Factors Determining the Crystal Phases of Zirconia Powders: A New Outlook

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The pH of the supernatant liquid in contact with a zirconia precipitate and the time taken to effect precipitation can be used to prepare either the monoclinic or the tetragonal phase of zirconia following calcination at higher (>400 °C) temperatures. Utilizing in situ X-ray diffraction, it has been observed that the precursors of either phase are first transformed to the tetragonal phase. The precursor that produces the monoclinic phase following heating to (about 450 °C or higher) and then cooling in air initially forms an intermediate tetragonal phase. Mechanisms based upon solution chemistry that attempt to explain the formation of a precursor that leads directly to tetragonal zirconia or directly to monoclinic zirconia are unable to adequately account for the present results.

Introduction

A number of papers have provided explanations for the factors which determine the low-temperature crystalline phases of zirconia. As zirconia shows polymorphism, the transformation between the tetragonal and monoclinic phases, and vice versa, has attracted attention both in academic and in industrial research laboratories. Special attention has been paid to the retention of the metstable tetragonal phase at low temperatures.

Garvie[1,2] proposed a "crystal size theory". According to this view, microcrystals below a critical size of about 30 nm are stabilized against the tetragonal to monoclinic (t → m) transformation because of the lower surface energy of the tetragonal phase. For those crystals above this critical size, the surface energy is insufficient to offset the thermodynamic driving force to form the m-phase; hence, these particles are susceptible to transformation. Later, the presence of water vapor was observed to accelerate the t → m transformation.[3,4] It was found that both precipitation kinetics and the final pH of the supernatant liquid were involved in the formation and stabilization characteristics of crystalline phases in zirconia calcined at low-to-intermediate temperatures.[5,6] Clearfield[7-10] advanced a basis for explaining the control of zirconia phases during precipitation. Clearfield[10] invoked mechanisms that involved the rate of polymerization of the Zr^{4+} species. In Clearfield's view, refluxing dilute solutions of zirconyl chloride results in a precipitation of colloidal zirconia where particles are formed slowly enough so that an ordered three-dimensional structure is developed and this leads to the tetragonal phase.[7] Rapid precipitation does not allow ordering, and this less ordered material produces a monoclinic phase. In his view, the crystal structure is present in the precipitate or is formed at low-temperature calcination.

In this study, we have used a high-temperature X-ray diffraction (HTXRD) technique to analyze the formation and transformation of crystalline phases of zirconia that have been obtained by precipitation at different pH ranges.

Experimental Methods

Hydrous zirconium oxide samples were precipitated from a zirconium tetrachloride solution (0.3 M; prepared from anhydrous $ZrCl_4$) by the addition of a predetermined amount of base needed to produce a desired pH of the solution in contact with the solid. The required amount of base was added very rapidly (dumping). Since any ammonium chloride remaining in the precipitated material following the washing procedure should thermally decompose below 500 °C, most materials were precipitated using ammonium hydroxide. However, a pH greater than about 10.5 cannot be attained when ammonium hydroxide is used. Consequently, sodium or potassium hydroxide was used when a final pH greater than about 10.5 was desired. At a pH of about 10.5, excess ammonium hydroxide could be added because of the buffering action of the ammonium chloride formed during the precipitation reaction. Since a buffering action does not result when potassium or sodium hydroxide was used, it is much easier to attain a desired pH that is less than 10.5 using ammonium hydroxide. Therefore rapid precipitation at pH values less than 10.5 was achieved by rapidly adding an amount of ammonium hydroxide needed to attain the desired pH. The actual amount of base required to yield a certain pH was obtained from a "standard" titration curve. In all precipitations, the zirconium salt solution was stirred rapidly.

Precipitations were also carried out by the slower addition of base. In this procedure a calculated amount of base (ammonium hydroxide for pH of 10.5 or less) was added dropwise to a stirred zirconium salt solution at a rate that caused the desired amount of base to be added in a targeted time.

