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Ultrafine microsphere particles of zirconium titanate produced by homogeneous dielectric-tuning coprecipitation*

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Zirconium titanates are widely used in electrical (common microwave dielectrics) and optical devices as well as in bifunctional catalysis and structural ceramics. In this paper, ultrafine amorphous solid microsphere precursor particles of zirconium titanate ($Zr_xTi_{1-x}O_2$) with possibly tailored intraparticle nanostructure (i.e., nanosized pores) were synthesized by a "dielectric-tuning" solution coprecipitation method, in which inorganic salts were dissolved in a simple water-alcohol mixture and homogeneous nucleation and growth of particles were then induced by heating at temperatures below 100°C. Near-monodispersed particles were obtained. Particle sizes (nanometers to a few micrometers in diameter) were controlled by adjusting the process parameters such as salt concentration, alcohol-to-water volume ratio, temperature, and heating time. Nanosphere particles were produced with a rapid microwave heating nucleation-control scheme. Transmission electron microscopic analysis of each individual microsphere indicates that uniform nanostructures (a few nanometers in pore size) as well as compositional homogeneity (in terms of the Zr/Ti ratio) have been obtained inside each amorphous microsphere. *In situ* high-temperature X-ray diffraction data show that no phase segregation was observed in as-preprared microspheres and the transition from amorphous to the single-crystalline $ZrTiO_4$ phase occurred around 650°C for a composition of Zr/Ti = 1. Interestingly, thermal analysis (DTA/TGA) data indicate that the solution synthesis condition seems to affect the crystallization activation energy and onset temperature, which varies from 530 to 680°C. © *2003 Kluwer Academic Publishers*

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1. Introduction

Zirconium titanate (ZT)-based ceramic materials (in the form of solid solutions) have many unique properties: high resistivity, high dielectric constant (thus providing high charge storage capacity), high permittivity at microwave frequencies, and excellent temperature stability of microwave properties [1, 2]. These materials have an extremely wide range of applications such as in microwave telecommunications (as capacitors, dielectric resonators in filters and oscillators) and in catalysis (as effective acid-base bifunctional catalysts and photocatalysts) [3, 4]. In the form of thin films, they also find advanced applications in piezoelectric sensors, transducers, ultrasonic motors, hydrocarbon sensors, integrated microwave devices, refractory materials, high-temperature pigments, composites for high-temperature corrosive environments, and thin-film optics [5–9]. In addition, ZT powders (crystalline $Zr_xTi_{1-x}O_4$) can be good precursor materials for the synthesis of other valuable electroceramics such as lead zirconate titanate (PZT) or lanthanum doped PZT (PLZT) [10, 11]. PZT is the electroceramic material most widely used in industrial applications as actuators and transducers.

As is true for many other materials, ultrafine-grained, high-quality powders of ZT are in great demand. Fine powders are necessary precursors for making monolithic ceramics via casting as well as ceramic films via a coating process. For such a binary (two-metal-elements) oxide system, compositional homogeneity and microstructure uniformity (low or no phase segregation) are very important. It is well known that powder characteristics (such as particle size, shape, size distribution, agglomeration, crystallite size, and chemical and phase composition) determine, to a large extent, the microstructures developed during sintering and thus affect the properties of ceramic materials [12, 13]. On the other hand, it is necessary to use fine and single-phase ZT powder to obtain fine and sinterable PZT powders by the partial oxalate method [14].

Various chemical solution synthesis methods have been developed as alternatives to the conventional solid-state-reaction route in order to obtain high-purity and more homogeneous materials. The solid-state reaction normally requires high temperatures (1200–1700°C) over a prolonged period for the homogeneous materials synthesis from the mixed crystalline ceramic oxides ZrO_2 and TiO_2 [9, 15–17] and also requires posttreatment such as energy-intensive grinding/milling procedures for powder formation. Still, this process usually leads to inhomogeneous, coarse, and multiphase powders of poor purity [18]. Amorphous precipitates or precursor gels are usually produced through chemical solution routes, which are characterized by their unparalleled ability to generate ultrafine, high-purity, and stoichiometric ceramic powders at low processing temperature. Pure oxide materials can be obtained by thermal processes of dehydration and crystallization of precursor precipitates, gels, or particles. Several major wet-chemical routes that have been studied for synthesis of ZT materials include the following:

1. *Sol-gel processes*: In classical hydrolytic sol-gel procedures (i.e., simultaneous hydrolysis of metal alkoxides and modified alkoxides), metal alkoxide or modified alkoxide salts are dissolved in an alcohol to prepare a precursor gel, which is then dried, calcined, and ground to fine powder [9, 18–24]. ZT powders have also been prepared via sol-gel processing of reactive hydroxoperoxo compounds [16, 17, 25, 26]. In this process, titanium tetrachloride and zirconyl chloride are mixed in anhydrous methanol at room temperature and then mixed with aqueous hydrogen peroxide, followed by the chemical precipitation of gels $[MO(O_2)(H_2O)_x$ $(M = Ti, Zr;\ x > 2)]$ via slow addition of aqueous ammonia solution. Use of hydrogen peroxide seems to improve coprecipitation and also decrease the crystallization temperature of amorphous precipitated gels. In another sol-gel procedure, the ZrO_2 and TiO_2 sols are actually produced by inhomogeneous chemical precipitation using inorganic salt precursors and then peptized with mineral acid [27–29]. Microfibers [27] and microspheres [28] have been produced by this procedure. Nonhydrolytic sol-gel processes for preparing ZT have also been published [18, 30, 31].
2. *Synthesis from metallorganic salts*: Hydrazine carboxylate dihydrate of zirconium and titanium and their solid solution $[ZrTiO_2(N_2H_3COO)_4{\cdot}4H_2O]$ have been prepared as precursors to fine $ZrTiO_4$ particles [32, 33]. The fine-particle formation was achieved via low-temperature (<300°C), autocatalytic exothermic decomposition of the precursors.
3. *Chemical precipitation and coprecipitation of metal salts from aqueous solutions*: Ikawa *et al.* [34, 35] achieved coprecipitation of $Zr(SO_4)_2$ and $Ti(SO_4)_2$ using concentrated ammonia water. Krebs and Condrate [36] used chloride salts in the preparation of solutions, which were then precipitated by addition of ammonium hydroxide. Leoni *et al.* [1] produced ZT nanopowders in a very simple way by chemical precipitation of an aqueous solution of $TiCl_4$ and $ZrOCl_2$ using ammonia. Composite gel particles have also been prepared by chemical processing of anatase as the inner core (10–25 nm) coated with *in situ*–precipitated amorphous zirconia as the outer core, which was obtained from controlled hydrolysis of zirconyl chloride using ammonia at $pH = 9–10$ [37].
4. *Mixed-cation oxides via thermal decomposition of polymeric precursors* (the classical Pechini method): Lessing [38] has given an excellent review of this method for preparation of mixed-cation oxide ceramics. Various groups have attempted to employ the method specifically for synthesis of ZT (e.g., [2, 8, 14, 38–40]. This method is based on chelation or complexation of multiple cations by a hydroxycarboxide acid such as citrate or oxalate. Typical preparation involves dissolution of salt(s) in a mixture of citric acid and ethylene glycol, gel formation by heat (90–100°C) and complete water elimination, and then polymeric precursor formation through the polyesterification reaction by long-time aging at moderate temperatures (130–140°C) in an oven. Agglomerated ceramic powders are then produced by thermal decomposition or calcination at temperatures greater than 800°C. The greatest

advantage of this method is the achievement of random/homogeneous distribution of cations (at the atomic level) in an amorphous polymer solid, which reduces phase segregation after calcination. However, powders produced by this method are usually irregular in shape, strongly agglomerated (because of the thermal decomposition step), and widely distributed in size.

5. *High-energy ball milling*: Stubicar *et al.* [41] synthesized $ZrTiO_4$ oxide powder by ball milling an equal molar powder mixture of ZrO_2-TiO_2 and post-anneal processing. A fully amorphous structure appeared during ball milling and requires further thermal processing for crystallization.

