Anomalous compressive behavior in CeO$_2$ nanocubes under high pressure

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Abstract. High-pressure angle-dispersive x-ray diffraction measurements have been performed on bulk and nanocrystalline cubic CeO$_2$ with mean sizes of 4.7 and 5.6 nm. It is found that the compressibility of the nanocrystals is lower than the bulk when a threshold pressure is reached. This critical pressure is found to
be 10 GPa for 4.7 nm and 16 GPa for 5.6 nm CeO$_2$ nanocubes. The particle size dependence of the threshold pressure for the hardening of CeO$_2$ nanoparticles is quite unusual. First-principles electronic calculations show that the increased bulk modulus of the nanocrystal is due to the strengthening of the surface Ce–O bonds resulting in a much larger shear modulus than in the bulk and consequently hardening the shell surface.

1. Introduction

Nanocrystals with the size of 1–100 nm are known to exhibit behavior distinct from the bulk. Extensive studies have shown that the mechanical and electronic properties are dependent on the crystallite size. Recently cerium oxide (CeO$_2$) has attracted a great deal of attention due to its industrial applications, e.g. in solid oxide fuel cells [1, 2], solar cells, electrolyte and in self-cleaning ovens as a hydrocarbon catalyst and oxygen-purification catalyst [3]–[5]. Previous studies revealed that most of these applications originate from its oxygen-vacancy defect at the surface [6], especially at the (001) terminated surface [7]. Thus, the synthesis of nanometer-sized CeO$_2$ (nano-CeO$_2$) particles with (001) surface is highly desirable [8, 9]. In order to broaden the practical application of CeO$_2$, the stability of CeO$_2$ nanocrystals needs to be investigated in detail. The study of the particle size effect on the bulk modulus and on possible solid–solid phase transformations will help to improve our understanding of the structural stability and the mechanical properties of nanostructured CeO$_2$ [10]–[20]. In this work, we report the compressive behavior of nano-CeO$_2$ with (001) terminated surface studied by in situ high pressure x-ray diffraction (XRD) and first-principles calculations. At low pressure, the compressibility of the nanocrystals is very similar to the bulk. A sudden change in compressibility was observed at 10 GPa (16 GPa) for 4.7 nm (5.6 nm) CeO$_2$ nanocubes. It is revealed, via first-principles electronic structure calculations, that the lower compressibility of the nanocrystal is directly related to the formation of stronger Ce–O bonds at the surface thus enhancing the hardness of the surface.

2. Experimental and theoretical

In the present study, compression behavior of two nano-CeO$_2$ cubes with average particle sizes of 4.7 and 5.6 nm prepared by a recent method [8], which allows the control of the shape and size of the nanocrystal, is investigated. The samples were characterized by transmission electron microscopy (TEM) measurements using a Titan FEI 80–300 equipped with a field emission gun and an electron energy loss spectrometer (EELS). The structure, average particle...
Figure 1. TEM characterization of as-synthesized CeO$_2$ samples. (a) TEM image for nano-CeO$_2$ sample with average particle size of 5.6 nm. (b) Selected area electron diffraction pattern of (a). (c) HRTEM image of two nanoparticles from (a). (d) and (e) two different particle size distributions of CeO$_2$ nanoparticles with an average particle size of 5.6 and 4.7 nm, respectively.

size and particle morphology of the two samples examined are reported in Figure 1. The TEM images in Figure 1(a) show that the as-synthesized size distributions of the two CeO$_2$ nanocrystals are quite uniform. Grain size distribution was estimated by counting about 300 nanoparticles which show a Gaussian distribution (solid line in figures 1(d) and (e)) with average particle size of 5.6 ± 0.2 nm and 4.7 ± 0.2 nm with standard deviation of about 12% and 17%, respectively. As shown in Figure 1(b), these nanoparticles have a crystalline fluorite structure with a predominately cubic-like morphology. The high resolution TEM image in Figure 1(c) shows the internal atomic lattice for two single nanocrystals terminated at the (001) surfaces. EELS measurements for the nanocubes were carried out using a Titan FEI 80–300 equipped with a field emission gun. From the Ce M5 and M4 peaks, it is clear that Ce ions in the nanocubes are Ce$^{4+}$. The ratio of Ce:O is found to be about 1:2 within experimental uncertainty.