In all cases, the hydrous zirconium oxide was collected by filtration. The collected gel was washed by repeated cycles of redispersion in distilled water and filtration. Washing was continued for a minimum of eight cycles, each using approxi-

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[†] University of Kentucky.
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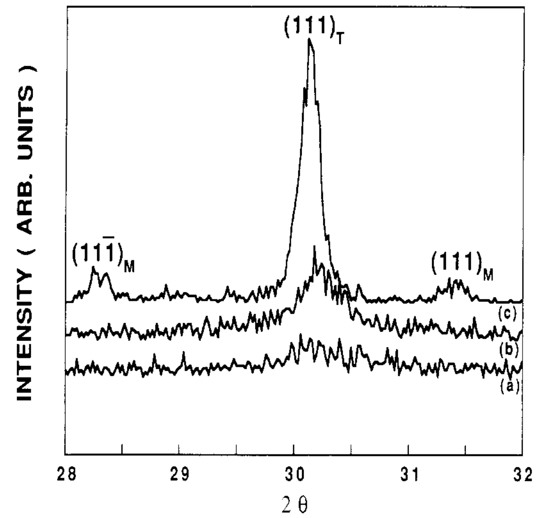

Figure 1. X-ray diffraction patterns from ZrO_2 precipitated at a pH of 3.0. Start temperature and end temperatures of the patterns are (a) 351–371, (b) 377–397, and (c) at 800 °C.

mately 100 mL of water/g of zirconia, until a negative test for Cl^- was obtained. Unless otherwise specified, the hydrous oxide was dried in air at 120 °C. After drying, the material was calcined at a particular temperature for a specified time as indicated in the Results.

The high-temperature X-ray diffraction work was carried out using a Scintag PAD X θ–θ diffractometer which is outfitted with a constant-potential X-ray generator operating at 45 kV/40 mA with a Cu target ($\lambda_{CuK\alpha}$ = 0.154 059 8 nm), a Buehler high-temperature XRD furnace with a beryllium window and Pt/Rh heating strip, and a liquid nitrogen cooled germanium single-crystal solid state detector. The significant advantage of using a θ–θ goniometer is that the specimen is horizontal and is undisturbed by the goniometer movements. Also, this geometry ensures that the high-temperature furnace need not rotate, and the same volume of sample is observed during the experiment.

A 10% Rh/Pt thermocouple (type S) was welded to the sample surface of the heating strip to enable temperature measurement of the sample. About 50 mg of powder was placed on a Pt/Rh heating strip, and a few drops of methanol was added, making a thin paste. After a few minutes, the alcohol evaporated, leaving a thin filmlike suspension of sample on the heating strip. The high-temperature furnace is provided with internal baffles to reduce thermal radiation directly to the water cooled walls of the furnace. A calibrated Micristar temperature controller maintains the selected heating or cooling rates and provides for precise control of the strip temperature to about ±1 °C throughout the experiment. The sample temperature is likely below the strip temperature by 10–20 °C due to radiative loss from the diffracting surface of the powder. Data acquisition and analysis were performed using a version 1.6 of Scintag's DMS-2000 (Data Management Systems) software. This software provides a number of convenient application packages such as automated rapid data collection, deconvolution of overlapping peaks, determination of peak breadth at half-maximum intensity, interactive graphics, etc.

Results

Precipitation of zirconia at different pH's yield different amounts of the tetragonal phase after the sample has been calcined at 500 °C for 4–6 h and then cooled in air in the furnace.[5,6] The present study was undertaken to observe the crystallization and phase transformation phenomena in zirconias precipitated at different pH's using in situ XRD.