Among the aforementioned synthesis routes, few could produce ultrafine ZT powders containing aggregation-free, monodispersed microsphere particles. Some routes such as the classical sol-gel process [9, 20–22] and some polymeric precursor methods [14] involve the use of expensive metal alkoxide salt(s) or commercially unavailable metallorganic salts. Most routes, such as gel-forming via precipitation or polymeric precursor methods, still require the undesirable procedure of grinding dried gels into powders with no control of particle shape. Irregular-shaped powdered ceramic particles are difficult both to handle and to use on an industrial scale, and thus spherical particles are preferred for the many distinct advantages they offer [27, 28]. The submicron spherical ZT particles reported by Hirano *et al.* [20], obtained by controlled hydrolysis of metal alkoxides, are agglomerated. Only one paper has been identified so far that describes the production of dispersed, sphere-shaped ZT particles [28]. However, the size of the reported "microspheres" was in the range of 15–50 μm, which is quite large for applications that require ultrafine particles (i.e., submicron to a few micrometers in diameter). Higher densities achievable using finer powders can result in sintered ceramic bodies with a higher dielectric constant [19]. The objective of our work is to investigate a methodology that allows the production of such ultrafine-sized dispersed microspheres and nanospheres.

Recently, a homogeneous precipitation methodology termed *dielectric-tuning solution synthesis* (DTS) has been studied using inorganic salts in a mixed alcohol-water solution. In principle, the dielectric property of the solution and, thus, the solubility of the hydrolyzed metal species as well as the nucleation and growth of particles can be tuned by varying the alcohol content in the mixed solution and the solution temperature. The dielectric-tuning precipitation approach has proven successful in producing ultrafine monodispersed microspheres of single oxide precursor materials such as zirconia and titania [42–45]; however, this technique has never been attempted for producing multiple oxide materials. Production of barium titanate (a binary oxide material) by single-step dielectric-tuning coprecipitation of mixed barium and titanium salt solution was proven unfeasible due to the differences in salt precipitation/crystallization behavior, which caused phase segregation and inhomogeneity in the precipitates. Hu *et al.* reported a new approach to synthesizing nanocrystalline monodispersed microspheres of barium titanate by a two-step process: DTS synthesis of titania microspheres plus low-temperature hydrothermal conversion [46, 47].

In this paper, we explore the applicability of the dielectric-tuning method for producing microspheres of another binary oxide material (i.e., ZT). The present work demonstrates that the single-step, low-temperature dielectric-tuning *coprecipitation* has produced high-quality ZT powder products—monodispersed microspheres containing homogeneous composition (with no crystalline phase segregation) and uniform amorphous nanopore structures. In addition, preliminary results from microwave hydrothermal experiments indicate a potential method for effective, controlled synthesis of ZT nanosphere particles. Because the ZT precursor particles generated via solution or sol-gel synthesis as described above are generally amorphous, thermal annealing processes need to be applied to convert the material into the desirable crystalline powder. *In situ* high-temperature X-ray diffraction (HTXRD) and thermal analysis (differential thermal analysis/thermal gravimetric analysis, TGA/DTA) were utilized to study the crystallization process from amorphous powders, in addition to other characterizations such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Single-phase ZT powders were obtained at relatively low calcination temperature.

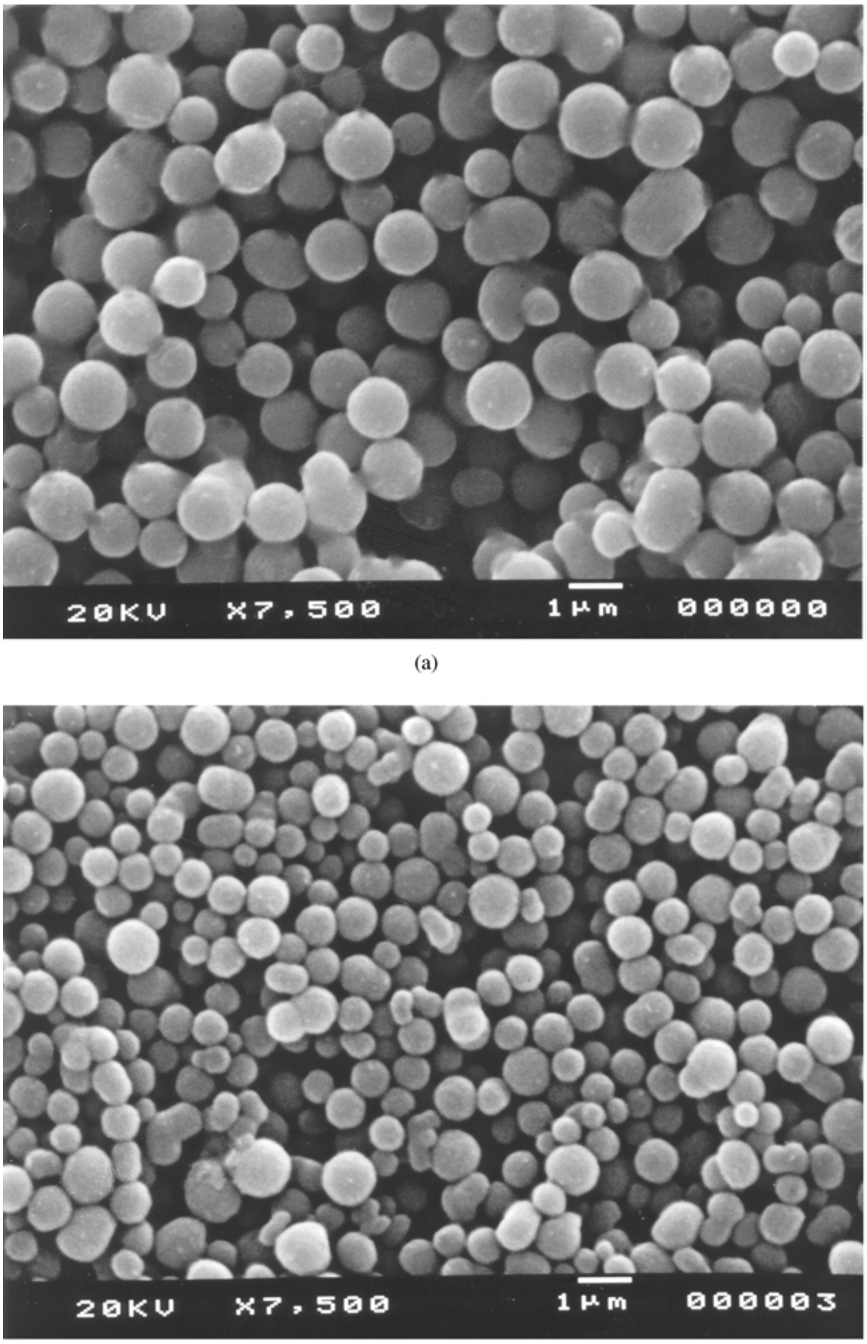
2. Experimental

2.1. Solution preparation

Titanium tetrachloride (5.56 mL of $TiCl_4$ 99.6%, Alfa Aesar, Ward Hill, MA) was slowly added to ice-cold aqueous HCl solution (2.85 mL of 1.0 N HCl added in approximately 20 mL deionized distilled water) that was constantly stirred in a 50-mL volumetric flask. The acidity is needed to minimize the explosive generation of orthotitanic acid [$(Ti(OH)_4$]. The final concentration of $TiCl_4$ was made up as 1.0 M. The stock solution was freshly prepared and usually left overnight before use. Stock solutions for zirconyl chloride (1.0 M, $ZrOCl_2$ 99.0%, EA Science)) and hydroxy propyl cellulose (HPC, 0.1 g/cm^3) were also prepared for convenience in conducting multiple experiments.

