Electronic Structures of $Ce_xHf_{1-x}O_2$ (x=0.5 and 0.75) Mixed Oxides

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Abstract

Density functional theory (DFT) calculations of electronic energy bands of $Ce_xHf_{1-x}O_2$ (x=0.5 and 0.75) are investigated within the generalized gradient approximation (GGA) and taking into account relativistic contributions. Nonlinear core corrections terms are used. Our plotted band structures show that the valence bands are separated from the conduction bands by an indirect band gap of 4.14eV, from X to Γ and direct band gap of 4.18eV at X for $Ce_{0.75}Hf_{0.25}O_2$. For $Ce_{0.5}Hf_{0.5}O_2$, the indirect band gap is 3.56eV from X to Γ and direct band gap of 3.84eV at Γ. Hence, the fundamental band gap in these alloys are indirect. We found a direct band gap of 5.90eV for CeO_2 at the Γ point, in good agreement with experiment. We also calculated lattice parameters of 5.28Å and 5.37Å for $Ce_{0.5}Hf_{0.5}O_2$ and $Ce_{0.75}Hf_{0.25}O_2$ respectively. Hf doping in ceria (CeO_2) results in reduced band gap compared to pure ceria. From the density of states (DOS) plot, the band gap is formed predominantly from O2p and (Ce, Hf)5d states from valence and conduction bands respectively. The calculated wide band gap of the oxides show that they are active in ultraviolet (UV) radiation and so can be applied as UV blockers.

Keywords: Density functional theory, Lattice parameter, Band structure, Band gap, Density of states

INTRODUCTION

Due to reducing property and high oxygen storage capacity (OSC) of ceria, it is commonly used as a catalyst for many chemical processes. Unfortunately, the applications of pure ceria are deficient at high temperature. And so to make ceria well applicable at broad range of temperatures, dopants must be added to it. This enhances its characteristic properties. Researchers have shown that doping of hafnia (Hf) into the ceria lattice highly enhances the oxygen storage capacity (OSC), thermal stability and reducibility of the produced mixed oxide [1-5]. $Ce_xHf_{1-x}O_2$ mixed oxides are used as catalysts in CO oxidation [6], as three way catalyst (TWC) [7] and for soot oxidation [8].

Ceria-hafnia mixed oxides are also useful because of their oxygen storage/release properties [9-11] that find applications in oxygen storage capacitors, nuclear reactors and thermal barrier coatings. It has already been shown that $Ce_xHf_{1-x}O_2$ for x=0.5 and 0.75 crystallizes in the cubic fluorite structure [12-16].

As the size of SiO_2 gate dielectric films used in complementary oxide semiconductor (CMOS) devices is reduced, the current leakage in the gate becomes high [17-19]. Hence, the need to replace the SiO_2 gate dielectrics with a high dielectric material which permits high gate capacitance without leakage current. Many researches have been carried out in order to find a substitute for future use [20-22]. Many high dielectric materials were discovered which can replace SiO_2. Among them is $Ce_xHf_{1-x}O_2$ [23].

The introduction of Hf gives rise to modifications of electronic structure of CeO_2. Unfortunately, theoretical informations about the electronic properties of $Ce_xHf_{1-x}O_2$ is very scarce. The aim of this present work is to study the electronic structures of the mixed oxides using density functional theory (DFT) calculations.

The knowledge of the electronic structures of these mixed oxides would aid in the design of gate oxide in microelectronics and energy related applications such as solid oxide fuels, gas-sensors and optics.

COMPUTATIONAL METHOD

The electronic properties of the mixed oxides are investigated using electronic structure calculation based on the generalized gradient approximation (GGA) within the density functional theory (DFT) [24,25]. The exchange correlation energy of the electrons is described in the GGA. The GGA functional from Perdew, Burke and Ernzerhof [26] is used to model the exchange and correlation energy of the electrons. Ultrasoft pseudopotential in the plane wave basis sets as implemented within the quantum espresso package is used [27]. A plane wave cutoff kinetic energy of 100Ry was chosen. Calculations were performed on 12 atoms supercell of the fluorite structures. A 6x6x6 k-point grid was used to obtain a well converged sampling of the Brillouin zone. The k integration over the Brillouin zone is performed using the Monkhorst and Pack mesh [28]. Scalar relativistic calculation [29-31] is done and non-linear core correction terms are also included [32].

