

High Yield Hydrothermal Synthesis of Nano-Scale Zirconia and YTZP

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Many techniques exist to synthesize zirconia and YTZP with a nano-scale particle size, but a recently developed hydrothermal precipitation procedure has shown promise in producing highyield quantities of well-dispersed 8-10 nm zirconia and YTZP. Using bicine as a complexing agent, a homogeneous solution of zirconyl nitrate and yttrium nitrate is formed; after hydrothermal treatment, 8-10 nm tetragonal zirconia or YTZP particles are precipitated. With the modified hydrothermal procedure, powder yield was increased to 100 g of powder per liter of reactant solution without significantly changing the powder characteristics. X-ray diffraction and Raman spectroscopy were used to verify that the tetragonal phase was formed in the 1YTZP composition. Complementary particle size measurements were made using dynamic light scattering, BET nitrogen adsorption, and X-ray diffraction; differences in measured particle size are discussed, and all three techniques verify the 8-10 nm particle diameter. Particle morphology and impurity content were measured with transmission electron spectroscopy and X-ray fluorescence, respectively. To overcome the increased likelihood of agglomeration that accompanies the increased synthesis, wash solutions of deionized water, bicine, and oxalic acid were compared, and the particle-particle interactions of nano-YTZP in these wash solutions and in ethanol are modeled with modified DLVO theory. The results show that yttria leaching is prevented and dispersion is promoted by laundering with a solution of oxalic acid and dispersing into deionized water, both adjusted to a pH value of 9.

I. Introduction

N ANO-SCALE zirconia materials offer unique mechanical properties, such as enhanced transformation toughening with less dopant, and superplastic deformation behavior.¹⁻³ Several authors have demonstrated that high-density, nano-grain ceramics can be fabricated with nano-scale zirconia materials.^{4,5} However, authors have expressed skepticism in whether nano-scale materials could be synthesized in industrial quantities.⁶ For example, many popular chemical-vapor synthesis methods^{7,8} require significant time and energy to produce relatively small amounts of material. However, the perception that nano-scale materials are only practical for small-scale research purposes is becoming discarded thanks, at least in part, to recent developments in wet-chemical precipitation,^{9–11} sol–gel synthesis,^{12–14} and hydrothermal techniques.^{15–17} In fact, several grades of nano-zirconia materials are commercially available from a variety of sources.

One synthesis technique in particular, developed by Kimel and Adair,¹⁸ is of particular interest for manufacturing larger quantities of nano-zirconia. With this procedure, stable aqueous suspensions of 8–10 nm zirconia or yttrium-doped tetragonal zirconia polycrystals (YTZP) are hydrothermally prepared by taking advantage of the complexation chemistry of the system.

Before precipitation, the participating metal ions are kept in a dissolved state by a complexing agent to produce a homogeneous solution. Precipitation takes place when the complex is broken and large amounts of metal ions are released into the solution. When this occurs, the supersaturation of the solution is extremely high, and almost all of the energy available for growth is consumed in the formation of nuclei. As a consequence, little growth of the nuclei occurs and the resulting particles are ultra-fine in size.

The choice of complexing agent in Kimel and Adair's¹⁸ work was based on several considerations. First, the complexing agent needed to form a stable complex with the metal ions over a wide range of pH values. Second, the complexing agent should impart charge to the surface of the newly formed particles to promote dispersion in suspension after precipitation. From previous studies^{19–21} and experimental verification, bicine (N,N-bis(2-hydroxyethyl)glycine) was selected as the appropriate complexing agent.

In the development of the technique by Kimel and Adair, the concentration of zirconium in solution produced a relatively small mass (~25 g) of nano-YTZP per liter of stock solution. For this to be an economical process, the yield of nano-scale material should be as high as possible and practical.

