Nanocrystallization and Phase Transformation in Monodispersed Ultrafine Zirconia Particles from Various Homogeneous Precipitation Methods

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Monodispersed ultrafine (nano- to micrometer) zirconia precursor powders were synthesized by three different physicochemical methods: (I) forced hydrolysis, (II) homogeneous precipitation in inorganic salt solutions, and (III) hydrolysis/condensation of alkoxide. The forced hydrolysis method produced monoclinic nanocrystalline particles (cube shaped) of nanometer scale, which depended largely on the initial salt concentration. Methods II and III, both involving the use of alcohol as a solvent, exhibited a faster particle formation rate and generated amorphous ultrafine (submicrometer) monodispersed microspheres, indicating that the presence of alcohol may have stimulated particle nucleation due to its low dielectric property (and, thus, the low solubility of nucleus species in mixed water–alcohol solutions). Nucleation and growth of the particles in solutions are discussed based on the measurements obtained by small-angle X-ray scattering (SAXS) and dynamic light scattering (DLS). High-temperature X-ray diffraction (HTXRD) and TGA/DTA studies elucidated the differences in phase transformation for different types of powders. The most interesting finding was the nonconventional monoclinic nanocrystal nucleation and growth that occurred prior to transformation to the tetragonal phase (at 1200°C) during the heat treatment of the nanocrystalline powders produced by the forced hydrolysis.

I. Introduction

ADVANCED ceramic materials are in high demand for use in structural or functional applications. Monodispersed ultrafine (i.e., submicrometer to nanosize) ceramic particles are important building blocks used in the fabrication of advanced ceramic materials having improved properties (mechanical, electrical, optical, magnetic, thermal, ionic conducting, and catalytic). Production of ceramic powders is by no means a new research subject; however, practical methods are still needed for synthesizing high-quality ultrafine powders with required characteristics in terms of their size, size uniformity, morphology/shape, microstructure, composition purity, crystallinity, etc. These characteristics of the precursor powders significantly affect the later-stage processing and sintering properties and eventually determine the microstructure and performance of the final ceramic materials. For example, spherical particle shape and narrow distribution of size help to reduce serious microstructural defects in ceramics (due to the particle packing heterogeneities) by enhancing the powder flow and packing efficiency in green bodies.[1]

Of particular interest to this study was the synthesis and characterization of monodispersed zirconia precursor particles, which are rather important in the fabrication of various modern zirconia-based or zirconia-containing ceramics.[2] Increasing interest in zirconia ceramics may be attributed to their unique set of properties, which includes high refractoriness and corrosion resistance, good mechanical strength, high fracture toughness and hardness, ionic conduction, high melting point, low thermal conductivity at high temperature, and thermal stability and resistance to thermal shock.[3] Zirconia is an important component in diverse structural ceramics and specialty ceramics with potential applications such as the following: (1) advanced structural/transformation-toughened ceramics (wear parts such as bearings, shapes, and seals; engine and machine components; cutting and abrasive tools; mill media; refractories), (2) electronic components (PZT piezoelectric ceramics and zirconate dielectric ceramics), (3) sensors/probes (for oxygen transport and detection) and solid electrolytes (for fabrication of fuel cells), (4) catalytic materials or supports with unique properties, (5) pigments (ceramic colors), and (6) thermal barrier coatings or thermal shield.

As such, an intense interest has grown in preparing zirconia powders with controlled particle size and crystal structure. Diverse physical and chemical synthesis routes have been reported in the literature for ultrafine zirconia particle production. Low-temperature aqueous chemical processing has been the leading contender among the low-cost processes for ultrafine ceramic powder synthesis.[4] In particular, hydrolysis (and condensation) under hydrothermal conditions and homogeneous precipitation are common approaches. Typical methods using the hydrolysis approach include forced hydrolysis in aqueous solutions of inorganic salt[5–7] and hydrolysis/condensation of metal alkoxides in alcohol solutions.[8–12] An organic solvent such as alcohol is always involved in the alkoxide hydrolysis/condensation method. Recently, alcohol solvent was also reported to play an important role in inducing homogeneous precipitation of hydrous oxide particles in aqueous solutions of inorganic salts.[5]

Formation of hydrous-zirconia particles by the above-mentioned methods has been studied extensively. However, characterization of the ultrafine powder product, particularly comparative studies of the monodispersed particles produced from different particle synthesis processes, has not been reported in previous studies. One of the important issues is to understand the nanocrystal evolution/nucleation, growth, and

crystalline-phase transformation during the heat treatment of zirconia powders. The critical parameters that need to be controlled are grain size and phase transformation of zirconia as a second phase in order to ensure that the zirconia-containing materials have the required properties.[13] So far, most studies in crystallization and phase transformation of zirconia have been conducted on poor-quality particles or gel materials prepared by simple chemical precipitation.

This study focuses on the characterization of monodispersed powder products produced by the three particle-forming processes. Comparison studies of particle-synthesis processes are also provided. *In situ* high-temperature X-ray diffraction (HTXRD) studies showed variation in the behavior of zirconia crystallization and phase transformation for powders obtained from various synthesis methods. Knowledge of the nanocrystal formation characteristics and phase transformation can help in determining the optimal thermal treatment process used in the fabrication of advanced zirconia-based ceramics.

II. Experimental Procedure

High-purity zirconium salt ($ZrOCl_2 \cdot xH_2O$, 99.99%, FW 178.3), technical-grade zirconium tetrabutoxide in 80% butyl alcohol, and 200 proof reagent-grade absolute ethyl alcohol were purchased from Aldrich Chemical Co. (Milwaukee, WI). Isopropyl alcohol (99.99%) was ordered from VWR (Oak Ridge, TN). All water used in the study was doubly distilled and deionized, so that the electrical conductivity was maintained below 18 mmho/cm. All solvents were used as received; no further modifications or purification were performed.

Three different methods were used in this study for the synthesis of ultrafine hydrous-zirconia particles:

(I) Forced hydrolysis in aqueous inorganic salt solutions: A 1.0*M* $ZrOCl_2$ aqueous solution was usually prepared as a stock solution and kept in a refrigerator at 4°C to avoid possible hydrolytic aging at room temperature. (Note: In a several-month-old solution, SAXS measurements indicated the presence of zirconium species larger than the ~4.5 Å radius of gyration zirconium tetramers which exist in the fresh solution.) Various concentrations (ranging from 0.01 to 2.0*M* dissolved zirconium, typically 0.05*M* for preparation of powder characterization sample) of $ZrOCl_2$ aqueous solutions were then prepared from the stock solution and incubated at 100°C for 3 days.

(II) Homogeneous precipitation in solutions of inorganic salt dissolved in mixed water–alcohol solvents: The same $ZrOCl_2$ stock solution was used. In addition, isopropyl alcohol was used as a dielectric-tuning agent for the alcohol–water mixture solvent and hydroxyl propyl cellulose (HPC) as colloidal particle dispersant, which added steric forces between particles. For this study, the mixture solution containing $ZrOCl_2$ (0.05 to 0.2*M*) and HPC (2.0×10^{-3} g/cm³) in mixed alcohol–water solution (volume ratio of isopropyl alcohol to water = 5) was incubated at 100°C for several hours to days.

