Mechanical and electronic properties of CeO$_2$ under uniaxial tensile loading: A DFT study

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Abstract

CeO$_2$ is a promising candidate for materials utilized in solid oxide fuel cells (SOFCs) due to its high ionic conductivity. The high operating temperature of SOFCs results in residual thermal stress in the materials. In this work, for the first time, we studied simultaneously the mechanical and electronic behavior of CeO$_2$ under different uniaxial tensile loading directions using density functional theory. CeO$_2$ shows strong anisotropic mechanical and electronic behavior under uniaxial tensile strain that it has the highest ideal strength and fracture strain along [100] direction. Meanwhile, [100] tensile strain also leads to the largest band gap reduction compared with the other two strain directions. The analysis of the mechanism shows that the highest strength along [100] direction is from the highest Young’s modulus and surface energy. While the analysis on the band gap variation using a theoretical model previously developed by us suggest that the largest average bond length and dielectric susceptibility variation leads to the largest band gap reduction when [100] tensile strain is applied to CeO$_2$. Therefore, the current study provides a meaningful insight into the mechanical and electronic properties of CeO$_2$ under stress, which is vital for its application as SOFCs’
Introduction

Solid oxide fuel cell (SOFC) [1] is a conversion device which produces electricity directly from oxidizing a fuel, such as H$_2$ or CO [2]. It is regarded as one of the most promising energy technologies due to its high power density and wide applications ranging from small auxiliary power units to stationary power plants [3]. In addition, it is advantageous also because of its nonpolluting emissions and low greenhouse gas generation [4]. Despite the geometry (planar and tabular) of a SOFC, there are principally three components, including the porous anode, cathode and the dense electrolyte membrane. The cathode catalyzes the oxygen reduction reaction while the anode catalyzes the fuel oxidation reaction. The electrolyte membrane serves to separate the air and fuel and is ideally a pure oxygen ion conductor [5]. What hinders the commercialization of SOFCs on the large scale is its high operating temperature, usually 500 - 1000°C [6], which brings problems and demands for the materials used in the cell. For instance, the high temperature requires the chemical and physical stability while the cycling operation leads to residual thermal strain in the materials which may degrade the mechanical and electronic properties such as strength and conductivity. Thus, for the reliable application of materials on SOFCs, it is vital to understand their mechanical and electronic properties under strain.

CeO$_2$ is a rare earth oxide which has cubic fluorite structure giving it enough space for the formation and migration of oxygen vacancy [7]. CeO$_2$ also possesses good physical and chemical stability with high concentration of oxygen vacancy [8]. Besides, the ready redox between Ce$^{3+}$ and Ce$^{4+}$ endows it good catalytic activity [9]. Thus, CeO$_2$-based materials are proper candidates for utilization either as electrodes or electrolytes because of their high catalytic activity and/or ion conductivity [10]. For electrolytes, high ionic conductivity and low electronic conductivity is wanted for the minimum voltage loss while for anodes, good catalytic performance is wanted for the efficient conversion of fuel(s). Researchers have been attempting to understand the
mechanical and electronic properties of CeO$_2$ under strain which results from the thermal stress [11]. A wide range of experimental and theoretical work have previously been done on CeO$_2$ for application as SOFC anodes and electrolytes [12, 13]. However, it is to our knowledge that not one paper has investigated both the mechanical and electronic properties of CeO$_2$ simultaneously under strain.

In this work, we study both the mechanical and electronic behavior of CeO$_2$ under different uniaxial tensile loading directions by means of density functional theory (DFT). The results suggest that CeO$_2$ shows strong anisotropy in both the mechanical and electronic properties. Combining Griffith theory with our DFT results successfully explain the anisotropic strength of CeO$_2$. The anisotropic variation of band gap is also explained by a theoretical model proposed by us before which verifies the validity of the model. The findings presented in this work provide meaningful results for application of CeO$_2$ in SOFCs.

**Computational Methods**

First-principles calculations based on density functional theory are performed to simulate the effect of uniaxial tensile strain on CeO$_2$. We use the PBE functional as is implemented in the VASP software package [14] for calculations of the elastic constants. The electronic structures for electrons are described by projector augmented wave (PAW) method. Wave functions are represented in plane-wave basis truncated at 650 eV. For integrations within the Brillouin zone, we employ Γ-centered k-point grids with a density equivalent to that of $8 \times 8 \times 8$. The geometry relaxations are performed with a conjugate-gradient algorithm. The convergence threshold for electronic self-consistent field (SCF) and forces acting on the atoms are $1 \times 10^{-6}$ and $0.01$ eV·Å$^{-1}$, respectively. To obtain the strain-stress curves, a small uniaxial tensile strain was applied sequentially to the unit cell which is relaxed in the previous step. The stress is defined as the force per deformed area and the strain is defined as the true strain. This method has been proved to be an effective tool to study the intrinsic failure mechanism of materials at the atomic scale [15, 16]. The Young’s moduli of
CeO$_2$ are calculated by the Voigt-Reuss-Hill method as implemented in VASP.