The scale-up of a precipitation procedure is often accompanied by a greater tendency for agglomeration. The increased yield of particulate also generates increased solids loading, particle number concentrations, and ionic strength in the precipitant solution. According to conventional DLVO theory (named for authors Derjaguin and Landau,²² Verwey and Overbeek²³), which models attractive and repulsive interactions between particles in suspension, increased solution ionic strength leads to double layer compression and lower energy barriers to agglomeration. The double layer thickness, or Debye–Hückel length (κ^{-1} , m) is a characteristic measurement of the distance that the counterion cloud extends into the suspension, and can be calculated with the equation²⁴

$$\kappa^{-1} = \left(\frac{8000\pi e^2 N_{\rm A}I}{\varepsilon_0 k_{\rm d} k_{\rm B}T}\right)^{\frac{1}{2}} \tag{1}$$

where *e* is the charge of an electron, N_A is Avogadro's number, *I* is the suspension ionic strength in mol/L, ε_0 is the permittivity of free space, k_d is the relative dielectric constant of the medium, k_B is Boltzmann's constant, and *T* is absolute temperature. Thus the Debye–Huckel length diminishes with $\Gamma^{-1/2}$.

For the synthesis procedure in question, a fourfold increase in yield equates to a fourfold increase in ionic strength, calculated by

$$I = \frac{1}{2} \sum_{i} Z_i^2 c_i \tag{2}$$

where z_i is the valence of a dissolved species *i*, and c_i is the molar concentration. Referring to Eq. (1), this increase in

H. Chan-contributing editor

Manuscript No. 29389. Received March 01, 2011; approved July 22, 2011. † Author to whom correspondence should be addressed. e-mail: christopher.szepesi@ am.umicore.com

ionic strength compresses the double layer by a factor of 2, which can be significant on the length scale of nano-particles. For successful processing into green bodies and, ultimately, high-density ceramics, the increased probability of agglomeration must be accounted for with a washing procedure that avoids the increased likelihood of agglomeration.

The usefulness of the precipitation process detailed in this work, however, is that yields are only limited by the solubilities of the reagents used. Upon precipitation, particles are surrounded by a protective colloid layer, which acts as an effective barrier to irreversible agglomeration. The process also allows flexibility in the concentration of dopant incorporated into the material.

In the current work, nano-YTZP yields have been increased to as high as 100 g/L (10 wt%) by increasing the metal ion and bicine concentrations (along with appropriate pH value compensation) without changing the product properties and without irreversible agglomeration. The effect of washing solution additives on particle dispersion is also presented, and an effective washing and dispersion procedure is identified, which minimizes agglomeration during laundering despite the increased likelihood in the high-yield formulation.

II. Materials and Methods

Figure 1 presents a schematic flow diagram of the synthesis procedure. Please note that the powder recovery and green forming steps are outside the scope of this report. Nano-scale zirconia and YTZP were prepared using zirconyl nitrate hydrate and yttrium nitrate hexahydrate (Sigma-Aldrich, Milwaukee, WI) as the sources for zirconium and yttrium ions, respectively, with bicine (>99% titration, Sigma-Aldrich) added to complex the ions in aqueous solution. The molar ratio of bicine to Zr⁴⁺ was kept at 2:1.¹⁸ Typical concentrations of zirconyl nitrate were on the order of 0.5-1.0M with yttrium nitrate added to produce between 1 and 4 mol% yttria doping. Appropriate amounts of CO2-free deionized water, bicine, zirconyl nitrate, and yttrium nitrate were added to solid tetramethylammonium hydroxide pentahydrate (TMAOH, >97%, Sigma-Aldrich) in a Nalgene bottle. The mixture was shaken overnight, forming a translucent white solution. The water contained in the TMAOH, when released during agitation, acted as a medium in which the other reagents could dissolve. The pH of the mixture was > 13.



Fig. 1. A modified procedure to increase yield of hydrothermally synthesized 8–10 nm YTZP is illustrated in this flow chart.

After agitation, the mixture was placed into a modified Parr hydrothermal vessel with a Teflon lining, described in more detail elsewhere.¹⁸ The mixture was treated for 8 h at 200°C and cooled to room temperature.

