

# Theoretical Material Research with First Principle Calculation Aiming at High-efficiency Hydrogen Production Using Solar Thermochemical Energy

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## Research Article

### Keywords:

**Posted Date:** January 24th, 2022

**DOI:** <https://doi.org/10.21203/rs.3.rs-1278972/v1>

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# Abstract

In recent years, hydrogen energy has been attracting attention, and the hydrogen gas production using solar thermal energy has been conducted. The studies of Kodama *et al.* were reported that the cyclic reaction can efficiently produce the hydrogen gas through a two-step thermal redox reaction with the cerium oxide. The transition metal doping into the cerium oxide improved the reaction efficiency. In our work, we considered the doping effect on the thermal two-step redox reaction. As a result of the calculation by the DV-X $\alpha$  method, it was clarified that the doped cerium oxide becomes a strong bond, the large BOP value without changing the ceria crystal structure in the two-step thermal redox reaction. The theoretical calculation results corresponded to the reaction efficiency improvement of the thermal reaction in experimental results.

# Introduction

Energy is essential, and the continuous energy production is one of the global problems. There are various forms of energy in the world, especially a hydrogen energy has attracted much attention in recent years. The reason is that the diversity of energy production can be created by converting the earth's abundant water into energy, and the dependence of the energy production on existing petroleum materials can be reduced.

In recent days, the global hydrogen gas production is about 700 billion Nm<sup>3</sup>, enough to supply the fuels for more than 600 million fuel cell vehicles. However, about half of the hydrogen gas is made from natural gas, nearly 1/3 of the hydrogen is made of crude oil in the refineries, and most of the hydrogen gas is consumed in the refineries<sup>1</sup>. From this background, many studies have also been reported on the sustainable production of the hydrogen energy from solar thermal energy, focusing on solar energy that can be used permanently<sup>2-5</sup>. Solar energy, typed by renewable energy, irradiates energy from the sun to the earth. It is equivalent to an enormous amount of about 4 million EJ (1 EJ = 1,018 J) per year<sup>6</sup>.

The amount of energy theoretically extracted could be about 19,000 EJ, and the amount of energy that can be technically extracted is estimated only about 1,900 EJ. It is also estimated to consume just about 20 EJ energy per year in human living. If we could convert a vast amount of solar energy into other energy, we could get enough energy for our living<sup>7</sup>. So, it makes sense to use solar energy for hydrogen energy production. In addition, various studies have been conducted on the supply chain, such as the transport and operation of the hydrogen energy<sup>8</sup>. Hydrogen gas is also transported by tanker and truck after being converted into liquid hydrogen or liquid fuels such as methanol, ammonia, and methylcyclohexane (MCH). The basis for producing hydrogen energy is also making significant progress, so the importance of hydrogen energy production is increasing<sup>1, 9-10</sup>. In laboratory experiments<sup>11-16</sup>, many hydrogen gas production demonstration experiments using beam down solar concentrators have been conducted<sup>17-20</sup>, and it is expected that commercialization of hydrogen gas production will become possible.

In hydrogen gas production, a two-step thermal redox reaction is used. The two-step thermal redox reaction is a cyclic redox reaction consisting of a reduction reaction (1st step: eqn.1) with oxygen desorption at high temperatures ( $> 1,000\text{ }^{\circ}\text{C}$ ) and an oxidation reaction (2nd step: eqn.2) with oxygen adsorption at low temperatures ( $< 1,000\text{ }^{\circ}\text{C}$ ). In the thermal oxidation reaction (2nd step), it is possible to decompose water molecules and efficiently produce hydrogen gas under high temperature steam<sup>14</sup>.



In addition to the hydrogen production reaction, the thermal redox reaction can also be used for  $\text{CO}_2$  reforming methane<sup>21-22</sup>, so the application of the two-step thermal redox reaction is wide.

In the two-step thermal redox reaction, various metal oxides have been used as catalytic reaction ceramics to improve hydrogen gas production efficiency. Hercynite ( $\text{FeAl}_2\text{O}_4$ ) was used by Ehrhart and his colleagues at the beginning of the hydrogen gas production study<sup>23</sup>. Wong *et al.* explored thermochemical heat storage (TCS) materials using thermal redox reactions in  $\text{Co}_3\text{O}_4/\text{CoO}$  and  $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$ <sup>24</sup>. Other research groups have also reported the two-step thermal redox reactions such as  $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$ ,  $\text{Co}_3\text{O}_4/\text{CoO}$ , and  $\text{CuO}/\text{Cu}_2\text{O}$ <sup>25-29</sup>. Kodama *et al.* have reported various hydrogen-producing materials using  $\text{Fe}_3\text{O}_4/\text{c-YSZ}$ ,  $\text{NiFe}_2\text{O}_4$ <sup>30</sup>,  $\text{NiFe}_2\text{O}_4/\text{m-ZrO}_2$ ,  $\text{Fe}_3\text{O}_4/\text{m-ZrO}_2$ <sup>31</sup>,  $\text{Fe}_3\text{O}_4/\text{m-ZrO}_2/\text{MPSZ}$ <sup>32-33</sup>. Among these experiments, the research on cerium oxide has been promoted in recent years<sup>34-37</sup>. Cerium oxide is a type of lanthanoid oxide ( $\text{CeO}_2$ ) used as an Oxygen Storage Capacity (OSC) material. It was found to be apply to not only a catalyst but also a thermal two-step redox reaction.

In the hydrogen gas production studies, it was found that cerium oxide increases the hydrogen gas production efficiency and the redox reaction cyclability<sup>38</sup>. Furthermore, doping transition metals into cerium oxide further increase the efficiency and cyclability has also been reported<sup>39-41</sup>. Although it is clear from the experimental facts that cerium oxide-based materials are effective, the following point are not clear.

(i) The hydrogen gas production properties of doped cerium oxide exceed those of pure cerium oxide.

As a specific point, we decided to focus on the stability of the crystal structure. It is the bond strength between the metal ions and the oxygen ions in the cerium oxide. The thermal reduction reaction means that the oxygen ions in cerium oxide are defective, while the thermal oxidation reaction is that the oxygen is taken into the cerium oxide crystal. So, the oxygen atoms adsorption and desorption are the critical matter during the thermal redox reaction. In addition, the experimental fact that the reaction efficiency and cyclability are improved by the transition metal doping into cerium oxide. It was expected that the transition metal doping into cerium oxide changes to chemical bonds suitable for the redox reaction cycle. Based on these hypotheses, we tried to solve the question (i).