**Results and Discussion**

We calculated the lattice constant, elastic mechanical parameters ($C_{11}$, $C_{12}$ and $C_{44}$) and band gap of CeO$_2$ to validate our methodology. Table 1 lists the comparison between our results and previously reported experimental and theoretical results. It can be seen that all the values calculated in this work are in good accordance with previous results with no large difference between either the first-principles methods or classical methods. In order to accurately reproduce the band gap values, all the band gap results are calculated using HSE06 hybrid functional. The band gap is calculated to be 3.23 eV which matches well with the experimental values considering the band gap of CeO$_2$ is morphology and/or size dependent properties [17,18]. Therefore, comparison of the mechanical and electronic data of CeO$_2$ between our results and the literature in table 1 validate our calculation methodology.

**Table 1.** Comparison of the elastic constants ($C_{11}$, $C_{12}$, $C_{44}$) and band gap of CeO$_2$ in this work between the previous experimental and theoretical results. MD stands for molecular dynamics.

<table>
<thead>
<tr>
<th></th>
<th>method</th>
<th>Lattice constant (Å)</th>
<th>$C_{11}$ (GPa)</th>
<th>$C_{12}$ (GPa)</th>
<th>$C_{44}$ (GPa)</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>DFT</td>
<td>5.39</td>
<td>359 (PBE)</td>
<td>111 (PBE)</td>
<td>60 (PBE)</td>
<td>3.23 (HSE06)</td>
</tr>
<tr>
<td>Ref.</td>
<td>Exp.</td>
<td>5.42</td>
<td>354 [19]</td>
<td>101</td>
<td>53.2</td>
<td>2.9-3.4</td>
</tr>
<tr>
<td>Ref.</td>
<td>GGA</td>
<td>5.40</td>
<td>355 [20]</td>
<td>139</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>Ref.</td>
<td>LDA+U</td>
<td>5.47</td>
<td>450 [21]</td>
<td>102</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>Ref.</td>
<td>MD</td>
<td></td>
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</tbody>
</table>
Figure 1 shows the stress response as a function of applied strain. All the tensile stresses linearly increase with the strain at the initial loading stage and the slope of the [100] curve is the sharpest, suggesting that the modulus along [100] direction is the highest, while the moduli along the other two directions are much lower and are close to each other. This suggests that CeO$_2$ can resist the largest deformation along [100] uniaxial loading direction, while it is much weaker resisting uniaxial loading along [110] and [111] directions. After the initial stage, the stresses show nonlinear increase with the strain and the slope of the curves gradually decrease, indicating softening of the structure. With further increase of the tensile strain, structural failure occurs and the fractured structures are shown in Figure 1b. The maximum stress along [100] uniaxial tensile loading is 69.7 GPa, while they are 16.2 and 13.5 GPa for [110] and [111], respectively. Furthermore, the structure failure for [100] happens when the strain reaches 0.47, followed by 0.32 for [110] and 0.22 for [111]. The corresponding mechanical values retrieved from Figure 1a are listed in Table 2. These data suggest that when CeO$_2$ is subjected to uniaxial tensile loading, the fracture will mostly happen when the loading direction is along [111] direction while [100] displays the highest strength among the three low-index directions.

**Figure 1.** (a) The calculated stress-strain relations of CeO$_2$ under different uniaxial tensile loading; (b) The fractured structures of CeO$_2$ under different uniaxial tensile loading.
Table 2. Ideal strengths and fracture strains of CeO$_2$ under different tensile loading directions

<table>
<thead>
<tr>
<th>Direction</th>
<th>[100]</th>
<th>[110]</th>
<th>[111]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal strength (GPa)</td>
<td>69.7</td>
<td>16.2</td>
<td>13.5</td>
</tr>
<tr>
<td>Failure strain</td>
<td>0.47</td>
<td>0.32</td>
<td>0.22</td>
</tr>
</tbody>
</table>

In order to explain the anisotropic fracture strength of CeO$_2$ along different uniaxial tensile loading directions, the well-established Griffith criterion is adopted [22]. According to Griffith theory, the fracture strength of material is expressed by the following equation,

$$\delta_f = \sqrt{\frac{2\gamma_s Y}{\pi a}}$$  \hspace{1cm} (1)

where $\sigma_f$ is the value of the stress at which fracture occurs, $\gamma_s$ is the surface energy of newly created surface due to crack propagation, $Y$ is the Young’s modulus and $a$ is half of the crack length. So for materials with cracks, this equation indicates that fracture occurs when the incremental release of stored strain energy caused by the increase in crack length becomes larger than the increase in surface energy by creation of new surface area. It should be noted that Eq.1 can also be used to estimate the ideal strength of a perfect material where $a$ is considered as the lattice constant instead of half the crack length.

