic effect into account, the result will be in good agreement with the experiment. Based on this, the important adsorption spectrum and energy loss function deduced from the frequency-dependent dynamical dielectric function for CeO_2 , $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_2$, $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$ and $\text{Ce}_{0.75}\text{Ni}_{0.25}\text{O}_2$ obtained by CASTEP are shown in Figs. 9 and 10(a). It is obvious that the main structures are well produced. From Fig. 9 (a), we know that the first peak in adsorption spectrum

Table 4
Calculation of the imaginary part $\varepsilon_2(\omega)$ of dielectric function for CeO_2 , including other experimental measurements and available theoretical data.

CeO_2	Present work	Calc ^a	Calc ^a	Exp ^a	Exp ^a
Peak position	3.5	2.5	3.2	3	3.66
	10.4	10	9.5	8.0	8.46
	20.6	21	22.3	20	

^a From Ref. [54].

^a From Ref. [74].

^a From Ref. [21].

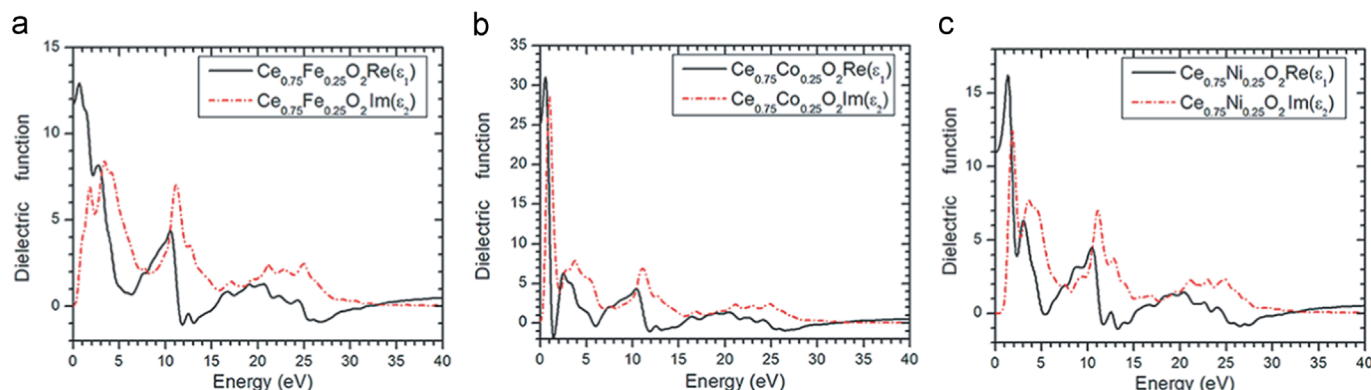


Fig. 7. (Color online) Dielectric of function for the structure of (a) $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_2$, (b) $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$, and (c) $\text{Ce}_{0.75}\text{Ni}_{0.25}\text{O}_2$, respectively.