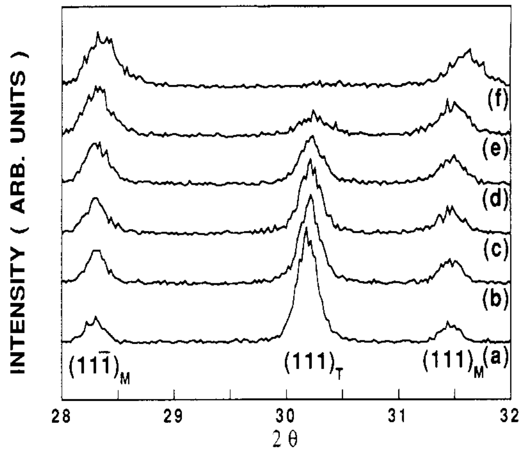

Figure 2. Phase transformation occurring upon cooling for ZrO_2 precipitated at pH 3.0. Start temperature and end temperatures of the patterns are (a) 532–511, (b) 486–467, (c) 462–443, (d) 440–421, (e) 394–376 °C and (f) room temperature.

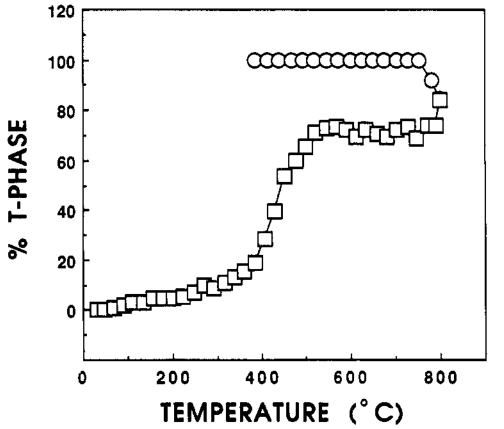

Figure 3. Percentage tetragonal phase as a function of temperature upon heating (○) and cooling (□), for ZrO_2 precipitated at pH 3.0.

Several X-ray diffraction patterns obtained at increasing temepratures during heating in air of a material precipitated at a pH 3.0 are shown in Figure 1. The tetragonal peak at about 30.2° 2θ appears first upon heating to about 450 °C, and this phase persists during heating to 800 °C. About 15% of the t-phase was transformed to the m-phase after holding the sample at 800 °C for 10 min (Figure 1c). On cooling, no further phase transformation occurred until the sample temperature had decreased to 532 °C; the transformation to monoclinic phase occurred progressively as the temperature decreased from about 532 °C to room temperature. The progressive transformations upon cooling of this material are represented by the XRD patterns shown in Figure 2.

The crystal phase data obtained during heating and then cooling a sample precipitated at a pH of 3.0 are shown in Figure 3; the percent tetragonal phase calculated from the XRD patterns versus the median temperature of each XRD trace temperature is plotted. Crystallization occurred at about 450 °C to produce essentially 100% tetragonal phase. Holding the sample at 800 °C caused some t → m transformation; however, the rate of transformation was slow as the sample was cooled at 20 °C/min from 800 to about 500 °C. Further cooling from ca. 500 to 375 °C results in an acceleration in the rate of the t → m transformation. The transformation continues below 200 °C to produce a material that is essentially the monoclinic phase. The rapid, "autocatalytic-type" transformation occurs over a narrow temperature range.

The data obtained in the dynamic in situ XRD studies represent averages over one minute. It required 1 min to obtain reasonable intensity data for the 2θ range that was scanned; during this minute the temperature changed by 20 °C. The temperature plotted in Figure 3 therefore represents the temperature of the midpoint of the 20 °C interval. Likewise, the XRD pattern at the lowest 2θ value corresponds to the lowest temperature for the experiment where the temperature is increased; thus, the $(11\bar{1})_m$ and the $(111)_t$ peaks will be recorded at different temperatures. What is important in considering these in situ X-ray data is the difference from one XRD scan to the next.

For the material precipitated at a pH of 14, crystallization occurred at about 450 °C to produce the tetragonal phase (Figure 4a). This tetragonal phase was stable during heating to 800 °C. Immediately beginning the cooling cycle at 20 °C/min caused the t phase to remain unchanged until 320 °C. On cooling from about 320 °C to room temperature, the "autocatalytic-type" transformation (Figure 4a) occurred to produce greater than about 85% monoclinic zirconia.