Figure 2a shows the structures of the three low-index surfaces of CeO$_2$. The surface energy is calculated by the following equation,

$$\gamma_s = (E_{\text{surface}} - nE_{\text{bulk}})/2S$$  \hspace{1cm} (2)

where $E_{\text{surface}}$ is energy of one of the low-index CeO$_2$ slabs with vacuum, $E_{\text{bulk}}$ is energy of bulk CeO$_2$ unit cell, and $S$ is the corresponding surface area. The surface energies of the (100), (110) and (111) surfaces are calculated to be 1.704, 1.214 and
0.834 J/m², respectively, which is consistent with previously reported energy order that \((100) > (110) > (111)\), further suggesting the reliability of our methods. Figure 2b shows the visualization of Young’s modulus of CeO₂ which is realized by an open source program ELATE [23], using the elastic tensor values calculated by VASP. The Young’s modulus of CeO₂ along [100], [110] and [111] are 307, 187 and 165 GPa, respectively, which follows same order as surface energy as \([100] > [110] > [111]\). Therefore, according to Eq. 1, the fracture strengths of CeO₂ along the three uniaxial tensile loading directions have the order of \([100] > [110] > [111]\), which matches exactly with the results in Figure 1a and Table 2. Thus, the highest strength of CeO₂ along [100] direction is attributed to the highest surface energy and Young’s modulus, which demonstrates that the different surface energies and Young’s modulus determine the anisotropic mechanical strength of CeO₂ under different uniaxial tensile loading directions.

![Figure 2.](image)

Figure 2. (a) The structure of the three low-index surfaces of CeO₂; (b) Visualization of Young’s modulus of pristine CeO₂ in 3-dimensional.

For application of CeO₂ as either the electrode and electrolyte material in SOFCs, it is important to study its electronic properties under strain. Figure 3a shows the band gap changes induced by the tensile strain along the three different loading directions and Figure 3b shows the corresponding DOS and pDOS of the structures at the specific
strains. It can be seen that with the increase of uniaxial tensile strain, the band gap of CeO$_2$ all decrease. The band gap drops tremendously from 3.2 eV to almost zero when CeO$_2$ is subjected to [100] tensile strain, while the band gap drops slightly to approximately 3 eV for [110] and [111] tensile loading. This suggests that the band gap for CeO$_2$ is quite sensitive for [100] tensile strain.

![Figure 3](image.png)

**Figure 3.** (a) Band gap changes induced by different uniaxial tensile loading directions; (b) Corresponding partial density of electronic states of CeO$_2$ at the largest strain before fracture.

In order to study the mechanism of the band gap variation, we have previously developed a theoretical model which can explain and predict the band gap change of oxides under epitaxial strain [24]. This model is proposed based on the well-established theories in solid state physics that the band gap of a material is influenced by the first Fourier coefficient of the crystal field, which is determined by the interatomic distances and dielectric screening. Therefore, the model to predict the band gap (E$_g$) variations induced by epitaxial strain is expressed as the following equation:

$$\frac{\Delta E_g(\eta)}{E_g} = -\frac{1}{2} \left( \frac{\Delta \chi(\eta)}{\chi(0)} + 2 \cdot \frac{\Delta d(\eta)}{d(0)} \right)$$  \hspace{1cm} (3)$$

where 0 represents the unstrained case while $\eta$ represents the epitaxial strain, $\Delta A = A(\eta) - A(0)$, $d$ represents the average metal-oxygen bond length. The $\chi$ represents the dielectric susceptibility which is calculated by $\chi = \varepsilon_{\infty} - 1$, where $\varepsilon_{\infty}$ is the
ion-clamped dielectric constant of the material. $\varepsilon_\infty$ is estimated by the perturbation DFT techniques as implemented in VASP. According to the model, the band gap will decrease along with the decreased atomic distances and/or weakened dielectric screening owing to the decreased crystal filed in the crystal and vice versa. However, it should be noted that the model as expressed in Eq.3 only provides qualitative prediction since the influence of structural and dielectric factors on the band gap variations are considered independently. The model aims at explaining the mechanism of band gap variations when epitaxial strain is applied, whereas the current study focuses on uniaxial tensile strain. The model is used here to explain the anisotropic electronic behavior of CeO$_2$ under different uniaxial tensile loading directions thus to verify the validity of the model under a broader scenario.