(III) Alkoxide hydrolysis and condensation: Zirconium tetra-*n*-butoxide (0.1 and 0.2*M*) solution in ethyl alcohol was mixed at room temperature (22°C) with an equal volume of water–ethyl alcohol solution (0.2, 0.4, and 0.6*M*). The water-to-alkoxide molar concentration ratio was maintained at 2.0. All solution incubations or agings were carried out in closely capped glass vials or Nalgene plastic bottles. Milky white zirconia sol solutions obtained by the above procedures were centrifuged and washed with deionized water several times and freeze-dried.

The evolution and growth of hydrous-zirconia ultrafine sol particles in liquid solutions were monitored with a custom-designed dynamic light scattering (DLS) spectrometer. Before the nucleation, early-stage polymeric cluster formation and growth during the forced hydrolysis of zirconia tetramers was measured by small-angle X-ray scattering (SAXS) at the Oak Ridge National Laboratory (ORNL) user facility. A detailed description of the DLS spectrometer and the SAXS instrument is provided by Hu *et al.*[5,6]

Several techniques were used for powder characterizations and calcination. A scanning electron microscope (SEM) (Joel JSM-T220A) and a Jeol 100CXII transmission electron microscope (TEM) were used to image the size, morphology, and microstructure of the powder particles (i.e., sol particles dried at room temperature), while the powder's surface area was measured by the multipoint BET nitrogen adsorption technique (Gemini, Micromiretics, Georgia). Powder samples were analyzed with a Harrop Model ST-736 thermogravimetric analyzer/differential thermal analyzer (TGA/DTA) for preliminary phase-transition information. The total gas flow in each experiment was 100 mL/min (20% O_2 and 80% N_2), which was regulated by mass flow controllers from MKS Industries, Inc. Approximately 0.167 g of powder sample was transferred into an alumina sample holder, which was then placed into the TGA/DTA. The sample was heated from ambient to 1200°C at a rate of 200°C/h.

An *in situ* HTXRD instrument at the ORNL HTML user facility was utilized for extensive studies of powder crystallization and phase transition. The HTXRD work was carried out using a Scintag PAD X θ–θ diffractometer which was outfitted with a constant-potential X-ray generator operating 45 kV/40 mA with a Copper target ($\lambda_{CuK\alpha}$ = 1.540598 Å), a Bueler high-temperature XRD furnace with a beryllium window, a thin Pt/Rh heating strip, and a liquid-nitrogen-cooled germanium single-crystal solid-state detector. There are several significant advantages of using a θ–θ goniometer: (1) the specimen is on a horizontal heating strip and is undisturbed by the goniometer movement, (2) there is no need for the high-temperature furnace to rotate, and (3) the same volume of sample is observed during experimentation.[14] During a sample test, powders were dispersed in methyl alcohol or ethyl alcohol to form a slurry and then spread onto the top surface of the Rh/Pt heating strip. After alcohol evaporation, a thin layer of powder was uniformly distributed on the strip surface. To precisely maintain and measure the sample temperature (±1°C), a surrounding heater was used around the heating strip and a 10% Rh/Pt thermocouple (type S) was welded to the bottom surface of the thin heating strip. In addition, the high-temperature furnace was provided with internal baffles to reduce thermal radiation directly to the water-cooled walls of the furnace. The high-temperature chamber allowed for variation in atmospheric composition; however, these experiments were all conducted in flowing air at 1 atm. Data were taken by heating the sample to predetermined temperatures (30°, 100°, 400°, 600°, 800°, 1000°, 1200°, 1400°C) at a heating rate of 0.5°C/min, and then cooling the sample to 30°C at a rate of 50°C/min. The holding time at each predetermined temperature was 1 h before the XRD scan began. Data acquisition was performed using DMS-NT software (Scintag Inc., Cupertino, CA) and data analysis was undertaken using Jade software (Materials Data Inc., Livermore, CA). Crystallite size was estimated from the broadening of the X-ray diffraction peaks, using the Scherrer equation from the diffraction peak breadths (full width at half-maximum).

III. Results and Discussion

The three different synthesis processes generated zirconia particles with different characteristics. Figure 1 shows a representative TEM photograph of zirconia particles produced by the forced hydrolysis of 0.075*M* $ZrOCl_2$ in aqueous solution. Near cubic-shaped, nanosize particles with a narrow size distribution (~50 nm average size) were obtained. Each of the particles was an aggregate of many needlelike, small primary particles measuring ~3 nm (rod diameter) by 5 nm (rod length). This TEM observation on the shape of primary particles agrees with our earlier SAXS studies.[6] Depending on the initial dissolved Zr concentration (0.05 to 0.5*M*), particle sizes ranged
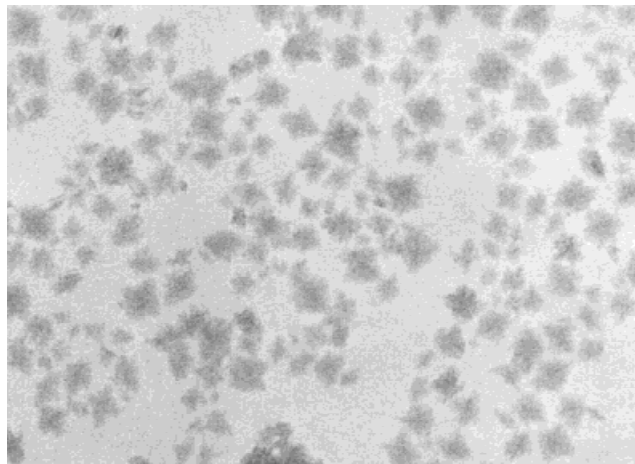
Fig. 1. Nanosize monoclinic zirconia particles with narrow size distribution produced from forced hydrolysis of aqueous solution of zirconyl chloride salt.

from tens to several hundred nanometers. Also, as the initial Zr concentration was increased from 0.01 to 0.2M, the particle size (Fig. 2) and hydrolysis reaction kinetics increased. In addition, the shape of the particle became more cubelike. However, increasing the zirconium concentration to greater than 0.2M inhibited the kinetics because of the high acidity and reduced the particle size. This observed effect of $ZrOCl_2$ concentration on particle size is in agreement with the most recent results obtained by Matsui and Ohgai.[15] They determined that H^+ ion concentration produced during hydrolysis plays a significant role in regulating the secondary particle size of hydrous zirconia. Detailed studies on nanoscale particle synthesis by the forced hydrolysis of this system at low zirconium concentrations (<0.2M) has been extensively explored in our earlier work.[5,6]

In contrast, particles obtained from the homogeneous precipitation of $ZrOCl_2$ in water–isopropyl alcohol solutions are perfect monodispersed microspheres, with sizes ranging from nanometers to a few micrometers. The lower the initial zirconium concentration in the mixed water–alcohol solvent, the smaller the microsphere size. Typical SEM photographs are shown in Fig. 3 The exact particle nucleation and growth
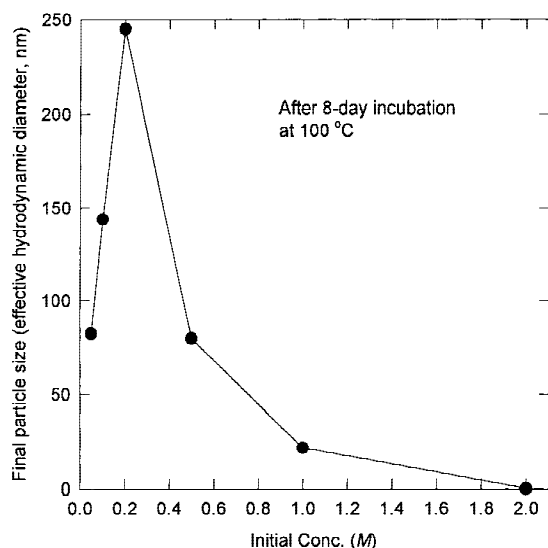