There is a significant difference between the heating/cooling characteristics of zirconia. This is produced by either rapid or slow precipitation with a final supernatant liquid pH of about 10.5.[11] This difference is more noticeable at lower calcination temperatures. The slowly precipitated material forms the t-phase at about 450 °C when heated to this temperature at 20 °C/min in air. Surprisingly, the rapidly precipitated material also forms the t-phase at about 450 °C under the same heating conditions. Furthermore, both materials produce an exotherm of the same magnitude per unit weight at about 450 °C.[6] Thus the heating characteristics of the two materials are nearly the same; however, upon cooling in air dramatic differences are noted. The slowly precipitated material may be maintained at 400–500 °C for 4 h (and even up to 100 h) with the formation and retention of the t-phase and can be cooled to room temperature in air without loss of the t-phase. The rapidly precipitated material may likewise be heated to 400–600 °C for 4–100 h where it forms the t phase; however, upon cooling to room temperature in air, the t → m transformation occurs so that 80–95% of the material is in the monoclinic form. The extent of transformation is a function of both the highest calcination temperature and the period of time the sample is calcined. Furthermore, the temperature and time needed to effect a specified fraction of t → m transition may depend upon the specific sample of rapidly precipitated material.

Thus, the zirconia obtained by rapid or slow precipitations behaves differently upon cooling when heated at lower temperatures (400 °C). However, when these samples are heated to higher temperatures, the situation is different. For this pH range, rapid precipitation at pH 10.5 produces a material that forms the t-phase first. This t-phase was stable on heating to 800 °C; on cooling, the t → m transformation occurred in the temperature range 300–25 °C (Figure 4b). Similar results were obtained for the slowly precipitated material (Figure 4c).