Table 3 lists the band gap changes of CeO$_2$ under different uniaxial tensile loading directions at the largest strain before fracture. The values for $\Delta$Eg/Eg obtained by DFT calculation (Figure 3) and our analytical model (Eq. 3) are listed for comparison. For [100] uniaxial tensile strain, there is large increase in the dielectric susceptibility and average Ce-O bond length, therefore, according to the model, the band gap variation is predicted to be $\sim$860%, suggesting that there would likely be a band gap close, which matches quite well with the DFT results that the band gap decreases to almost zero (Figure 3a). As for the cases of [110] and [111] tensile strains, the dielectric susceptibilities decrease slightly while the average bond lengths increase slightly, the band gap variations are calculated to be as small as 2.2% and -1.9%, respectively, which also matches well with the DFT results that the band reduction is less than 10%. There is discrepancy of the prediction between the model and DFT results on the band gap variation when [110] uniaxial tensile strain is applied where the model predicts a slight increase in the band gap while the DFT results show that there is slight drop. This discrepancy results from the qualitative nature of the model. The analyses presented here elucidate the band gap variation of CeO$_2$ is from the average bond length and dielectric susceptibility changes during the loading of uniaxial tensile strain. Although the model is proposed when studying the influence of epitaxial strain,
the good correlation between the values predicted by the model and the DFT results in this study suggest the validity of the model under the scenario of uniaxial tensile strain. It is further speculated that the model is valid for broader situations, i.e., if the data of average ionic bond length and dielectric susceptibility of an oxide is known, the model can provide qualitative prediction on the band gap variation of materials.

Table 3. Relative band gap changes calculated at the ideal tensile strain along different loading directions. $\Delta \chi$ and $\Delta d$ represent the variation in the dielectric susceptibility and average Ce-O bond length as referred to the unstrained case. [model] refers to the relative band gap variations estimated with the analytical model expressed in Eq. (3), while [DFT] refers to the values obtained directly from the DFT calculations as shown in Figure 3.

<table>
<thead>
<tr>
<th>Tensile Direction</th>
<th>$\Delta \chi / \chi$</th>
<th>$\Delta d / d$</th>
<th>$\Delta E_g / E_g$ [model]</th>
<th>$\Delta E_g / E_g$ [DFT]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[100]</td>
<td>15.926</td>
<td>0.710</td>
<td>-867.32%</td>
<td>-95.83%</td>
</tr>
<tr>
<td>[110]</td>
<td>-0.219</td>
<td>0.088</td>
<td>2.20%</td>
<td>-5.25%</td>
</tr>
<tr>
<td>[111]</td>
<td>-0.069</td>
<td>0.054</td>
<td>-1.97%</td>
<td>-6.86</td>
</tr>
</tbody>
</table>

Conclusions

In this work, the ideal strength and fracture strength of CeO$_2$ under three uniaxial tensile loading directions are calculated by means of first-principles methods. It is found that CeO$_2$ has the highest ideal strength of 69.7 GPa along the [100] direction, while it has the lowest ideal strength of 13.5 GPa along the [111] direction. Griffith theory combined with our DFT results suggest that the strong anisotropic mechanical strength results from the large difference in the surface energy and Young’s modulus for the three low-index crystalline surfaces. Electronic property analyses show significant difference of the band gap reduction among the three tensile loading directions where CeO$_2$ is quite sensitive to the tensile strain along [100]. The band gap drops to only 0.22 eV when CeO$_2$ is maximally strained along [100] while the band
gap only slightly decreases when maximally strained along the other two directions. An analytical model developed previously by us is used to qualitatively unravel the anisotropic mechanism of the band gap variation. The band gap changes can be explained in terms of the structural and dielectric property variations that alter the crystal field and thus the bonding-antibonding splitting. The present work not only presents the anisotropic mechanical and electronic behaviors of CeO₂ under uniaxial tensile strain but also provides microscopic mechanism that can explain the anisotropy, thus provides meaningful results for applications of CeO₂ in SOFCs and other fields where both mechanical and electronic properties need to be considered. This work also demonstrates that uniaxial tensile loading can be used to tune the electronic properties of CeO₂.

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References