Fig. 2. Influence of initial $ZrOCl_2$ salt concentration on the size of final colloidal sol particles.

mechanisms are not clear. Nucleation occurs probably by either hydrolytic reactions or a salting-out phenomenon. Growth could be via diffusive molecular (i.e., tetramer) deposition or an aggregation of primary particles. However, the effect of isopropyl alcohol can be explained rather well by the dielectric property of the water–isopropyl alcohol solvent. The presence of the isopropyl alcohol reduced the dielectric constant of the solution. Furthermore, elevation of the incubation temperature also contributed to a reduction in the dielectric constant of the mixed water–isopropyl alcohol solvent. The solubility of the zirconium species in solution becomes lower when the dielectric constant of the solvent is decreased. Particle formation in the mixed solvent could occur at temperatures (such as 60°C) that are too low for forced hydrolysis to take place. Therefore, particle formation could be totally attributed to the salting-out phenomenon due to the dielectric constant reduction, instead of hydrolytic condensation. On the other hand, the presence of isopropyl alcohol dramatically enhanced the particle formation kinetics. Precipitation in a mixed water–alcohol system could be completed in as little as 1 h, rather than days as required for forced hydrolysis.

The sol–gel method using alkoxides as molecular precursors has been a very popular approach for monodispersed ceramic powder production. In this study, hydrous zirconia powder samples were also prepared by this method by using optimal conditions as reported in the literature (i.e., 0.1M zirconium alkoxide, 0.2M water in ethanol).[11] Powders produced by this method were used only as a baseline product for comparison with the powders obtained from the other two methods using the inorganic salt precursor. Hydrolysis and condensation of zirconium tetrabutoxide in ethanol–water solution produced submicrometer-size microspheres, as shown in the SEM photograph (Fig. 4).

The growth of hydrous zirconia sol particles in $ZrOCl_2$ solutions, in the presence and absence of isopropyl alcohol, was monitored with the DLS spectrometer (Fig. 5). Note that the early-stage data (when the particle size was less than 5 nm during the induction period) for the forced hydrolysis process (Fig. 5(a)) was measured with the SAXS instrument. It can be seen that the forced hydrolysis was a relatively slow process, usually taking days to complete. Under equivalent conditions (i.e., the same initial zirconium concentration and aging temperature), the presence of the isopropyl alcohol shortened the induction period dramatically and also increased the particle growth rate. The shape of the growth curve shown in Fig. 5(b) indicated a possible uncontrolled aggregation of microspheres and further agglomeration of the aggregates. Such colloidal coagulation eventually generated large agglomerates that were beyond the size measuring capability of the DLS spectrometer. The agglomerates must have been loosely bound and easily dispersed because the SEM photograph showed individually separated microspheres. On the other hand, we can see that the forced hydrolysis method produced nanosize particles, whereas the particles produced by the mixed solvent system were much larger under the conditions shown in Fig. 5(b) (isopropyl alcohol was 50 vol%). However, the particle size in the mixed solvent system is controllable, and smaller or even nanosize monodispersed microsphere production can be achieved (Fig. 3). Detailed results from extensive studies of homogeneous precipitation in mixed solvent systems are reported elsewhere.

The postsynthesis characterization of powders prepared by various methods was also a part of this study. First, BET analysis of cube-shaped powders formed by forced hydrolysis (of 0.05M $ZrOCl_2$, 100°C, 3 days), microsphere powders by mixed-solvent precipitation (0.05M $ZrOCl_2$ containing 50 vol% isopropyl alcohol, 100°C, 15 h), and the original $ZrOCl_2$ salt precursor showed specific surface areas of approximately 23.75 m²/g, <0.01 m²/g, and negligible amounts, respectively. Figure 6 shows typical nitrogen adsorption/desorption data for cube-shaped zirconia powder formed by forced hydrolysis. We observed that the freeze-drying process caused a significant
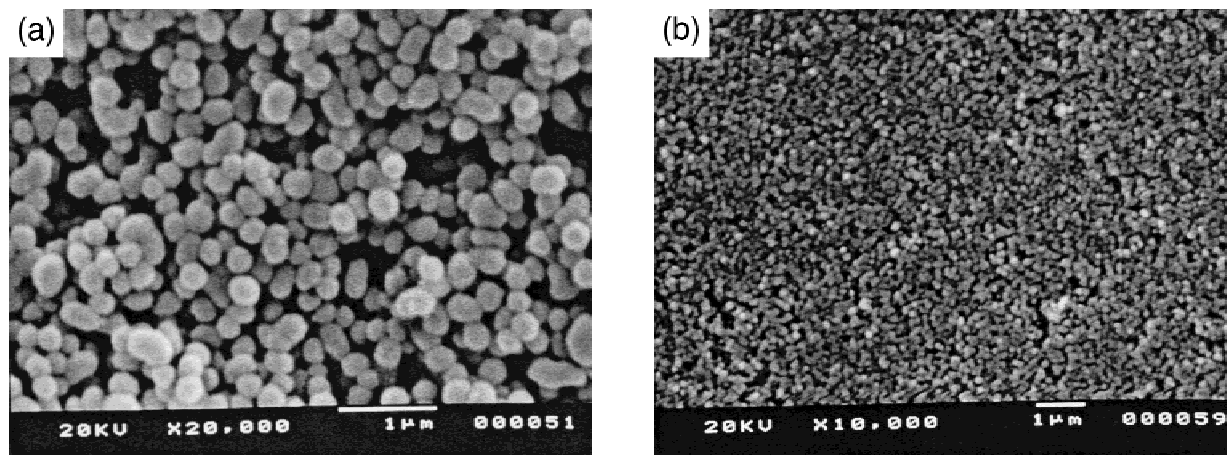
Fig. 3. Monodispersed zirconia microspheres by homogeneous precipitation of $ZrOCl_2$ in mixed alcohol–water solutions: (a) submicrometer-size spheres produced from 0.2*M* $ZrOCl_2$ 50 vol% alcohol–water solutions incubated at 100°C for 2.5 h; (b) nanometer-size spheres produced from 0.05*M* $ZrOCl_2$ 50 vol% alcohol–water solutions incubated at 100°C for 2.5 h.
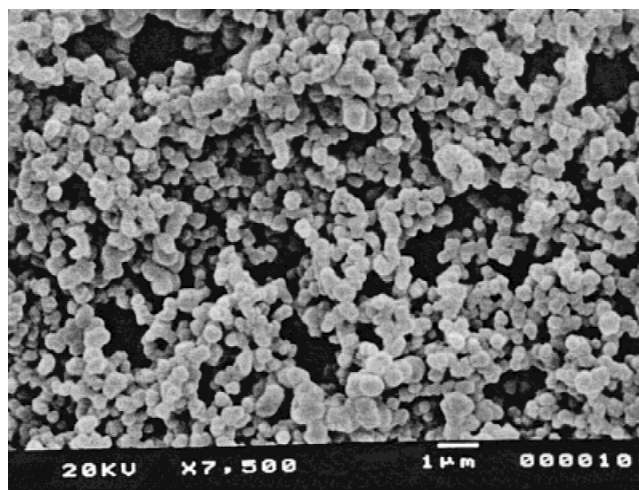

