In situ x-ray diffraction study of the pressure-induced phase transformation in nanocrystalline CeO_2

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The x-ray-diffraction study of nanosized CeO_2 was carried to pressures of 38.6 GPa using an energy dispersive synchrotron-radiation technique in a diamond-anvil cell. At a pressure of 22.3 GPa, nano-CeO_2 starts to transform to an orthorhombic α-$PbCl_2$ structure. This pressure is significantly lower than the transition pressure of 31 GPa for phase transformation in the bulk CeO_2. The high-pressure phase is unquenchable and distorts to a hexagonal structure upon release of pressure to ambient conditions. The nanosized cubic fluorite phase has a bulk modulus (B_0) of 328 ± 12 GPa, much higher than that of the macrosize CeO_2 with a B_0 of 230 GPa. There is a large volume decrease of 9.4% in phase transformation from the fluorite to α-$PbCl_2$ structure. Such a phase transformation may occur via a large volume collapse and an unstable high-pressure phase causing a reduction of transition pressure in this type of nanomaterial.

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I. INTRODUCTION

Pressure-induced phase transformations in fluorite-type compounds have been the subject of some recent studies.[1] Pressure-induced post-fluorite phases are of geophysical interest, and hence several fluorite-type dioxides have been subjected to high pressures up to 70 GPa and temperatures around 1000 °C, in a laser-heated diamond-anvil cell.[2,3] In materials that are quenched after high-pressure high-temperature treatment, phase transformations to denser structures have been reported.[1–6] Pressure Raman studies on the alkaline-earth difluorites have shown that they undergo a cubic-to-orthorhombic phase transformation at elevated pressure.[1–3,6–8] CeO_2 has the same type of structure as the dioxides and has been found to incorporate into the orthorhombic structure at pressures around 31 GPa at room temperature.[7,8]

There is now a considerable interest to investigate high-pressure behavior of nanosized materials due to their novel properties, which may differ from that of the macrosize materials.[9–13] Studies on nano-oxides indicate that the decrease of particle size significantly changes the compressibility and the transition pressure. Some of these oxides display lower transition pressure with a decrease in particle size.[9,11,13] Such findings are contrary to the general model for most nanomaterials, including sulfides and oxides, which exhibit higher transition pressures with a decrease in particle size.[10,12] Large volume collapse in this type of pressure-induced phase transformation is the explanation assigned to such observations.[10] However, to deepen our understanding of this new high-pressure phenomenon in the nanomaterial field, more experimental documentation is needed. To this end, we have carried out an *in situ* x-ray-diffraction study of nano-CeO_2 up to pressures of 38.6 GPa. We found that at room temperature the cubic fluorite phase of nano-CeO_2 undergoes a pressure-induced phase transformation at 22.3 GPa, which is remarkably lower than the pressure of 31 GPa occurring in the corresponding bulk CeO_2. Another structure phase was also observed in the recovered sample. These results are presented below.

II. EXPERIMENTS

The sample used here was commercial nanosized CeO_2, with a particle size of 9–15 nm. It was identified as a cubic fluorite structure ($Fm3m$,225) by using x-ray diffraction and Raman spectroscopy.[7,14] Because of the size effect, the x-ray-diffraction peaks are quite broad. Raman spectroscopy displays a peak at 467 cm^{-1}, which is a little higher than the peak at 465 cm^{-1} observed in the bulk CeO_2. This peak can be assigned to the triply degenerate first-order Raman-active peak (F_{2g}) of the cubic fluorite structure CeO_2.[7,15]

Diamond with a 400-μm culet was used in a gasket diamond-anvil cell. The gasket consisted of a hardened spring steel 400-μm thick, pre-indented to 65 μm. A 150-μm diameter hole was packed with CeO_2 powder mixed with a fractional amount of platinum powder. Pressure was checked with the well-known equation of state (EOS) of platinum (Pt). Energy dispersive x-ray-diffraction spectra were collected with a fixed $2\theta\,(=11°)$ on the bending magnet beam line at the Cornell High Energy Synchrotron Source (CHESS), Cornell University. The energy calibration was done by the well-known radiation source (^{55}Fe and ^{133}Ba). The angle calibration was done by using six peaks of the standard Au powder.

