Martensitic Phase Transformation of Isolated HfO$_2$, ZrO$_2$, and Hf$_x$Zr$_{1-x}$O$_2$ (0 < x < 1) Nanocrystals**
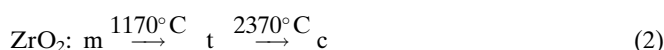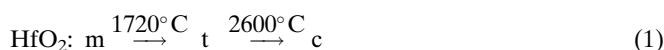
By *Jing Tang, Feng Zhang, Peter Zoogman, Jason Fabbri, Siu-Wai Chan, Yimei Zhu,* Louis E. Brus,* and *Michael L. Steigerwald**

We previously reported that, during the reactions to make nanocrystals of HfO$_2$ and Hf-rich Hf$_x$Zr$_{1-x}$O$_2$, a tetragonal-to-monoclinic phase transformation occurs that is accompanied by a shape change of the particles (faceted spherical to nanorods) when the temperature at which the reaction is conducted is changed from 340 to 400 °C. We now conclude that this concomitant phase and shape change is a result of the martensitic transformation of isolated nanocrystals in a hot liquid, where twinning plays a crucial role in accommodating the shape-change-induced strain. That such change was not observed during the reactions forming ZrO$_2$ and Zr-rich Hf$_x$Zr$_{1-x}$O$_2$ nanocrystals is attributed to the higher driving force needed in those instances compared to that needed for producing HfO$_2$ and Hf-rich Hf$_x$Zr$_{1-x}$O$_2$ nanocrystals. We also report here the post-synthesis, heat-induced phase transformation of Hf$_x$Zr$_{1-x}$O$_2$ (0 < x < 1) nanocrystals. As temperature increases, all the tetragonal nanocrystals transform to the monoclinic phase accompanied by an increase in particle size (as evidenced by X-ray diffraction and transmission electron microscopy), which confirms that there is a critical size for the phase transformation to occur. When the monoclinic nanorods are heated above a certain temperature the grains grow considerably; under certain conditions a small amount of tetragonal phase appears.

1. Introduction

Hafnia (HfO$_2$) and zirconia (ZrO$_2$) are so similar in many physical and chemical aspects that they are called twin oxides, and their similarity is attributed to their similar crystal structures. Both oxides have three polymorphs, i.e., monoclinic, tetragonal (t), and cubic (c). In the bulk, they are stable as the monoclinic phase at room temperature and then, as the temperature increases, they transform to the tetragonal phase and, eventually, to the cubic phase.[1]

$$\text{HfO}_2\text{: m} \xrightarrow{1720°\text{C}} \text{t} \xrightarrow{2600°\text{C}} \text{c} \tag{1}$$

$$\text{ZrO}_2\text{: m} \xrightarrow{1170°\text{C}} \text{t} \xrightarrow{2370°\text{C}} \text{c} \tag{2}$$

The cubic phase has the fluorite structure, and the other polymorphs are distorted versions of this structure. The high-temperature phases, tetragonal and cubic, can not be quenched to room temperature, although these phases (when stabilized by doping) are far more important in technological applications than the low-temperature phase materials. The stabilization of tetragonal and cubic phases of hafnia and zirconia can be achieved mainly by two routes: 1) by incorporating cation dopants—the inclusion of divalent or trivalent and oversized/undersized tetravalent cation dopants (such as Mg^{2+}, Ca^{2+}, Cr^{3+}, Y^{3+}, and virtually any of the rare earth ions) introduces oxygen deficiencies that stabilize the tetragonal or cubic phase; and 2) by controlling their size—in many oxide systems (such as Al$_2$O$_3$, TiO$_2$, ZrO$_2$, and Fe$_2$O$_3$) differences in surface energies stabilize, as nanoparticles, polymorphs that are metastable in the bulk. Garvie[2] predicted that pure ZrO$_2$ is stabilized in the tetragonal form at room temperature when the (spherical) particle size is less than 30 nm, owing to the lower free surface energy of the tetragonal form than that of the monoclinic. Navrotsky[3] used high-temperature oxide solution calorimetry to measure the enthalpy of ZrO$_2$ as a function of polymorphism

[*] Dr. M. L. Steigerwald, Dr. J. Tang, Prof. L. E. Brus
Department of Chemistry
Materials Research Science and Engineering Center
Columbia University
New York, NY 10027 (USA)
E-mail: mls2064@columbia.edu
Dr. Y. Zhu
Center for Functional Nanomaterials
Brookhaven National Laboratory
Upton, NY 11973 (USA)
E-mail: zhu@bnl.gov
Dr. F. Zhang, Prof. S.-W. Chan
Department of Applied Physics and Applied Mathematics
Materials Research Science and Engineering Center
Columbia University
New York, NY 10027 (USA)
P. Zoogman
Harvard University
Cambridge, MA 02138 (USA)
J. Fabbri
Fairfield University
Fairfield, CT 06824 (USA)

DOI: 10.1002/adfm.200500050

and surface area, and her results confirmed crossovers in polymorph stability at the nanoscale.

HfO$_2$ and ZrO$_2$ are isomorphous in each phase; they have strikingly similar monoclinic lattice parameters and the same space group ($P2_{1/c}$), and thus they form a series of solid solutions, Hf$_x$Zr$_{1-x}$O$_2$, over the complete concentration range ($0 < x < 1$) in the bulk. We previously reported that solid-solution Hf$_x$Zr$_{1-x}$O$_2$ nanoparticles over a wide range of x, in either the tetragonal or the monoclinic phase, can be formed. The ZrO$_2$ and HfO$_2$ nanocrystals were made by condensation of the metal halide (MX$_4$) and metal isopropoxide (M(O^{i}Pr)$_4$), while the solid-solution Hf$_x$Zr$_{1-x}$O$_2$, nanoparticles were made by the cross-condensation reaction between MX$_4$ and M(O^{i}Pr)$_4$ in a coordinating reaction environment.[4,5] It was found that the temperature at which these preparative reactions are run has a significant effect on the resulting nanoparticles. When the reaction is run at ~340 °C, roughly spherical, albeit faceted, particles with pure or predominantly tetragonal phase form, whereas at higher synthesis temperatures (~400 °C), the particles form as nanorods and, at the same time, the phase changes to monoclinic.