This study aims to explain theoretically the experimental facts concerning the above question (i) contents by using DV-X $\alpha$  molecular orbital calculation. The DV-X $\alpha$  method was developed by D. E. Ellis (Northwestern University) and H. Adachi (Kyoto University)<sup>42-46</sup>. The self-consistent field method (SCF method) proposed by Hartree in 1928 and includes the Hartree-Fock-Slater method proposed by J. C. Slater<sup>47</sup>. The electronic potential proposed by Slater is called "X $\alpha$  potential," and the DV-X $\alpha$  method is another name for the Hartree-Fock-Slater method. The DV-X $\alpha$  method has the advantage of numerically evaluating the electronic state of a substance. Therefore, accurate calculation results can be obtained for the *d*- or *f*-orbitals of the metal atoms. Due to the above advantages, the DV-X $\alpha$  method is used in the theoretical calculations for cluster models of the doped cerium oxide.

## Result And Discussion

### Evaluation of BOP

In the metal-doped ceria, it was suggested that the stability of the ceria crystal structure was improved by doping the transition metals, as described in the introduction. We used the BOP value as a parameter of bond strength to discuss the stability of the ceria crystal structure. If the BOP values become larger, the more overlap in the wave functions between the two atoms, and the bond become a strong bond. In this study, to discuss the stabilization of the metal-doped crystal structure, we consider the bond strength between the doped metal atom (M) and the surrounding oxygen atoms in the M@Ce<sub>12</sub>O<sub>8</sub><sup>36+</sup> cluster model. We discuss the stability of the crystal structure in the doped ceria by comparing the BOP values between the M-O two atoms.

At first, we focused on the doping of Mn, Fe, Co, and Ni as the 3*d*-orbital transition metals to discuss the doped ceria with Mn, Fe, Co, and Ni reported by Kodama *et al.*. We also report the theoretical calculation results of the ceria with Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn as doped-metal species.

The BOP table for the M@Ce<sub>12</sub>O<sub>8</sub><sup>36+</sup> cluster models, M = Ce (non-substitution) and M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn (substitution) is shown in Table 1. The horizontal items show the type of the doped metal, and the vertical items show the valence of the doped metal. The valence of the doped metal was varied from tetravalent (M<sup>4+</sup>) to trivalent (M<sup>3+</sup>) in each 0.05 valent, and each cell was colored by gradient according to the obtained BOP values, blue and red for larger and smaller values, respectively.

As can be seen from the Table 1, comparing the BOP values change with the doped metal species and the BOP values with the valence changes, it was found that the BOP value changes are more marked at the difference of the doped metal species. With and without doping the transition metal, the difference shows that the BOP values are large in transition metal-doped ceria than in undoped ceria. This calculation result means that the transition metals doping into ceria would stabilize the ceria crystal structure. If the ceria crystal structure would be unstable and its structure completely collapses in the redox reaction, the efficiency of the thermal redox reaction would show less reactive because it will not have cyclability. On the other hand, if the crystal structure would be stable without the collapse of the metal-doped ceria, the

reactivity and cyclability of the thermal two-step redox reaction will be enhanced. Moreover, Kodama *et al.* reported that thermal redox reactivity increases with Mn or Fe doped ceria. So, it was suggested that the interatomic bonding in Mn- and Fe-doped ceria becomes stronger than in undoped ceria. It makes the crystal structure stabilization more suitable for thermal redox reactions.

Table 1

The BOP table for the  $M@Ce_{12}O_8^{36+}$  cluster models (M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ce). The maximum value (1.967) is set to blue and the minimum value (0.671) to the red, each cell is colored by gradient according to the obtained BOP values, blue for larger values and red for smaller values.

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ce
4.00	1.435	1.567	1.513	1.453	1.391	1.315	1.187	1.047	0.935	0.692
3.95	1.435	1.567	1.512	1.452	1.391	1.314	1.187	1.046	0.935	0.691
3.90	1.434	1.566	1.512	1.452	1.390	1.314	1.186	1.046	0.934	0.690
3.85	1.433	1.566	1.511	1.451	1.390	1.313	1.186	1.045	0.934	0.689
3.80	1.433	1.565	1.510	1.450	1.389	1.313	1.185	1.045	0.933	0.688
3.75	1.432	1.565	1.510	1.450	1.388	1.312	1.185	1.045	0.933	0.687
3.70	1.432	1.565	1.509	1.449	1.388	1.312	1.185	1.044	0.932	0.686
3.65	1.431	1.564	1.508	1.448	1.387	1.312	1.184	1.044	0.932	0.685
3.60	1.431	1.564	1.508	1.448	1.387	1.311	1.184	1.043	0.931	0.684
3.55	1.430	1.564	1.507	1.447	1.386	1.311	1.183	1.043	0.931	0.683
3.50	1.430	1.563	1.506	1.447	1.386	1.310	1.183	1.042	0.931	0.682
3.45	1.429	1.563	1.506	1.446	1.385	1.310	1.182	1.042	0.930	0.681
3.40	1.428	1.562	1.505	1.445	1.385	1.309	1.182	1.042	0.930	0.679
3.35	1.428	1.562	1.504	1.445	1.384	1.309	1.181	1.041	0.929	0.678
3.30	1.427	1.562	1.504	1.444	1.383	1.308	1.181	1.041	0.929	0.677
3.25	1.427	1.561	1.503	1.444	1.383	1.308	1.180	1.040	0.928	0.676
3.20	1.426	1.561	1.502	1.443	1.382	1.307	1.180	1.040	0.928	0.675
3.15	1.426	1.561	1.502	1.442	1.382	1.307	1.180	1.039	0.927	0.674
3.10	1.425	1.560	1.501	1.442	1.381	1.306	1.179	1.039	0.927	0.673
3.05	1.424	1.560	1.501	1.441	1.381	1.306	1.179	1.039	0.927	0.672
3.00	1.424	1.560	1.500	1.440	1.380	1.305	1.178	1.038	0.927	0.671

The calculated BOP values were compared with the experimental results of each metal-doped ceria (doped with M = Mn, Fe, Co, Ni). The calculated BOP values of Mn and Fe doped ceria had larger than that of Ni and Cu doped ceria. Therefore, the bond between the doped metal atom and the surrounding oxygen atoms is strong in Mn and Fe doped ceria, which relates to the stoichiometric thermal redox reaction. The bond is weak in Ni and Cu doped ceria, which relates to the nonstoichiometric thermal redox reaction. From this fact, it is understood that when the bonds are strong, the doped ceria crystal does not easily collapse, while when the bonds are weak, the doped ceria crystal easily collapses. The BOP values suggest that the contribution of doping to the stabilization of the crystal structure of ceria. Moreover, the BOP values were arranged in M = V, Cr, Mn, order for each doped metal species. Even in the same period

metals, it was suggested that the V, Cr, and Mn doping into ceria improves the reaction performance of the thermal reduction reaction.

