

Stability of the Ce₂O₃ phases: A DFT+*U* investigation

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We report a first-principles investigation of the energetics and structure properties of CeO_{1.50} in the hexagonal (La₂O₃), cubic (bixbyite), and monoclinic structures. Our calculations are based on density functional theory within the local density approximation (LDA), generalized gradient approximation (GGA), LDA+*U*, and GGA+*U* functionals. The hexagonal (cubic) structure is 53 meV/CeO_{1.50} (57 meV/CeO_{1.50}) lower in energy than the cubic (hexagonal) structure using LDA+*U* (GGA+*U*), which is consistent (in disagreement) with experimental observations. Thus, these results might indicate a superior description of cerium oxides by the LDA+*U* functional. We found that $V_0^{\text{CeO}_{1.50,\text{hexagonal}}} \approx V_0^{\text{CeO}_{2,\text{fluorite}}}$, while $V_0^{\text{CeO}_{1.50,\text{cubic}}}$ is 4%–9% larger than $V_0^{\text{CeO}_{2,\text{fluorite}}}$, where V_0 is the equilibrium volume per f.u. Therefore, only the results for CeO_{1.50} in the cubic structure can explain the volume expansion of CeO₂ upon reduction conditions, which supports experimental observations of a cubiclike structure for partially reduced CeO₂. The volume expansion is due to the change in the oxidation state of the Ce atoms from Ce^{IV+} in CeO₂ to Ce^{III+} in CeO_{1.50} without changes in the lattice structure.

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Cerium oxides (CeO_{2-x}, 0 ≤ *x* ≤ 1/2) and related compounds such as Ce_{1-x}Zr_xO₂ play an important role in catalysis.¹ CeO_{2-x} is a key component in automotive three-way catalyst used to decrease pollutants from combustion exhaust.^{2,3} Catalysts based on Pt-CeO_{2-x} and Au-CeO_{2-x} have been investigated for the water-gas-shift reaction^{4,5} (CO+H₂O → CO₂+H₂) and Rh-CeO_{2-x} for the steam-reforming reaction⁶ (C₂H₅OH+H₂O → 2CO+4H₂), which are key steps in fuel processing technology to generate H₂. Furthermore, cerium oxides have been extensively investigated as a support for vanadium catalysts.⁷

The main role of cerium oxides in catalysis has been attributed to the ability to easily take up and release oxygen under oxidizing and reducing conditions, respectively, which is known as oxygen storage capacity (OSC).¹ Thus, the reduction of CeO₂ in the fluorite structure into CeO_{1.50} in the hexagonal LaO_{1.50} structure (CeO₂ → CeO_{1.50}+1/4O₂) plays an important role in OSC.^{1,8} It has been reported that partially reduced CeO₂ is stable in the cubic structure up to *x* ~ 0.40, which can be reoxidized to CeO₂ by exposure to an oxidizing environment.¹ For example, CeO_{1.66} and CeO_{1.68} have a cubic superstructure with the lattice parameter twice as large as for the fluorite CeO₂ structure.⁹ Thus, the phase transformation of partially reduced CeO_{2-x} (cubic structure) into CeO_{1.50} (hexagonal structure) occurs only for oxygen compositions close to 1.50. Therefore, it is important to understand the stability of the different phases of CeO_{1.50}, in particular, the stability of the hexagonal structure compared to the cubic phase of CeO_{1.50}.

The theoretical description of Ce-based compounds has been a challenge for theoretical calculations based on density functional theory (DFT) employing local or semilocal exchange-correlation (XC) functionals due to the localized and extended behavior of the Ce 4*f* states in Ce-based compounds.¹⁰ Recent calculations employing DFT+*U*,¹¹⁻¹⁴ in which a Hubbard *U* term is added to the local density approximation (LDA) or generalized gradient approximation (GGA),¹⁵ yielded the correct ground state solution (insulator) of cerium oxides, in particular, for CeO_{1.50}, which cannot be

obtained by plain DFT calculations; e.g., DFT-LDA/GGA yields a metallic solution for CeO_{1.50}.^{11,13} Furthermore, LDA+*U* and GGA+*U* results are in excellent agreement with hybrid functional calculations,¹³ in which a percentage of the exact Fock exchange is added to the XC functional. Thus, DFT+*U* yields a superior description of the cerium oxide properties than plain DFT; however, as for plain DFT calculations, DFT+*U* rely on the choice of a particular XC functional to which the Hubbard *U* is added, e.g., LDA+*U* or GGA+*U*, as well as on the value of the effective Hubbard *U* term.