To remove reaction byproducts, a displacement washing procedure was employed. Three wash solutions were chosen for this study: 0.01M oxalic acid(aq) (A.C.S. grade, Fisher Scientific, Hanover Park, IL), 0.01M bicine(aq) (minimum 99% titration, Sigma Aldrich), and deionized water, each adjusted to pH 9 with tetraethylammonium hydroxide (20 w/w solution in water, Sigma Aldrich) to minimize yttrium dissolution.^{25–27} The rationale behind the choice of these particular reagents will be discussed later in this article. All laundering was carried out in Nalgene containers to minimize contamination from glassware at elevated pH values. All suspensions were washed until a constant conductivity was achieved. In the final washing (dispersion) step, the solids loading was adjusted to 20 wt% by adding an appropriate amount of dispersing solution.

Dispersion was evaluated in washed suspensions using dynamic light scattering (DLS) to measure particle size distribution (Malvern ZetaSizer, Model Nano S; Malvern Instruments, Worcestershire, U.K.) and zeta potential (ZetaPALS Zeta Potential Analyzer, Brookhaven Instrument Corporation, Holtsville, NY). Suspensions were diluted to optical transparency into pH-adjusted deionized water or ethanol for these measurements. Particle interaction energies and suspension stability were calculated in the STABIL[©] v4.5 computer program²⁴ based on a modified DLVO theory used by Kimel and Adair. The Hamaker constant used for tetragonal YTZP was 8.8 \times 10^{-20} J, 28 and the approximation for small values of ka (ratio of particle size to double layer thickness <<1) was used in the calculation. The size of the adsorbed layers for the oxalate and bicine molecules was the same as in Kimel and Adair (0.37 and 0.75 nm, respectively). Suspension stability is further characterized by the agglomeration probability, α , described by the equation²⁴

$$\alpha = \frac{\int_2^\infty \frac{\exp(V_A(d)/k_B T)}{s^2} ds}{\int_2^\infty \frac{\exp(V_T(d)/k_B T)}{s^2} ds}$$
(3)

This value is also calculated with the Stabil[©] software,²⁴ where $V_A(d)$ is the attractive energy curve, $V_T(d)$ is the total energy curve, and *s*, the homologous separation distance, is

$$s = \frac{a_1 + a_2 + d}{a_1 + a_2} \tag{4}$$

 a_i is the diameter of particle *i*, and *d* is the separation between overlapping double layers. When employing these models, it was assumed that particles were spherical, molecularly smooth, with charges evenly distributed over the particle surface.

The product was further characterized through measurement of specific surface area by N_2 adsorption (Gemini II 2370 Surface Area Analyzer, Micromeritics Instrument Corporation, Norcross, GA), crystal structure and crystallite size by X-ray diffraction (PAD V X-ray Diffractometer, Scintag, Inc., Sunnyvale, CA), phase determination by Raman spectroscopy (Model PI-ECL-785-300-FC Raman Spectrometer, InPhotonics, Inc., Norwood, MA), and compositional analysis by X-ray fluorescence (Philips 1600/10 Wavelength Dispersive XRF, courtesy of the Mineral Lab, Lakewood, CO). Crystallite size was estimated from peak broadening of the (011) reflection in the XRD pattern of dried powder with the Scherrer equation,

$$d_{\rm XRD} = \frac{K\lambda}{\Delta_{2\theta}\cos\theta} \tag{5}$$

where K is a shape factor (usually equal to 0.9), and $\Delta_{2\theta}$ is the peak width in radians, and θ is the diffraction angle.²⁹

The product was also observed using a transmission electron microscope (Philips 420T TEM; FEI Company, Hillsboro, OR) in the electron microscopy facility of the Materials Research Institute at the Pennsylvania State University.

Average agglomeration number (AAN), which estimates the average number of primary particles in an agglomerate, was calculated as the ratio of the cube of the mean particle size measured by light scattering (hydrodynamic diameter, D_{DLS}) to the cube of the equivalent spherical diameter measured by BET gas adsorption times a packing fraction, assuming spherical particles.³⁰ The equivalent spherical diameter is given by

$$d_{\rm BET} = \frac{6}{(SSA \times \rho)} \tag{6}$$

where d_{BET} is an equivalent spherical diameter (µm), *SSA* is the specific surface area (m²/g), and ρ is the density of the material (g/cm³). The equivalent spherical diameter was converted from a surface area basis to a volume basis, *D*, for comparison with the volume-based hydrodynamic diameter with the equation³⁰

$$\log(D) = \log\left(\frac{6}{\rho SSA}\right) + \frac{4.6}{s_{\rm w}^2} \tag{7}$$

where s_w is the width of the particle size distribution, usually taken as 4 or 5 for a log-normally distributed powder.