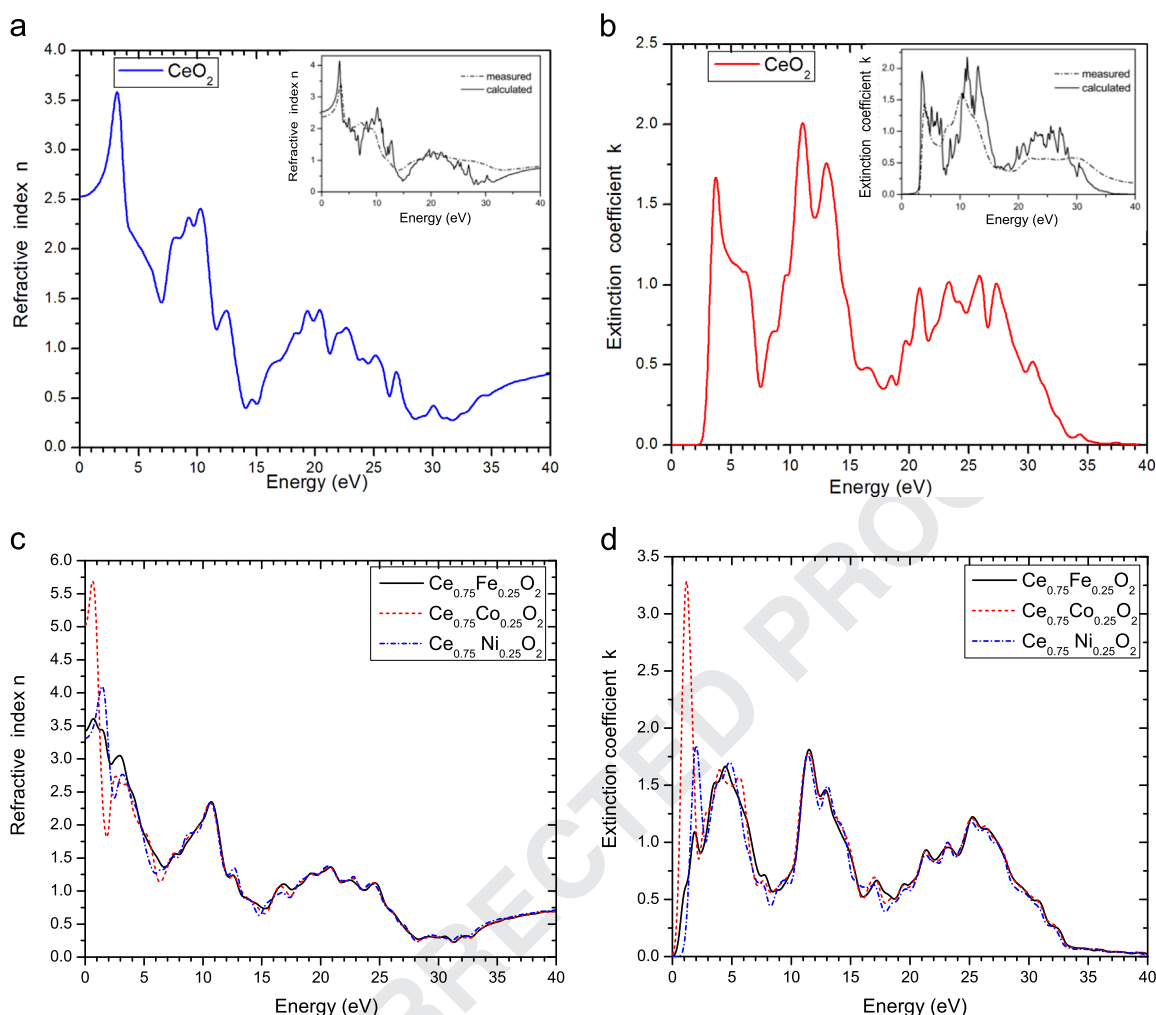


Fig. 8. (Color online) Calculated optical properties of CeO_2 : (a) the refractive index n , (b) the extinction coefficient k . The inset shows measured and calculated in (a) and (b) taken from Ref. [13], respectively. Calculated optical properties of the refractive index n and the extinction coefficient for $\text{Ce}_{1-x}\text{M}_x\text{O}_2$ ($x=0.25$) are presented at (c) and (d), respectively.

Table 5

Calculated refractive index for CeO_2 , including other experimental measurement and available theoretical data.

CeO_2	Present work	Calc ^a	Exp ^a
$n_{(0)}$	2.54	2.54	2.35
n	3.65	4.2	3.4
Maximum energy (eV)	3.2	3.0	3.2

^a From Ref. [13].

has a shifting of about 1.5 eV to higher energy for CeO_2 (6 eV) compared with the experiment [21], and the second peak of absorption is situated at about 13.2 eV, corresponding to the experimental peak at 13.0 eV. The third quite broad peak of absorption is at 27.5 eV corresponding to the experimental peak at 30.0 eV. This is in good agreement with the other calculation (5.5 eV, 12.8 eV and 22.5 eV for the first, second and third peaks of absorption, respectively) [77]. For the doped structure, the first, the second and the third peaks in adsorption spectrum have the shifting of about 0.5 eV, 1.5 eV and 1.5 eV to lower energy, respectively. Compared with CeO_2 , the graphic shape is almost unchanged. This is mainly due to the effect of the impurity band introduced by Fe (or Co, Ni) atoms. According to de Broglie relation [$E = h \cdot \nu$, here E is the energy, h is the Planck constant, ν is the frequency.] and the relationship between the band gap and the