In this work, we addressed the following problems employing DFT+*U* calculations: (i) Stability of CeO_{1.50} in the hexagonal, cubic, and monoclinic structures. (ii) Volume expansion effect of CeO_{2-x} upon reduction conditions. (iii) Performance of the LDA+*U* and GGA+*U* functionals in the study of cerium oxides, in particular, the stability of the bulk CeO_{1.50}.

The spin-polarized calculations are based on DFT+*U* and employ the projected augmented wave (PAW) method,¹⁶⁻¹⁸ as implemented in the Vienna *ab initio* simulation package (VASP).^{19,20} In DFT+*U*, a Hubbard *U* term corresponding to the mean-field approximation of the on-site Coulomb interaction is added to the LDA or GGA functionals. We employed the rotationally invariant approach,¹⁵ in which the Coulomb, *U*, and exchange, *J*, parameters do not enter separately, but only the difference is meaningful ($U_{\text{eff}}=U-J$). An effective Hubbard parameter of 5.30 eV (LDA+*U*) and 4.50 eV (GGA+*U*) was added only for the Ce 4*f* states, which was used in previous first-principles calculations for cerium oxides.^{13,21} For comparison, LDA and GGA calculations were also performed. The Ce 4*f* states were considered in the valence for all calculations. Furthermore, we also performed GGA calculations in which the Ce 4*f* states were considered as part of the core, which was previously used in the study of the OSC in cerium oxides.⁸ The frozen core states are treated fully relativistically, while the valence states are treated by the scalar relativistic approximation; i.e., spin-orbit coupling is not taken into account for the valence

states. A plane-wave cutoff energy of 400 and 800 eV were chosen for the total energy and stress tensor calculations, respectively. The Brillouin-zone integrations were performed using a \mathbf{k} mesh of $(10 \times 10 \times 5)$, $(4 \times 4 \times 4)$, and $(4 \times 4 \times 3)$ for the hexagonal, cubic, and monoclinic structures, respectively. All forces are optimized up to be smaller than $0.01 \text{ eV}/\text{\AA}$.

All the rare-earth sesquioxides, under a temperature of $\sim 2000^\circ \text{C}$, crystallize in one or three crystal structures,^{22,23} namely, hexagonal,²⁴ monoclinic,²⁵ and body-centered cubic (bcc) structure.²⁶ The hexagonal structure (*A* type, space group $P\bar{3}2/m1$, No. 164) has 2 f.u. ($\text{CeO}_{1.50}$) per unit cell, in which there are two internal parameters ($u_{\text{Ce}}, u_{\text{O}}$) to be determined in addition to the two lattice parameters (a_0, c_0).²⁴ The monoclinic structure (*B* type, space group $C2/m$) has 6 f.u./unit cell. There are three and five nonequivalent Ce and O atoms, respectively.²⁵ The bcc structure (*C* type, space group $Ia\bar{3}$, No. 206), which is also known as a bixbyite structure, has 16 f.u./unit cell.²⁶ There are four internal parameters and one lattice parameter to be determined, i.e., ($u_{\text{Ce}}, x_{\text{O}}, y_{\text{O}}, z_{\text{O}}$, and a_0). There is a close relation between the bixbyite $\text{CeO}_{1.50}$ structure and the fluorite CeO_2 structure; i.e., the bixbyite structure can be derived by removing 25% of the oxygen atoms and then by rearranging the remaining atoms somewhat. The structures are shown in Fig. 1, while the results for the lattice parameters are summarized in Table I.