Fig. 4. Monodispersed zirconia microspheres produced by hydrolysis/condensation of zirconium tetra-*n*-butoxide.

degree of particle aggregation and caking, which may be responsible for the low specific surface area of dried powders. Preliminary studies on the crystallization and phase transitions of the zirconia powders and $ZrOCl_2$ salt were conducted by the TGA/DTA measurements (Fig. 7). It is clear that the microspheres produced by mixed-solvent precipitation showed similarities to the salt precursor in both TGA and DTA plots, except that the salt seems to be more hydrated and thus lose more weight during heating. In the TGA curve, the microsphere powders show a total weight loss percentage similar to the theoretical weight loss value (22.61%) of $Zr(OH)_4$ or $ZrO_2·2H_2O$.[16] Thus, the composition of the microspheres is thought to be similar to $ZrO_2·2H_2O$, which may result from combination of zirconyl tetrameric cations. There was a sudden loss of weight around 450°C for both microspheres and salt. The cube-shaped particles formed by forced hydrolysis were the least hydrated and showed no sudden weight loss at 450°C.

In the DTA plot (Fig. 7(b)), the endothermic peak(s) and a large weight loss appear between room temperature and 200°C, corresponding to the thermal dehydration or evaporation of physically adsorbed water. At about 450°C, a narrow, sharp exothermic peak appeared for both microspheres and the salt sample, indicating the crystallization of zirconia. Previous studies have shown similar exothermic peaks in this temperature range (400–460°C) and are referred to as "glow exo-

therms." Various temperatures for the exotherm have been reported around 430°, 400°, 420–440°, and 460°C.[17–20] The glow exotherm was attributed to a rapid release of bound hydroxyl groups, which is a prerequisite for crystallization.[1,17,21–23] Others think that the exotherm is due to the transformation of zirconium oxyhydroxide to the amorphous oxide; that is, $ZrO(OH)_2 \rightarrow ZrO_2·H_2O$.[20] Most recently, two possible separate transformation events were proposed to occur at the same "glow" temperature: (1) crystallization of amorphous materials into small-size single-domain crystals and (2) exothermal events commonly referred to as a glow phenomenon, wherein small crystals coalesce into large particles containing one or more grain boundaries.[14] The sudden change in slope of the DTA curves between 900° and 1200°C (Fig. 7(b)) is an indication of a phase transition, corresponding to monoclinic-to-tetragonal transformation as shown later by XRD data (Fig. 8). Nevertheless, the DTA curve for the cube-shaped particles produced by forced hydrolysis shows no obvious sharp peak at 450°C, only a broad curvature between 200° and 600°C.

It is well known that zirconia is a typical polymorphic material which may exist in monoclinic, tetragonal, cubic, and orthorhombic crystalline forms at different temperatures.[24] At room temperature, zirconia has the monoclinic baddeleyite structure, which is thermodynamically stable below 1150°C. At a temperature of approximately 1150°C, the first displacive martensitic phase transition from monoclinic to tetragonal phases occurs.[25,26] At still higher temperature of approximately 2370°C, the tetragonal phase transforms into cubic phase with a fluorite-type crystal structure which is stable up to the melting point (2680 ± 15°C).[27,28] However, the phase formation and transformation behavior of hydrous-zirconia powders are affected significantly by various synthesis conditions or processing parameters such as pH, aging time, reaction temperature, precursor concentration, solvent type, and variation of precursor salt[1,29–32] and, thus, may not always follow the traditional phase transition route. The two zirconia powders and the $ZrOCl_2$ were further analyzed by HTXRD, a complementary technique to TGA/DTA. Figure 8 presents the XRD spectra at various temperatures for cube-shaped zirconia powders synthesized by forced hydrolysis. It can be seen that without any heat treatment, the cube-shaped nanoparticles are monoclinic crystalline material (with crystallite sizes of approximately 14 nm at 30°C). Particularly noteworthy, the monoclinic peaks (at both 28.174° and 31.467° 2θ) gradually increased in intensity when the sample was heated from 30°, 100°, 400°, 600°, 800°, up to 1000°C (1-h holding time at each temperature), indicating further nucleation/growth of the monoclinic nanocrystals inside the powder particles. Further
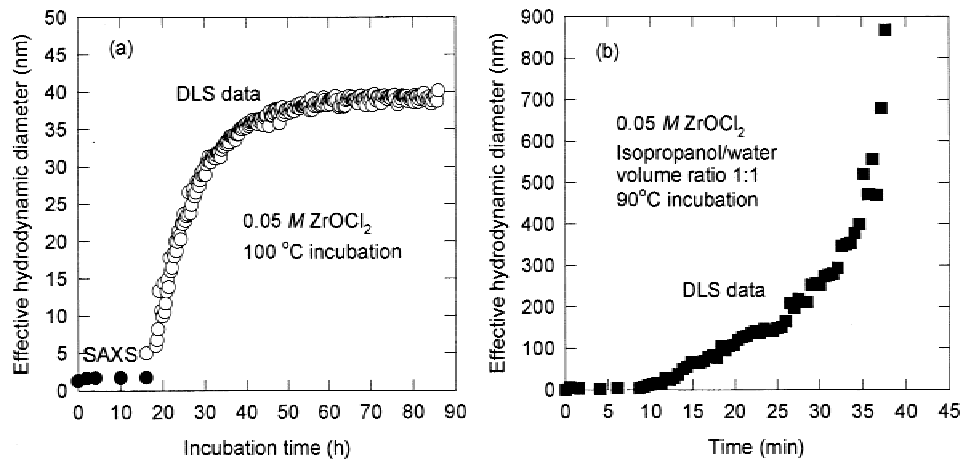
Fig. 5. Growth of zirconia sol particles in thermally incubated solutions of $ZrOCl_2$: (a) no alcohol solvent, forced hydrolysis; (b) with alcohol solvent in solution, mixed-solvent precipitation.
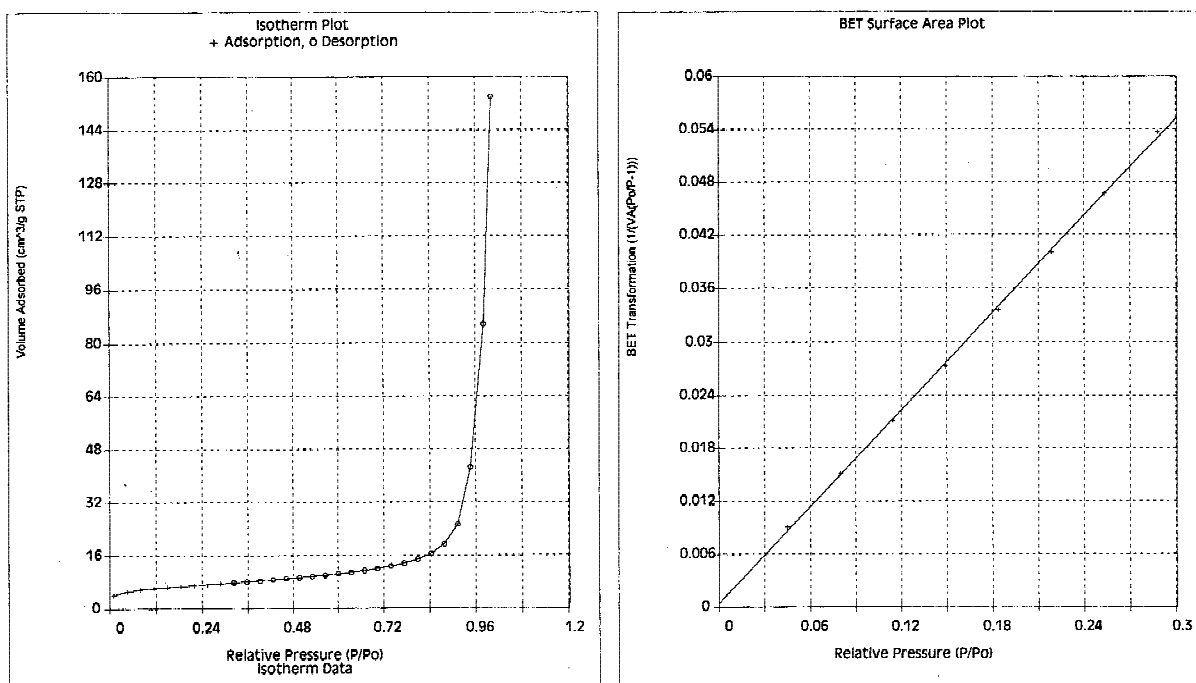