In situ high pressure angular dispersive XRD experiments were performed on nano-CeO$_2$ samples with average particle size of 5.6 ± 0.2 nm and 4.7 ± 0.2 nm and a bulk-CeO$_2$ sample (average particle size of about 100 µm and 99.9% purity) up to 28 GPa. In the high pressure experiments, CeO$_2$ powders were mounted in a 300 µm-diameter hole of the T301 stainless-steel gasket in a Mao-Bell diamond-anvil cell. The XRD measurements at ambient temperature were performed on beamline BL13A with an imaging plate detector at the KEK Synchrotron Radiation Facility in Japan. Monochromatized x-rays (0.42713 Å) were collimated to 50 × 50 µm and irradiated at the center of the sample. A pressure transmitting medium of 16 : 3 : 1 methanol : ethanol : water solution was used. The sample pressure was measured by
Some selected XRD patterns for a nano-CeO$_2$ sample with an average particle size of 4.7 nm at different applied pressures during compression. No new phase was clearly observed up to 27.8 GPa.

ruby fluorescence method. All XRD patterns were fitted by the Rietveld method [21] to extract unit cell parameters.

3. Results and discussion

Figure 2 shows the XRD patterns recorded at selected pressures on the 4.6 nm nano-CeO$_2$ sample. No evidence of a possible new phase was detected at pressures below 28 GPa. This result differs from that observed for a 12 nm nano-CeO$_2$ sample where a phase transition was identified at 26.5 GPa, by Raman measurements [22]. Figure 3 shows the compressive behavior of the three CeO$_2$ samples. The results for the bulk-CeO$_2$ sample are consistent with data reported in [23]. Recently, it was shown that it is impossible to derive a unique set of lattice parameters for nanocrystals [24] from the positions of the Bragg reflections. It is reasoned that the ‘apparent’ lattice parameters which depend on the diffraction vectors $Q$ ($Q = 2\pi/d$, where $d$ is the lattice $d$-spacing) can be used to distinguish the surface and bulk structures. For nanocrystals, large $Q$s are more sensitive to the core and conversely, smaller $Q$s are sensitive to the surface. To this end, several reflections, (111) (220) (311) and (400), are selected to examine the surface and bulk effects. Positions of the Bragg peaks were determined from profiles fit to the experimental data. The results for CeO$_2$ nanocubes are summarized in figure 4. In both cases, it is clearly seen that the ‘apparent’ $d$-spacings are different for different $Q$ values. In fact, the ratio of the $d$-spacing ($d/d_0$ relative to ambient pressure) for smaller $Q$s varies much less than those at higher $Q$s. This strongly indicates that the compressibility of the surface layers of the nanocrystal is enhanced as compared with the bulk [25]. The surface layers are more difficult to compress at high pressure. More significantly, at lower pressures, within the experimental limit of accuracy, ratios of the $d$-spacing of nanocubes are almost identical to the bulk. It is observed that the $d$-spacing ratio starts to deviate from the bulk at 10.6 GPa in the 4.7 nm nanocube and increased to 13.8 GPa in the 5.6 nm nanocube. The existence of a size-dependent onset threshold

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Figure 3. Compressibility as a function of pressure for bulk-CeO$_2$ and two nano-CeO$_2$ samples with average particle sizes of 4.7 and 5.6 nm obtained from in situ high pressure XRD measurements.

Figure 4. Variation of relative $d$-spacing ($d/d_0$) for 4.7 nm nano-CeO$_2$ for different Bragg reflections as a function of pressure (see text).

(critical) pressure is quite unusual and will be discussed below. This behavior, apparently, has not been reported before for other nanometer-sized particles.

Being aware of the potential shortcoming of an average lattice parameter for nanocrystals, the compressive behavior of nano-CeO$_2$ is now compared with bulk-CeO$_2$. It is shown in figure 3 that the compressibilities of the nano-CeO$_2$ samples are similar to bulk-CeO$_2$ below 10 GPa and 16 GPa for 4.7 nm and 5.6 nm nano-CeO$_2$ samples, respectively. When the pressure is increased,
Figure 5. Compressibility obtained from \textit{ab initio} calculations as a function of pressure for bulk-CeO$_{2-x}$ with different compositions, i.e. Ce$_{16}$O$_{32}$ (pure CeO$_2$), Ce$_{16}$O$_{31}$, Ce$_{16}$O$_{30}$ and Ce$_{16}$O$_{24}$ (pure Ce$_2$O$_3$) together with experimental results for bulk-CeO$_2$ and two nano-CeO$_2$ samples with average particle sizes of 4.7 nm and 5.6 nm obtained from \textit{in situ} high pressure XRD measurements.

The equations of state (volume versus pressure curve) of the nanocrystals begin to deviate from bulk-CeO$_2$. Beyond the onset critical pressure, the nanocrystals become harder to compress. The results indicate that the smaller the particle size, the lower the onset pressure on the deviation of the compressibility from the bulk.