The cubic structure has the largest equilibrium volume per f.u., V_0 , among the calculated structures, while the monoclinic structure has the smallest one, i.e., ($V_0^{\text{monoclinic}} < V_0^{\text{hexagonal}} < V_0^{\text{cubic}}$). This trend was obtained by all XC functionals. For the hexagonal structure, LDA+ U underestimates V_0 by 3.2%, while GGA+ U overestimates by 3.3% compared with experimental results,²⁴ i.e., similar magnitudes, but opposite directions. For the cubic phase, there are experimental results only for $x=1.53$ and 1.68.^{9,23} For $x=1.53$, which is the closest oxygen composition to $x=1.50$, LDA+ U yields almost the experimental equilibrium volume, i.e., a difference smaller than 0.2%; however, GGA+ U overestimates V_0 by 4.6%. In contrast to the results obtained for the hexagonal phase, the LDA+ U and GGA+ U functionals yield unexpected small and large deviations for V_0^{cubic} , which might indicate a large uncertainty in the equilibrium lattice constants of $\text{CeO}_{1.50}$ in the cubic phase. The monoclinic structure has not been experimentally observed for $\text{CeO}_{1.50}$.²³

Experimental studies have obtained that the equilibrium volume of CeO_2 increases upon reduction of CeO_2 under H_2 atmosphere; e.g., $V_0^{\text{CeO}_2}$ increases up to $\sim 7\%$ at partial reduction conditions.^{27,28} Using the equilibrium volumes of CeO_2 in the fluorite structure per f.u. [39.36 (LDA+ U), 41.37 (GGA+ U), 38.71 (LDA), and 40.92 \AA^3 (GGA)]¹³ and our results obtained in this work for the reduced $\text{CeO}_{1.50}$ in the cubic phase, we found that $V_0^{\text{CeO}_{1.50, \text{cubic}}}$ increases by 4%–9% compared to the equilibrium volume of CeO_2 . Furthermore, we found that $V_0^{\text{CeO}_2} \approx V_0^{\text{CeO}_{1.50, \text{hexagonal}}}$. Therefore, only the results obtained for $\text{CeO}_{1.50}$ in the cubic structure can explain the volume expansion of CeO_2 upon reduction conditions, which provides further evidences for a cubiclike structure for partially reduced CeO_2 . We explain the lattice expansion ef-

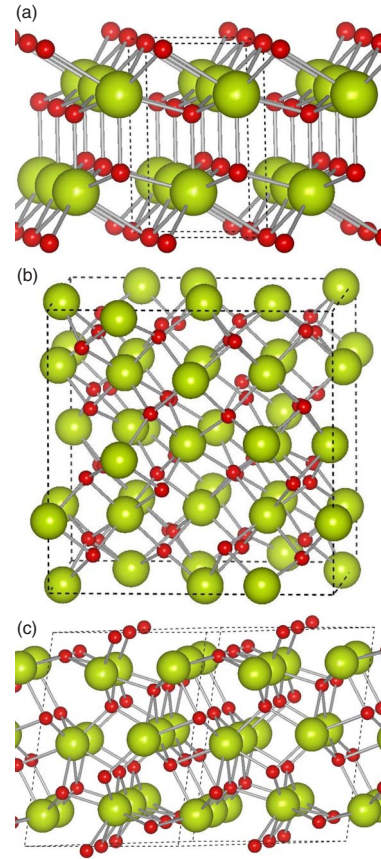


FIG. 1. (Color online) Bulk structures of $\text{CeO}_{1.50}$. (a) Hexagonal La_2O_3 structure. (b) Cubic bixbyite structure. (c) Monoclinic structure. The large and small balls indicate Ce and O atoms, respectively. The cells indicated by dashed lines are the primitive ones for the hexagonal and monoclinic structures and the conventional one for the cubic bixbyite structure.

fect of CeO_2 upon reduction conditions as a consequence of the changes in the oxidation state of the Ce atoms upon reduction conditions and of the high stability of the cubiclike structure of CeO_2 upon reduction conditions. For example, Ce atoms change the oxidation state from $\text{Ce}^{\text{IV}+}$ in CeO_2 to $\text{Ce}^{\text{III}+}$ in $\text{CeO}_{1.50}$, which implies a change in the size of the Ce atoms from 0.97 to 1.14 \AA ,^{29,30} respectively, and hence induces an expansion of the equilibrium volume. Thus, our results suggest that the high stability of the cubiclike structures of CeO_2 upon reduced conditions play an important role in the volume expansion effect.