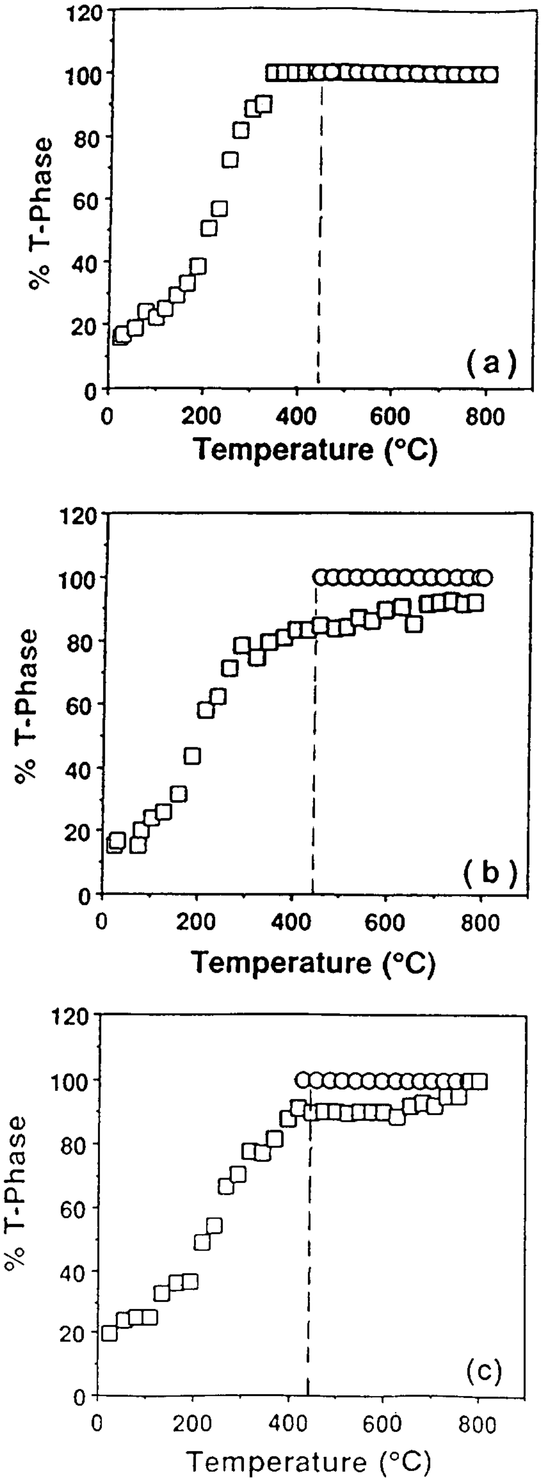

Figure 4. (a) Percentage tetragonal phase versus temperature for ZrO_2 precipitated at a pH of 14.0; (b) ZrO_2 rapidly precipitated at a pH of 10.5; and (c) ZrO_2 precipitated slowly at a pH of 10.5 (heating (○) and cooling (□)).

The relationship between the crystallite size calculated from X-ray line broadening and temperature is shown in Figure 5 for the material precipitated rapidly at a pH of 10.5. The crystallite size calculated from the peak width at half-maximum intensity of the tetragonal (111) profile is in the range 8–9 nm and it increases to about 11 nm at 800 °C. On cooling, the transformation from the tetragonal phase to the monoclinic phase begins at about 290 °C. The crystallite size from X-ray line broadening of the tetragonal (111) profile does not change significantly on cooling to 290 from 800 °C. The crystallite size of the fraction that is in the tetragonal phase on cooling below 290 °C remains at about 11 nm. The crystallite size from the peak width at half-maximum intensity of the monoclinic $(11\bar{1})$ peak after transformation is also constant and in the range 9–10 nm, which is slightly smaller than the parent tetragonal crystals. This is in agreement with

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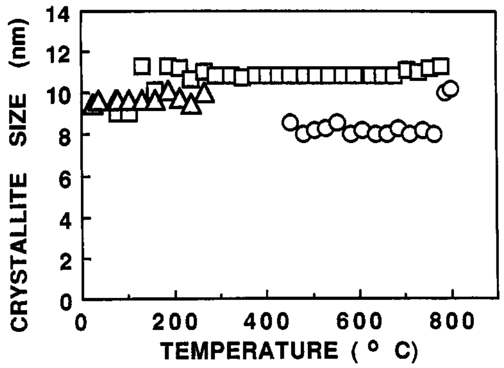

Figure 5. Relationship between the crystallite size and temperature for ZrO_2 precipitated rapidly at a pH of 10.5. (○) Crystallite size obtained from peak width at half-maximum intensity of the tetragonal (111) peak on heating, (□) crystallite size on cooling, and (△) the crystallite size from monoclinic $(11\bar{1})$ peak after transformation. Note that the crystallite size of monoclinic particles after transformation is smaller than that of the parent tetragonal particles.

our earlier TEM studies.[12] Note that the crystallite size of either the tetragonal or monoclinic crystals is in the range 8–12 nm, which is less than the critical particle size of 30 nm proposed by Garvie.[1,2] Even more important than the smaller crystal size predicted by Garvie is the fact that the monoclinic phase has smaller X-ray crystal size than the tetragonal phase. Thus, whereas we would expect, according to Garvie's theory, the monoclinic phase to have a larger crystallite size than the crystal that they are formed from, we observe that the monoclinic crystal has a smaller size than the tetragonal form. Thus, on the basis of only on X-ray crystal size, the monoclinic crystal would have a higher surface energy than the tetragonal crystal and not a lower surface energy as required by Garvie's theory.

An important observation is that the crystallization occurred to produce the tetragonal phase irrespective of the pH of precipitation or the time taken to attain a final pH, provided the sample was heated to 800 °C. The t → m transformation occurs on cooling in air much more rapidly than in an inert gas. For example, the pH 10.5 material must be held at 800 °C in helium for hours to effect the transformation.

Discussion

The material that results from the precipitation of zirconia is a mixture of complex polymers. It is logical to base our attempt to understand the process leading to these polymers upon simple, well documented inorganic complexes.