Table 2

The BOP table for the  $M@Ce_{12}O_8^{36+}$  cluster models arranged according to the period and group of the periodic table. When the maximum value (2.117) is set to blue and the minimum value (0.509) to the red, each cell is colored by gradient according to the obtained BOP value, blue and red for larger and smaller values, respectively.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1																		
2																		
3																		
4				1.435	1.567	1.513	1.453	1.391	1.315	1.187	1.047	0.935						
5				1.563	1.935	1.995	1.860	1.718	1.605	1.372	1.095	0.975						
6				1.615	1.984	2.117	1.980	1.825	1.710	1.494	1.173	0.958						
7																		
			La系	0.509	0.692	0.854	0.870	0.867	0.867	0.867	0.874	0.874	0.881	0.891	0.899	0.907	0.908	1.125
			Ac系															

Next, the results will be described in the case of doping into the ceria with the  $4d$  and  $5d$  transition metal and the lanthanoid metal elements. We report the results of doped ceria with Zr to Cd of the  $4d$  transition metal element, Hf to Hg of the  $5d$  transition metal element, and La to Yb of the lanthanoid metal element.

Table 2 shows the BOP values of the  $M@Ce_{12}O_8^{36+}$  cluster model,  $M = Ce$  (unsubstituted) and  $M = 4d$  and  $5d$  transition metal elements and the lanthanoid metal elements. The substituted metal elements are arranged according to the periodic table, with the group and the period on the horizontal and the vertical axis, respectively. The valence of the substituted doped metal is set at quadrivalent ( $M^{4+}$ ), and the colors of each cell by gradient according to the obtained BOP value, blue and red for larger and smaller values, respectively.

The results in Table 2 suggested that the metal-doping with the  $3d$  transition metals stabilizes the ceria crystal structure rather than with the lanthanoid metals. In addition, focusing on the group of doped metal elements, the result of the BOP value was larger in the order of the  $3d$ ,  $4d$ , and  $5d$  transition metals. In doping with the  $3d$ ,  $4d$ , and  $5d$  transition metal elements, it was easily understood that the stability was changed due to the number of electrons occupied by the outermost orbitals. The bond between the doped metal atom and the oxygen atom (M-O) became more stabilized by doping with the 5, 6, and 7 group metals. On the other hand, doping with the lanthanoid metals, which have the f-orbital in the outer shell, the stability in the ceria crystal structure could not be effective.

Table 2 shows the doping usefulness of the transition metal atoms with  $d$ -orbitals, and the stability depends on the number of electrons occupied by the  $d$ -orbitals. In addition, when the  $4d$  and  $5d$  transition metals were doped, the crystal structure was more stable than the  $3d$  transition metals. Therefore, it was

considered that the index for the suitable hydrogen production materials was given about the metal-doped ceria material, which has not yet been synthesized.

## Evaluation of p-DOS

The BOP change depending on the doped metal is described in sections 3-1. Although all of them have the same crystal structure of the fluorite type, the difference in the bond strength could be explained by the magnitude of the interaction between the doped metal and the oxygen atom in the  $M@Ce_{12}O_8^{36+}$  cluster model. Here, it will be described that the features of the doped ceria with the  $3d$  transition metals, and the relation between the doped metal atoms and the oxygen atoms. The p-DOS results show the  $3d$  orbital of the transition metal and the  $2p$  orbital of the first nearest oxygen atom in each  $M@Ce_{12}O_8^{36+}$  cluster model.

Figure 1 shows the p-DOS in each transition metal's  $3d$  orbitals, and Fig. 2 shows the p-DOS in the  $2p$  orbitals of the oxygen atom in each  $3d$  transition metal-doped  $M@Ce_{12}O_8^{36+}$  cluster model ( $M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ce$ ). In both cases, the vacuum level was set as 0 eV as the reference level. From Fig. 1, doping into ceria significantly changes the electronic state of the  $3d$  orbitals. The  $d$ -orbital levels are shifted to lower energy as the atomic number of the doped metal increases. On the other hand, Fig. 2 shows little change in the peak position or peak shift regardless. This result suggested that the effect of doping the transition metal was small on the electronic state of oxygen.

Therefore, it was suggested that the interaction between the oxygen atom and the cerium atoms affected the bond state between the doped metal atom and the oxygen atom (M-O). In other words, the stabilization of the ceria crystal can be achieved by doping transition metal atoms which do not prevent the spatial expansion of electrons on cerium and oxygen atoms. It is because that most of the bonds in the ceria crystal are composed of the bonds between the cerium atoms and the oxygen atoms (M-O). The bond strength shown in the results of Tables 1 and 2 is dependent on the doped central metal.

Next, Figs. 3 and 4 show the result of doping the  $4d$  and  $5d$  transition metal into the ceria. The p-DOS in the  $2p$  orbital of oxygen in Figs. 3 and 4, as in Fig. 2, shows little change in the peak position or peak shift. These results also indicated that there is no significant difference in the behavior of electrons on oxygen atoms, and that the stability in ceria crystal structure is determined by doped transition metal atoms.

It was suggested that the bond strength is formed by the interaction between the doped metal atoms and the oxygen atoms. We confirmed whether the bond strength (the BOP value) between the doped metal atom and oxygen atoms (M-O) is related to the HOMO and LUMO levels and the bandgap in each metal-doped ceria. In Table 3, LUMO and HOMO levels and the bandgap based on based on the reference level as the vacuum levels in the  $M@Ce_{12}O_8^{36+}$  cluster model. Fig. 5 shows the values summarized in Table 3 regarding energy levels on the vertical axis and for each doped metal on the horizontal axis. The LUMO and HOMO levels and the bandgap of each  $M@Ce_{12}O_8^{36+}$  cluster model are related to the stability in

Table 1. The vanadium(V) doped ceria has the lowest bandgap of 0.066 eV, the BOP value of 1.567 (V<sup>4+</sup>) is the largest BOP value among the 3*d* metal-doped ceria.