2.2. Titania microsphere synthesis

The titania synthesis procedure was slightly modified from the one developed previously [46, 47]. Routinely, a sample mixture contains 0.05–0.2 M $TiCl_4$, 0.002 g/cm^3 HPC, and isopropyl alcohol. It was found that an *RH* ratio (i.e., the volumetric ratio of isopropyl alcohol to the aqueous part) of 3 yields the best results in the growth of the titania microspheres. The HPC was used to enhance the dispersion of microsphere particles. The mixture was kept in a 40-mL tightly sealed glass vial and incubated at 100°C for 24 h. After the growth of the microspheres, the milky suspension was then cooled with cold water to room temperature ($\sim$22°C). The suspension was then neutralized with drops of 5 N NH_4OH under constant stirring with a magnetic stir



(a)

(b)

Figure 1 SEM photographs of ultrafine microspheres of single oxide precursor particles. (a) ZrO_2 particles. Conditions: $[ZrOCl_2] = 0.1$ M, $RH = 3/1$, $T = 100°C$, $t = 24$ h, HPC $= 2.0 \times 10^{-3}$ g/cm^3. (b) TiO_2 particles. Conditions: $[TiCl_4] = 0.1$ M, $RH = 3/1$, $T = 100°C$, $t = 24$ h, HPC $= 2.0 \times 10^{-3}$ g/cm^3.

bar. Neutralization was required due to the fact that microspheres tend to dissolve into the deionized water during the washing and centrifugation processes. Sample washing with deionized water removes chloride and ammonia.

2.3. Zirconia microsphere synthesis

The procedure for dielectric-tuning synthesis of zirconia was reported in detail previously [42]. In this work, conditions were similar to those used for synthesis of titania. This single-metal oxide particle synthesis serves as a control for the binary oxide (ZT) particles as described below.

2.4. Synthesis of ZT microspheres

A 30-mL mixture containing zirconyl chloride, titanium tetrachloride, HPC, filtered deionized water, and isopropanol was kept in a 40-mL, screw-capped glass vial. The mixed solution was then incubated for a predetermined amount of time at 100°C in order to produce ZT microspheres. The conditions controlled for the ZT synthesis were salt concentrations (C) 0.025–0.2 M $ZrOCl_2$ and 0.025–0.2 M $TiCl_4$, volume ratio of isopropanol over aqueous solution (*RH*) from 1 to 5, HPC concentration fixed at 0.002 g/cm^3, the heating temperature (T) typically at 100°C, and incubation heating time (t) varying from 15 min to 24 h. Equal molar concentrations of zirconyl chloride and titanium tetrachloride were used to prepare each ZT sample. To stabilize the microspheres, the ZT particle suspension was routinely neutralized with 5 N NH_4OH before washing with deionized water (twice).

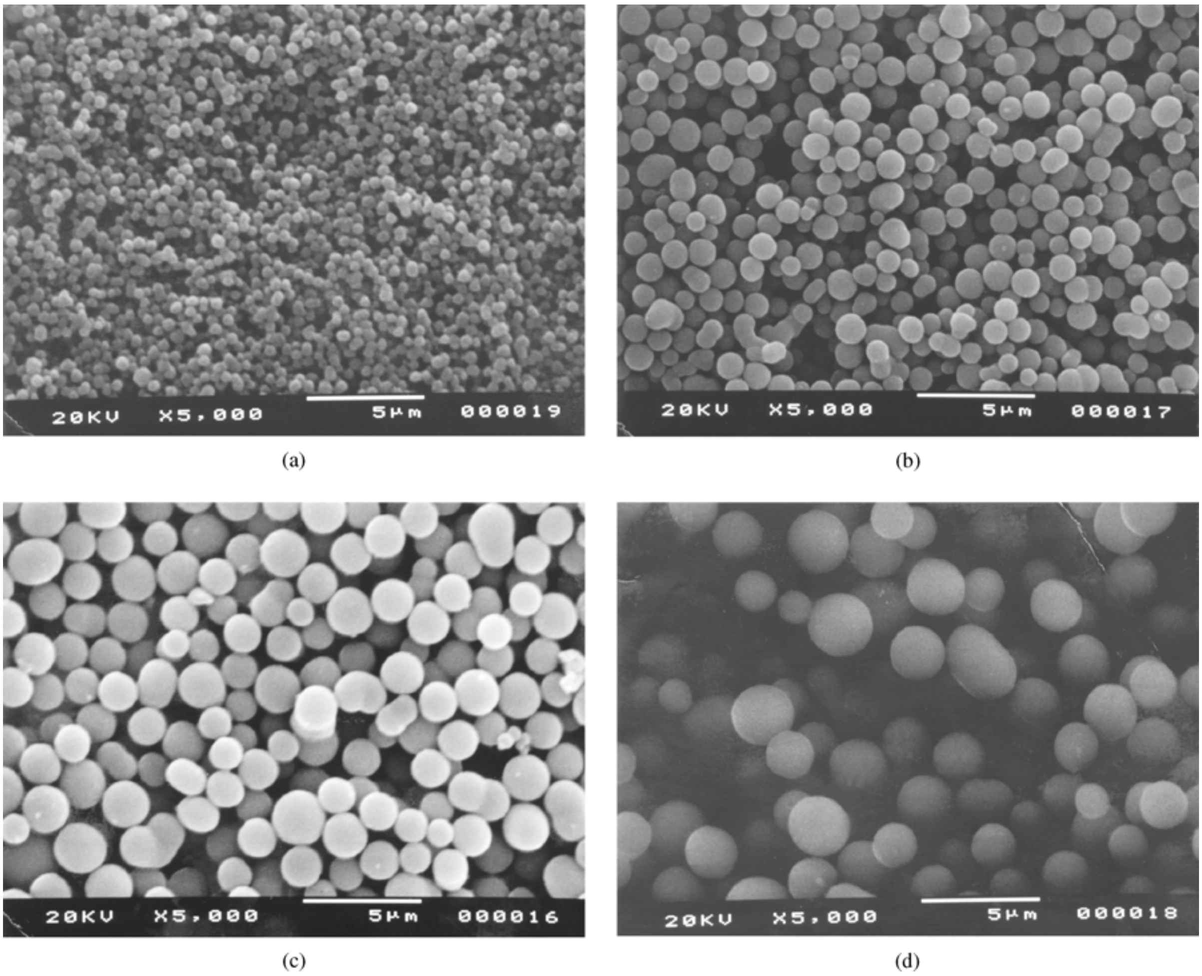
2.5. Characterization of particle samples

The evolution of particle size and morphology with reaction time was analyzed by SEM (JSM-T220A, JEOL) in which the particles were spread and air-dried on conductive carbon tape that was attached to a cylindrical brass stub. The particles on the stub were plasma coated with gold (Hummer 6.2 sputtering system, Anatech LTD) for 3–4 min in preparation for SEM imaging. Room-temperature X-ray diffraction (RTXRD, Scintag) was used for phase identification and analysis of crystallite size in the oxide powder samples. The crystallization process of the amorphous powders and the phase transformation in the temperature range of 27 to 1200°C were monitored in real time by a HTXRD (for detailed instrument description, see [48]). Complementary DTA/TGA was also performed (alumina crucible, sample weight 100 mg) using the following conditions: heating rate, 5°C/min; peak temperature, 1250°C; and air flow, 100 cm^3/min. Specific surface areas of dried powder samples were analyzed using a nitrogen adsorption analyzer (Micromeritics, Atlanta, GA).