III. Results and Discussion

(1) Synthesis Procedure and Characterization

Treatment time, reaction pH, and temperature were kept the same as optimized in the Kimel and Adair procedure¹⁸ (8 h at 200°C in a Teflon-lined hydrothermal vessel). These conditions were chosen to hydrothermally decompose the bicine–zirconium complex and precipitate the tetragonal phase. Adair²⁶ and Denkewicz *et al.*³¹ have generated solubility diagrams for the Zr–H₂O and Y–H₂O systems and have shown that hydrothermal precipitation at pH values above 12 is necessary to produce the stabilized tetragonal phase.

Alkaline metal bases are normally avoided in achieving such a high pH because of possible deleterious effects during subsequent processing, such as sintering. Consequently, a concentrated organic base needed to be identified to adjust solution pH without drastically increasing solution volume. tetramethylammonium hydroxide Solid pentahydrate (TMAOH, >97%, Sigma-Aldrich, Milwaukee, WI) is readily available, and, when mixed as a solid with the solid acidic metal ion salts, forms a highly alkaline aqueous solution by the release of water contained within the reagent structures. Excess water can then be added to adjust the metal ion concentrations to the desired levels. Treatment time and temperature were kept the same as optimized in the Kimel and Adair procedure¹⁸ (8 h at 200°C in an unstirred Teflon-lined hydrothermal vessel).

Zirconium concentration within the stock solutions was limited to about 0.8M due to the volume increase associated with higher reagent concentrations. Yields from these stock solutions routinely achieve 100 g/L of nano-scale YTZP upon hydrothermal treatment using the modified procedure described in Fig. 1.

An often overlooked, but critical element in the solution synthesis of nano-particulates is the laundering and recovery steps to remove spectator ions while maintaining a well-dispersed system. To remove reaction byproducts, several washing steps are typically required. This is done with a standard displacement washing procedure in which solids are concentrated from suspension by centrifugation, supernatant is decanted and replaced with fresh wash solution, and solids are redispersed with moderate ultrasonication. However, for the higher yield of zirconia, it was uncertain what wash procedure was most appropriate.

Figure 2 illustrates an example of the particle size distributions of several washed suspensions as measured by dynamic light scattering. Note that this particle sizing technique gives a measurement of hydrodynamic diameter, D_{DLS} , which is affected by light scattering from the double layer. To confirm the primary particle size, BET surface area and XRD peak broadening were also used. Surface area values were measured to be between 100 and 120 m²/g, which corresponds to a d_{BET} between 8 and 10 nm using Eq. (6).

Equation (6) assumes that particles are spherical in shape, which is a reasonable assumption, given the particles shown in the TEM micrographs in Fig. 3, which shows undoped zirconia and 1YTZP particles washed with oxalic acid solution. Crystallite size calculations from XRD peak broadening, shown in Fig. 4 for a 1YTZP sample, using the Scherrer equation, result in values similar to those calculated from surface area measurements. Therefore, from surface area measurements, XRD analysis and TEM observations, it is concluded that particles have an average diameter between 8 and 10 nm.

However, these calculated values are in slight disagreement with the hydrodynamic diameter determined by light scattering. As particles are in a suspended, charged state during measurements with this technique, a slight shift in the position of the primary particle mode, as illustrated in Fig. 2 with different wash solutions, suggests a difference in double layer thickness with wash solution.^{32,33} In fact, the particle size measured by light scattering being larger than that measured by BET surface area, XRD, and TEM, verifies that the double layer thickness and adsorbed species affect the particle size measured by the light scattering technique.^{34,35} This effect and corrections for it are discussed in the following section.