III. RESULTS AND DISCUSSION

Figure 1 shows x-ray spectra of nano-CeO_2 up to pressures of 38.6 GPa in this study. The unit-cell parameters are calculated from the positions of the x-ray-diffraction peaks of the starting sample at one atmosphere pressure, which show a pure cubic fluorite phase with $a_0 = 5.416 \pm 0.012$ Å in agreement with the powder-diffraction value of $a_0 = 5.411\,34(12)$ Å for the bulk CeO_2.[14] With increasing pressure, new peaks of the high-pressure phase started to occur at a pressure of 22.3 GPa, which is significantly lower than the

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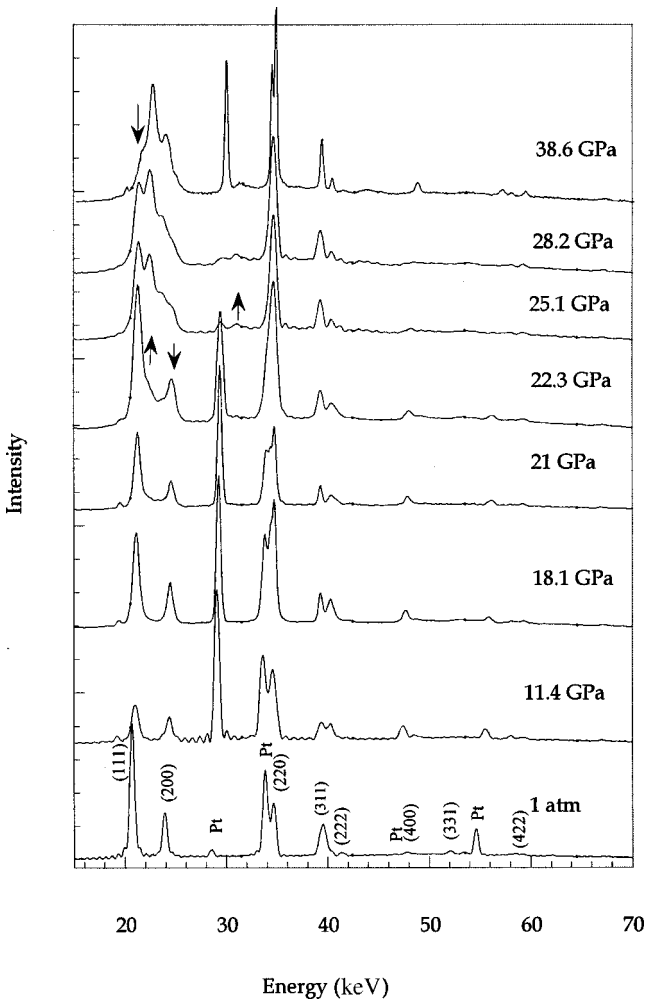

FIG. 1. X-ray diffractions of nano-CeO_2 up to pressures of 38.6 GPa. The downward arrow↓represents the disappearance of main peaks belonging to the starting phase of CeO_2, and the upward arrow ↑ represents the appearance of some peaks of the high-pressure CeO_2 phase.

phase-transition pressure of 31 GPa occurring in the corresponding bulk CeO_2.[7,8] Complete phase transformation to the high-pressure phase did not occur until a pressure as high as 38.6 GPa. This indicates that the phase transformation is quite sluggish and much slower than that taking place in the bulk material. It is suggested that a high-energy hindrance might be a factor that prevents the rapid formation of a high-pressure phase in nano-CeO_2.