Fig. 6. BET specific surface area analysis of cube-shaped, nanosize zirconia powders.

crystallization/growth of the monoclinic crystallites occurs until their transition to the tetragonal phase (at 31.167° 2θ) around 1200°C. The tetragonal phase exists between 1200° and 1400°C and monoclinic phase is completely transformed into the tetragonal phase at 1400°C. This type of monoclinic-phase-growth XRD data with increasing temperature is reported here for the first time. When the temperature dropped from 1400°C back to 30°C, the tetragonal phase was completely transformed to the monoclinic phase, which is the stable phase at room temperature. No metastable tetragonal phase stabilization was observed. In addition, the percentage ratio of monoclinic phase to tetragonal phase (m/t) is shown on the left-hand side of each XRD spectrum in Fig. 8. (Note: Data are presented in the same manner later in Figs. 9, 10, and 11.) This phase percentage ratio was estimated from the integrated peak intensity according to the method of Garvie and Nicholson.[33]

In contrast to the cube-shaped particles, microspheres produced by mixed-solvent precipitation and $ZrOCl_2$ salt precursor are "amorphous" to X-rays if they are not heat-treated

above 400°C (Figs. 9 and 10). For both microspheres and the salt the tetragonal phase appears first as the temperature is increased. Then the monoclinic phase evolves at higher temperatures and coexists with the tetragonal phase. The tetragonal phase exists from the crystallization temperature (400°C for microspheres and 600°C for the salt) all the way to 1400°C. However, when the temperature is cooled down to 30°C or room temperature, only monoclinic phase is present. Evidently, during the solution synthesis the presence of the isopropyl alcohol increases the particle growth rate by enhancing the aggregation of zirconium species in the solution but inhibits the ordered, hydrolytic arrangement of zirconium tetrameric species and, thus, the monoclinic crystalline phase formation in the microspheres. It is also worthwhile to note that the mixed-solvent synthesis conditions (such as aging time, temperature, alcohol-to-water volume ratio) affect the thermal crystallization and phase-transition behavior of the microsphere powders. We plan to report detailed studies of such effects later.

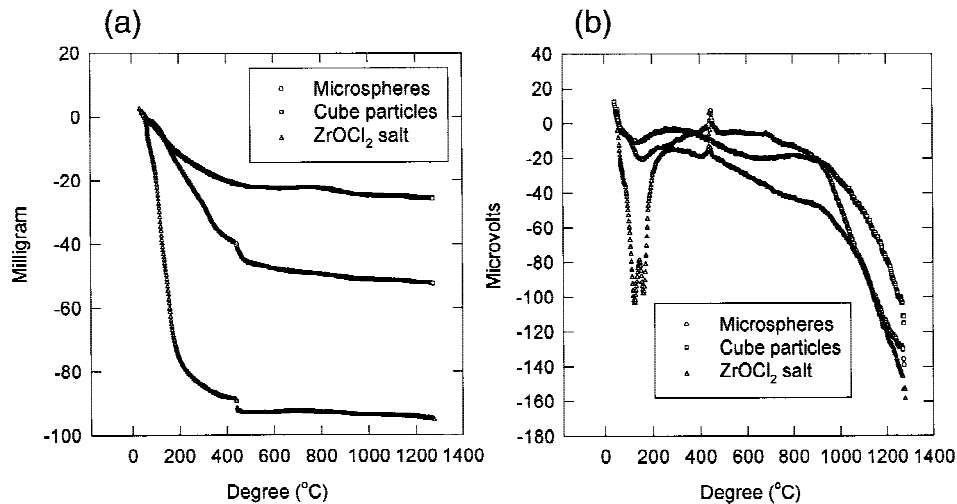As a baseline for comparison, the microsphere powders pre-

Fig. 7. Comparisons of TGA/DTA data of zirconia powders and precursor inorganic salt: (a) TGA plot, (b) DTA plot.
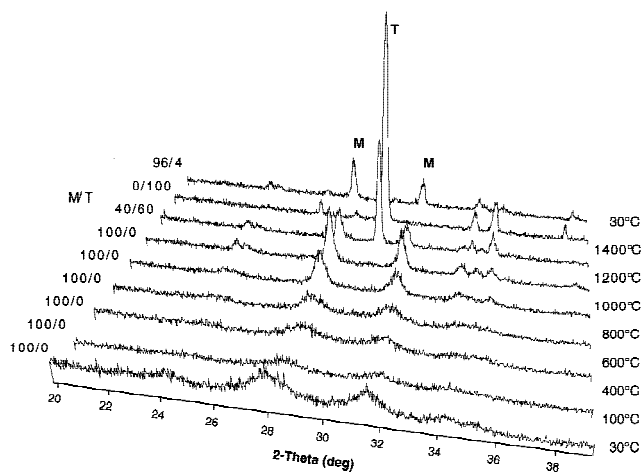

Fig. 8. HTXRD analysis of nanocrystalline cube-shaped zirconia particles synthesized by forced hydrolysis.
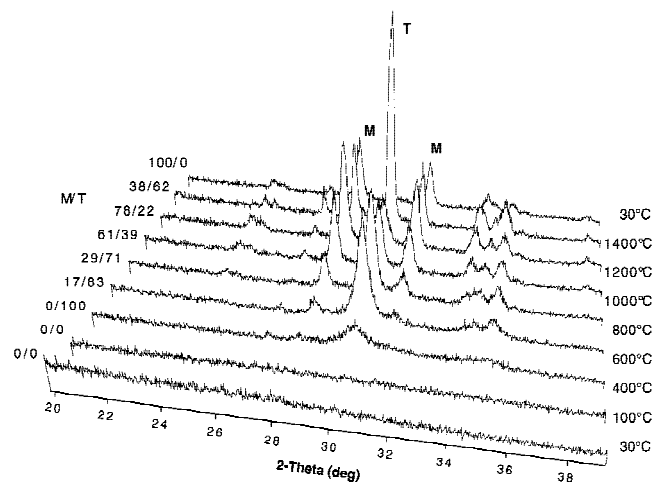

Fig. 9. HTXRD analysis of ultrafine zirconia microspheres synthesized by mixed-solvent precipitation.