The relative total energies per f.u., ΔE_{tot} , with respect to the hexagonal structure are summarized in Table II. $\Delta E_{\text{tot}}^{\text{structure}} = E_{\text{tot}}^{\text{structure}} - E_{\text{tot}}^{\text{hexagonal}}$. We found that the monoclinic structure has the highest energy among the three studied structures, which was expected; i.e., there is no reported observation of the monoclinic structure for $\text{CeO}_{1.50}$. The LDA+ U , GGA+ U , and GGA ($4f$ state in the core) functionals obtained $\Delta E_{\text{tot}}^{\text{monoclinic}} \approx 125 \text{ meV}$, while the LDA and GGA functionals yielded about 50 meV. Thus, the localization of the Ce $4f$ states increases the stability of the hexagonal structure compared with the monoclinic phase.

The hexagonal structure has the lowest total energy

TABLE I. Structural parameters of $\text{CeO}_{1.50}$ in the hexagonal, monoclinic, and cubic structures. Equilibrium volume V_0 per f.u., equilibrium lattice constants (a_0, b_0, c_0), internal parameters, and angle between the lattice vectors, β , for the monoclinic structure.

Hexagonal structure (A type)						
	V_0 (\AA^3)	a_0 (\AA)	c_0 (\AA)	u_{Ce}	u_{O}	
LDA+ U^a	38.46	3.87	5.93	0.2441	0.6463	
GGA+ U^a	41.03	3.92	6.18	0.2471	0.6448	
LDA ^a	36.11	3.77	5.88	0.2429	0.6413	
GGA ^a	38.67	3.83	6.08	0.2459	0.6430	
GGA ^b	41.75	3.94	6.20	0.2485	0.6445	
Expt. ^c	39.72	3.89	6.06	0.2454	0.6471	
Monoclinic structure (B type)						
	V_0 (\AA^3)	a_0 (\AA)	b_0 (\AA)	c_0 (\AA)	β	
LDA+ U^a	37.88	13.92	3.58	9.23	99.14	
GGA+ U^a	40.38	14.24	3.65	9.44	99.28	
LDA ^a	35.04	13.53	3.47	9.07	99.20	
GGA ^a	37.85	13.94	3.57	9.27	99.57	
GGA ^b	41.01	14.30	3.67	9.50	99.18	
Cubic structure (C type)						
	V_0 (\AA^3)	a_0 (\AA)	u_{Ce}	x_{O}	y_{O}	z_{O}
LDA+ U^a	43.39	11.16	0.4701	0.3893	0.1481	0.3782
GGA+ U^a	45.45	11.33	0.4716	0.3887	0.1482	0.3792
LDA ^a	40.35	10.89	0.4793	0.3860	0.1440	0.3773
GGA ^a	42.99	11.12	0.4789	0.3874	0.1452	0.3775
GGA ^b	46.54	11.42	0.4699	0.3904	0.1489	0.3783
Expt. ^d	43.44	11.16				
Expt. ^e	42.85	11.11				

^aPAW calculations with the Ce $4f^1$ state in the valence

^bPAW calculations with the Ce $4f^1$ state in the core.

^cExperimental results, Ref. 24.

^dReference 23; result for $\text{CeO}_{1.53}$.

^eReference 9; result for $\text{CeO}_{1.68}$.