The XRD measurements were also ambiguous in differentiating between the cubic and tetragonal phases of zirconia in the 1YTZP product. Because of crystallite size effects, peak broadening obscures any splitting associated with the tetragonal phase. Therefore, to conclusively determine which phase was produced, Raman spectra were taken on samples of dry-pressed powder. Figure 5 illustrates such a spectrum of a 1YTZP product, which exhibits the six vibrational modes associated with the tetragonal phase, not the single mode associated with the cubic phase.³⁶ A seventh mode was attributed to residual organics.

XRF was used to determine impurity concentrations and to verify the level of yttrium doping within synthesized particles. Typical impurities are given in Table I and consist



Fig. 2. Hydrodynamic diameter measurements by dynamic light scattering (DLS) show good dispersion in 10 w/w YTZP suspensions. Differences in primary mode may be attributed to variations in double layer thickness and hydrodynamic diameter with wash solution additive.



Fig. 3. TEM micrographs of (a) undoped zirconia and (b) 1YTZP, both washed with oxalic acid solution, confirm particle sizes measured by BET surface area and XRD peak broadening as between 8 and 10 nm.



Fig. 4. XRD analysis reveals that either the cubic or tetragonal phase is present in as-synthesized 1YTZP. Calculation of particle size from peak broadening using the Scherrer equation yields crystallite sizes between 8 and 10 nm.

of low levels of sodium, magnesium, silicon, phosphorus, and titanium.

A yttrium concentration between 1.5 and 3 mol% is a routine target composition to produce transformation toughening behavior in the final ceramic body.^{2,37} With their procedure, Kimel and Adair¹⁸ were able to produce zirconia containing 1.7 mol% yttria. XRF measurements for batches prepared with a 1.5 mol% yttria initial input indicate a final concentration of between 0.8 and 1 mol%. An advantage of this synthesis technique, however, is that it allows flexibility in composition by simply adjusting the beginning recipe.

(2) Washing and Dispersion

Several previous studies have demonstrated that wet processing routes provide the best possible mechanism for obtaining "bulk" nano-crystalline ceramics because wet processing does not call for extremely high pressures for consolidation as are needed with conventional dry forming techniques.^{38–40} Uncontrolled agglomeration can also be prevented because wet processing routes use the nano-particles in a dispersed state. Traditional dry-powder green forming techniques, widely employed in industry, have also been shown to be useful with nano-scale materials.^{41–44} However, aggregation and poor powder flow characteristics, resulting from a large number of particle–particle contacts and high internal friction, routinely result in inhomogeneities that can compromise both the green and final microstructures.^{17,42,45–47} To recover a material suitable for further processing, either wet or dry, particles should first be well dispersed in a medium free of reaction by-products and spectator ions. With this in mind, wash solution additives were chosen to promote dispersion as well as prevent the loss of yttrium dopant from synthesized particles.

Bicine (N,N-bis(2-hydroxyethyl) glycine) is already present in this material system as a zirconium complexing agent used



Fig. 5. Raman spectrum (using a 785.493 nm laser excitation source) of 1YTZP dry-pressed powder exhibits a pattern verifying the presence of the tetragonal phase with peaks at 145, 268, 314, 463, 604 (shoulder), and $639 \text{ cm}^{-1.44}$ The peak at 418 cm⁻¹ is attributed to residual bicine on particle surfaces.

 Table I.
 Typical Impurity Concentrations (in ppm) Present

 in 1YTZP Samples Washed in Ethanol (Zr-735-E) and Water

 (Zr-735-W and Zr-741)