To explain the experimental observation, first-principles electronic structure calculations were performed to study (i) the composition effect on the compressible behavior of bulk-CeO$_{2-x}$, and (ii) the pressure effect on model CeO$_2$ nanocrystals. Density functional theory-based first-principles total energy calculations were carried out using the pseudopotential plane wave program VASP [26]. The core electrons are replaced by a projector-augmented-wave (PAW) potential. The LDA + U Hamiltonian was used to account for the strong on-site Coulomb repulsion between the electrons in the localized Ce 4f orbitals [27, 28]. We first calculated compression behaviors for four compositions, i.e. Ce$_{16}$O$_{32}$ (pure CeO$_2$), Ce$_{16}$O$_{31}$, Ce$_{16}$O$_{30}$ and Ce$_{16}$O$_{24}$ (pure Ce$_2$O$_3$). As shown in figure 5 the calculated EOS for the bulk material is in very good agreement with experiment. More importantly, by reducing the oxygen content in bulk-CeO$_{2-x}$, the compressibility increases. This result strongly indicates that the reduction of compressibility for CeO$_2$ nanocubes observed here could not be caused by a composition effect. For a nanocrystal of a few nanometers in size, it is expected that there will be a core region which behaves similarly to the bulk under pressure, and a surface layer which may respond quite differently to pressure. The surface/volume ratio in nanocrystals is known to affect the compressive property of CeO$_2$ anocystallites [29]–[31]. It is impractical to perform first-principles calculations to study the bulk modulus on a nanocrystal with the size dimension used in this study [32]. However, it is not unreasonable to investigate the surface compressive property with the simple model shown in figure 6. This model consists of 8 Ce–O bilayers, with cell dimensions corresponding to the nanocrystal of 4.33 nm, which is comparable in size to the CeO$_2$ anocubes studied here (4.7 nm and 5.6 nm). The Ce–O slabs are separated with a vacuum region of 1 nm. First, all the atoms
Figure 6. Supercell geometry used in ab initio calculation. The slab system consists of 8 Ce–O bilayers, corresponding to a nanocrystal of 4.33 nm, with a vacuum region of 1 nm. The supercell is illustrated by solid lines.

are relaxed to reach an equilibrium structure. (Note that we treated all layers in the same way, not dividing into the core-layer and the surface layer.) To mimic the effect of pressure, the cell dimensions along x-, y- and z-axes are reduced according to a preset volume. In order to constrain the compressed volume, it is necessary to fix the z-coordinates of the oxygen atoms in the O-deficient CeO$_2$ (001) (top surface layer) [33]–[37] while allowing the lateral dimensions (x–y-plane) together with all atoms at other layers to fully relax in the geometry optimization. Figure 7(a) shows the changes in calculated Ce–O bond length when the volume of the nanocrystal is reduced (pressure is increased). In the figure, $V$ is the volume of the nanocrystal at a given pressure and $V_0$ is its initial value at zero pressure. This simple model reproduces the essence of the results that the compressive effect is manifested mostly by the surface layers. It clearly shows that Ce–O bonds in the third and the fourth bilayer are almost identical to the bulk but the Ce–O bond in the surface bilayer is much shorter and those in the second bilayer are longer than the bulk value. Figure 7(b) shows changes in Ce–O bond lengths ($D_{\text{Ce–O}}/D_{\text{Ce–O}}^0$) relative to that at ambient pressure with the volume (pressure). It is seen that the Ce–O bond in the surface bilayer is much more difficult to compress than those in other bilayers. Due to inward relaxation of oxygen atoms and outward relaxation of the Ce atoms in the surface bilayer, the Ce–O bonds in the surface bilayer rotate toward the surface plane of the nanocrystal. Similar behavior is also observed in subsequent bilayers but to a lesser degree. Results of first-principles calculations suggest that shorter and stronger Ce–O bonds are near the surface of the nanocrystal forming a hard shell which is harder to compress.

To quantify the enhanced hardening of the surface layer in the nanocrystal, surface elastic moduli are estimated by theoretical calculations. The calculations follow a strategy [38] which has been demonstrated to describe differences in the surface elastic property from that of the bulk in a boron doped diamond surface [38]. In this case, calculations were performed on a model with a slab of 6 bilayers of CeO$_2$ (12 layers) representing the surface [38, 39]. Small strains were applied to the equilibrium lattice to determine the resulting change in the total
Figure 7. Calculated Ce–O bond properties at different $V/V_0$. (a) Ce–O bond length at surface layer, second layer, third layer and fourth layer. (b) Deduced Ce–O bond length changing ratio ($D_{Ce-O}/D_{0,Ce-O}$, 0 denotes the balanced structure for each layer) at varying $V/V_0$.