We have also studied the post-synthesis, heat-induced phase transformation of the nanoparticle powder. The tetragonal Hf$_x$Zr$_{1-x}$O$_2$ nanoparticles ($0 < x < 1$) transform to the monoclinic phase as the temperature increases, accompanied by an increase in the grain size, as evidenced by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). This is consistent with the critical size effect as predicted by Garvie.[2] Isothermal transformation kinetics are also observed for the nanocrystal transformation. When the monoclinic nanorods are heated, the grain size increases considerably above a certain temperature and, under certain conditions, a small amount of tetragonal phase appears.

Martensitic transformations are well known in bulk solid-state materials.[6] A martensitic transformation is diffusionless—all of the atoms in a crystal domain move simultaneously, and the same interatomic connectivity is retained throughout, although the actual distances and angles change. In view of the evidence we present below, we conclude that the concomitant shape and phase changes we observe result from martensitic phase transformations within isolated particles.

2. Results and Discussion

2.1. Martensitic Phase Transformation During Synthesis

As mentioned previously, it has been found[5] that, in the reaction to make HfO$_2$ nanocrystals using Hf(O^{i}Pr)$_4$ and HfCl$_4$, the reaction tempera-

ture has a significant effect on the characteristics of the resulting particles. When the reaction temperature is ~340 °C, the particles are faceted, and the XRD pattern of the particles can be attributed to the cubic phase. It is difficult to distinguish between the tetragonal and the cubic phases from XRD alone; however, electron diffraction analysis of individual particles shows that the particles are single crystals with $P4_2/nmc$ symmetry. Raman data further confirm that these faceted HfO$_2$ nanoparticles are predominantly, if not exclusively, tetragonal. When the preparative reaction is conducted at ~400 °C, HfO$_2$ nanorods form and, at the same time, the phase of the particles changes to monoclinic as determined from both XRD and electron-diffraction analysis.

A similar effect was observed in the synthesis of Hf-rich Hf$_x$Zr$_{1-x}$O$_2$ nanoparticles. For example, the reaction of Hf(O^{i}Pr)$_4$, ZrCl$_4$, and HfCl$_4$ in a 2:1:1 molar ratio gives Hf$_{0.66}$Zr$_{0.34}$O$_2$ nanoparticles; when run at 340 °C the reaction yields faceted particles of the tetragonal phase, and when run at 400 °C it yields nanorods of the monoclinic material. Transmission electron micrographs of the faceted particles and nanorods of Hf$_{0.66}$Zr$_{0.34}$O$_2$ are shown in Figure 1, along with the corresponding XRD patterns.

Although it may take 2 h at 340 °C to form tetragonal particles that are uniform and faceted, particles already start to form after keeping the reaction at 340 °C for only 10 min.
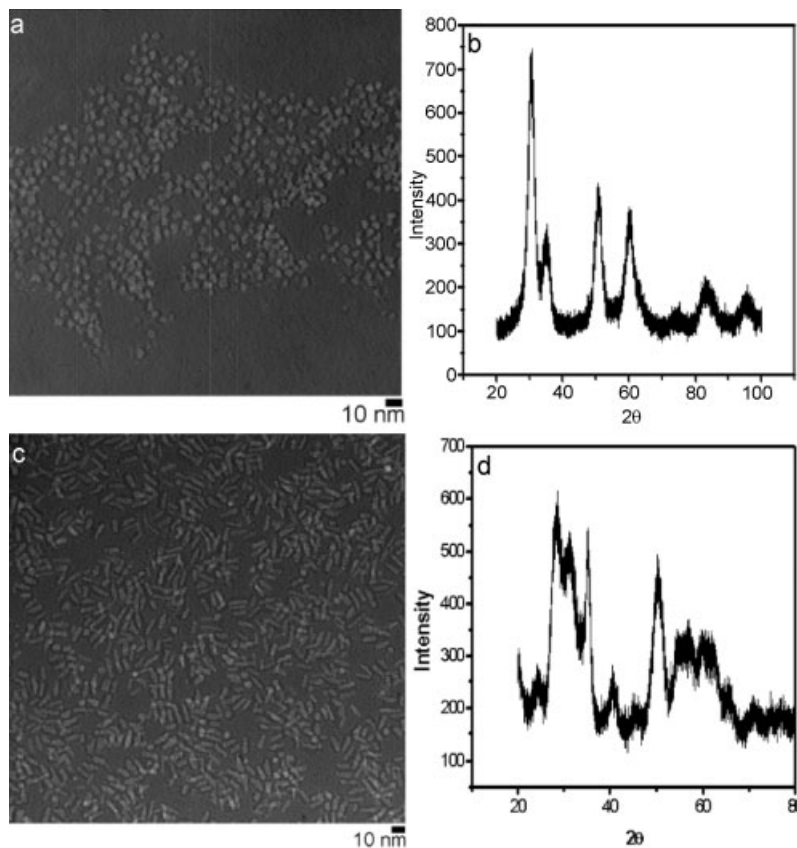
Figure 1. TEM image and the corresponding XRD pattern of tetragonal (a,b) and monoclinic (c,d) Hf$_{0.66}$Zr$_{0.34}$O$_2$ nanocrystals resulting from reacting Hf(O^{i}Pr)$_4$ with ZrCl$_4$ and HfCl$_4$ (2:1:1) at 340 °C and 400 °C, respectively.