Table 3  
The LUMO (eV), HOMO (eV) level, and the bandgap (eV) in each M@Ce<sub>12</sub>O<sub>8</sub><sup>36+</sup> cluster model based on the reference level as the vacuum level.

	LUMO	HOMO	Gap
Ti	8.592	7.638	0.954
V	8.708	8.642	0.066
Cr	8.617	8.492	0.125
Mn	8.585	8.300	0.285
Fe	8.537	8.099	0.439
Co	8.615	8.362	0.253
Ni	8.613	8.142	0.472
Cu	8.607	7.893	0.714
Zn	7.744	7.606	0.137
Ce	8.598	7.222	1.376

The bandgap is the largest at 1.376 eV in the undoped ceria, with the BOP value of 0.692 (Ce<sup>4+</sup>). It is the smallest BOP value compared to the 3*d* transition metal-doped ceria. However, there is no relationship, such as a smaller bandgap tends to have larger BOP values, or a larger bandgap tends to have smaller BOP values. Next, the HOMO and LUMO levels are explained. The highest HOMO level is 7.638 eV with the V-doped ceria, while the lowest HOMO level is 7.222 eV with the undoped pure ceria. At first, there seemed to be a correlation between the HOMO level and the BOP values. However, there is no correlation between the stability of the ceria crystal structure (BOP values) and the HOMO level, as a similar relationship between the BOP values and the bandgap. Fig. 5 shows the LUMO level colored blue and the HOMO level colored red. It indicates that there is no significant difference in the LUMO levels in each metal-doped ceria. Therefore, it seemed that there is also no relationship between the LUMO level and the BOP value.

The HOMO, LUMO levels, and the bandgap results for 4*d* and 5*d* transition metals show similar results to the 3*d* transition metal-doped ceria. Therefore, there is no relationship between the BOP values and the

HOMO, LUMO levels, or bandgap values for each metal-doped. The results of each detail calculation are summarized in SI 3, 4, 5 and 6.

In Fig. 6, p-DOS in the  $2p$  orbitals of the oxygen atoms are shown in each  $3d$  transition metal-doped  $M@Ce_{12}O_8^{36+}$  cluster model ( $M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ce$ ). The HOMO level in each  $M@Ce_{12}O_8^{36+}$  cluster model is the reference level. As shown in Fig. 2, there is no difference in the shape of the peak profile, but there is a difference in the peak positions. It was considered that a slight energy shift is one of the effects of metal doping into ceria.

## Evaluation of bonding orbitals and antibonding orbitals

The difference of the bond strength between the doped metal atom and the surrounding oxygen atoms (M-O) greatly affects the stability of the ceria crystal structure. Bonding and antibonding orbitals in molecular orbitals will be described in this section. Interactions between the doped metal atom and the surrounding oxygen atoms in each  $M@Ce_{12}O_8^{36+}$  cluster model are explained by interpreting the bonding and antibonding orbitals

In Fig. 7, the bonding orbitals between the metal atom and the surrounding oxygen atoms are shown on the right, and the antibonding orbitals are shown on the left for each doped metal atom, based on the reference level as the vacuum level in each  $M@Ce_{12}O_8^{36+}$  cluster model. From Fig. 7, the peaks of the bonding orbital component are concentrated around at 5-7 eV except for the Zn-doped ceria. It means that there was no difference in the factors which strengthened the bonds even if the kind of the doped metal changed. However, focusing on the antibonding orbital component, the peak of the antibonding orbital component shifts to the lower energy side. So, when the atomic number of the doped metal atom is increased, the orbitals of the antibonding component are more occupied below the HOMO level. Then, it was suggested that more electrons are occupied in the antibonding orbital component, which weakens the bonds between the doped metal atom and the oxygen atoms (M-O).

Next, it is shown the bonding and antibonding of the  $3d$  orbitals of the doped metal atom and the  $2p$  orbitals of the oxygen atoms in Figs. 8 and 9. Then, the energy level in Fig. 8 based on the reference level as the vacuum level, in Fig. 9 based on the reference level as the HOMO level in each in  $M@Ce_{12}O_8^{36+}$  cluster model. In Fig. 8, the distribution of the bonding and antibonding orbital components, whose peak does not change in Fig. 7. This indicated that the bonding between the doped metal atom and the oxygen atoms depends on the magnitude of the interaction between the  $3d$  orbitals and the  $2p$  orbitals of the oxygen atoms. When the doped metal is changes, there is no change in the bonding orbital component between the  $3d$  orbitals of the doped metal atom and the  $2p$  orbitals of the oxygen atoms. It was suggested that these factors are reflected in the BOP results shown in Table 1. From the result in Fig. 9, it can be clearly seen that the antibonding orbital component increases below the HOMO level.

Compared Figs. 1 and 2 with Fig. 8, it was understood that the peak shifts of the  $3d$  orbitals shown in Fig. 1 are as well as the antibonding peaks in Fig. 8. The peak shifts of the p-DOS in the  $2p$  orbitals in Fig. 2

are as well as the bonding peaks in Fig. 8. This result supports the fact that most of the bonding orbitals are occupied by the  $2p$  orbitals of the oxygen atoms, while most of the antibonding orbitals are occupied by the  $3d$  orbitals of the doped metal atom. The antibonding orbital component is mainly occupied by the  $3d$  orbitals of the doped metal atom, and the energy level also changes depending on the doped metal elements.

Here, it is shown that the electronic state of the  $2p$  orbitals of the oxygen atoms does not change even in the case of not only the  $3d$  transition metal-doped but also  $4d$  and  $5d$  transition metal-doped. The results of the bond composition between the metal  $4d$ ,  $5d$  orbitals and the oxygen  $2p$  orbitals show in Figs. 10 and 11 based on the reference level as the HOMO level in each  $M@Ce_{12}O_8^{36+}$  cluster model. From these results, the energy level of the antibonding orbital component changes while the bonding orbital component does not change. This tendency is like the case of the  $3d$  transition metal-doped. Moreover, the magnitude of the bonding orbital is higher in order of the  $3d$ ,  $4d$ , and  $5d$  orbitals. Based on the spread of the  $d$ -orbital, it was suggested that the  $5d$  transition metal doping stabilizes the cerium oxide crystal structure, as shown in Table 2.