3. Results and discussion

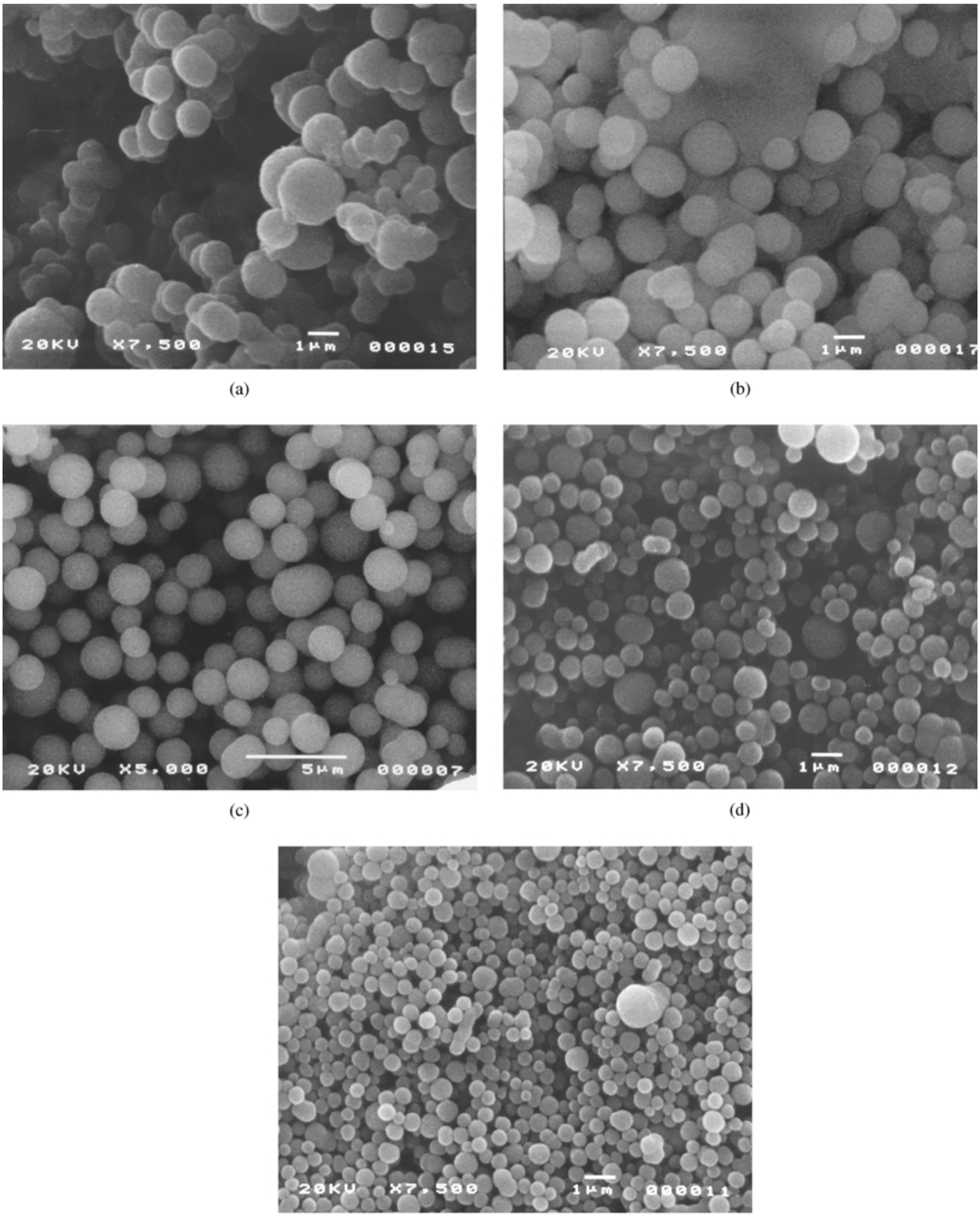
Single oxide precursor particles for zirconia and titania, which were used as a control test, are shown in Fig. 1. The dielectric-tuning precipitation method has previously proven successful for the production of single-metal oxide precursor particles [42, 44, 45]. However, the objective of this work is to determine if such a method can apply to the synthesis of binary metal oxides, in particular the production of ultrafine ZT precursor particles. It is unknown if inhomogeneous composition or crystalline-phase segregation can occur during coprecipitation of mixed salts, due to different precipitation/crystallization kinetics.

The process parameters for ZT synthesis include initial metal salt concentration (C, Zr/Ti molar ratio fixed at 1), isopropanol content in solution (*RH* ratio, a volume ratio of alcohol to aqueous solution), temperature (T), incubation heating time (t), and HPC concentration (fixed at 2.0×10^{-3} g/cm^3 for use in this study). Results shown in Fig. 2 clearly demonstrate that near-monodispersed microspheres of binary oxide (ZT) precursor particles can be produced when both zirconium chloride and titanium tetrachloride are mixed at equimolar concentrations in the initial synthesis solutions. The significant effect of the initial metal ion concentration in mixed solutions on the particle size is also shown in Fig. 2. With increases in metal salt molar concentration from 0.025 M to 0.2 M, the



(a) (b) (c) (d)

Figure 2 Near-monodispersed microspheres of binary oxide (ZT) precursor particles showing the effect of metal salt concentration on particle size. Conditions: $RH = 3/1$, $T = 100°C$, $t = 24$ h, HPC $= 2.0 \times 10^{-3}$ g/cm^3. (a) $C = 0.025$ M. (b) $C = 0.05$ M. (c) $C = 0.1$ M. (d) $C = 0.2$ M.

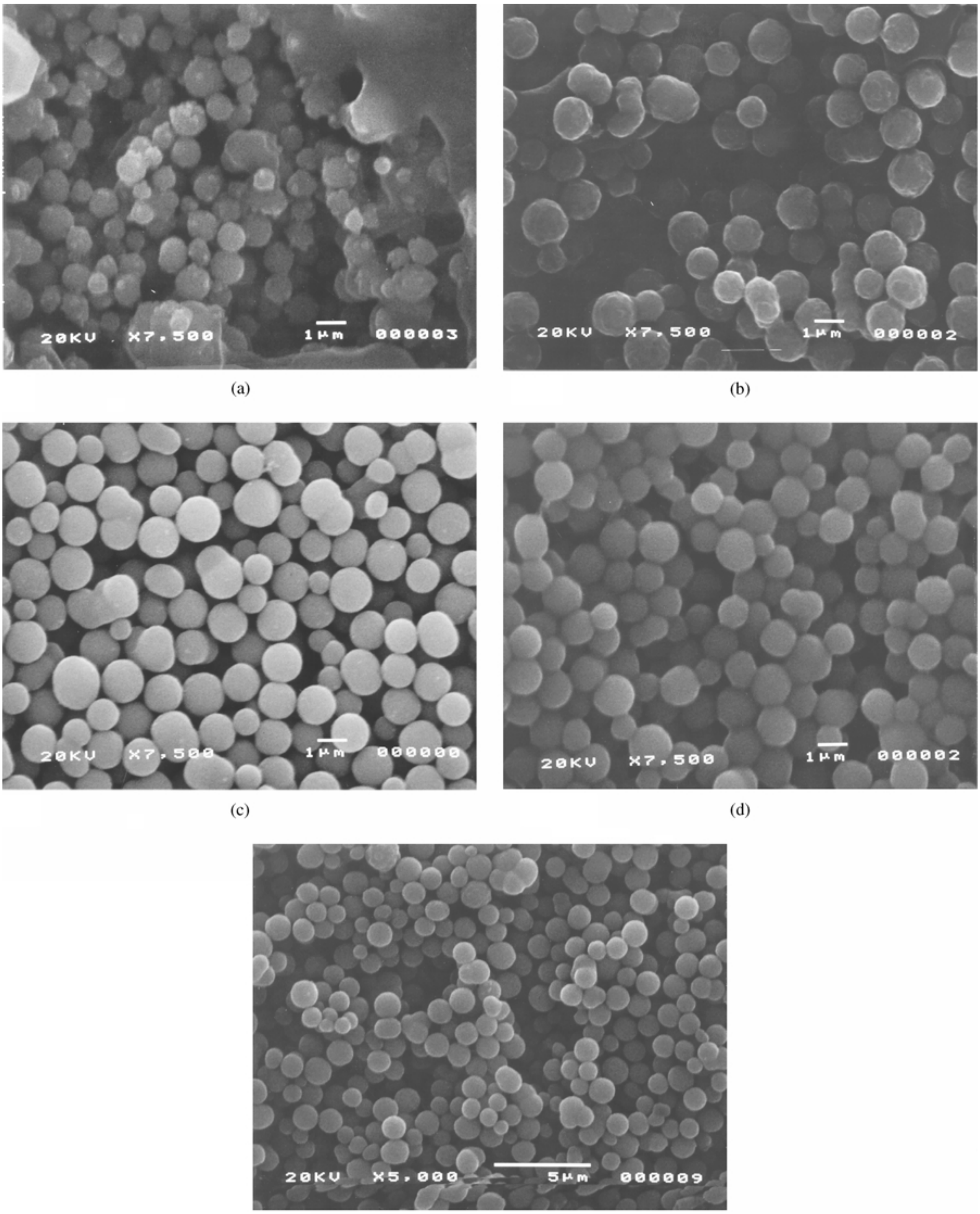


(a) (b) (c) (d) (e)

Figure 3 Effect of alcohol volume fraction (*RH* ratio) on ZT particles. Conditions: $C = 0.1$ M, $T = 100°\mathrm{C}$, $t = 24$ h, HPC $= 2.0 \times 10^{-3}$ g/cm^3. (a) *RH* = 1/1. (b) *RH* = 2/1. (c) *RH* = 3/1. (d) *RH* = 4/1. (e) *RH* = 5/1.