Moreover, raising the temperature from 340 to 400 °C usually takes at least 30 min, therefore we believe the monoclinic nanorods (either HfO$_2$ or Hf-rich Hf$_x$Zr$_{1-x}$O$_2$) formed at ~400 °C are transformed from tetragonal particles that already form at lower temperatures.

Such correlated changes in shape and phase of the particles has been observed in several cases of the hydrothermal synthesis of ZrO$_2$.[7,8] Nishizawa et al.[7] reported that cubic zirconia crystallizes into small mosaic particles when an amorphous zirconia gel was treated hydrothermally at 130 °C, however, at reaction temperature of 320 °C, an abrupt change of the particle phase and shape occurs—monoclinic rods formed. Noh et al.[8] reported that, as the reaction temperature increases from 150 to 200 °C during the hydrothermal processing of amorphous zirconium hydroxide and tetragonal zirconia powder, the particle shape changes from spherical to rod-like and the particle phase changes from tetragonal to monoclinic. These authors speculate that the monoclinic rods form through the dissolution and reprecipitation, or by coagulation of very fine particles in a highly oriented fashion.

The present case differs from these examples in one important aspect—in the previous examples the average volume of the monoclinic rods is much larger than the average volume of the corresponding tetragonal/cubic spherical particles (for example, the size of the cubic and monoclinic ZrO$_2$ crystallites are reported to be 11–18 nm and 150 × 30 nm, respectively;[6] while the tetragonal spherical particles are reported to be 20–30 nm in diameter, and the monoclinic rods 50 nm in diameter and 200–400 nm in length[7]), while in the present case, the average volume of the nanorods is close to that of the tetragonal spherical particles. For example, in the case of HfO$_2$, the average volumes of the faceted tetragonal particles (5.5 nm) and the monoclinic rods (3.2 × 10.1 nm) are 87 and 83 nm^3, respectively. Moreover, in our case the average surface area of the monoclinic HfO$_2$ nanorods is actually larger than that of the tetragonal particles (~121 nm^2 and ~95 nm^2, respectively) with similar volume. The thermodynamic argument advanced by Garvie[2] claims that, for a sufficiently large surface-area-to-volume ratio, particles of HfO$_2$ should convert to the tetragonal phase. Were this mechanism operating, the nanorods should also be in the tetragonal phase (in fact these nanorods should be even more favored than the spheroid particles to be in the tetragonal phase). However, in Garvie's arguments, the surface energies are assumed to be isotropic; our results on relative surface areas suggest that this may actually not be the case.

Macroscopic shape change of nanoparticles during phase transformation has also been observed in the high-pressure phase transformation of CdSe and Si nanoparticles, in which the change of the particle shape acts as an indicator of the transformation mechanism.[9] With several important pieces of evidence shown below, we believe that the concomitant shape and phase changes of the HfO$_2$ and Hf-rich Hf$_x$Zr$_{1-x}$O$_2$ nanoparticles is a result of a martensitic phase transformation.

It has long been known that the t → m transformation, or vice versa, in ZrO$_2$ and HfO$_2$ is martensitic.[10] A martensitic phase transformation is diffusionless, and all the atoms in a crystal move simultaneously in a coordinated fashion. The change of crystal structure is achieved by a deformation of the parent phase. An invariant plane exists between the parent and product phase, which means twins and lattice slips typically result. A martensitic transformation is usually accompanied by changes in volume and shape and can be triggered by hydrostatic and shear stresses. For ZrO$_2$, the t → m transformation is associated with a 5 % volume expansion. The martensitic phase transformation of ZrO$_2$ has been intensively studied due to the theoretical interest in understanding this important transition and its technological importance, as it contributes to the toughening of ceramics.

We believe that the concomitant shape and phase transformations occurring in the reactions producing HfO$_2$ and Hf-rich Hf$_x$Zr$_{1-x}$O$_2$ nanocrystals results from a martensitic phase transformation, based on the following evidence:

1) High-resolution imaging and diffraction investigations show that twinning structures often occur in the monoclinic nanorods, while the spherical tetragonal nanoparticles are defect free. Figure 2a shows a representative high-resolution (HR)TEM image of a monoclinic Hf$_{0.66}$Zr$_{0.34}$O$_2$ nanorod, in which the twinning elements are clearly identified, and the twin plane (100) is marked by a dashed line. Figure 2b is a Fourier transform of the corresponding HRTEM image, and twinning is further confirmed by the spot splitting in the diffraction pattern. Extensive HRTEM analysis of the nanorods showed that they generally have the same growth direction and the twin
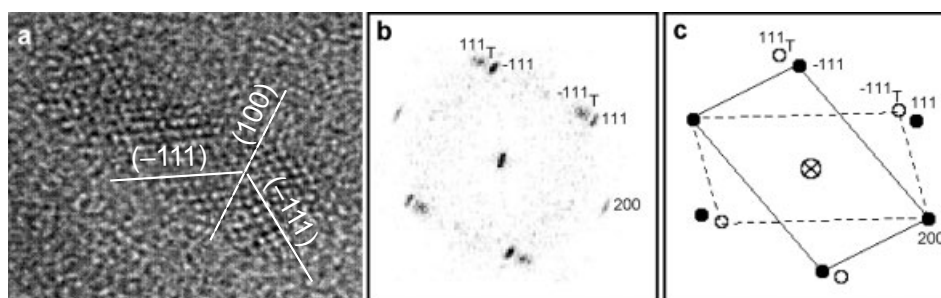

Figure 2. a) HRTEM image of a Hf$_{0.66}$Zr$_{0.34}$O$_2$ nanorod. The (100) twinning plane is denoted by the dashed line. b) The corresponding diffraction pattern obtained from Fourier-transforming the image in (a). c) Schematic diagram of the diffraction pattern in (b), showing the twinning relation between the two crystals. The subscript "T" in (b,c) refers to twinning.

planes are always either (100) or (001). In practice, however, there is no need to distinguish between the (001) and (100) twinning in the HRTEM images, as their twinning angles related to the (111) lattice are very similar (the angle between (100) and (111) is 49.8°, while the angle between (001) and (111) is 50.9°) due to the small difference (~3 %) between the *a* and *c* lattice parameters of monoclinic HfO$_2$ or ZrO$_2$.