absorption edge [73] [$\lambda(A \cdot h \cdot c - \lambda E_g) = (h^2 \cdot c^2 / d^2) \cdot \ln^2(1/T)$, here λ is wavelength, A is transition coefficients of direct band gap, T is transmissivity, d is thickness and E_g is value of band gap.], we know that the absorption shoulder for pure CeO_2 is 354 nm, this is consistent with the experiment [13]. And the absorption shoulder for $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_2$, $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$ and $\text{Ce}_{0.75}\text{Ni}_{0.25}\text{O}_2$ are 850 nm, 2200 nm and 1200 nm, respectively. It is obvious that the absorption edges have a red shift for $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_2$, $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$ and $\text{Ce}_{0.75}\text{Ni}_{0.25}\text{O}_2$, respectively, as asserted by the experimental report [31] that the Co doping causes the change in band gap and red shift when compared to the undoped CeO_2 NPs. This attributes to the different band gap corresponding to the different absorption edge, i.e., when the conduction band is extended, the absorption spectrum is wider. Significantly, the electronic transitions occur between Ce-5d, O-2p and Ce-4f owing to the Ce-5d, Ce-4f and O-2p states dominating the top of valence band and Ce-5d being located at the bottom of conduction band (in Figs. 3–5), leads to charge density redistribution in the charge of the top of valence band after Ce atom was replaced by Fe (or Co, Ni).

The energy-loss function has a large effect on usage of material, i.e., the narrower scope can explain the sharper peak of energy loss. As shown in Fig. 10(a), the two peaks at about 6.9 and 15.5 eV for CeO_2 , these are in good agreement with the other experimental result [21] and calculated value [78] for CeO_2 . Therefore, our result reproduces the positions of the peaks that are determined by