among the three studied structures employing the LDA+ U and LDA functionals, which is consistent with experimental observations.²⁴ However, in contrast with experimental results, the cubic structure has the lowest total energy using the GGA+ U and GGA (Ce $4f$ states in the valence and in the core) functionals. To cross-check this particular discrepancy between the XC functionals, which may depend on the performance of the PAW potentials to describe Ce-based compounds, we performed calculations employing the all-electron full-potential linearized augmented plane-wave (FP-LAPW) method, as implemented in the WIEN2K package.³¹ For the FP-LAPW calculations, the core states were treated fully relativistically, while the semicore and valence states are treated by the scalar relativistic approximation. We found that $\Delta E_{\text{tot}}^{\text{cubic}} = -47$ (GGA+ U), -96 (GGA), $+64$ (LDA+ U), and 43 meV (LDA), which are consistent with the PAW results. Hence, these results are not an artifact from the PAW potentials. Hence, the present results might indicate that the LDA+ U functional provides a superior description of the stability of the $\text{CeO}_{1.50}$ compounds compared with the GGA+ U functional. For the FP-LAPW calculations, the optimized PAW LDA+ U and GGA+ U structures were used,

while for LDA and GGA the structures were fully optimized using the FP-LAPW method. Atomic forces are not implemented in the WIEN2K package within the DFT+ U framework.

As mentioned in the Introduction, the reduction energy to reduce CeO_2 into $\text{CeO}_{1.50}$ ($\text{CeO}_2 \rightarrow \text{CeO}_{1.50} + \frac{1}{4}\text{O}_2$) is an important quantity, and it has been the subject of several recent studies.^{12–14,32} We found that the relative total energy differ-

TABLE II. Relative total energy ΔE_{tot} of $\text{CeO}_{1.5}$ given in meV/f.u. in the hexagonal, monoclinic, and bcc structures. $\Delta E_{\text{tot}}^{\text{structure}} = E_{\text{tot}}^{\text{structure}} - E_{\text{tot}}^{\text{hexagonal}}$.

	Hexagonal	Cubic	Monoclinic
LDA+ U^a	0.00	+53	+128
GGA+ U^a	0.00	-57	+123
LDA ^a	0.00	+31	+52
GGA ^a	0.00	-111	+56
GGA ^b	0.00	-105	+122

^aPresent study: Ce $4f$ states in the valence.

^bPresent study: Ce $4f$ states in the core.

ence between the hexagonal and cubic structures is only few tenths of meV/f.u., hence, the choice of the CeO_{1.50} structure does not play a critical role in the calculation of the reduction energy. This finding is in contrast to the relative reduction energy difference of 0.82 eV between cubic and hexagonal structures reported in Ref. 32. This large difference is due to the approximation of the complex cubic bixbyite structure by the fluoritelike structure with 25% of oxygen vacancies, as reported in Ref. 32. Therefore, conclusions based on that particular approximation should be taken with caution.

As mentioned above, LDA+*U* yields a superior description of the stability of CeO_{1.50}, and hence, bulk modulus calculations were performed using only the LDA+*U* functional. The bulk modulus B_0 for the different phases were obtained by fitting the relaxed potential energy surface (13 regularly space volumes) to the Murnaghan's equation of state. We obtained 1.30, 1.53, and 1.24 Mbar for the hexagonal, cubic, and monoclinic structures, respectively, while $B_0=2.10$ Mbar for CeO₂ using LDA+*U*.¹³ Thus, the formation of oxygen vacancies in the fluorite CeO₂ structure and changes in the oxidation state of the Ce atoms decreases the bulk modulus from 2.10 to 1.53 Mbar. Furthermore, B_0 decreases from 1.53 to 1.30 Mbar due to the phase transition from the cubic to the hexagonal structure.

In summary, we reported DFT+*U* and DFT calculations

for the CeO_{1.50} system in the hexagonal, cubic, and monoclinic structures. We found that the LDA+*U* and LDA functionals yielded the lowest total energy for the hexagonal structure, which is consistent with experimental observations; however, GGA+*U* and GGA (Ce 4*f* states in the valence or in the core) calculations are in contrast with the experimental results. Therefore, our results might indicate that LDA+*U* provides a superior description of the cerium oxides than the GGA+*U* functional. Plain DFT calculations yield a metallic solution for CeO_{1.50}. However, the stability of CeO_{1.50} and structure properties are consistent with DFT+*U* calculations. Furthermore, we explain the volume expansion effect of the CeO₂ upon reduction conditions, as a consequence of the changes in the oxidation state of Ce atoms from Ce^{IV+} in CeO₂ to Ce^{III+} in CeO_{1.50} and due to the high stability of the partially reduced CeO₂ in the cubiclike structure.

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