As mentioned above, twinning is usually a typical result of martensitic phase transformation, and (001) and (100) are the typical invariant twin planes during the martensitic phase transformation of bulk ZrO$_2$ and HfO$_2$.[11] The shape change during the phase transformation can be directly related to twinning to accommodate the local strain due to the shape change. Therefore, the twinning structures observed in these monoclinic nanorods provide very important evidence that the correlated shape and phase changes result from the martensitic phase transformation. Recently, Shen et al.[12] directly observed the t→m phase transformation induced by the electron beam in TEM, and showed the shape change from t-ZrO$_2$ spheres to m-ZrO$_2$ ellipsoids with dilation and contraction along orthogonal [110] directions and invariant plane strain along (001) twin planes, which is in accordance with martensitic phase transformations.

2) A small percentage of spherical particles were always found in the monoclinic nanorods system, which suggests a coexistence of the two distinct phases. For example, Figure 3a is a TEM image of the Hf$_{0.75}$Zr$_{0.25}$O$_2$ particle obtained from reaction of Hf(O^{i}Pr)$_4$ with ZrCl$_4$ and HfCl$_4$ (molecular ratio 3:1:2) at 400 °C, in which both faceted particles and nanorods are present. The Hf$_{0.46}$Zr$_{0.54}$O$_2$ particles formed from reacting Hf(O^{i}Pr)$_4$ with Zr(O^{i}Pr)$_4$, ZrCl$_4$, and HfCl$_4$ (molecular ratio (1:1:1:1) at 400 °C were found by XRD to be a mixture of the tetragonal and monoclinic phases. Low-resolution TEM of this sample (Fig. 3b) clearly shows that both faceted particles and nanorods were present in large amounts. HRTEM measurements on these particles find again that twinning exists extensively only in the monoclinic nanorods. In Figures 3c,d we show two examples of HRTEM images of Hf$_{0.46}$Zr$_{0.54}$O$_2$ nanorods, and in both particles the twin boundaries are identified, as denoted by the dashed lines. Therefore, from the structure analysis of this mixed-phase sample, the correlation between the shape and phase of the particles is unambiguously established: particles that have a faceted shape and an aspect ratio near unity are tetragonal, whereas those that have a cylindrical shape are monoclinic.

3) It was found that the elemental composition of the Hf$_x$Zr$_{1-x}$O$_2$ nanocrystals remains constant during the phase transformation of the Hf-rich Hf$_x$Zr$_{1-x}$O$_2$ nanocrystals in the reactions (i.e., they are tetragonal at 340 °C and transform to monoclinic at ~400 °C). Since the transformation is diffusionless, i.e., all atoms have the same neighbors in either phase, it is easy to understand that the composition of the system does not vary during the transformation.[10] This means that the system should always be considered as a single-component system, regardless of the number of components that would be counted for a conventional phase.
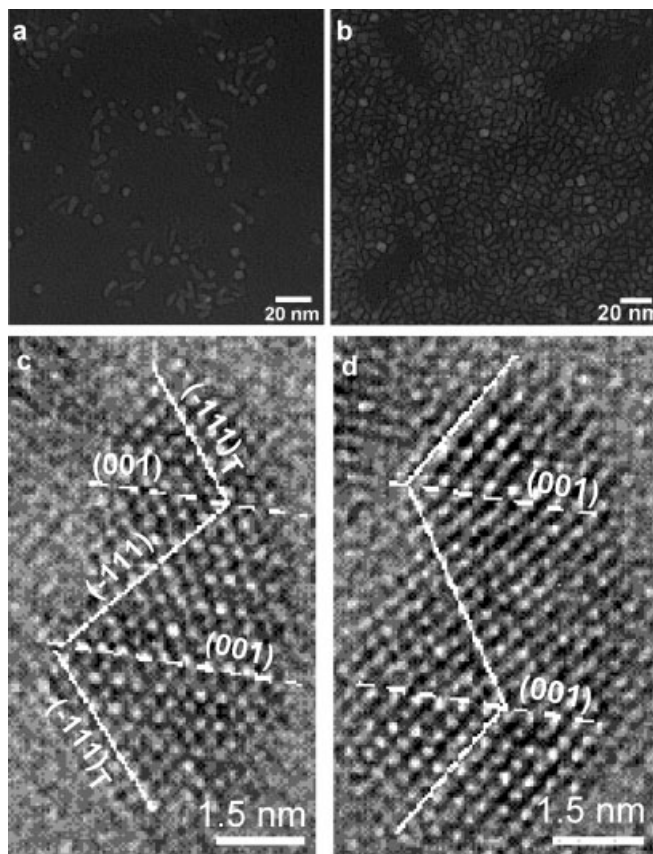
Figure 3. a) TEM image of particles obtained from reacting Hf(O^{i}Pr)$_4$ with ZrCl$_4$ and HfCl$_4$ (3:1:2) at ~400 °C. Although the majority of particles are monoclinic nanorods, a small number of spherical particles also coexist. b) TEM image of particles obtained from reaction of Hf(O^{i}Pr)$_4$ with Zr(O^{i}Pr)$_4$, HfCl$_4$, and ZrCl$_4$ (1:1:1:1) at ~400 °C. Both faceted particles and nanorods are present, while the XRD pattern shows a mixture of the tetragonal and monoclinic phases. c,d) Two examples of the HRTEM images of the nanorods shown in (b). Two twin boundaries are identified in each image, as denoted by the dashed lines.