The electronic configurations for Ce, Hf and O are Ce: Xe $4f^1$ $5d^1$ $6s^2$, Hf: Xe $4f^{14}$ $5d^2$ $6s^2$ and O: He $2s^2$ $2p^4$. For the constituent elements, the valence electron configurations used are: Ce- $5s^2$, $6s^2$, $5p^6$, $6p^6$ and $5d^1$, Hf- $5s^2$, $6s^2$, $5p^6$ and $5d^2$, O- $2s^2$ and $2p^4$. The f-electron is treated as a localized core state. The 3d excited state of Oxygen is included.

The iteration process was repeated until the calculated total energy of the crystals converged to less than 1mRyd. Convergency was achieved in nine iterations for the alloys and in seven iterations for CeO_2.

RESULTS AND DISCUSSION

We have used first principles calculation to investigate the electronic structures of ceria-hafnia for x=0.5 and x= 0.75. Both alloys crystallize in the cubic fluorite structure as shown in Figure 1 and 2. For comparison purpose, we calculated the band gap of CeO_2, although many DFT calculations of the electronic and structural properties of CeO_2 have been performed [33-43]. Ceria is a lanthanide oxide with the cubic fluorite structure. Ceria is a wide band gap material with valence and conduction band built primarily from O2p states and Ce5d states respectively. Between these two bands lies a narrow Ce4f band. Experimentally, the O2p-Ce5d band gap is about 6eV [44].

In this work, the lattice parameters of CeO_2, $Ce_{0.5}Hf_{0.5}O_2$ and $Ce_{0.75}Hf_{0.25}O_2$ are calculated to be 5.41Å, 5.28Å and 5.37Å respectively. The band energies at high symmetry points for $Ce_{0.5}Hf_{0.5}O_2$ and $Ce_{0.75}Hf_{0.25}O_2$ from DFT-PBE calculations are given in Table 1 and 2. The valence band energy at each point is represented by E_v while the conduction band energy is represented by E_c. The valence band maximum and conduction band minimum are represented with bold fonts. For easy comparison, the band gaps (E_g) of CeO_2, $Ce_{0.5}Hf_{0.5}O_2$ and $Ce_{0.75}Hf_{0.25}O_2$ are listed in Table 3. The band gap presented is between O2p and (Ce,Hf)5d states.

The electronic band structures of $Ce_{0.5}Hf_{0.5}O_2$ and $Ce_{0.75}Hf_{0.25}O_2$ are given in Figure 3 and 4 respectively. For $Ce_{0.5}Hf_{0.5}O_2$, the direct band gap is 3.84eV at Γ while the indirect band gap $X \rightarrow \Gamma$ is 3.56eV. Therefore, the fundamental band gap of the alloy is indirect (3.56eV). For $Ce_{0.75}Hf_{0.25}O_2$, the direct band gap is 4.18eV at X while the indirect band gap which is also the fundamental band gap is 4.14eV from $X \rightarrow \Gamma$ is 3.56eV. From the band structure plot, both mixed oxides are wide band gap insulators. They show good UV light absorption region. They could be used as photocatalysts. Light having energy within the band gap energies of these oxides can be absorbed by them.

As we have taken 4f-orbitals in core part of Ce and Hf basis set so f orbital bands are absent in the shown energy band. From DOS plots in Figure 5 and 6, energy bands of $Ce_xHf_{1-x}O_2$ (x=0.5 and 0.75) are divided into five parts. The first energy band in the valence band are mainly due to 2s states of O atom. The next two regions contain the contribution of Ce-p and Hf-p orbitals respectively. The region just below the Fermi level E_F is predominately p states of O, with only a small contribution from d-Ce and d-Hf states. Above the Fermi level, the region is predominately d states of the metals with a very small contribution of their s-states. That means valence bands are formed mostly by oxygen p states, while conduction bands are formed majorly by Cerium and Hafnium 5d states. Therefore, we conclude that the 5d electrons of Ce, 5d electrons of Hf atoms and 2p electrons of O atom play a major role in deciding the size of band gap.
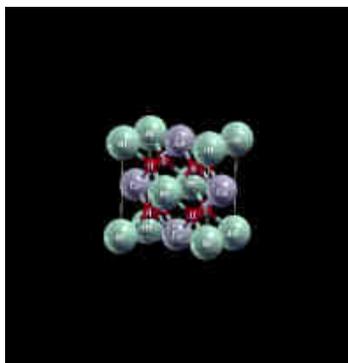

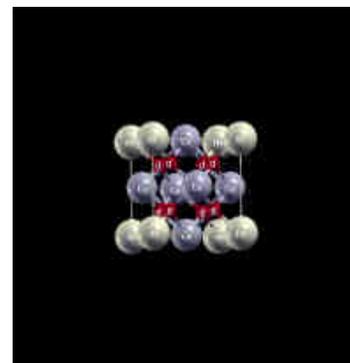**Figure 1: Ball and Stick representation of $Ce_{0.5}Hf_{0.5}O_2$**

Figure 2: Ball and Stick representation of $Ce_{0.75}Hf_{0.25}O_2$

Table 1: Band energies at high symmetry points in $Ce_{0.75}Hf_{0.25}O_2$. The valence band maximum is set to zero.