The high-pressure phase of CeO_2 can be effectively indexed to an orthorhombic cell with $a_0=5.641(2)$, $b_0=6.647(5)$, $c_0=3.481(4)$ Å, $V_0=130.53(8)$ Å^3 and four units of CeO_2 per unit cell at a pressure of 38.6 GPa. The bulk modulus was calculated to be 326(9) GPa, which is a little higher than 304 GPa found in the bulk CeO_2 by Duclos *et al.*[8] The unit-cell volume was extrapolated to ambient conditions and is 9.4% denser than the cubic fluorite. Upon release of pressure, the high-pressure orthorhombic phase becomes unstable and transforms to a different structure at a pressure of 4.0 GPa with the appearance of a few peaks that cannot be refined in both the cubic fluorite and the orthorhombic structures. This recovered phase then remains stable to ambient conditions (Fig. 2). This is significantly different from the recovered phase in the bulk material, which has a cubic fluorite structure. The phase obtained can be well fitted to a hexagonal structure with $a_0=8.368(11)$, $c_0=10.693(15)$ Å, $V_0=648.43(27)$ Å^3 (Table I), which is 2% less dense than the cubic fluorite phase at one atmosphere pressure due to a little distortion from the cubic structure.

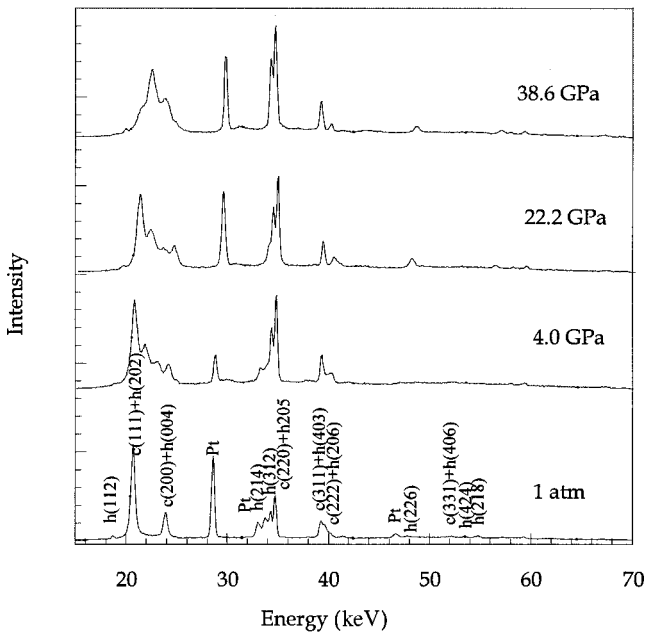

FIG. 2. X-ray diffractions of nano-CeO_2 with decompression to ambient conditions. The peaks at one atmosphere are marked with *c* and *h*, which represent the cubic fluorite phase and the hexagonal phase, respectively. The volume ratio of two phases is difficult to determine based only on the coexisting peaks.

Figure 3 shows the EOS data of nano-CeO_2 to pressures of 38.6 GPa. A fit to the Birch-Murnaghan EOS of the cubic

TABLE I. Observed and calculated d spacings of CeO_2 with the hexagonal structure at ambient conditions, which are recovered from high pressures. The unit-cell parameters are $a_0=8.368(11)$, $c_0=10.693(15)$ Å $Z=16$, with $V_0=648.43(27)$ Å^3.

hkl	d_{obs} (Å)	d_{calc} (Å)	d_{obs}-d_{calc} (Å)
101	5.969	5.101	−0.028
112	3.459	3.295	0.165
202	3.125	2.999	0.126
004	2.706	2.673	0.033
214	1.917	1.913	0.004
312	1.888	1.881	0.007
205	1.862	1.842	0.020
403	1.633	1.615	0.018
206	1.647	1.599	0.048
226	1.352	1.357	−0.005
406	1.241	1.270	−0.029
424	1.211	1.218	−0.007
218	1.184	1.201	−0.017