4) Thus far, the t→m phase transformation has only been observed in HfO$_2$ and Hf-rich Hf$_x$Zr$_{1-x}$O$_2$ nanocrystals. We believe that similar correlated shape and phase changes would occur in ZrO$_2$ and Zr-rich Hf$_x$Zr$_{1-x}$O$_2$ nanocrystals as well, but a higher driving force is needed for these systems. Although ZrO$_2$ and HfO$_2$ have many very similar chemical and physical properties, they still do show some differences in their phase-transformation behavior. For example, Wolten[10] studied the monoclinic–tetragonal phase changes in pure ZrO$_2$ and HfO$_2$ with high-temperature diffractometry and found that the hysteresis loops associated with the transformations of ZrO$_2$ and HfO$_2$ have similar shapes (which are typical of martensitic transformations), but the widths of the loops differ greatly for the two materials, i.e., 200 °C for ZrO$_2$ and only 20–30 °C for HfO$_2$. Martensitic-phase-transformation kinetics are controlled by nucleation and growth and, as growth velocities are usually very fast, it is believed that these transformations are nucleation-controlled. Wolten conceived that nucleation is easier in HfO$_2$ and also that the smaller volume change during the trans-

formation in HfO₂ could contribute to the narrower hysteresis loop. Chen et al.[13] studied the martensitic phase transformation of small ZrO₂ and HfO₂ particles embedded in metal and ceramic matrices. They found that the transformation enthalpy of HfO₂ is 75 % higher than that of ZrO₂, and that HfO₂ has a much higher driving force and therefore a substantially less-stringent nucleation condition for the phase transformation. Their experiments showed that the t → m phase transformation is easier for HfO₂ particles than ZrO₂ particles. In the study of the phase transformation of a HfO₂–ZrO₂ solid solution in a Al₂O₃ matrix, Claussen et al.[14] found that the tetragonal Hf$_{0.5}$Zr$_{0.5}$O₂ particles readily transform to the monoclinic phase when induced by electron irradiation in TEM, while the tetragonal ZrO₂ particles in the same matrix are much more difficult to transform under identical TEM conditions; this again confirms that alloying ZrO₂ with HfO₂ increases the driving force needed for the phase transformation.

Therefore, the fact that we observed the t → m transformation only for HfO₂ and Hf-rich Hf$_x$Zr$_{1-x}$O₂ nanoparticles is consistent with the fact that HfO₂ has a higher driving force for the phase transformation and thus transforms more easily than ZrO₂.

5) The correlated shape and phase changes have also been seen during the post-synthesis, heat-induced phase transformation of the particles, even for ZrO₂ and Zr-rich Hf$_x$Zr$_{1-x}$O₂ nanoparticles. Owing to the removal of surfactant and the presence of strong van der Waals interactions between the particles, the particles tend to aggregate significantly, and the density of the isolated particles is generally low. Figure 4a shows a TEM image of the Hf$_{0.66}$Zr$_{0.34}$O₂ nanorods obtained by heating the originally faceted tetragonal particles at 400 °C in Ar (TEM image of the original particles is shown in Fig. 1a) for 0.5 h. Clearly, a small number of nanorods start to appear. This is also seen in heated ZrO₂ and Zr-rich nanoparticles, even though such a transformation has not been observed during the synthesis reactions. Figure 4b shows a TEM image of ZrO₂ nanorods after heating the originally 4 nm tetragonal spherical ZrO₂ nanoparticles at 900 °C in air for 1 h. However, in all these cases, the percentage of the nanorods is small as the phase transformation is dominated by the other pathway— grain-size increase; details of this will be discussed below. Hence, we believe the t → m phase transformation of the nanoparticles is facilitated in the surfactant (trioctylphosphine

oxide, TOPO) and this is probably due to the enhancement of the nucleation in the presence of the surfactant.

Figure 5a shows the crystal structures of the tetragonal and monoclinic phases of Hf$_x$Zr$_{1-x}$O₂ $(0 < x < 1)$ nanoparticles, viewed close to the [010] direction. The dashed lines on the left unit cell indicate the crystal shear associated with the t → m phase transition. The angular difference of 9.2° is also indicated
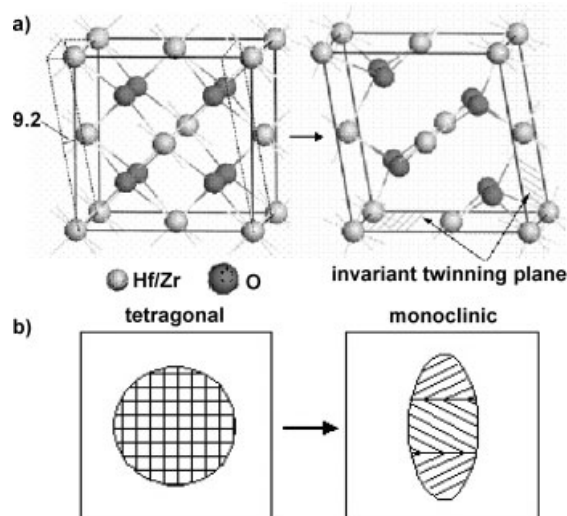
Figure 5. a) Crystal structures of the tetragonal and monoclinic phases of Hf$_x$Zr$_{1-x}$O₂ $(0 < x < 1)$ nanoparticles viewed along the [010] direction. The marked 9.2° angle on the left indicates the change of β (the angle between the *a*- and *b*-axes) between the two phases. The (100) and (001) invariant planes during the phase transformation are also indicated. b) The martensitic t → m phase transformation is schematically represented, going from left to right, and indicates that the particles undergo size and shape changes, and also that twins form.