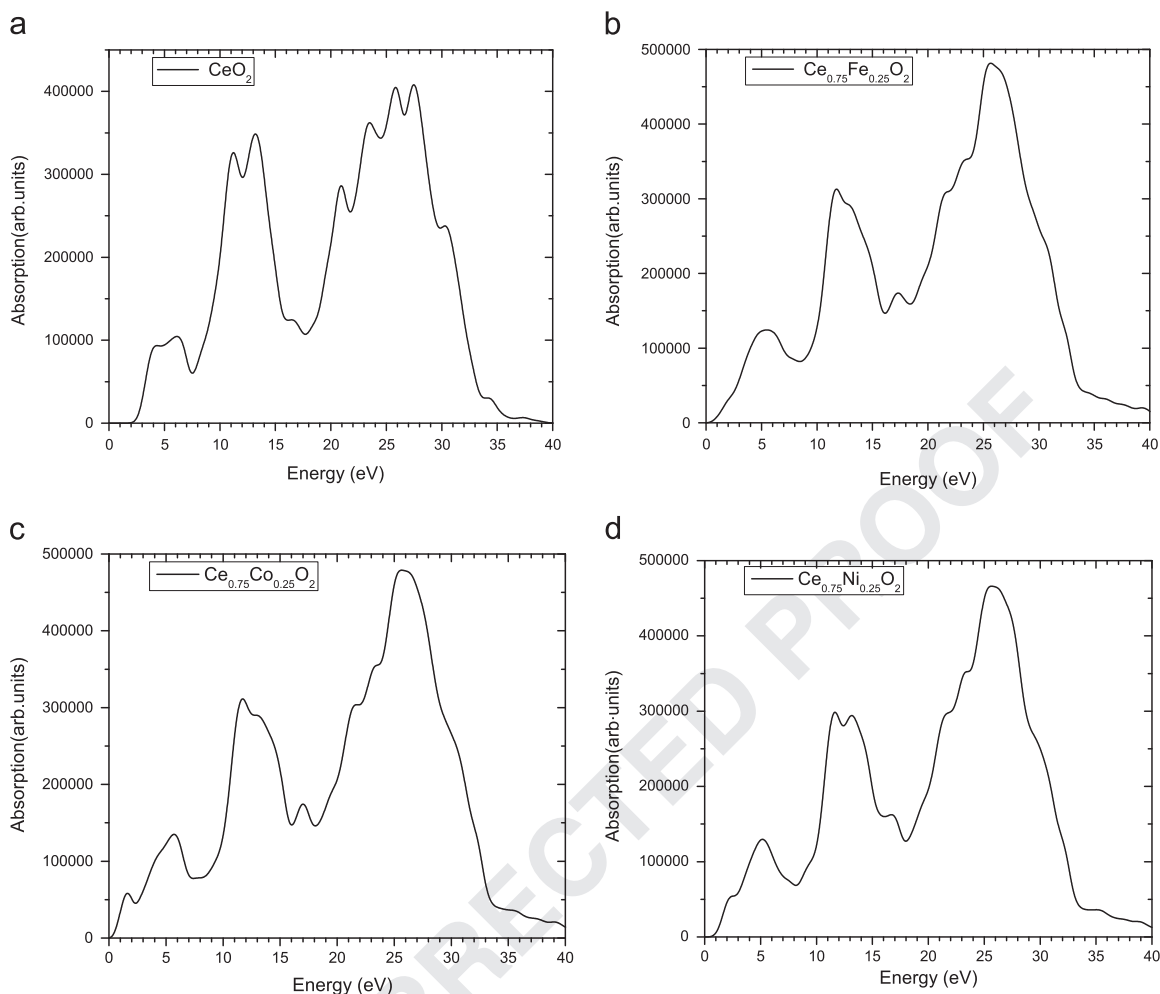


Fig. 9. (Color online) Absorption spectra for the structure of (a) CeO_2 , (b) $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_2$, (c) $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$, and (d) $\text{Ce}_{0.75}\text{Ni}_{0.25}\text{O}_2$, respectively.

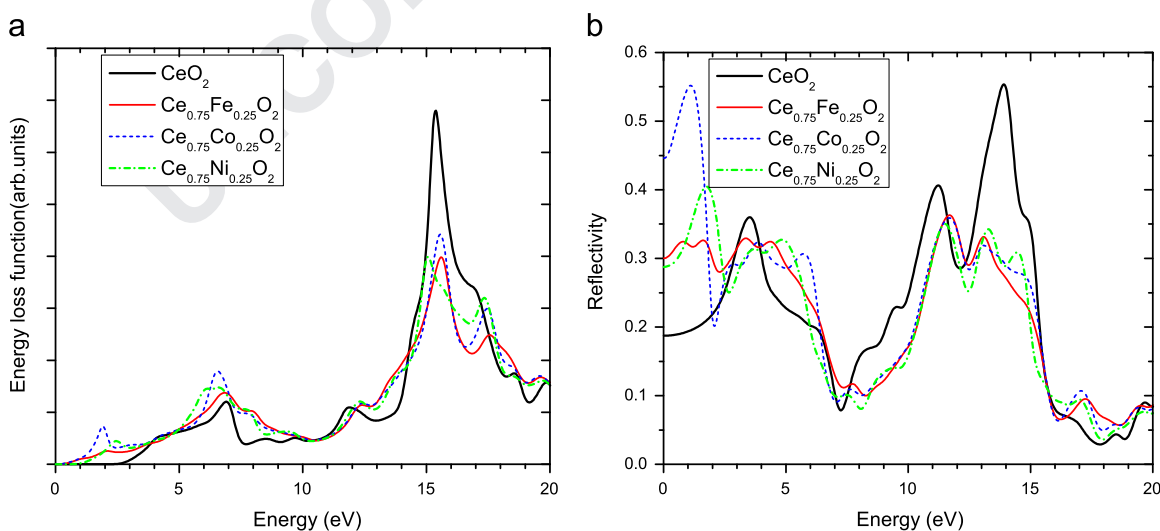


Fig. 10. (Color online) Calculated (a) energy loss function and (b) reflections of $\text{Ce}_{1-x}\text{M}_x\text{O}_2$ ($\text{M}=\text{Fe}, \text{Co}, \text{Ni}; x=0.25$) obtained from the CASTEP calculation, respectively.

inter-band transitions with good accuracy. For the doped structure, the primary peak emerges at 6.8, 6.5 and 6.0 eV for $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_2$, $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$ and $\text{Ce}_{0.75}\text{Ni}_{0.25}\text{O}_2$, while the second quite broad peak of energy loss function is situated at about 15.5, 15.5 and 15.0 eV, and they change little, compared with pure CeO_2 . As the energy loss function corresponds to the energy loss of

electron traversing, these peaks can elucidate the electron of O-2p states leaping into the unoccupied conduction band.