energy, from which we could deduce the elastic constant. They are identified as proportional to the second-order coefficient in a polynomial fit of total energy as a function of the distortion parameter $\delta$ [40]. For most materials, it has been found that the hardness correlates better with the shear modulus than the bulk modulus [38, 41]. Results of the calculations reported in table 1 clearly show that all the elastic components of the surface model are larger than in the bulk. The shear modulus in the $x$–$y$-plane, viz $c_{22}$, is similar for both the surface and the bulk. In contrast, the larger elastic moduli ($c_{12}$, $c_{44}$, $c_{33}$, $c_{66}$, $c_{23}$) in the surface involve displacements (strains) in the $z$-direction reflecting the hardness of the CeO$_2$ (001) surfaces. In particular, the $c_{33}$, strain along the $z$-axis, is about five times that of the bulk-CeO$_2$. Additional calculations at $V/V_0 = 0.97$ show the elastic moduli increase with pressure, which is in good agreement
with the experimental observation of a gradual decrease in compressibility. A way to measure the degree of anisotropy in bonding between atoms in different planes is to compute the shear anisotropy factor $A$ [39] which is defined as:

$$A_{(001)} = \frac{4c_{66}}{c_{11} + c_{22} - 2c_{12}}.$$

For an isotropic crystal, the factor $A$ must be one as for fcc bulk-CeO$_2$. A value smaller or greater than unity is a measure of the degree of elastic anisotropy possessed by the crystal. For the surface, $c_{22}$ equals $c_{11}$ and $A_{(001)}$ is found to be 1.35 at ambient pressure which is significantly larger than unity. The anisotropy factor increases further to 1.60 when $V/V_0 = 0.97$. These results demonstrate the existence of a very large elastic anisotropy in the (001) surface. The calculation presented here was performed on an infinite surface. However, the surface energy is dependent on the number of surface atoms, therefore the effect is dominant in smaller nanocrystals because the ratio of surface atoms to bulk atoms is higher. The particle size dependence of the threshold pressure is therefore not unexpected.

A strong surface Ce–O bond is substantiated by a comparison of the charge distribution in the (110) plane for bulk-CeO$_2$ with that at the surface for a CeO$_2$ nanocrystal. In figure 8, the charge densities for three different values of $V/V_0$ are shown. It is clear that charge density between the Ce and O atoms is higher in the surface bilayer compared to that in the bulk. Thus, the Ce–O bonds in the surface bilayer are more covalent, which should be stronger than the dominant ionic bond in the bulk. The Ce–O bond is mainly formed by p orbitals of O atoms and d and f orbitals of Ce atoms. As the pressure increases the charge density around the O atoms is found to remain roughly the same. In comparison, the charge density around the Ce atoms increases with pressure. More significantly, the charge density of the surface atoms increases much faster than that in the bulk. The results affirm that the increased hardness of nanocrystalline CeO$_2$ is due to a harder surface shell. The theoretical results are in agreement with the experimental observations. The size dependence of the threshold pressure for the deviation of the compressibility of the nanoparticles to bulk-CeO$_2$ is unusual. There could be two possibilities. First, the methanol : ethanol : water pressure transmitting medium may become non-hydrostatic at pressures over 10 GPa. It is reasonable to expect that the pressure gradient may affect particles of difference sizes resulting in an apparent difference in the critical pressure. If the observed results in figure 3 were caused by the pressure transmitting medium used, then using another pressure transmitting medium should give different results. Thus, to rule out this pressure transmitting medium effect, we further carried out high pressure XRD measurements for CeO$_2$ nanocubes using liquid N$_2$ as pressure transmitting medium, which becomes non-hydrostatic at pressures higher than a methanol : ethanol : water pressure.

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**Table 1.** Bulk modulus and elastic constants for bulk-CeO$_2$ and surface-slab-model.

| GPa | B  | c11 | c12 | c44 | c33 | c66 | c23 |
|-----|----|-----|-----|-----|-----|-----|-----|
| Exp | 230|     |     |     |     |     |     |
| Bulk| 211| 386 | 124 | 79  | 79  | 79  | 124 |
| Surface| 215| 394 | 135 | 85  | 423 | 128 | 154 |
| Surface ($V/V_0 = 0.97$) | 255| 562 | 317 | 111 | 445 | 131 | 222 |
transmitting medium. Similar results as in figure 3 were observed. This rules out the pressure transmitting effect for the size dependence of the threshold pressure for the deviation of the compressibility of the nanoparticles from bulk-CeO$_2$. The second explanation has been discussed earlier. The surface energy of a nanocrystal is dependent on the surface area (i.e. size). The smaller the nanocrystal, the larger its surface energy will be and the greater the hardening of the outer shell.

4. Conclusions

The compression behavior of nano-CeO$_2$ cubes with (001) terminated surface and average particle sizes of 4.7 and 5.6 nm has been investigated by in situ XRD and first-principles calculations. Deviation of the compressibility from bulk-CeO$_2$ is observed at different pressures for CeO$_2$ nanocubes with different sizes. The nanocubes are less compressible than bulk-CeO$_2$. First-principles calculations show that this interesting behavior can be attributed to the higher surface energy which increases with compression. The results presented here provide additional evidence that nanometer-sized particles, due to the high fraction of surface atoms, show novel behavior which is different from the corresponding bulk materials.

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