$(\beta = 99.2°$ for the monoclinic phase). The (100) and (001) invariant planes during the shear and phase transformation are also illustrated. Figure 5b schematically illustrates the concomitant changes in phase and shape, and the formation of twins of the HfO₂-ZrO₂ nanoparticles that result from the martensitic transformation in a hot liquid. The mechanism of the diffusionless martensitic transformation in solids has been previously discussed in detail.[6]

Although the volumes of the monoclinic rods are much larger than those of the tetragonal particles in the hydrothermal
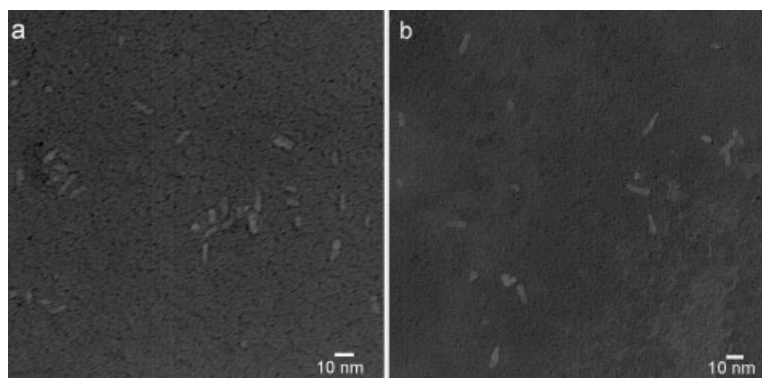
Figure 4. a) A small number of nanorods appear after heating the tetragonal Hf$_{0.66}$Zr$_{0.34}$O₂ particles (original TEM picture shown in Fig. 1a) at 400 °C in argon for 30 min. b) A small number of nanorods appear after heating the tetragonal ZrO₂ particles at 900 °C in air for 1 h.

synthesis of ZrO_2 mentioned above (in which correlated phase and shape changes also occurred), the possibility of a martensitic phase transformation cannot be excluded. Ellipsoidal nuclei could form as a result of the martensitic transformation and then subsequently grow into much larger rods.

2.2. Post-Synthesis Heat-Induced Phase Transformation

2.2.1. Tetragonal Nanocrystals

The precipitated powder of tetragonal nanoparticles was heated at various temperatures, and the $t \rightarrow m$ phase transformation was monitored by XRD. The XRD patterns of the 4 nm diameter ZrO_2 nanocrystals after being heated at 600, 900, 1000, 1100, and 1200 °C for 1 h are shown in Figure S1 of the Supporting Information. At 600 °C, there is no significant change in the XRD pattern; however, starting at 900 °C, the peaks narrow and several of the peaks split into doublets ($2\theta \sim 60$, 81° (900 °C), 35° (1000 °C)). These doublets are characteristic of the tetragonal phase. They are not resolvable in the XRD pattern of the as-synthesized particles (as well as those of the particles annealed at lower temperatures) due to the small particle size. The increase of crystallite size with the heating, indicated by the peak narrowing in the XRD spectra, is accompanied by the tetragonal-to-monoclinic phase transformation. Monoclinic peaks start to appear at 1100 °C, and heating the sample at 1200 °C for 1 h completes the transformation.

The average grain size can be calculated from the broadening of characteristic peaks in the XRD according to the Debye–Scherrer equation.[15] The (111) reflection of the tetragonal phase and the (111) and ($\bar{1}$11) reflections of the monoclinic phase are selected to represent the tetragonal and monoclinic particles, respectively. The relative fraction of tetragonal phase (t) can be determined from the relative XRD line intensities by the polymorph method using the following equation,[16]

$$t = \frac{I_{t(111)}}{I_{m(111)} + I_{m(\bar{1}11)} + I_{t(111)}} \tag{3}$$

in which $I_{t(111)}$, $I_{m(111)}$ and $I_{m(\bar{1}11)}$ represent the relative intensities of the tetragonal (111) peak and the two monoclinic peaks, (111) and ($\bar{1}$11), respectively.

The effect of the composition on the thermally induced phase transformation has also been studied. The phase-transition temperature of nanoparticles containing Hf is lower than that of pure ZrO_2 nanoparticles. For HfO_2 nanoparticles, the phase transformation starts at a much lower temperature—at 600 °C, a considerable amount of monoclinic phase is apparent; however, the phase transformation is not complete until 1200 °C. At a given temperature, the percentage of sample transformed increases with increasing Hf fraction, as seen in Figure 6a, which gives the percentage of the tetragonal phase as a function of temperature for the different compositions of $Hf_xZr_{1-x}O_2$ nanocrystals.

The average change in tetragonal grain size as a function of temperature for the different compositions of $Hf_xZr_{1-x}O_2$ is plotted in Figure 6b. In all cases, just as described above for the case of ZrO_2 nanocrystals, the tetragonal particles are indeed stabilized only below a certain size, and this critical size decreases with increasing Hf content. The critical-size effect on the phase stability is consistent with Garvie's prediction according to the difference of the surface energy between the tetragonal and monoclinic phases.[2]

The annealed particles were further characterized by TEM (examples are shown in Supporting Information, Fig. S2), and the increase in particle size is further confirmed. However, for the particles heated at 1000 °C or higher, most particles were considerably larger than the grain size calculated from the XRD pattern. This is explained by the fact that the particles are polycrystalline (as confirmed by the spotted ring pattern from the selected area electron diffraction on individual particles), and, therefore, each particle contains more than one grain. One thing we also noticed is that some small tetragonal particles retained their size, even after being heated at temperatures as high as 1100 °C.