Kpoints	E_v(eV)	E_c(eV)
L	-0.57	4.35
Γ	-0.20	**4.14**
X	**0.00**	4.18
W	-0.32	4.32
K	-0.32	4.34

Table 2: Band energies at high symmetry points in $Ce_{0.5}Hf_{0.5}O_2$. The valence band maximum is set to zero

kpoints	E_v(eV)	E_c(eV)
L	-0.61	4.20
Γ	-0.28	**3.56**
X	**0.00**	4.22
W	-0.36	4.32
K	-0.36	4.26

Table 3: Electronic band gap of CeO_2, $Ce_{0.75}Hf_{0.25}O_2$ and $Ce_{0.5}Hf_{0.5}O_2$

System	Direct E_g(eV)	Indirect E_g(eV)	Experimental E_g(eV)
CeO_2	5.90	5.68	6 (direct)
$Ce_{0.75}Hf_{0.25}O_2$	4.18	4.14	—
$Ce_{0.5}Hf_{0.5}O_2$	3.84	3.56	—

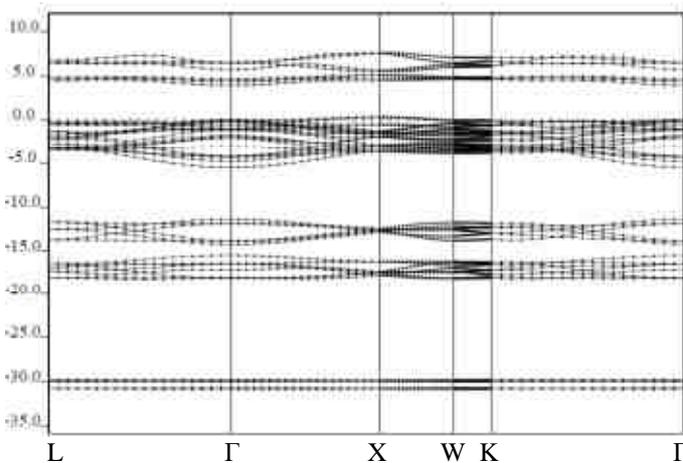**Figure 3: Electronic Band structure of $Ce_{0.5}Hf_{0.5}O_2$. The vertical axis represents the energy in eV while the horizontal axis represents the high symmetry points.**