	Zr-735-E	Zr-735-W	Zr-741
Na ₂ O	0.1	0.2	0.2
MgO	0.3	0.3	0.3
Al_2O_3	0.5	< 0.1	< 0.1
SiO ₂	< 0.1	< 0.1	0.1
P_2O_5	< 0.1	0.1	0.1
S	< 0.1	< 0.1	< 0.1
Cl	< 0.1	< 0.1	< 0.1
K ₂ O	< 0.1	< 0.1	< 0.1
CaO	< 0.1	< 0.1	< 0.1
TiO ₂	0.1	0.2	0.2
MnO	< 0.1	< 0.1	< 0.1
Fe ₂ O ₃	< 0.1	< 0.1	< 0.1
BaO	< 0.1	< 0.1	< 0.1
V	<100	<100	<100
Cr	<100	<100	<100
Ni	<100	<100	<100
Cu	<100	<100	<100
Zn	<100	<100	<100
As	<100	<100	<100
Sn	<200	<200	<200
Pb	<100	<100	<100
Mo	<100	<100	<100
Sr	<100	<100	<100
U	<100	<100	<100
Th	<200	<200	<200
Nb	<300	<300	<300
Rb	<100	<100	<100
Y	11 000	14 000	14 000
	(0.77 mol%)	(0.99 mol%)	(0.99 mol%)

during synthesis.¹⁸ Evidence suggests that during and after precipitation, bicine acts as a protective colloid preventing irreversible agglomeration of newly formed particles.⁴⁸ Also, the branched, flexible structure of bicine may allow it to act as a lubricant among particles during dry compaction.

Oxalic acid, another wash additive, has been shown to be effective in suppressing the leaching of yttrium from YTZP particles.⁴⁹ It has also been shown that adsorbed oxalate ions impart significant surface charge to YTZP particles, which provides an electrostatic barrier to irreversible agglomeration. $^{\rm 49}$

Deionized water was chosen as a control solution. All washes were conducted at a pH of 9, which is a minimum point in yttrium solubility in an aqueous environment.^{25–27} Washed samples were also dispersed in ethanol, adjusted to pH 9, to observe the effect of compressive capillary forces on aggregate strength during drying in a future study. Drying from ethanol, with a lower surface tension than water, was expected to decrease the compressive stress exerted on particles during solvent removal and, therefore, lower the average aggregate strength.

Particle size distributions from dynamic light scattering measurements given in Fig. 2 illustrate the effect of wash solution additive on dispersion. Modes at 26, 32, and 41 nm correspond to the measured size of primary particles of YTZP washed and dispersed in water, bicine, and oxalate, respectively. Modes at 20, 29, and 36 nm correspond to the measured size of primary particles of YTZP washed in water, oxalate, and bicine, respectively, and re-dispersed in ethanol. Variations in mode position may be attributed to differences in double layer thickness.^{34,35,50}

Charged particles in suspension attract counterions of opposite charge to balance the charge and maintain electroneutrality with the surrounding suspension. Counterions may adsorb to particle surfaces and may also congregate around the particle in a diffuse cloud. The former is called the Stern layer while the latter is referred to as the Guoy–Chapman layer. The double layer thickness can be calculated for samples dispersed under different conditions with Eqs. (1) and (2).

As each sample was diluted into pH-adjusted deionized water or ethanol for the particle size measurement, the ionic strength of each sample was around 2.5×10^{-4} mol/L (see Table II). Double layer thickness calculated with Eq. (1) for samples dispersed in water and ethanol was 19 and 11 nm, respectively. Xu⁵⁰ measured particle size shifts between 4 and 8 nm for similar double layer thicknesses. Particle size shift values for YTZP samples are summarized in Table II. In general, the double layer effects are greater for samples containing additives, such as oxalate and bicine. This is not unexpected as a diffuse layer of these ions surrounding a particle represents electrostatic heterogeneities that interact with the light used to interrogate the sample. Samples washed without additives do not contain these heterogeneities, so the measured hydrodynamic radius gives a more representative value of particle size.

Following the recommendation of Xu,⁵⁰ these observations illustrate the need to eliminate double layer effects, either by compression with a high ionic strength medium or by elimination of adsorbing ions, to obtain accurate particle size measurements using dynamic light scattering.