One important feature of a martensitic phase transformation is that it is athermal, meaning that the extent of the phase transformation is independent of time at a fixed temperature, and only changes by varying the temperature. This athermal character is a consequence of very rapid nucleation and growth, so rapid that the time taken can, under normal circumstances, be neglected. However, some studies on Y_2O_3-stabilized tetragonal ZrO_2 have shown that the transformation occurs isothermally over a certain temperature range.[17] Moreover, fine-grained ZrO_2 appears to exhibit an isothermal component in the transformation kinetics and this is attributed to the contribution of surface energy.[18] According to Grain and Garvie,[19] isothermal kinetics would be expected in a material that has a crystallite size less than 100 nm; above this size, the transformation should follow athermal kinetics. This isothermal kinetics has also been seen in our small tetragonal $Hf_xZr_{1-x}O_2$ nanoparticles. It is found that the percentage of the monoclinic phase increases with increased heating time at a certain temperature, and the transformation kinetics depends
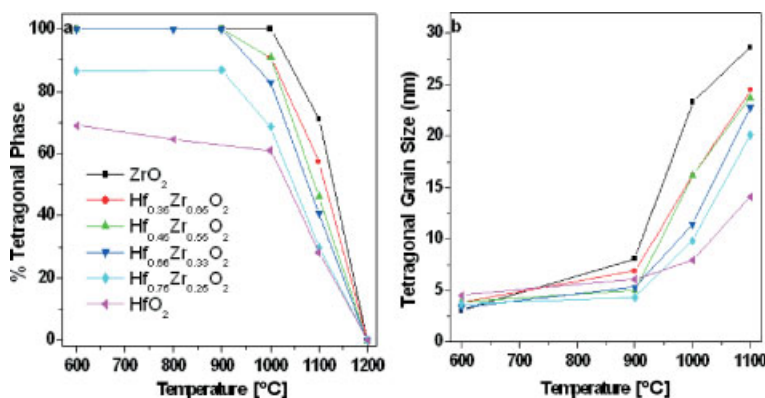

Figure 6. Percentage of tetragonal phase (a) and average tetragonal grain size (b) of $Hf_xZr_{1-x}O_2$ nanocrystals after being heated at various temperatures for 1 h.

dramatically on the temperature (see Supporting Information, Fig. S3). The transformation rate increases significantly at higher temperatures—for example, for ZrO_2 nanocrystals, it takes ~48 h at 1000 °C and 5 h at 1100 °C to complete ~90 % of the phase transformation, while at 1200 °C, the phase transformation completes within an hour. Again, we see greater phase-transformation rates with higher Hf content under equivalent conditions (see Supporting Information, Fig. S3a). It was also found that heating the ZrO_2 nanocrystals at 600 °C for 90 h produces basically no difference between its XRD pattern and that of the as-synthesized particles. This indicates that the crystallite-size increase depends strongly on the temperature and at low temperature, it does not increase as a function of time, and, thus, no phase transformation occurs with longer duration of heating. The average tetragonal and monoclinic grain size change during the isothermal phase transformation (see Supporting Information, Figs. S3b,c, respectively) shows that the average monoclinic grain size increases as the heating time increases, while the average tetragonal grain size decreases slightly.

2.2.2. Monoclinic Nanorods

The monoclinic $Hf_xZr_{1-x}O_2$ nanorods were also heated to see if any phase transformation would occur. For example, $Hf_{0.66}Zr_{0.34}O_2$ nanorods were heated to 600, 900, 1000, 1100, and 1200 °C for 1 h and the corresponding XRD patterns are shown in Figure S4 of the Supporting Information. Up to 900 °C, there is very little change in the XRD pattern; however, from 1000 °C, the peaks start to narrow and at 1100 °C, the peaks narrow considerably, and most of the peaks that could not be resolved (due to the small particle size) in the XRD pattern of the as-synthesized particles can now be clearly resolved. Moreover, the characteristic tetragonal peak at $2\theta \sim 30.2°$ appears at 1000 °C and becomes stronger at 1100 °C, but weakens at 1200 °C. Heating the nanorods at 1100 °C for a longer time (i.e., 3 h) also weakens the tetragonal peak, compared to heating at the same temperature for 20 min or 1 h. The fractions of the tetragonal phase after being heated at 1000, 1100, and 1200 °C for 1 h were 5.3, 14.5, and 2.6 %, respectively. The calculated average monoclinic grain size is 5.4, 14.4, and 25 nm, respectively, for samples heated at 1000, 1100, and 1200 °C for 1 h, and the corresponding average tetragonal grain size is 12.2, 22.2, and 27 nm, respectively.

TEM analysis of the heated nanorods sample shows that most of the nanorods still retain their shape and size after being heated at 900 °C, which is consistent with the essentially unchanged XRD pattern. TEM of the sample heated at 1000 °C (see Supporting Information, Fig. S5) shows that the nanorods have grown into irregular or nearly spherical particles. As the nanorods grow into nearly spherical particles, and when some of the particles are below the critical size, they could be stabilized in the tetragonal phase, and this may account for the appearance of the tetragonal phase at certain temperature; however, when the tetragonal particles continue to grow at higher temperature or for a longer time, they will transform to the monoclinic phase just as the as-synthesized tetragonal particles described above.