A species containing four Zr^{4+} ions in a square with double hydroxyl bridges linking them has been identified in solution and crystalline solids.[7,13] In addition, four water molecules are attached to each metal atom to complete the coordination sphere. Clearfield[10] proposed that rapid addition of a base increased the number of hydroxyls on this tetramer in a random fashion so that subsequent polymerization occurs rapidly in many directions. The result is a disordered array of tetramers which leads to the formation of the monoclinic phase on heating. On the other hand, if base addition is slow so that there is sufficient time for the tetramer species to form ordered sheets of $Zr(OH)_4 \cdot xH_2O$, then the tetragonal phase will result on heating. The formation of tetragonal phase nuclei was proposed to be less efficient at low pH. In a very alkaline medium (>pH 13.0), hydrous zirconia is slightly soluble:

$$Zr(OH)_4 \cdot xH_2O + OH^- \rightleftharpoons Zr(OH)_5^- \cdot xH_2O$$

The dissolution and reprecipitation of the hydrous oxide, a sluggish process at normal pH, occurs at high pH to produce the ordered sheets that lead to tetragonal phase.

The in situ XRD results presented above show that the mechanism proposed by Clearfield[10] does not adequately explain the factors that determine the crystal phase of zirconia. The tetragonal phase was first formed upon heating whether the pH is low, intermediate, or higher than 13.0. This condition is also true for both rapid and slow precipitation processes to a pH of 10.5. Thus, the precursors for the monoclinic or the tetragonal phase each form the tetragonal phase upon calcination and the stability of this tetragonal phase determines the ultimate phase that is formed.

Garvie[1,2] proposed that the excess surface energy of the small tetragonal crystals stabilizes the tetragonal form; only when crystal growth occurs to produce a crystal of about 30 nm does the surface energy effect become smaller than the energy of the t → m transformation. When the particle size is considered to be the same as the XRD crystallite size, the data in Figure 5 do not agree with Garvie's theory. Since a single zirconia particle may be composed of more than one crystal defined by XRD, the surface area is a more reliable measure of the particle size, and a measure of the surface energy. We have shown that the surface area of zirconia (and zirconium–hafnium mixed oxides) decreases from about 250 to 82 m^2/g during the exothermic event when the sample is heated at 20 °C/min as was done in the in situ XRD studies.[15] In the case of zirconia, the loss of surface area by crystal growth and the appearance of X-ray crystalline material occurs at the same temperature. Therefore, about 30 small zirconia particles coalesce to form a larger particle with a loss of 60% of the surface area. Further heating to 800 °C causes a further increase in the particle but not in XRD crystal size. Upon cooling there is a t → m transformation, and this occurs without a decrease in particle size that is reflected by the surface area. We believe that this is conclusive evidence that a loss in surface area, with a concurrent loss in surface energy, is not responsible for the t → m transformation. Surface energy decrease, if it is responsible for the transformation, must occur without a decrease in surface area.

It has been observed that the addition of sulfate to the surface of a precursor that would normally produce the monoclinic phase acts to stabilize the tetragonal phase.[11,14] This observation, in addition to the fact that the t → m transition occurs upon cooling much more readily in an oxygen containing atmosphere than in helium, suggests that the t → m transition is the reuslt of a surface phenomenon that triggers the crystal phase transformation.