From the calculation results of the bonding and antibonding components between the  $d$  orbitals of the doped metal atom and the  $2p$  orbital of the oxygen atom, it was considered that the oxygen atom is affected by the cerium atoms more than the doped metal atoms in the cerium oxide crystal. As can be seen in Table 2, the bonds between doped metal atoms and oxygen atoms with  $d$ -orbitals in their outermost shell orbitals are strong.

As shown in Fig. 12, the spread of the wave function in the  $3d$  orbital (#24  $t_{2g}$ :  $d_{xy}$  orbital) around the Cu metal atom is smaller than that in the case of the V doped. This result suggests that the ceria structure can be stabilized by the  $d$ -orbitals in the outermost shell orbitals, an appropriate number of electrons must be occupied in the outermost shell orbitals of the doped metal. Examples are given for the  $3d$  transition metals doping into the ceria, and the same applies to the case for the  $4d$  or  $5d$  transition metals doping into the ceria. Therefore, when a metal classified into group 5, 6, or 7 is doped, the bonds between the doped metal atom and the oxygen atom become stronger because the repulsion between electrons occupied on the  $d$ -orbital of the doped metal atom and those occupied on the  $2p$  orbital of oxygen is not too large, and the electrons occupied on more  $d$ -orbitals can participate in the bonds between the doped metal atom and the oxygen atoms.

As shown in Table 2, the strong bond in the order of  $3d$ ,  $4d$ , and  $5d$  orbitals is attributed to the fact that the wave functions of the  $2p$  orbitals of the oxygen atom and the  $d$ -orbitals of the doped metal atom are in phase with each other and that more electrons can be shared with the  $2p$  orbitals of the oxygen atom in the  $5d$  orbitals with the larger wave functions. In other words, it is important for stabilizing the ceria crystal structure to dope the metal atoms that do not prevent the spatial spread of cerium atoms and electrons on oxygen atoms in the ceria crystal.

## Conclusion

In the case of the *d*-orbital metal doping, the stability of the interatomic bond can be predicted by the overlap of the wave functions between the *d*-orbitals of the doped metal and the *2p* orbitals of the first nearest oxygen atom. As for the case of transition metal doping in the cerium oxide, the effect of doped metal atoms can be discussed by focusing on the interaction of the outermost orbitals of each atom. By evaluating whether the bonding orbitals between the metal and oxygen atoms are classified as the bonding or antibonding orbitals, it is possible to predict the stability of the crystal structure when the metal atoms are doped into ceria.

Theoretical study was carried out to solve the problem of (i) as mentioned in Section 1, considering that the stabilization of crystal structure leads to the improvement of the cyclicity and efficiency of thermal redox reaction. Then, the stabilization of the crystal structure was discussed focusing on the bonds between the doped metal atom and the oxygen atoms (M-O). Specifically, we concluded that the following factors stabilize the crystal structure when the metal atoms are doped in cerium oxide.

- (I.) The outermost shell orbital of the doped metal atom must be a *d*-orbital.
- (II.) The appropriate number of electrons must be occupied by the *d*-orbitals in the doped metal atom.
- (III.) The principal quantum number of the *d*-orbitals of the doped metal atom must be large.

In this study, we found that the cerium oxide crystal structure is stabilized depending on these factors. In addition, the doped ceria was expected to improve the cyclicity of the two-step thermal reaction and function as a hydrogen generating material whose crystal structure does not collapse during the thermal redox reaction.

## Method

### First Principle Calculation

This study aims to explain theoretically by using the DV-X $\alpha$  method. We calculated the electronic structures of the M@Ce<sub>12</sub>O<sub>8</sub><sup>36+</sup> cluster model composed of 12 cerium (Ce) atoms with the quadrivalent per Ce atom and 8 oxygen ions(O<sup>2-</sup>), in which the central atom (M) is substituted with another metal atom (M = *3d*, *4d*, and *5d* transition metals, and the lanthanoid metals) in each calculation model. In other words, we substituted the central M atom with the *3d* (M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn), *4d* (M = Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd), and *5d* transition metal (M = Hf, Ta, W, Re, Os, Ir, Au, Hg), or the lanthanoid metal (M = La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Ho, Tm, Yb, Lu). Then, M = Ce doped model (Ce@Ce<sub>12</sub>O<sub>8</sub><sup>36+</sup> = Ce<sub>13</sub>O<sub>8</sub><sup>36+</sup>) means that the cluster model is the pure cerium oxide with no substitution. The absolute coordinates of the calculated cluster model were determined by the reported experimental data. The M@Ce<sub>12</sub>O<sub>8</sub><sup>36+</sup> cluster model has a high symmetry of the fluorite type structure (Fm-3m), and the lattice constant of 5.411 Å. It has the central metal atom(M), the 8 oxygen atoms around the central atom, 12 cerium atoms are located on the outside of each oxygen atom.

The calculations are performed self-consistently until the difference in orbital populations between the initial and final states of the iteration by means of the DV-X $\alpha$  molecular orbital method is less than 0.0005 electrons. The calculations were also performed considering the Madelung potential in each cluster model.

## Declarations

## Acknowledgement

The authors appreciate Prof. H. Adachi (Kyoto Univ.) for permission to use a computational program. The authors express thanks to Drs. F. Izumi (Nat'l Inst. for Materials Sci., Japan) and K. Momma (Nat'l Museum of Nature and Sci., Tokyo) for permission to use a 3D visualizing program "VESTA". T.K. and T.I. is supported by JSPS KAKENHI Grant 20H00362.

## Author contributions

T. N. performed the research tasks such as the theoretical calculation. T.K. and T.I. designed this project. G. S. gave us new interpretation and the meaningful data (in Fig. 12). T.N., T.K., and T.I. contributed to the discussion of the results. T.N. and T.I. revised the manuscript.

## Competing interests

The authors declare no competing interests.

## Additional information

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## Figures

Figure 1

p-DOS for the  $3d$  orbitals of the doped metal atoms in the  $M@Ce_{12}O_8^{36+}$  cluster model, the vacuum level is the reference energy level ( $M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ce$ ).