3. Conclusions

We have studied the phase transformation of $Hf_xZr_{1-x}O_2$ ($0 < x < 1$) nanocrystals both during the synthesis reactions and as induced by heat after synthesis. We put forward the following conclusions:

1) HRTEM analysis shows that twinning extensively exists in the monoclinic nanorods, while the tetragonal nanocrystals are defect free. We conclude that the concomitant phase and shape changes during the synthesis of HfO_2 and Hf-rich $Hf_xZr_{1-x}O_2$ nanocrystals that occur as the temperature increases results from the martensitic phase transformation. That such change is not observed during the synthesis of ZrO_2 and Zr-rich $Hf_xZr_{1-x}O_2$ nanocrystals is attributed to the higher driving force needed to produce them, compared to that needed to produce HfO_2 and Hf-rich $Hf_xZr_{1-x}O_2$ nanocrystals.

2) As temperature increases, the tetragonal $Hf_xZr_{1-x}O_2$ ($0 < x < 1$) nanocrystals all transform to the monoclinic phase accompanied by the particle size growth as evidenced by XRD and TEM, which confirms that there is a critical size for the phase transformation to occur. The effect of composition on the phase transformation rate and the isothermal transformation kinetics have also been discussed.

3) When the monoclinic nanorods are heated, the grain size grows considerably after a certain temperature and, under certain conditions, a small amount of tetragonal phase appears.

4. Experimental

Nanocrystals of ZrO_2, HfO_2, and $Hf_xZr_{1-x}O_2$ were prepared according to literature methods [4,5]. Low-resolution TEM was performed using a JEOL 100cx microscope (accelerating voltage 100 kV). Higher-resolution structural characterization of the nanoparticles was carried out using a field-emission transmission electron microscope (JEOL 3000F) operating at 300 kV. The 300 kV instrument has a high-resolution pole-piece with a point-to-point resolution of 0.16 nm. The lattice images presented in this article were recorded using a high-resolution charge-coupled device (CCD) camera. Diffraction analysis for electron crystallography and measurement of lattice parameters were conducted for individual particles via fast Fourier transform of the images based on the computer code developed at Brookhaven National Laboratory. XRD patterns were recorded using either a Scintag X2 diffractometer or an Inel diffractometer with a Cu Kα radiation source. The elemental composition of the $Hf_xZr_{1-x}O_2$ nanoparticle samples was accurately determined by inductively coupled plasma (ICP) analysis (Desert Analytics, Tucson, AZ).

The heat-induced phase transformation of the particles was performed by heating the precipitated nanoparticle powder in a tube furnace (Lindberg) in air or Ar. The particles were then characterized by XRD and TEM. As the surfactant/ligand TOPO is usually lost during the heating process, it is difficult to disperse the resulting particles in an organic solvent. The heated powder was sonicated in hexane for 30 min and a drop of the suspension was deposited onto a TEM grid and dried in vacuo.

[1] F. Cardarelli, *Materials Handbook*, Springer, London **2000**.

[2] a) R. C. Garvie, *J. Phys. Chem.* **1965**, *69*, 1238. b) R. C. Garvie, *J. Phys. Chem.* **1978**, *82*, 218.

[3] A. Navrotsky, *Geochem. Trans.* **2003**, *4*, 34.

[4] J. Joo, T. Yu, Y. W. Kim, H. M. Park, F. Wu, J. Z. Zhang, T. Hyeon, *J. Am. Chem. Soc.* **2003**, *125*, 6553.

[5] J. Tang, J. Fabbri, R. Roberson, Y. Zhu, I. P. Herman, M. L. Steigerwald, L. E. Brus, *Chem. Mater.* **2004**, *16*, 1336.

[6] A. G. Khachaturyan, *Theory of Structural Transformations in Solids*, John Wiley & Sons, New York **1983**.

[7] H. Nishizawa, N. Yamasaki, K. Matsuoka, H. Mitsushio, *J. Am. Ceram. Soc.* **1982**, *65*, 343.

[8] H. J. Noh, D. S. Seo, H. Kim, J. K. Lee, *Mater. Lett.* **2003**, *57*, 2425.

[9] a) S. H. Tolbert, A. B. Herhold, L. E. Brus, A. P. Alivisatos, *Phys. Rev. Lett.* **1996**, *76*, 4384. b) J. N. Wickham, A. B. Herhold, A. P. Alivisatos, *Phys. Rev. Lett.* **2000**, *84*, 923.

[10] G. M. Wolten, *J. Am. Ceram. Soc.* **1963**, *46*, 418.

[11] E. C. Subbarao, H. S. Maiti, K. K. Srivastava, *Phys. Status Solidi A* **1974**, *21*, 9.

[12] P. Shen, W. H. Lee, *Nano Lett.* **2001**, *1*, 707.

[13] I. W. Chen, Y. H. Chiao, in *Science and Technology of Zirconia II* (Eds: N. Clauseen, M. Rühle, A. H. Heuer), American Ceramic Society, Columbus, OH **1984**, p. 33.

[14] N. Claussen, F. Sigulinski, M. Rühle, in *Science and Technology of Zirconia II* (Eds: N. Clauseen, M. Rühle, A. H. Heuer), American Ceramic Society, Columbus, OH **1984**, pp. 164–165.

[15] B. D. Cullity, *Elements of X-ray Diffraction*, Addison-Wesley, Reading, MA **1978**.

[16] M. I. Osendi, J. S. Moya, C. J. Serna, J. Soria, *J. Am. Ceram. Soc.* **1985**, *68*, 135.

[17] a) M. Hayakawa, K. Nishio, J. Hamakita, T. Onda, *Mater. Sci. Eng. A* **1999**, *273–275*, 213. b) H. Tsubakino, N. Matsuura, *J. Am. Ceram. Soc.* **2002**, *85*, 2102.

[18] H. S. Maiti, V. G. K. Gokhale, E. C. Subbarao, *J. Am. Ceram. Soc.* **1972**, *55*, 317.

[19] C. F. Grain, R. C. Garvie, *Bur. Mines Rep. Invest.* **1965**, 6619.

FULL PAPER