ZT-precursor particle size increased from submicrometer range to a few micrometers in diameter (Fig. 2). In addition, the *RH* ratio affects not only the size of particles but also their agglomeration state (Fig. 3). At a low *RH* ratio (1/1), particles show wide size distribution and are somewhat agglomerated (with an observed neck connection between microspheres). With higher *RH* ratios (up to 5/1), the particles obtained tend to become smaller and better dispersed.

The SEM images in Fig. 4 show the evolution of particles with incubation heating time. The particles seem to be further aged/densified with longer incubation time. At $t = 0.5$ h reaction time, the particles look like embryos that are soft, loosely packed microspheres, while some hydrolyzed metal salt species are not yet ready to be packed into microspheres. At a later time ($t = 1.5$ h), the microspheres are somewhat aggregated and gel-like. The wrinkled surfaces of the microspheres are likely due to the shrinkage of low-density gel particles with drying. After sufficient time (>3.5 h), dense and well-dispersed microsphere particles are formed. Although discrete particles were observed within a few hours of heating, the conversion yield (here defined as the percentage of metal ions converted into a



(a) (b) (c) (d) (e)

Figure 4 Kinetic process of ZT microsphere evolution with reaction time. Conditions: $C = 0.1$ M, $RH = 3/1$, $T = 100°\text{C}$, HPC $= 2.0 \times 10^{-3}$ g/cm^3. (a) $t = 0.5$ h. (b) $t = 1.5$ h. (c) $t = 3.5$ h. (d) $t = 6$ h. (e) $t = 24$ h.

microsphere mass), as shown in Fig. 5, indicates that it requires a much longer period of time (approximately a day) to complete the reaction when the initial molar concentrations of zirconium and titanium are 0.05 M.

The RTXRD spectrum for a typical as-prepared ZT powder is shown in Fig. 6. The general "hump" of the spectrum indicates the amorphous nature of the particles. Further, variation of the *RH* value from 1/1 to 5/1 does not change the shape of the spectrum or the amorphous nature of the particles. *In situ* time-resolved high-temperature XRD (HTXRD) measurements provided information on the evolution and kinetics of the crystallization of the amorphous ZT precursor particles into crystalline powders (Fig. 7). Again, we can see that the as-prepared ZT microsphere particles (at temperatures $<\sim 600°\text{C}$) were amorphous and did not contain any segregated phases such as monoclinic/tetragonal zirconia or anatase/rutile titania. This indicates that the zirconium and titanium salt precursors were converted into a pure amorphous

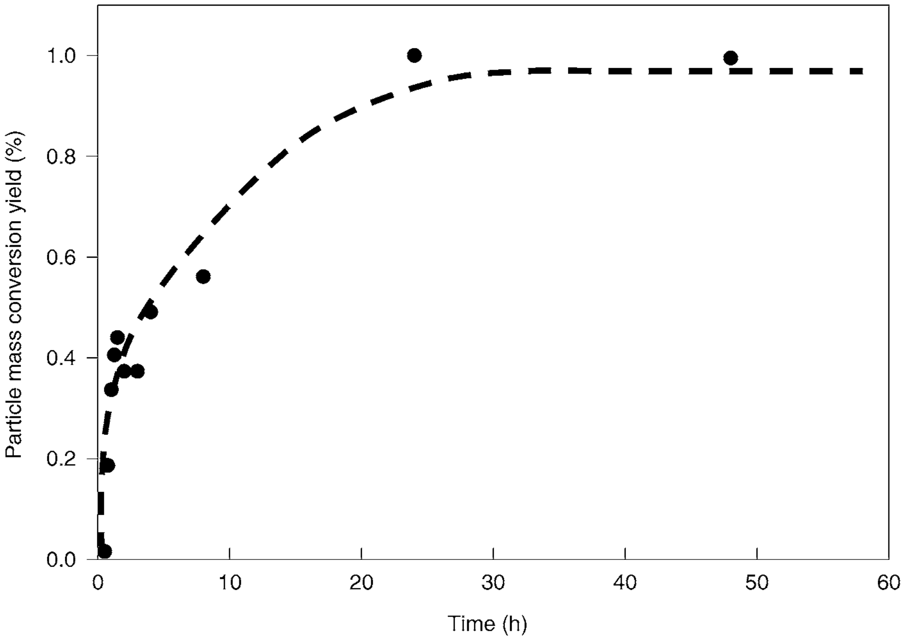


Figure 5 Conversion yield from metal ions into ZT microsphere solid mass at various times. Conditions: $C = 0.05$ M, $RH = 3/1$, $T = 100°C$, HPC = 2.0×10^{-3} g/cm^3.

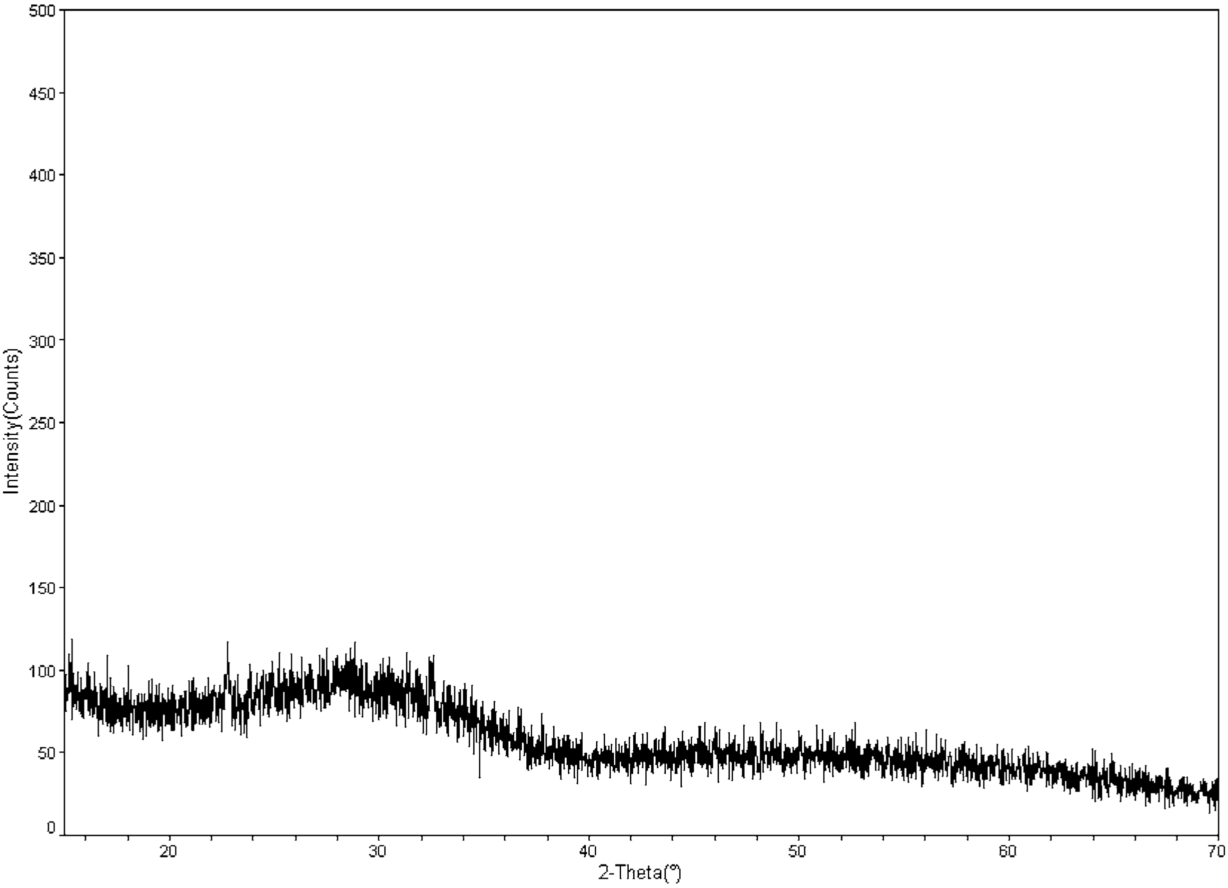


Figure 6 A typical RTXRD spectrum of as-prepared ZT microsphere particles. Sample preparation conditions: $C = 0.1$ M, $RH = 1/1$ to $5/1$, $T = 100°C$, $t = 24$ h, HPC = 2.0×10^{-3} g/cm^3. SEM images are shown in Fig. 3.