A reasonable view is that the surface sites responsible for the phase transformation are oxygen deficient. The generation of these sites depends, in addition to the rate

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Table I. Summary of the t → m Transformation Dependence upon the pH of Precipitation

pH range	initial phase[a]	transformation
up to about 7	tetragonal	tetragonal phase first appears at 450 °C on heating. The t → m transformation begins at 800 °C and about 30% transformation is complete up to 520 °C on cooling. The rate is accelerated on cooling further to room temperature and complete transformation occurs at room temperature (see Figure 3)
rapid precipitation at about 7–10.5	tetragonal	tetragonal phase first appears at 450 °C on heating, and this phase is stable up to 800 °C. About 20% transformation occurs very slowly on cooling to about 300 °C, and below 300 °C the rate of transformation is fast. The transformation is complete at room temperature (see Figure 4b). However, if heated at 500 °C for 4–6 h in a muffle furnace and cooled in air, the final structure consists of about 80% monoclinic phase, and about 20% tetragonal phase[6]
slow precipitation at about 7–10.5	tetragonal	tetragonal phase first appears at 450 °C on heating, and this phase is stable up to 800 °C. About 10% transformation occurs very slowly on cooling to about 400 °C, and below 400 °C the rate of transformation is accelerated. The transformation is complete at room temperature (see figure 4c). However, if heated at 500 °C for 4–6 h in a muffle furnace and cooled in air, the final structure is tetragonal phase[6]
13–14 or higher	tetragonal	tetragonal phase first appears at 450 °C on heating. This phase is stable up to 800 °C. On cooling the t → m transformation begins at 320 °C and is complete at room temperature (see Figure 4a). However, if heated at 500 °C even for more than 200 h and cooled in air, the final structure is t-phase

[a] Identified by high-temperature XRD.

of precipitation, upon the temperature the sample was heated to, the time to attain the temperature, the length of time held at the temperature prior to cooling, and the atmosphere. Thus either zirconia precursor forms the tetragonal phase upon heating. For the material rapidly precipitated to a pH of 10, factors are built in during precipitation and/or drying that readily produces surface defects that will cause the t → m transformation upon cooling in an oxygen containing atmosphere.

The transformation should therefore be considered in terms of a severity factor, θ:

$$\theta \propto f(t,T,E,P)$$

where θ = severity factor to effect phase transformation, t = time, T = temperature, E = environment, and P = preparative procedure. Environment refers to gas(es) in contact with the oxide. The t → m transformations are summarized in Table I for various pH of the supernatant liquid. All materials initially form the tetragonal phase upon heating to about 450 °C. The rapidly precipitated material at a pH of 10 requires the smallest θ for the t → m transformation and the material precipitated at a pH of about 14 the largest θ. For the material precipitated under acidic conditions, θ is larger than for the material precipitated at pH 10.5 but less than for the material precipitated slowly at pH 10.5.

Considering the in situ XRD data in this paper and the change in surface area with heating,[15] it appears that a qualitative description of crystallization and phase transformation can be represented in an idealized schematic as shown in Figure 6 (for simplicity the cross section of 4 particles, rather than nearly 30 particles in the real case, are shown). Small amorphous particles of zirconia crystallize and coalesce into a larger nonporous zirconia particle with all, or at least the dominant fraction, of the small particles forming individual distinct crystals with respect to XRD and TEM.[16] All zirconia samples, irrespective of the preparative procedure, undergo this transformation to produce a large particle comprised of numerous t-phase crystal domains. In the case of t → m transformation the severity factor, θ, determines how rapidly the t → m transformation occurs. It is proposed that the t → m transformation is triggered by the adsorption of oxygen on sites that are built in during the preparative procedure. In the larger polycrystal zirconia particle (B in Figure 6) the transformation to the monoclinic form should create an intercrystalline interface zone due to the mismatch of crystal planes of the monoclinic form that will be sufficiently disordered that it appears amorphous to X-rays; this is postulated to account for the slight decrease in X-ray crystal size for the t → m transformation.

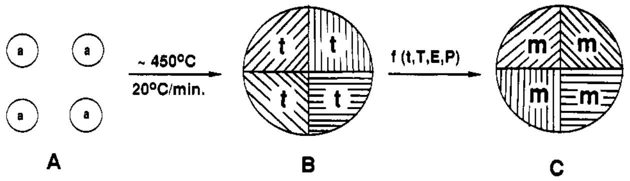

Figure 6. Idealized schematic of crystallization and phase transformation for ZrO_2.

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