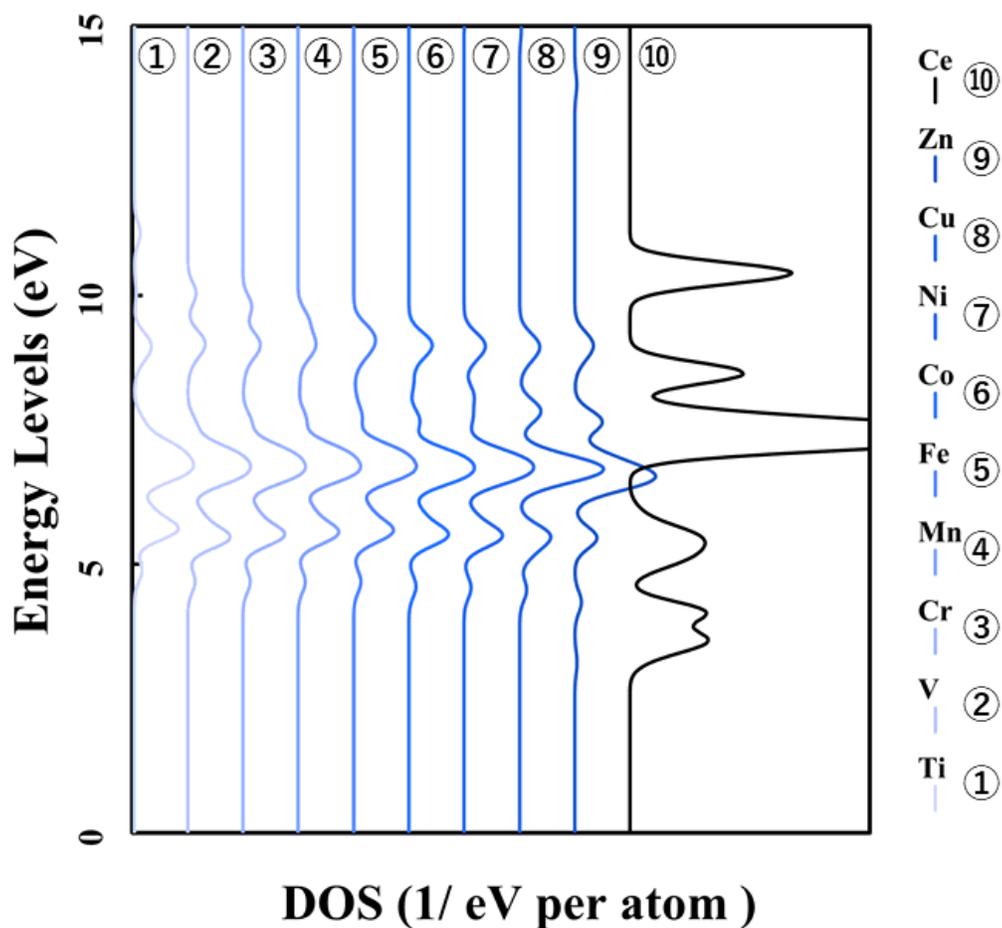


Figure 2

p-DOS for the  $2p$  orbitals of the oxygen atoms in the  $M@Ce_{12}O_8^{36+}$  cluster model, the vacuum level is the reference energy level ( $M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ce$ ).

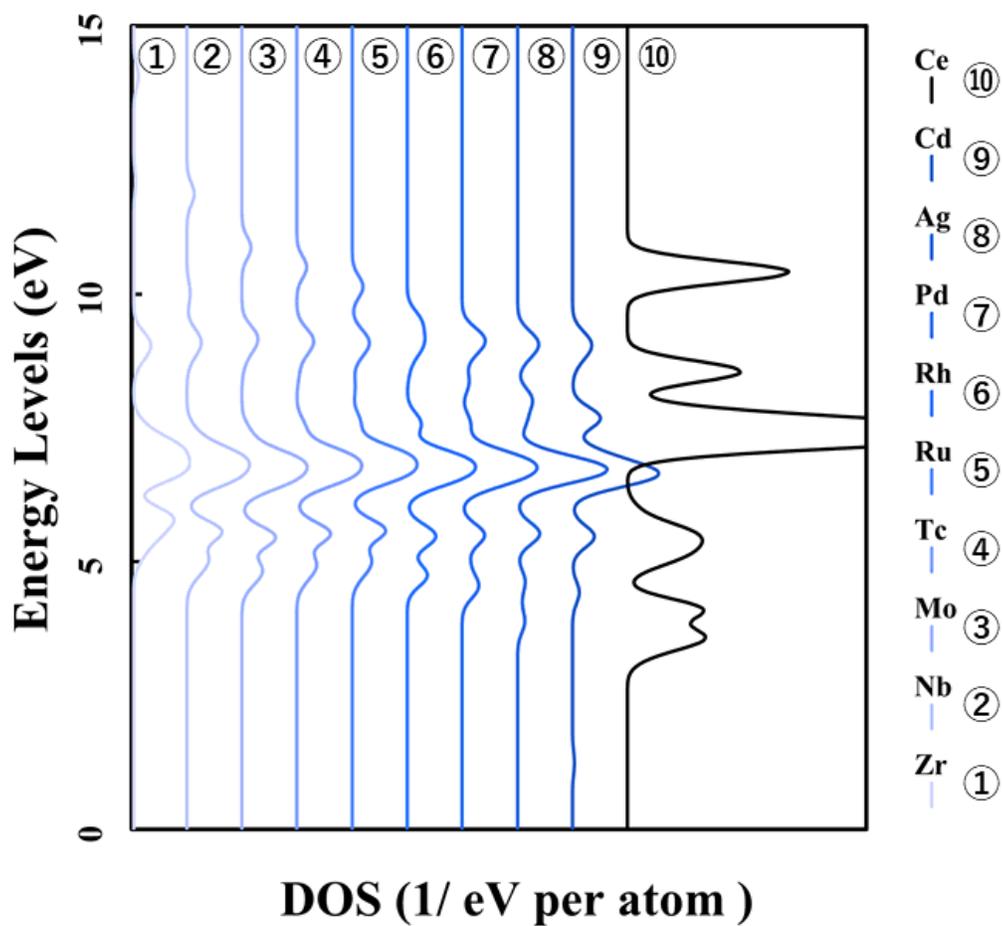


Figure 3

p-DOS for the  $2p$  orbitals of the oxygen atoms in the  $M@Ce_{12}O_8^{36+}$  cluster model, the vacuum level is the reference energy level ( $M = Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, Ce$ ).