ZT compound during the single-step dielectric-tuning coprecipitation.

HTXRD data (Fig. 7) show that crystallization from amorphous precursor particles occurred around 600°C, which agrees well with earlier reported values for amorphous ZT materials from sol-gel synthesis [9], from a polymer precursor route [2], and from high-energy dry ball milling of equal molar ZrO_2-TiO_2 powder mixture [49]. Single-phase $ZrTiO_4$ (orthorhombic, P*bcn* 60, disordered form, JCPDS 34-0415, lattice parameters: $a = 0.5035$, $b = 0.5487$, and $c = 0.4801$) evolved when the sample powder was heated up to ~600°C and also remained after the sample was cooled to room temperature (27°C). It is generally believed that the cations

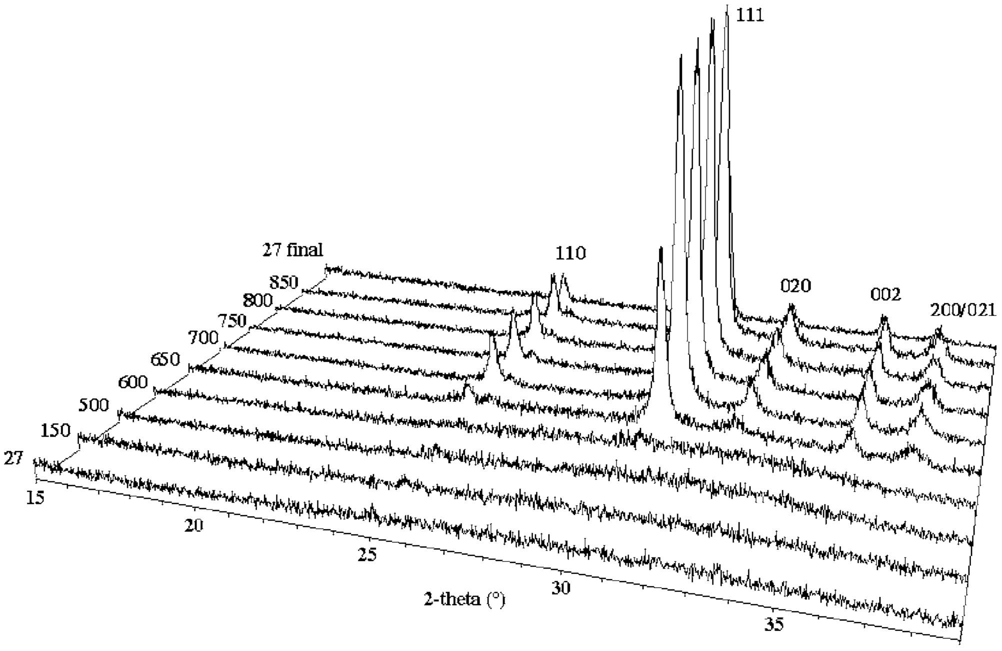


Figure 7 HTXRD spectra during *in situ* calcination of ZT microsphere particles. Sample preparation conditions: $C = 0.2$ M, $RH = 3/1$, $T = 100$°C, $t = 24$ h, HPC $= 2.0 \times 10^{-3}$ g/cm^3. Above ~600°C, peaks characteristic of single $ZrTiO_4$ phase are present.

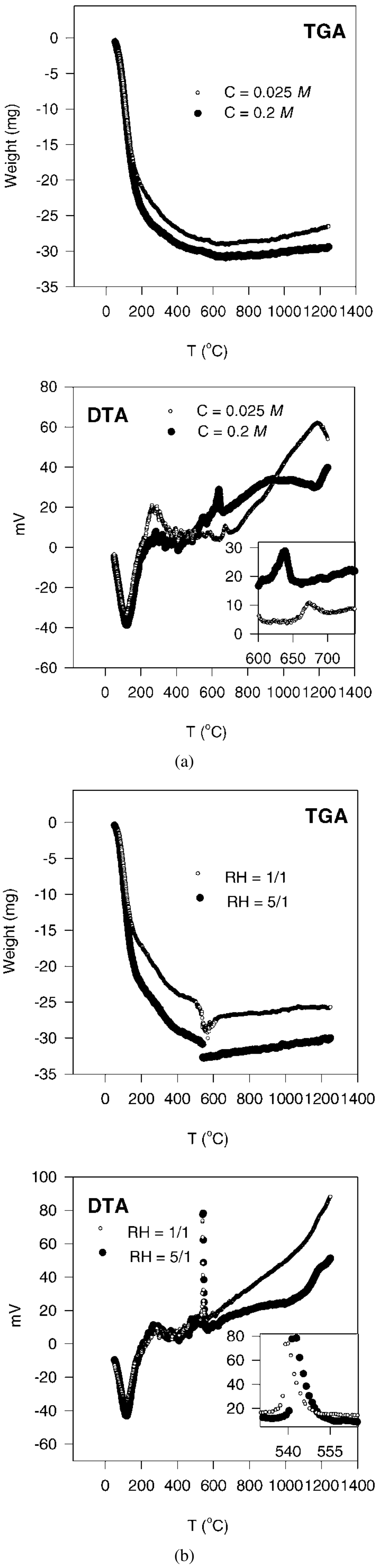
Zr^{4+} and Ti^{4+} are randomly distributed within the lattice. Based on the phase diagram of the system TiO_2-ZrO_2 [50], both baddeleyite and ZT solid solution are expected at room temperature for Zr/Ti = 1:1; however, we confirmed that no monoclinic zirconia is present in the sample. The HTXRD crystallization evolution spectra are similar for ZT powders from both synthesis concentrations (0.025 and 0.2 M).

DTA/TGA data for samples obtained from various conditions are shown in Fig. 8a and b. The TGA plots show that slower coprecipitation rate conditions (i.e., at lower salt concentration and lower *RH*) seem to generate less hydrated amorphous materials (and less shrinkage and weight loss). The large endothermic peak in the DTA plots (below 200°C) can be ascribed principally to water elimination from the pores of the particles. The exothermic peak around 200–400°C (and some smaller peaks up to ~500°C) could be due to the progressive removal of water molecules bonded into the pores of the solid plus the elimination of alcohol coupled in the particle during the coprecipitation. The significant sharp exothermic peak exhibited at temperatures varying from 530 to 680°C, depending on the concentration and *RH* (see inserts of DTA plots in Fig. 8), corresponds to the crystallization temperature from amorphous to $ZrTiO_4$ orthorhombic crystal. The lowest crystallization temperature for our samples was around 530°C. It is known that chemical processing influences the thermal crystallization behavior of ZT materials. Navio *et al.* [16, 17, 25] found that the formation of peroxo species of Ti and Zr seems to enhance the crystallization of $ZrTiO_4$ at a lower temperature, possibly because the peroxo bonding is broken easily after the thermal treatment. In our work, the shifts in crystallization peak clearly indicate that synthesis conditions (initial salt concentration and the *RH* ratio) affect the crystallization temperature significantly. Increasing the initial salt concentration caused a drop of the crystallization temperature from 675 to 630°C. Such crystallization temperature may be determined by the degree of hydration and the short-range order of the amorphous materials.