The calculated optical reflectivity is shown in Fig. 10(b). The calculated reflectivity for CeO_2 starts at about 18.5 % and has a maximum value of roughly 58% at about 14.0 eV. The experimental reflectivity starts with 20% [54], and the other calculation has a

maximum value of 60% at about 14.0 eV [77]. Thus, the interband transitions can determine the good accurate positions of the peaks that are reproduced by ours. From Fig. 10(b), we know that the high reflectivity is mainly located in two parts: one part is situated between 9.8 and 14.75 eV, and the other part is situated between 25.5 and 30.5 eV, which are all consistent with the previous calculation [77] and experiment [21]. From Fig. 10(b), we clearly know that the maximum values of reflectivity for $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_2$, $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$ and $\text{Ce}_{0.75}\text{Ni}_{0.25}\text{O}_2$ are all bigger than CeO_2 at lower energy. Especially, $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$ has a high reflectivity of about 55% at 1.5 eV, which shows that $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$ may be suitable as a high refractivity coating material.

4. Conclusions

The atomic, electronic and optical properties of $\text{Ce}_{1-x}\text{M}_x\text{O}_2$ ($\text{M}=\text{Fe}, \text{Co}, \text{Ni}; x=0, 0.25$) are studied by using the DFT + U method within the generalized gradient approximation (GGA) in the Cambridge Serial Total Energy Package (CASTEP) program. The computational results of the equilibrium lattice parameter, cell volume, bulk modulus and optical properties for CeO_2 are all in excellent agreement with the experiment and other calculations. Compared with undoped (CeO_2), when Ce is replaced by Fe (or Co, Ni) in CeO_2 , the lattice parameter, cell volume, bulk modulus and the bond length of Ce–O decreased. This reflects that the strength of chemical bond (Ce–O) in CeO_2 is stronger than $\text{Ce}_{1-x}\text{M}_x\text{O}_2$ ($\text{M}=\text{Fe}, \text{Co}, \text{Ni}; x=0.25$). The substitutional doping of Fe (or Co, Ni) in cubic CeO_2 leads to the band-gap (E_g) reduction. This reflects that the conductivity of $\text{Ce}_{1-x}\text{M}_x\text{O}_2$ ($\text{M}=\text{Fe}, \text{Co}, \text{Ni}; x=0.25$) is increased, and the feature of metallic is strengthened. Meanwhile, it is interesting to find that the substitutional doping of Fe (or Co, Ni) in CeO_2 obviously decreases the O 2p–Ce 4f gap and the O 2p–Ce 4f transition intensity. Based on the dielectric functions obtained, it is shown that the substitutional doping of Fe (or Co, Ni) in CeO_2 obviously increases the static dielectric constant ϵ_0 and refractive index n_0 . For example, the refractive index n_0 ranges from 2.54, 3.43, 5.02 to 3.33 for CeO_2 , $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_2$, $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$ and $\text{Ce}_{0.75}\text{Ni}_{0.25}\text{O}_2$, respectively. And the static dielectric constant ϵ_0 ranges from 6.4, 11.8, 25.0 to 11.0 for CeO_2 , $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_2$, $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$ and $\text{Ce}_{0.75}\text{Ni}_{0.25}\text{O}_2$, respectively. This is consistent with formula (2) and other experiments. Compared with the undoped CeO_2 , the shoulder of optical absorption also becomes narrow for $\text{Ce}_{1-x}\text{M}_x\text{O}_2$ ($\text{M}=\text{Fe}, \text{Co}, \text{Ni}; x=0.25$). From analysis the absorption spectrum, it can be found that the absorption edge of CeO_2 is observed at 354 nm, which is in agreement with the experimental value. And the absorption edge becomes wide and has a red shift for $\text{Ce}_{0.75}\text{Fe}_{0.25}\text{O}_2$, $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$ and $\text{Ce}_{0.75}\text{Ni}_{0.25}\text{O}_2$. Meanwhile, it can also be noted that CeO_2 has a step absorption peak at the absorption edge at 3.4 eV, which is in good agreement with the experiment, and it can be used in UV absorption application. Compared with the undoped CeO_2 , the doped system has steep absorption peaks ranging from 1.0 eV to 2.0 eV at lower energy, and it can be used for visible light absorption applications. The $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$ has a high refractive index and reflectivity, which shows that the $\text{Ce}_{0.75}\text{Co}_{0.25}\text{O}_2$ is suitable as a high-refractive index film material in single and multilayered optical coatings, compared with pure CeO_2 .

Acknowledgments

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