pared by the alkoxide hydrolysis/condensation method also tested by the HTXRD (Fig. 11) were found to be amorphous to X-rays at room temperature. Only the tetragonal phase (no monoclinic phase) appeared at temperatures from 600° to 1400°C. As always, the tetragonal phase was reversed to the monoclinic phase when the sample was cooled down from 1400° to 30°C. The crystallization temperature for the microsphere from mixed-solvent synthesis is around 400°C, which is much lower than that of the salt (~600°C) and the microspheres from the alkoxide method. Such tetragonal-phase evolution (corresponding to explosive crystallization or exotherm) from an amorphous material (i.e., hydrous zirconia gels) was reported previously.[17] Our current study is in agreement with earlier work on the tetragonal crystal evolution from amorphous zirconia gel materials. HTXRD data for the amorphous microsphere zirconia particles (Figs. 9 and 11) support the belief that the formation of tetragonal zirconia is closely related to the existence of amorphous zirconia because of their structural similarity. Topotatic crystallization on nuclei in the amorphous zirconia has been proposed as the mechanism of tetragonal zirconia formation under hydrothermal conditions.[34]

Table I shows the thermally induced nanocrystal evolution and growth for the $ZrOCl_2$ salt and the powders from the inorganic salt. It is obvious that with increasing temperature, the size of the crystallites increases. Nanocrystal growth depends on the methods of zirconia preparation. Monoclinic crystallite size increased from 9.3 to 41 nm when the cube-shaped par-

ticles were heated from 400° to 1000°C in air. Such monoclinic nanocrystal growth data agree very well with results reported previously by Murase and Kato[35] under a dry air or nitrogen atmosphere (Fig. 12). In addition, Murase and Kato found that the presence of water vapor during heat treatment stimulates monoclinic zirconia crystal growth significantly. For the microspheres by mixed-solvent precipitation, the nanocrystal growth of the metastable tetragonal phase as a function of temperature (below 1200°C) is comparable with the experimental crystallite size data previously reported by Garvie,[13] growing from 12.4 to 30 nm. In the case of heating $ZrOCl_2$ hydrated salt, the salt crystal (believed to have a tetramer structural unit $[Zr(OH)_2 4H_2O]_4{}^{8+})$[36] becomes X-ray amorphous at 100° and 400°C. By further increasing the temperature, crystallite size for the tetragonal phase grows from 12.3 to over 100 nm.

At temperatures higher than 1200°C, the effective crystallite sizes of the tetragonal phase for all samples shown in Table I are considerably larger (>100 nm) than the critical size (~30 nm) previously reported for the metastable zirconia.[34,35,37–39] Garvie's supporters believe that metastable tetragonal phase can be stabilized only for those tetragonal crystals less than 30 nm. In other words, crystallites smaller than 30 nm could exist in the tetragonal form while particles larger than this size would tend to transform to the more stable monoclinic form. Our 30°C data after cooling (Table I) clearly show that crystallite size after the heating cycle is greater than the 30-nm
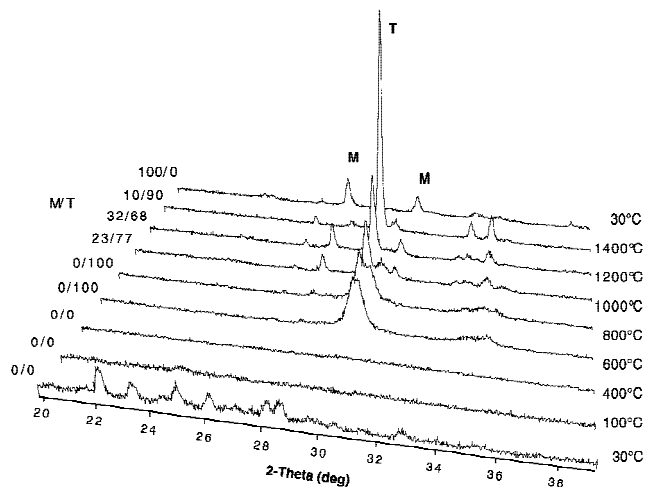
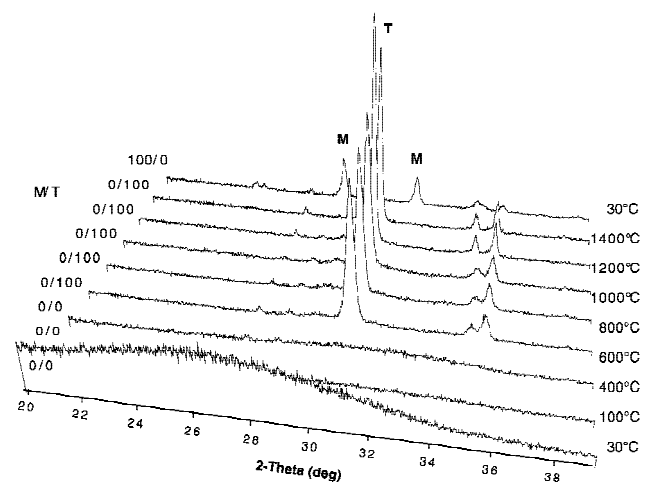**Fig. 10.** HTXRD analysis of zirconyl chloride octahydrate salt.

Fig. 11. HTXRD analysis of ziconia powders from hydrolysis/condensation of zirconium tetra-*n*-butoxide in ethanol solution.

Fig. 12. Correlation between nanocrystal growth of monoclinic zirconia and calcination temperature.

critical size. This may explain why in all of our samples no metastable tetragonal phase remained stable when the temperature cooled down to room temperature. Several earlier works reported that homogeneous precipitation produced zirconia powders which contained single metastable tetragonal crystals exceeding 100 nm.[1,4] They believed that the existence of the large tetragonal monocrystals was due to the very fine internal porosity or substructure of the closely oriented nanocrystallites within the domains. The fine internal porosity gave rise to a surface area/volume ratio sufficient to stabilize tetragonal zirconia by the same mechanism as in nanocrystalline powders.
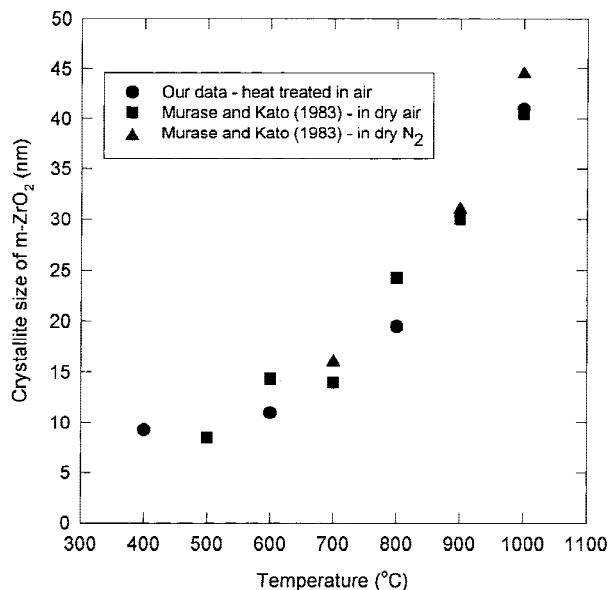
It is important to stress that for nanocrystalline cube-shaped nanoparticles, the monoclinic nanocrystal growth and phase transformation (monoclinic to tetragonal) that take place when the temperature is increased from 30° to 1400°C in air (Fig. 8) is an unusual but interesting case:

[amorphous + monoclinic]→[monoclinic(crystallization)] → [monoclinic + tetragonal] → [pure tetragonal]
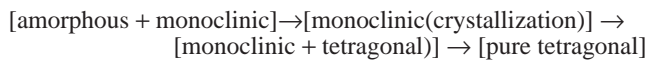
Traditionally, upon increasing calcination temperature, most amorphous zirconia precursor materials convert to the tetragonal phase first and then transform to monoclinic phase at higher temperature (~600°C); that is, tetragonal phase forms preferentially to the monoclinic phase during crystallization of amorphous hydrous zirconia.[1,39–41] In the case of nanocrystalline zirconia precipitated from acidic salt solutions by hydrothermal treatment, an important exception to the traditional crystallization route occurs.[7,32,42] According to Garvie's surface energy theory,[13,37] the existence of monoclinic nanocrystalline zirconia would be attributed to a lowering of the surface free energy under acidic conditions.[42] The stability of the metastable tetragonal phase has been attributed to the lower surface energy of the tetragonal phase compared with the monoclinic phase. The surface energy theory cannot explain entirely the findings of this study, particularly why monoclinic crystal evolution and growth occurred with increasing temperature, rather than tetragonal crystal evolution. In fact, an earlier work by Morgan reported phenomena that contradict the critical size theory.[42] He obtained ultrafine zirconia particles as small as 6

Table I. Size Determination of Nanocrystals Evolved in Powders during Heat Treatment by HTXRD

	Size (nm)							
	Cube-shaped zirconia powders by forced hydrolysis		Microspheres of zirconia by mixed-solvent precipitation		ZrOCl₂ salt precursor (as received)		Powders from alkoxide hydrolysis/condensation	
Temperature (°C)	Monoclinic phase	Tetragonal phase	Monoclinic phase	Tetragonal phase	Monoclinic phase	Tetragonal phase	Monoclinic phase	Tetragonal phase
400	9.3			12.4				
600	11.0		17.5	17.5	ND[‡]	12.3		33.5
800	19.5		21.0	21.0	ND	11.6		38.5
1000	41.0		25.5	25.3	30.0 to 45.0	42.8		40.0
1200	40.0 to 64.0	>100.0	33.0 to 49.0	30.0	90.0 to 100.0	>100.0		>100.0
1400	†	>100.0		45.0		>100.0		>100.0
30	60.0 to 100.0		44.0 to 48.0		60.5 to 68.0		52.5	

†Peak (or crystalline phase) does not exist. ‡Cannot be accurately determined from the XRD data.

nm in the monoclinic phase. Based on TEM particle size and XRD crystallite size, Srinivasan *et al.* also concluded that the tetragonal-to-monoclinic transformation does not appear to be due to a critical size effect.[43] When the primary particles aggregate together with the formation of necks, Déchamps *et al.* proposed a branched-chain model in which the tetragonal-to-monoclinic transformation in zirconia is independent of the size of the aggregate or domain.[4]

IV. Summary

Inorganic salt can be used as a good precursor in the production of monodispersed ultrafine ceramic powders and provides the same level of quality as that obtained using higher-cost alkoxide precursor. Ultrafine monodispersed zirconia particles were successfully synthesized by three different methods for comparative studies. The particle-synthesis methods were (1) forced hydrolysis of $ZrOCl_2$ in aqueous solutions, (2) mixed-solvent precipitation of $ZrOCl_2$ by adjusting the dielectric constant of the mixture solutions, and (3) hydrolysis/condensation of zirconium alkoxide. For the forced hydrolysis and mixed-solvent precipitation processes, SAXS and DLS were effective tools used to monitor the particle nucleation and growth of the sol particles. The forced hydrolysis is a slow process that produced monoclinic, cube-shaped nanoparticles of zirconia. In contrast, the mixed-solvent precipitation and the alkoxide method produced amorphous microspheres. Production of nanosize (<100 nm) microspheres can be achieved in the mixed-solvent precipitation of inorganic salt solutions. Powder characterizations indicated that the synthesis methods or processing conditions affect the behavior of crystallization and phase transition, which does not follow the traditional phase transformation route for zirconia. It was discovered that the cube-shaped particles produced from forced hydrolysis follow a unique nanocrystal evolution and growth pathway; that is, monoclinic crystals can evolve and grow before the appearance of tetragonal crystals during the heating process. The microspheres from mixed-solvent synthesis exhibit a mixture of tetragonal and monoclinical phases, while microspheres from alkoxide hydrolysis/condensation show a pure tetragonal-phase formation.

References

[1]B. Djuričić, S. Pickering, D. McGarry, P. Glaude, P. Tambuyser, and K. Schuster, "The Properties of Zirconia Powders Produced by Homogeneous Precipitation," *Ceram. Int.*, **21**, 195–206 (1995).

[2]R. H. J. Hannink and M. V. Swain, "Progress in Transformation Toughening of Ceramics," *Annu. Rev. Mater. Sci.*, **24**, 359–408 (1994).

[3]A. H. Heuer and L. W. Hobbs (Eds.), Advances in Ceramics, Vol. 3, *Science and Technology of Zirconia.* American Ceramic Society, Columbus, OH, 1981.

[4]M. Déchamps, B. Djuričić, and S. Pickering, "Structure of Zirconia Prepared by Homogeneous Precipitation," *J. Am. Ceram. Soc.*, **78**, 2873–80 (1995).

[5]M. Z.-C. Hu, M. T. Harris, and C. H. Byers, "Nucleation and Growth Kinetics for Synthesis of Nanometric Zirconia Particles by Forced Hydrolysis," *J. Colloid Interface Sci.*, **198**, 87–99 (1998).

[6]M. Z.-C. Hu, J. T. Zielke, J.-S. Lin, and C. H. Byers, "Small-Angle X-ray Scattering Studies of Early-Stage Colloids Formation by Thermohydrolytic Polymerization of Aqueous Salt Solutions," *J. Mater. Res.*, **14**, 103–13 (1999).

[7]A. Bleier and R. M. Cannon, "Nucleation and Growth of Uniform *m*-ZrO_2," *Mater. Res. Soc. Symp. Proc.*, **73**, 71–78 (1986).

[8]M. Chatry, M. Henry, and J. Livage, "Synthesis of Nonaggregated Nanometric Crystalline Zirconia Particles," *Mater. Res. Bull.*, **29**, 517–22 (1994).

[9]H. Kumazawa, T. Inoue, and E. Sada, "Synthesis of Fine Spherical Zirconia Particles by Controlled Hydrolysis of Zirconium Alkoxide in the High Temperature Range Above 50°C," *Chem. Eng. J.*, **55**, 93–96 (1994).

[10]H. Kumazawa, Y. Hori, and E. Sada, "Synthesis of Spherical Zirconia Fine Particles by Controlled Hydrolysis of Zirconium Tetrabutoxide in 1-Propanol," *Chem. Eng. J.*, **51**, 129–33 (1993).

[11]S.-K. Lee, I. Masaki, and M. Nobuyasu, "Influence of Alcoholic Solvent on Formation of Monodispersed Particles by Hydrolysis of Zirconia Tetra-*n*-butoxide," *J. Ceram. Soc. Jpn.*, **99**, 290–94 (1990).

[12]T. Ogihara, N. Mitzutani, and M. Kato, "Growth Mechanism of Monodispersed ZrO_2 Particles," *J. Am. Ceram. Soc.*, **72** [3] 421–26 (1989).