Using DTA, Macias *et al.* [26] has conducted a careful kinetic study of crystallization in ZT from an amorphous precursor (hydroxoperoxo compound of Zr and Ti) precipitated by ammonia from titanium or zirconium methanol solutions containing hydrogen peroxide. The same crystallization kinetics model they used should apply to crystallization of other amorphous materials such as those obtained by dielectric-tuning coprecipitation. The reaction rate of a solid-state transformation, obeying a nucleation and growth process, should follow the Johnson-Mehl-Avrami (JMA) kinetic model. The simplified model with Doyle's approximation can be written as

$$\ln\left[\ln\frac{1}{1-\alpha}\right] = n\ln\frac{AE}{\beta R} + 5.33n - 1.05\frac{nE}{RT}$$

where α is the reacted fraction, n is a parameter depending on the crystallization mechanism, A is the Arrhenius preexponential factor, E is the activation energy, β is the heating rate, R is the gas constant (= 8.3143 J K^{-1} mol^{-1}), and T is the absolute temperature. A plot of $\ln[-\ln(1-\alpha)]$ vs. $(1/T)$ should be a straight line of slope nE. For the ZT crystallization reaction from precursors, Macias *et al.* [26] determined that $n = 1.02$, which was explained by considering an agglomerated system constituted of a constant number of small particles as nuclei. In such a system, the rate of crystallization is controlled by random nucleation. Using the same method with the data shown in Fig. 8, we determined the activation energy E for our samples: 323 kJ/mol (for $RH = 5/1$), 290 kJ/mol (for $RH = 1/1$), 174 kJ/mol (for $C = 0.2$ M), and 139 kJ/mol (for $C = 0.025$ M). There seems to be a general trend of increase in activation energy with increasing *RH* and solution concentration



(a)

(b)

Figure 8 TGA/DTA analysis of ZT samples from various conditions. (a) Varying concentration from 0.025 to 0.2 M. (b) Varying *RH* from 1/1 to 5/1.

TABLE I Effect of *RH* ratio on specific surface areas and pore sizes in as-prepared ZT powder

Conc. C (M)	*RH* ratio	Surface area (m^2/g) (BET multipoint)	Surface area (m^2/g) (Langmuir)	Pore size[a] (nm)
0.1	2/1	489.80	854.51	Not measured
0.1	4/1	76.37	121.61	~4
0.1	3/1	0.8128	1.1318	Not determined
0.2	3/1	0.0568	0.0621	Not determined
0.05	3/1	1.1163	1.5944	~20

Conditions for sample preparation: $T = 100°C$, $t = 24$ h, HPC $= 2.0 \times 10^{-3}$ g/cm^3.

[a] Pore diameter at the peak of BJH adsorption dV/dD pore volume plot.

C. The activation energies for crystallization from the precursor powders prepared by our method are significantly lower than the value reported in the literature, i.e., 620 kJ/mol [26]. This means that our nanostructured precursor ZT powders are much easier to crystallize.

The performance of ZT-based devices depends on the compositional and microstructural features of the ZT material. High resolution TEM (Fig. 9, thin slice of crosssection of a microsphere) was used to examine these two aspects of as-prepared powders. Each individual particle looks essentially spherical [Fig. 9a] even under high magnification. Energy dispersive spectroscopy (EDS) analysis at three positions (A, B, and C) across the microsphere indicated that the chemical composition of the microsphere is homogeneous and identical. Fig. 9b also shows the homogeneous internal amorphous nanostructure with no phase segregation. The microsphere seems to contain some pores of a few nanometers in dimension. These intraparticle nanopores may explain why some of the samples have relatively high specific surface areas (Table I). Processing parameters such as the *RH* ratio may be tuned to tailor the intraparticle nanostructure of the microsphere in addition to the microsphere size and agglomeration state. Surface area data (see Table I) and TEM image (Fig. 9b) confirm the existence of the nanostructural mesopores inside some of the microsphere particles.

It was previously reported that when a high homogeneity level is not achieved, crystallization of TiO_2 is observed before crystallization into $ZrTiO_4$ [16, 17], whereas homogeneous gels crystallize directly into $ZrTiO_4$ below 700°C [22, 26, 28, 29, 51, 52]. In our dielectric-tuning coprecipitation process using equal molar Zr and Ti in starting solution, no phase separation or impurity phase (anatase) was observed in any of the ZT samples, because all our ZT precursor particles are purely amorphous. We can infer that titanium tends to coprecipitate with equal moles of zirconium to form amorphous ZT compounds. Otherwise, titanium will form the undesirable anatase/brookite phase if it precipitates out alone. In fact, this homogeneity in molecular composition (in terms of the Zr/Ti ratio) has been verified by the TEM/EDS technique. The compositions at three different positions inside the microsphere (Fig. 9a) show almost identical composition. However, when the molar ratio Ti/Zr = 2 was used in the initial mixture solution, we observed the crystalline

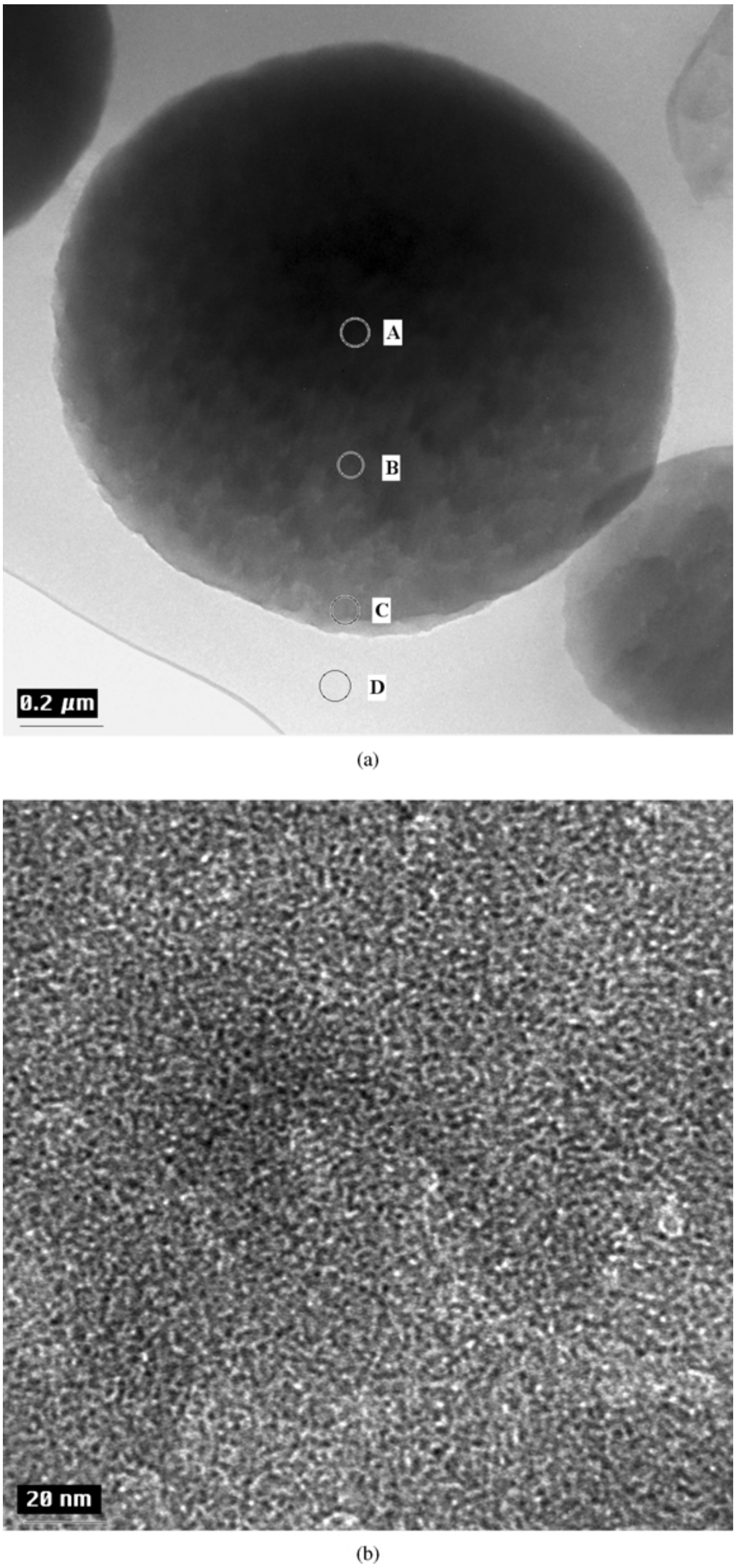
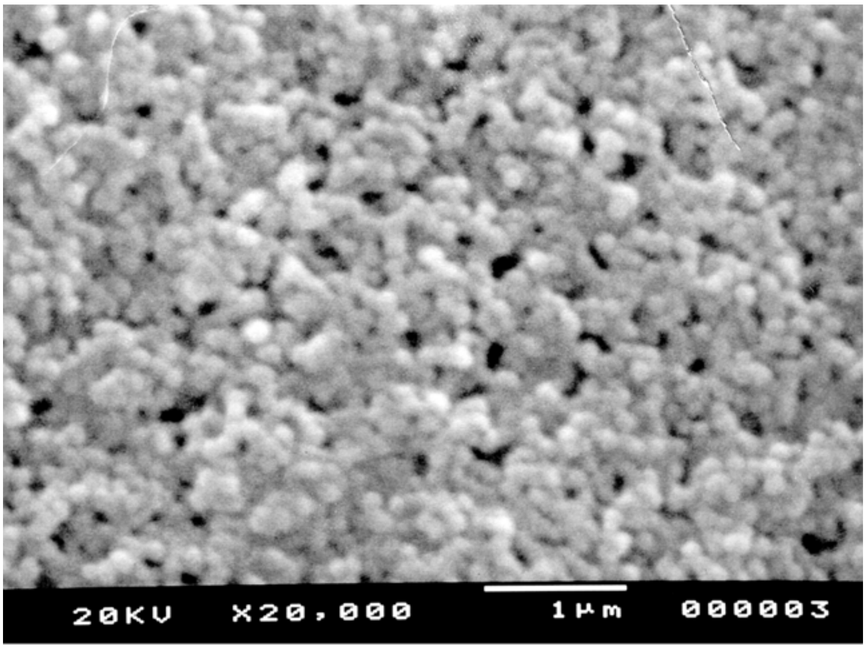