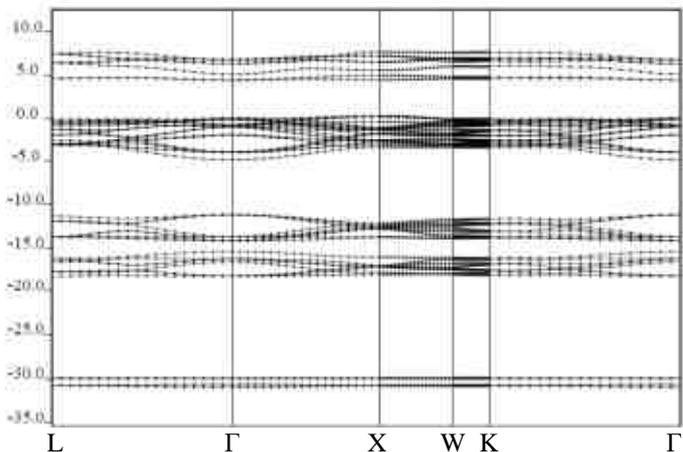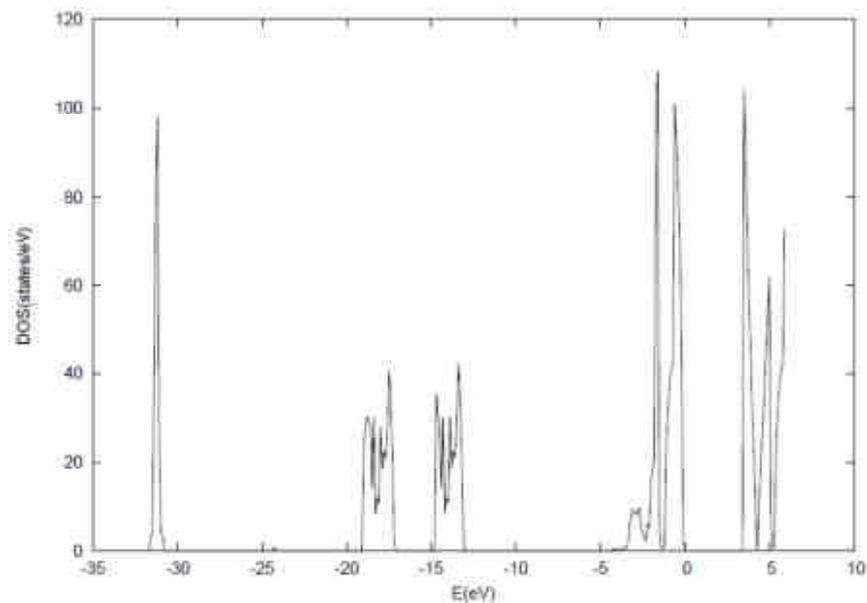**Figure 4: Electronic Band structure of $Ce_{0.75}Hf_{0.25}O_2$. The vertical axis represents the energy in eV while the horizontal axis represents the high symmetry points.**
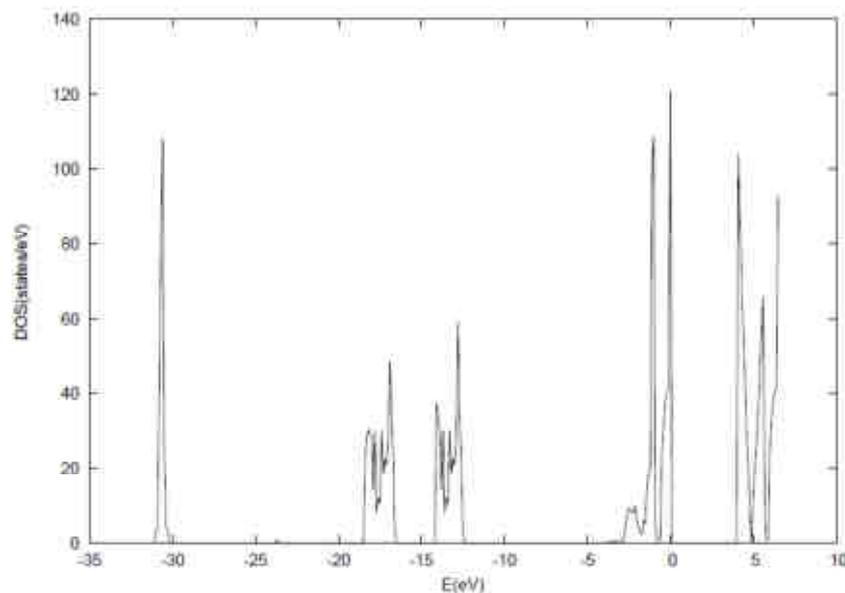
Figure 5: Density of states of $Ce_{0.5}Hf_{0.5}O_2$

Figure 6: Density of states of $Ce_{0.75}Hf_{0.25}O_2$

CONCLUSION

In summary, using density functional theory, we have studied the electronic properties of $Ce_{0.5}Hf_{0.5}O_2$ and $Ce_{0.75}Hf_{0.25}O_2$ within GGA for exchange correlation potential. In addition to the electronic band structure, we obtained the density of states.

Our calculations led to ground state electronic properties. We found that the fundamental band gaps of $Ce_xHf_{1-x}O_2$ are indirect band gaps, from X to Γ, of 3.56eV and 4.14eV respectively. The calculated direct band gap of CeO_2 of 5.90eV, at the Γ points, is in agreement with the result of experiments. The calculated band gap energy shows that the alloys can absorb in the short wavelength UV light and hence can find application in the UV metal-insulator-semiconductor light emitting diodes and UV light blockers.

We expect the calculated band gap of the mixed oxides to enable future comparisons with experimental measurements, such as optical reflectivity.

The electronic properties of the alloys can be studied using other methods for comparison purpose. The obtained results can be used as a reference data in studies of ceria-hafnia alloys with different x concentrations. We consider that the results obtained are only one predictive study, by expecting that our present research will induce more works on the mixed oxides.

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