Average agglomeration number, as defined earlier, estimates the average number of primary particles in an agglomerate.³⁰ The packing fraction within an agglomerate can be as low as 0.15 for a flocculated suspension, or as high as 0.74 for close packed spherical particles.³⁰ For random close packing, a value of 0.6 is typically used. Hydrodynamic diameter (D_{DLS}) and equivalent spherical diameter (d_{BET}) should be compared on a volume basis. Dynamic light scattering data are presented as a volume distribution, and the equivalent spherical diameter can be converted from a surface area basis to a volume basis (D_{BET}) with Eq. (7).³⁰

AAN values calculated with measured data are summarized in Table II; if the effect of the double layer on the measured hydrodynamic diameter is taken into account, then actual AAN values for each wash solution are likely to be close to 1. Therefore, good dispersion can be achieved with any of the chosen wash solutions. It should be noted that samples washed in water or bicine solution and dispersed in ethanol display broader particle size modes at larger sizes, which indicate that while primary particles are

Table II. Selected Characteristics of 1Y-ZrO₂ Powder Synthesized by Hydrothermal Precipitation

Sample (YTZP)	Wash treatment	D _{DLS} (nm)	Specific surface area (m ² /g)	d _{BET} (nm)	D _{BET} , Vol-basis (nm)	Particle size shift, D_{DLS} – D_{BET} (nm)	Average agglomeration number
Zr-781-B	Bicine _(aq) wash	29	108	9.2	17.9	11.1	2.5
Zr-781-BE	Bicine _(aq) wash, Dispersed in ethanol	33	124	8.0	15.6	17.4	5.7
Zr-781-O	$Oxalate_{(aq)}$ wash	35	96	10.4	20.2	14.8	3.1
Zr-781-OE	Oxalate _(aq) wash, dispersed in ethanol	29	113	8.8	17.1	11.9	2.9
Zr-781-W	DI water wash	23	124	8.0	15.6	7.4	1.9
Zr-781-WE	DI water wash, dispersed in ethanol	18	132	7.6	14.7	3.3	1.1

Table III. Solution Parameters Used for Calculations of Particle Interaction Energies

	Deionized water, pH 9	Oxalic acid, pH 9	Bicine, pH 9
[H ⁺] (mol/L)	10 ⁻⁹	10 ⁻⁹	10 ⁻⁹
$[OH^{-}] (mol/L)$	10^{-5}	10^{-5}	10^{-5}
[Tetramethyl ammonium ⁺] (mol/L)	4.9×10^{-4}	0.17	2.5×10^{-2}
$[Oxalate^{2-}]$ (mol/L)	_	0.01	_
$\begin{bmatrix} \text{Bicine}^{+/-} \end{bmatrix}$ (mol/L)	_	_	0.01
Conductivity (S/m)	1.4×10^{-3}	0.42	0.8
Ionic strength (mol/L)	2.5×10^{-4}	0.21	4.5×10^{-2}
Zeta potential (mV)	-30	-39	-37

dispersed in the suspension, some degree of agglomeration is occurring.

The degree of dispersion was further evaluated through measurements of zeta potential. Zeta potential determinations permit the calculation of particle-particle interaction energies using modified DLVO theory, which states that the total energy of interaction between two charged particles is the sum of the attractive (van der Waals) and repulsive (electrostatic, steric) energies between them. The Stabil^{\square} computer program²⁴ calculates the total interaction energies and forces based on several different models of interaction geometry. As the particles in question can be approximated as nano-scale spheres, the small ka (<0.5) spherical model was used. Parameters necessary for the calculation, such as lattice parameter⁵¹ and Hamaker constant,²⁸ were taken from the literature as 5.1 Å and 8.8×10^{-20} J, respectively. Particle radius was taken to be 5 nm, and the adsorbed layer thickness was 0.37 or 0.75 nm for oxalate and bicine wash solutions, respectively. Zeta potential was measured, and solution ionic strength was calculated from conductivity data taken during these measurements, which is given in Table III, and equivalent conductivity values for each ionic species taken from the literature.⁵² It should be noted that bicine is a zwitterion with both positive and negative charge at the working pH value⁵³ and, therefore, will not add to the overall conductivity. It should be taken into account, however, in calculating solution ionic strength.