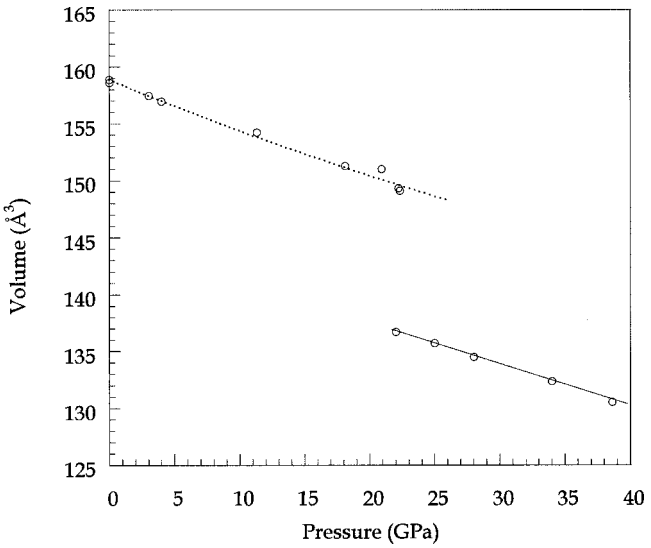

FIG. 3. The room-temperature equation-of-state data for nano-CeO_2. The dotted curves are the Birch-Murnaghan equation-of-state fits for the cubic fluorite phase with $B_0=328\pm12$ GPa, $B'=4$. The high-pressure orthorhombic phase has $B_0=326\pm9$ GPa, $B'=4$. The density change extrapolated back to one atmosphere pressure is 9.4% between two phases.

fluorite phase gives the bulk modulus $B_0=328\pm12$ GPa, when the bulk modulus pressure derivative is constrained to $B'=4.0$. This is significantly higher than that of the corresponding bulk CeO_2 with $B_0=230$ GPa.[8] This indicates that the reduction of particle size significantly increases the bulk modulus.

Previous studies on nanosized materials indicate that the decrease of particle size leads to a large elevation of phase-transition pressure and of bulk modulus in nanomaterials, including sulfides and oxides, as compared to the bulk materials.[9–13] Recent studies on γ-Fe_2O_3 and rutile (TiO_2) show that the decrease of particle size results in a significant reduction of the phase-transition pressure in the pressure-induced solid-solid phase transformations.[10,12] The elevation of transition pressure in the pressure-induced solid-solid phase transformation has been explained by a higher surface energy between the phases involved in nanosized materials compared to the bulk materials. This is in agreement with the predictions of homogenous deformation theories.[13] Conversely, the reduction of transition pressure in another type of nanometric material has been interpreted by the large collapse in volume upon phase transformation due to the formation of the high-density high-pressure phase.[10] Our results obtained strongly support the existence of the transition-pressure reduction in nanomaterials. So far, in addition to CeO_2, only two of the above-mentioned nanomaterials including γ-Fe_2O_3 and rutile (TiO_2) have been reported in the literature.[10,12] It is surprising that the corresponding high-pressure phases are unstable on release of pressure or upon increase of temperature. The nanosized rutile (TiO_2) transforms to the α-PbO_2 phase at a lower pressure with the reduction of particle size, but with increasing temperature, the α-PbO_2 phase incorporates into the original rutile phase.[12] Even though the nanosized γ-Fe_2O_3 was mostly fitted to the hexagonal structure at high pressures in the literature,[10] it is actually more reasonable to be substituted by a rhombohedral structure at high pressure due to a pressure-induced distortion. Upon release of pressure, it is recovered with the hexagonal phase. The above observations imply that the large volume collapse and the existence of an unstable high-pressure phase may lead to the reduction of transition pressure in nanomaterials compared to the corresponding bulk materials.

IV. CONCLUSION

This study has described the high-pressure room-temperature behavior of the nanosized CeO_2. The bulk modulus of the cubic fluorite structure nano-CeO_2 is 328 ± 12 GPa with an assumption of a pressure derivative of 4.0. This clearly indicates that the reduction of particle size leads to a significant elevation of the bulk modulus of CeO_2. The nano-CeO_2 starts to transform on loading to an orthorhombic structure of space group *Pnam* at 22.3 GPa, which is significantly lower than the transition pressure of 31 GPa for the corresponding bulk CeO_2. Moreover, the reduction of particle size results in a quite sluggish dynamic process in the pressure-induced phase transformation of nano-CeO_2. Upon release of pressure, the high-pressure orthorhombic phase becomes unstable. At a pressure of 4.0 GPa, it transforms to the hexagonal structure and then remains stable to ambient conditions. Thus, it may be suggested that a large volume collapse and the existence of an unstable high-pressure phase lead to a reduction of the transition pressure in nano-CeO_2.

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