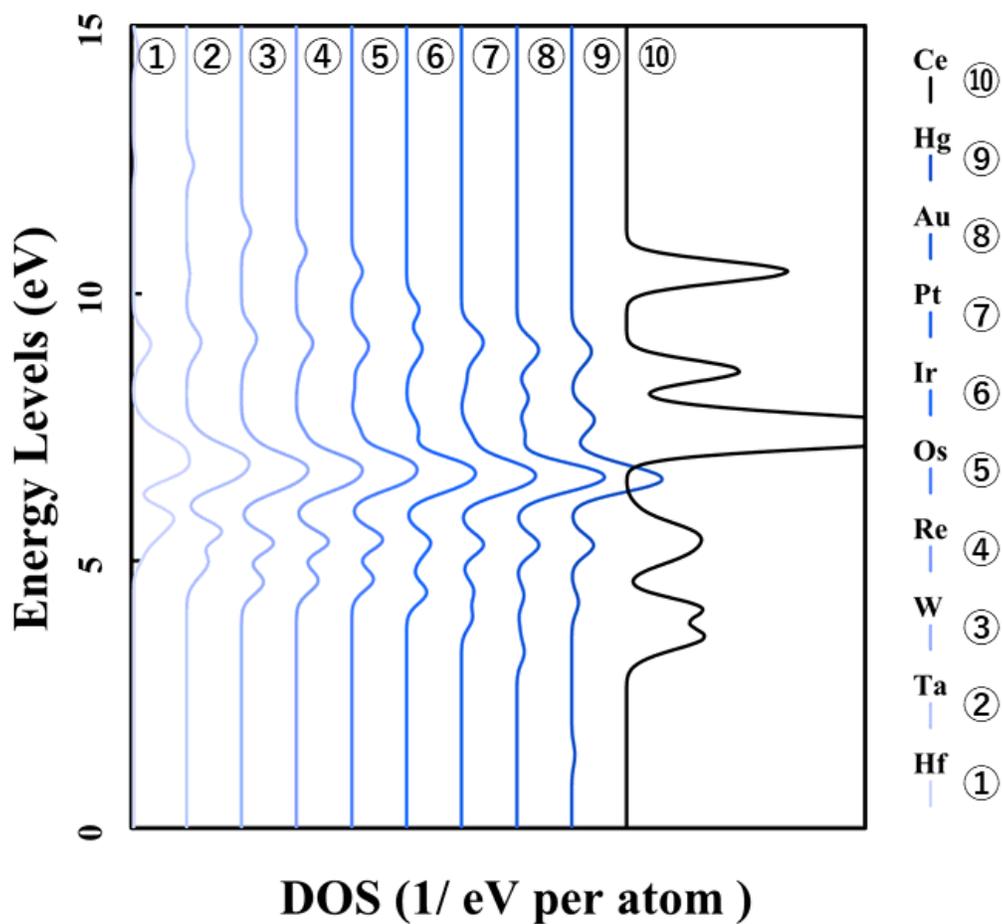


Figure 4

p-DOS for the  $2p$  orbitals of the oxygen atoms in the  $M@Ce_{12}O_8^{36+}$  cluster model, the vacuum level is the reference energy level ( $M = \text{Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Ce}$ ).

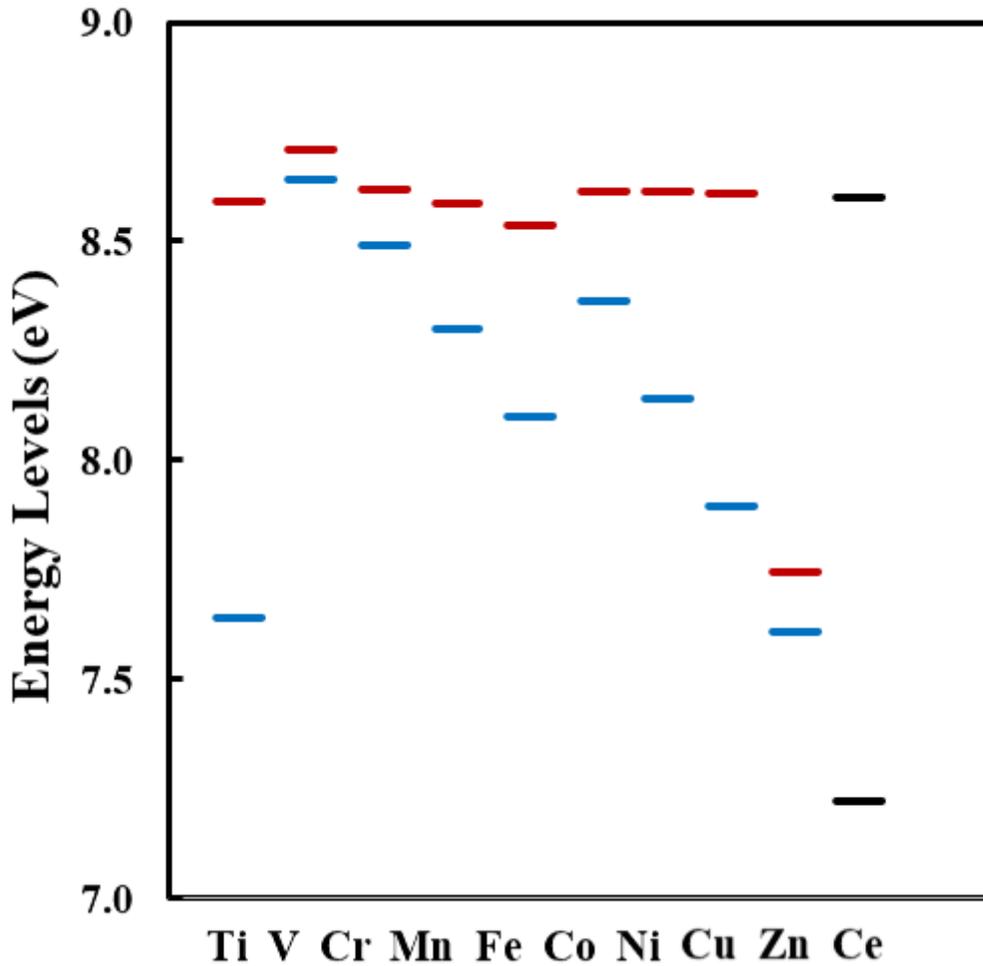


Figure 5

The LUMO (eV), HOMO (eV) level, and the bandgap (eV) in each  $M@Ce_{12}O_8^{36+}$  cluster model based on the reference level as the vacuum level, as described in Table 3. The HOMO level is colored in blue and the LUMO level is colored in red. In the undoped pure ceria, the HOMO level and the LUMO level are colored in black.