The interaction energy curves calculated for YTZP in the three wash solutions are given in Fig. 6. For a suspension to maintain good dispersion, a positive energy barrier greater than thermal energy (approximately 3–4 kT) should exist among suspended particles. In the YTZP–water system, this energy barrier exists, indicating that particles will tend not to agglomerate if they collide. For nano-scale particulates, even steric barriers as small as those provided by the bicine (0.75nm) and oxalate (0.35 nm) provide an electrosteric barrier to agglomeration by truncating the short range van der Waals interactions at a distance of twice the diameter of the adsorbed molecule. In the YTZP–oxalate and YTZP–bicine systems, there are no positive energy barriers, indicating a net attraction between particles, but there is a finite energy minimum provided by the oxalate and bicine adsorbed

Total Interaction Energy Summary, 10nm YTZP



Separation Distance (nm)

Fig. 6. The Stabil[©] computer $\operatorname{program}^{24}$ was used to calculate interaction energy curves for YTZP washed in pH 9 deionized water, pH 9 0.01*M* bicine solution, and pH 9 0.01*M* oxalic acid solution. Repulsive and attractive energies are added to compute the total interaction energy based on the spherical particle model. YTZP washed with oxalate solution and dispersed in water displays the greatest energy barrier to agglomeration due to the high zeta potential and low ionic strength. The inset illustrates a steric barrier to agglomeration when the energy curve ends at a distance of twice the diameter of the adsorbed organic molecule (bicine or oxalate).

layers, illustrated in the inset of Fig. 6. Thus, the size of the adsorbed oxalate ions and bicine molecules on the 10 nm diameter provides electrosteric dispersion even though no net repulsive energy barrier is present.

The value of α reflects the likelihood that two particles will collide with enough energy to overcome the repulsive energy barrier and come to a separation distance where the attractive van der Waals interactions dominate the overall particle interactions. The α value is calculated as the ratio of the attractive energy (integrated over the separation distance between two particles) to the total energy (also integrated over the separation distance between two particles). As noted



Fig. 7. The Stabil[©] computer program²⁴ was used to calculate the probability of agglomeration based on the total interaction energy and attractive interaction energy curves. The agglomeration probability, α , is the likelihood that two particles will collide with enough energy to come to a separation distance where the attractive van der Waals interactions dominate. YTZP washed in water and dispersed in water or oxalic acid at pH 9 display the lowest aggregation probability.

in Fig. 7, the aggregation probability is highest for YTZP particles washed and dispersed in oxalic acid and bicine solutions, 0.90 and 1.0, respectively; α is lowest for YTZP particles washed and dispersed in DI water or washed in DI water and dispersed into oxalic acid solution, 0.09 and 0.06, respectively.

From these calculations, it is apparent that both the YTZP-water and YTZP-bicine systems promote dispersion. However, under these conditions, leaching of dopant is not prevented.⁴⁹ The major drawback of the YTZP-oxalate system is its ionic strength, which is the greatest of the three wash solutions. Particles in this system exhibit the greatest zeta potential; however, a high ionic strength medium compresses the double layer surrounding the charged particles, thus decreasing the repulsive energy between them. By decreasing the ionic strength, surface charge compensation by counterions extends further into the surroundings, thus increasing the double layer thickness and the repulsive energy barrier, as illustrated in Fig. 6. Therefore, to simultaneously prevent dopant leaching and promote dispersion, YTZP particles were first washed in pH 9 oxalic acid and dispersed in the final step into pH-adjusted deionized water.

IV. Conclusions

By modifying a hydrothermal technique, crystalline, 8-10 nm, tetragonal 1YTZP has been produced with a low impurity content and a yield as high as 100 g/L. The crystal structure was established with XRD and Raman spectroscopy, and the particle size was confirmed using dynamic light scattering, BET surface area measurements, TEM observations, and XRD peak broadening. The enhanced tendency for agglomeration in high-yield batches was successfully suppressed by the bicine protective colloid. An effective washing and dispersion procedure was identified in which precipitated suspensions were washed with aqueous oxalic acid, pH adjusted to a value of 9, and dispersed in the final step into pH-adjusted deionized water. The effect of double layer thickness on measurement of hydrodynamic radius using dynamic light scattering was discussed. Taking into account double layer effects on the measured particle size, AAN values are near unity, indicating good dispersion with this procedure. Interaction energy curves based on DLVO theory were calculated to illustrate the observed dispersion behavior.

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