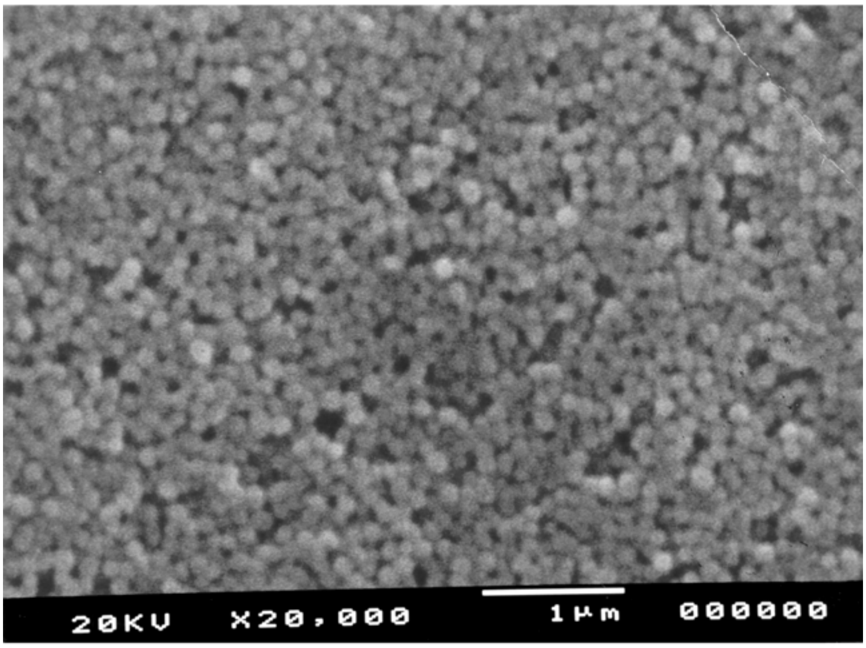
Figure 9 High-resolution TEM image of (a) crosssection of a ZT microsphere and (b) the homogeneous nanoporous amorphous phase inside the microsphere. Point D is located within the resin for TEM sample preparation. Sample synthesis conditions: $C = 0.1$ M, $RH = 2/1$, $T = 100°\mathrm{C}$, $t = 24$ h, HPC $= 2.0 \times 10^{-3}$ g/cm^3.

titania (anatase/brookite phase) in the as-prepared sample. With heat treatment from 27 to 1200°C, the rest of the amorphous phase in the titania-containing sample converts the $ZrTiO_4$ phase while the titania phase coexists. Obviously, there is a certain tolerance of deviation from an equal molarity Ti/Zr ratio within which single-crystalline $ZrTiO_4$ phase will form. Clearly, the ratio of Ti/Zr $= 2$ is beyond this tolerance.

Relative to the hydrothermal process, which usually uses autoclave vessels heated in a conventional oven, microwave heating represents an efficient and controllable means for hydrothermal processing due to



(a)



(b)

Figure 10 SEM image of ZT nanosphere particles by the rapid microwave heating process. (a) Microwave heating for 2 s. (b) Microwave heating for 5 s. Conditions: $C = 0.05$ M, $RH = 3/1$, $T =$ not measured, HPC $= 2.0 \times 10^{-3}$ g/cm^3.

the potential uniform volumetric heating. We explored the feasibility of microwave hydrothermal synthesis of monodispersed ZT nanoparticles. Fig. 10a and b show SEM photos of ZT particles obtained by a rapid microwave heating incubation at 2 and 5 s, respectively. Under similar conditions, microwave heating required a very short time to produce much smaller, more uniform dispersed nanosphere particles than the conventional oven incubation. The rapid burst of nucleation of larger population density of nuclei in the solution may explain the smaller size. The microwave heating rate could be used as an important parameter to control the particle size. This exploratory result clearly indicates that microwave hydrothermal processing should be developed further as a potential route to produce nanoparticles. Detailed investigation on monodispersed particle synthesis using a well-controlled microwave system will be reported elsewhere.

It is worthwhile noting that the dielectric-tuning coprecipitation is different from the chemical precipitation reported by Leoni *et al.* [1], although both process may use the same mixed zirconium and titanium salts. The chemical precipitation process is hard to control and inhomogeneous and produces precipitates in the form of nonsphere agglomerates. In contrast, the dielectric-tuning process generates a homogeneous nucleation and growth environment, is controllable by varying alcohol content and temperature, and produce precipitates consisting of dispersed, near-uniform-sized microspheres.

4. Conclusion

We report a method to synthesize ultrafine dispersed spherical particles of zirconium titanate (with near uniform size ranging from a few nanometers to a few micrometers). A low-temperature (<100°C) wet-chemical synthesis method—dielectric-tuning solution coprecipitation—has been demonstrated to produce near-monodispersed ZT microsphere and nanosphere particles. This method could be generally applied to many other binary or multiple-metal oxide systems. Particle size and morphology as well as intraparticle nanostructure (nano- or mesopores) may be tailored by simply tuning the processing parameters such as initial metal ion concentration, alcohol volume fraction, heating rate, and heating temperature. We have shown that the dielectric-tuning coprecipitation method generates ZT microsphere particles having homogeneous composition at the molecular level, no phase segregation, and the uniform microstructure at the nanometer scale in each microsphere. Such homogeneity and uniform nature of amorphous ZT precursor particles may have contributed favorably to the low crystallization temperature measured by DTA/TGA. We have also demonstrated that microwave heating coupled with the dielectric-tuning coprecipitation approach can be used to produce dispersed nanosphere particles.

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