Figure 6

-DOS for the  $2p$  orbitals of the oxygen atoms in the  $M@Ce_{12}O_8^{36+}$  cluster model, the HOMO level in each  $M@Ce_{12}O_8^{36+}$  cluster model is the reference energy level. (M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ce)

Figure 7

Energy levels of the bond composition between the doped metal and the oxygen atoms based on the reference level as the vacuum level in the  $M@Ce_{12}O_8^{36+}$  cluster model ( $M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ce$ ). The bonding and antibonding orbital components are on the right and left side, respectively.

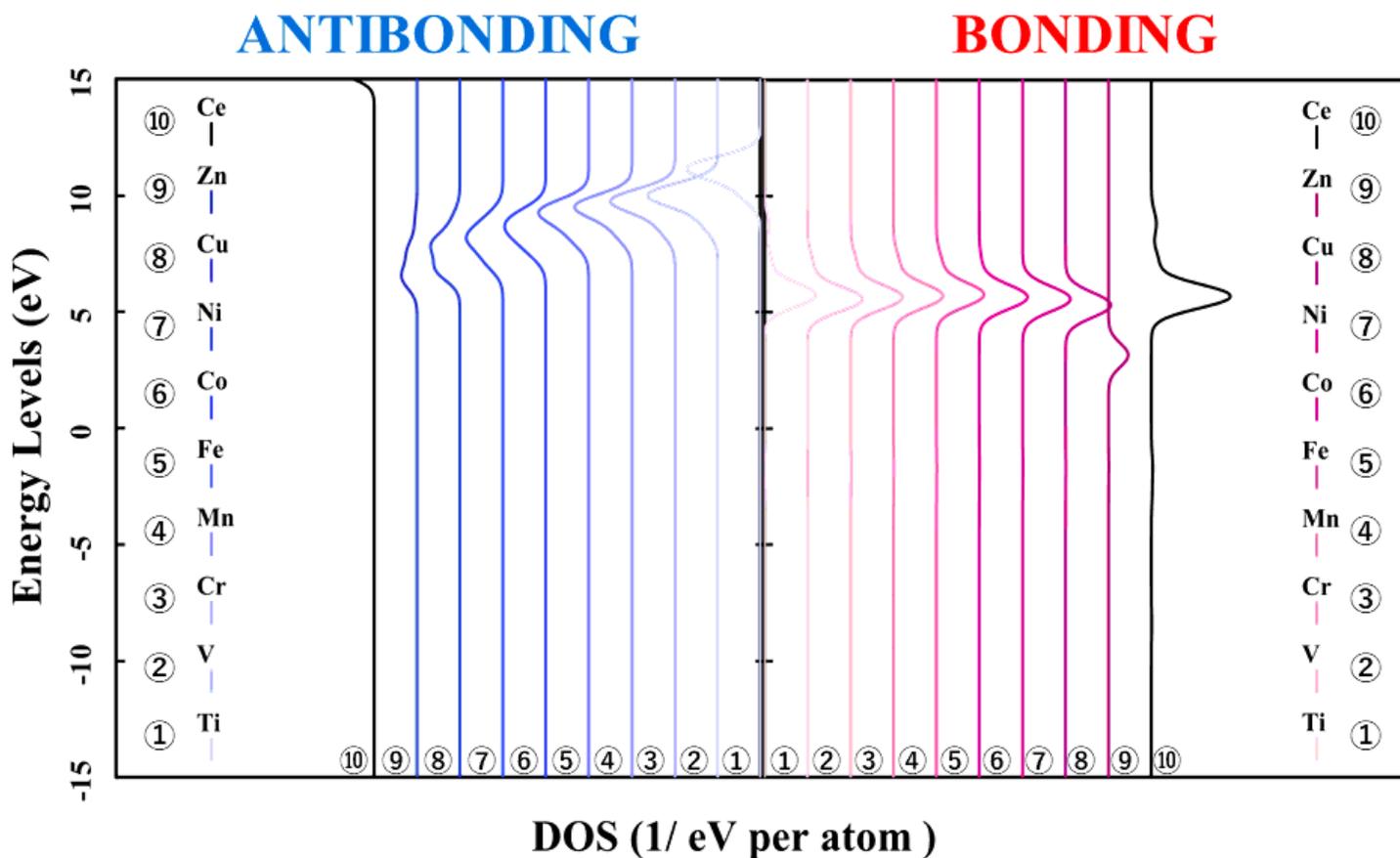


Figure 8

Energy levels of the bond composition between the metal  $3d$  orbitals and the oxygen  $2p$  orbitals based on the reference level as the vacuum level in the  $M@Ce_{12}O_8^{36+}$  cluster model ( $M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ce$ ). In the undoped ceria, the bond composition between the metal  $5d$  orbitals and the oxygen  $2p$  orbitals. The bonding and antibonding orbital components are on the right and left side, respectively.

## Figure 9

Energy levels of the bond composition between the metal  $3d$  orbitals and the oxygen  $2p$  orbitals based on the reference level as the HOMO level in the  $M@Ce_{12}O_8^{36+}$  cluster model ( $M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ce$ ). In the undoped ceria, the bond composition between the metal  $5d$  orbitals and the oxygen  $2p$  orbitals. The bonding and antibonding orbital components are on the right and left side, respectively.

## Figure 10

Energy levels of the bond composition between the metal  $4d$  orbitals and the oxygen  $2p$  orbitals based on the reference level as the vacuum level in the  $M@Ce_{12}O_8^{36+}$  cluster model ( $M = Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd$ ). In the undoped ceria, the bond composition between the metal  $5d$  orbitals and the oxygen  $2p$  orbitals. The bonding and antibonding orbital components are on the right and left side, respectively.

## Figure 11

Energy levels of the bond composition between the metal  $5d$  orbitals and the oxygen  $2p$  orbitals based on the reference level as the vacuum level in the  $M@Ce_{12}O_8^{36+}$  cluster model ( $M = Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg$ ). In the undoped ceria, the bond composition between the metal  $5d$  orbitals and the oxygen  $2p$  orbitals. The bonding and antibonding orbital components are on the right and left side, respectively.

## Figure 12

Comparison of the wave functions (visualized by VESTA) of the bonding orbitals:  $t_{2g}$  (# 26) in V doped and Cu doped ceria are visualized, the isosurface level is set to 0.025 for both.

## Supplementary Files

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