[13]R. C. Garvie, "The Occurrence of Metastable Tetragonal Zirconia as a Crystallite Size Effect," *J. Phys. Chem.*, **69** [4] 1238–43 (1965).

[14]R. Srinivisan and B. H. Davis, "Glow Phenomenon and Crystallization: Evidence That They Are Different Events for Hafnium–Zirconium Mixed Oxides," *J. Colloid Interface Sci.*, **156**, 400–405 (1993).

[15]K. Matsui and M. Ohgai, "Formation Mechanism of Hydrous-Zirconia Produced by Hydrolysis of $ZrOCl_2$ Solutions," *J. Am. Ceram. Soc.*, **80** [8] 1949–56 (1997).

[16]Y. T. Moon, H. K. Park, D. K. Kim, and C. H. Kim, "Preparation of Monodisperse and Spherical Zirconia Powders by Heating of Alcohol–Aqueous Salt Solutions," *J. Am. Ceram. Soc.*, **78** [10] 2690–94 (1995).

[17]J. Livage, K. Doi, and C. Mazieres, "Nature and Thermal Evolution of Amorphous Hydrated Zirconium Oxide," *J. Am. Ceram. Soc.*, **51**, 349–53 (1968).

[18]E. D. Whitney, "Observations on the Nature of Hydrous Zirconia," *J. Am. Ceram. Soc.*, **53** [12] 697–98 (1970).

[19]M. T. Torrolvo, M. A. Alario, and J. Soria, "Crystallization Behavior of Zirconium Oxide Gels," *J. Catal.*, **86**, 473–76 (1984).

[20]S. A. Selim and T. M. E. Akkard, "Thermal Decomposition, Pore Structure and Heats of Immersion of Zirconia Gel," *J. Appl. Chem. Biotechnol.*, **27**, 58–66 (1977).

[21]G. Gimblet, A. A. Rahman, and K. S. W. Sing, "Thermal and Related Studies of Some Zirconia Gels," *J. Chem. Technol. Biotechnol.*, **30**, 51–64 (1980).

[22]P. D. L. Mercera, J. G. Van Ommen, E. B. M. Doesburg, A. J. Burggraaf, and J. R. H. Roos, "Zirconia as a Support for Catalysts—Evolution of the Texture and Structure on Calcination in Air," *Appl. Catal.*, **57**, 127–48 (1990).

[23]R. Srinivasan, M. B. Harris, S. F. Simpson, R. J. Deangelis, and B. H. Davis, "Zirconium Oxide Crystal Phase: The Role of the pH and Time to Attain the Final pH for Precipitation of the Hydrous Oxide," *J. Mater. Res.*, **3**, 787–97 (1988).

[24]G. Fisher, "Zirconia: Ceramic Engineering's Toughness Challenge," *Am. Ceram. Soc. Bull.*, **65** [10] 1355–60 (1986).

[25]E. Ryshkewitch and D. W. Richerson, *Oxide Ceramics, Physical Chemistry and Technology*, 2nd ed. General Ceramics, Haskell, NJ, 1985.

[26]C. J. Howard, R. J. Hill, and B. E. Reichert, "Structures of the ZrO_2 Polymorphs at Room Temperature by High-Resolution Neutron Powder Diffraction," *Acta Crystallogr.*, Sect. B, **44**, 116–20 (1988).

[27]P. Aldebert and J.-P. Traverse, "Structure and Ionic Mobility of Zirconia at High Temperature," *J. Am. Ceram. Soc.*, **68**, 34–40 (1985).

[28]D. K. Smith and C. F. Cline, "Verification of Existence of Cubic Zirconia at High Temperature," *J. Am. Ceram. Soc.*, **45**, 249–50 (1962).

[29]X. Bokhimi, A. Morales, O. Novaro, M. Portilla, T. López, F. Tzompantzi, and R. Gómez, "Tetragonal Nanophase Stabilization in Nondoped Sol–Gel Zirconia Prepared with Different Hydrolysis Catalysts," *J. Solid State Chem.*, **135**, 28–35 (1998).

[30]M. C. Silva, G. Trolloard, O. Masson, R. Guinebretiere, A. Dauger, A. Lecomte, and B. Frit, "Early Stages of Crystallization in Gel Derived ZrO_2 Precursors," *J. Sol–Gel Sci. Technol.*, **8**, 419–24 (1997).

[31]M. L. Rojas-Cervantes, R. M. Martin-Aranda, A. J. Lopez-Peinando, and J. De D. Lopez-Gonzalez, "ZrO_2 Obtained by the Sol–Gel Method: Influence of Synthesis Parameters on Physical and Structural Characteristics," *J. Mater. Sci.*, **29**, 3743–48 (1994).

[32]R. P. Denkewicz, Jr., K. S. TenHuisen, and J. H. Adair, "Hydrothermal Crystallization Kinetics of *m*-ZrO_2 and *t*-ZrO_2," *J. Mater. Res.*, **5** [11] 2698–705 (1990).

[33]R. C. Garvie and P. S. Nicholson, "Phase Analysis in Zirconia Systems," *J. Am. Ceram. Soc.*, **55**, 303 (1972)

[34]E. Tani, M. Yoshimura, and S. Somia, "Formation of Ultrafine Tetragonal ZrO_2 Powder under Hydrothermal Conditions," *J. Am. Ceram. Soc.*, **66**, 11–14 (1983).

[35]Y. Murase and E. Kato, "Role of Water Vapour in Crystallite Growth and Tetragonal–Monoclinic Phase Transformation of ZrO_2," *J. Am. Ceram. Soc.*, **66**, 196–200 (1983).

[36]T. C. Mak, "Refinement of the Crystal Structure of Zirconyl Chloride Octahydrate," *Can. J. Chem.*, **46**, 3491–97 (1968).

[37]R. C. Garvie, "Stablization of the Tetragonal Structure in Zirconia Microcrystals," *J. Phys. Chem.*, **82**, 218–24 (1978).

[38]T. Mituhashi, M. Ichihara, and U. Tatsuke, "Characterization and Stabilization of Metastable Tetragonal ZrO_2," *J. Am. Ceram. Soc.*, **57**, 97–101 (1974).

[39]R. Srinivasan, B. H. Davis, O. Burlcavin, and C. R. Hubbard, "Crystallization and Phase Transformation Process in Zirconia: An *In-Situ* High-Temperature X-ray Diffraction Study," *J. Am. Ceram. Soc.*, **75**, 1217–22 (1992).

[40]M. Yashima, T. Kato, M. Kakihana, M. A. Gulgun, Y. Matsuo, and M. Yoshimura, "Crystallization of Hafnia and Zirconia During the Pyrolysis of Acetate Gels," *J. Mater. Res.*, **12**, 2575–83 (1997).

[41]G. T. Mamott, P. Barnes, S. E. Tarling, S. L. Jones, and C. J. Norman, "A Dynamic High Temperature XRPD Study of the Calcination of Zirconium Hydroxide," *Powder Diffr.*, **3** [4] 234 (1988).

[42]P. E. D. Morgan, "Synthesis of 6 nm Ultrafine Monoclinic Zirconia," *J. Am. Ceram. Soc.*, **67** [10] C-204–C-205 (1984).

[43]R. Srinivasan, L. Rice, and B. H. Davis, "Critical Particle Size and Phase Transformation in Zirconia: Transmission Electron Microscopy and X-ray Diffraction Studies," *J. Am. Ceram. Soc.*, **73** [11] 3528–30 (1990).   □