

Hydrothermal Synthesis of Spherical Perovskite Oxide Powders Using Spherical Gel Powders

Jae Young Choi, Chong Hee Kim,* and Do Kyung Kim*

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Taejeon 305-701, Korea

Spherical perovskite oxide powders, composed of fine particulates, were prepared by using spherical gel powders under hydrothermal conditions. Spherical PbTiO_3 , BaTiO_3 , and SrTiO_3 powders were synthesized from spherical TiO_2 gel powders, and spherical PbZrO_3 powder from spherical ZrO_2 gel powder. Spherical $\text{Pb}(\text{Zr}_{0.5}, \text{Ti}_{0.5})\text{O}_3$ and $\text{Ba}(\text{Zr}_{0.5}, \text{Ti}_{0.5})\text{O}_3$ powders were prepared from spherical ZrTiO_4 gel powders. Lead acetate trihydrate, barium hydroxide octahydrate, and strontium hydroxide octahydrate were used as the sources of A-site ions in each perovskite oxide (ABO_3). The spherical TiO_2 and ZrO_2 gel powders were prepared by thermal hydrolysis of titanium tetrachloride and zirconium oxychloride, respectively, and spherical ZrTiO_4 gel powder by thermal hydrolysis of a mixture of them in alcohol-water mixed solvent. During the hydrothermal treatment, the spherical gel powders retained their spherical shape to produce spherical perovskite oxide powders, composed of nanometer-sized particulates.

I. Introduction

HYDROTHERMAL powder synthesis has been known as a powerful method for the preparation of fine, high-purity, and homogeneous powders of various single-component and multicomponent oxide powders.¹ Furthermore, powders with particle sizes in the nanometer to centimeter range can be synthesized depending on the configuration of the hydrothermal equipment. Recently, multicomponent oxide powders, especially, perovskite oxide powders, have attracted attention for their useful electronic applications such as dielectric, piezoelectric, electrostrictive, and transparent electrooptic ceramics.^{2,3} It has been commonly accepted that an unagglomerated spherical powder with a narrow size distribution is the most desirable state for the compacting and sintering of ceramics.⁴ However, in the hydrothermal powder synthesis of some perovskite powders, it has been known to be difficult to obtain spherical powders because of the formation behavior. Powders with needle, plate, and cubic shapes were formed in the hydrothermal synthesis of lead zirconium titanate,⁵⁻¹⁰ lead titanate,¹¹⁻¹⁵ and lead zirconate.⁹

Generally, hydrothermal synthesis utilizes the treatment of aqueous solutions or suspensions of precursor gel powders at elevated temperatures and pressures. The precursor gel powders are usually nanometer-sized gels precipitated from metal

salts (chlorides, nitrates, sulfates, and so on) or metal alkoxides.⁵⁻¹⁵ On the other hand, several researchers have used spherical gel powders in hydrothermal synthesis.¹⁶⁻¹⁹ In their work, spherical titanium hydrous oxide¹⁶⁻¹⁸ was synthesized by the controlled hydrolysis of titanium tetraethoxide, and spherical strontium titanium hydrous oxide carboxylate¹⁹ by the controlled hydrolysis of quinaisopropoxystrontium titanium octanoate. The hydrous oxide powders, by hydrothermal treatment, were crystallized to their oxides, which retained their spherical shape, composed of nanometer-sized particulates.

In this study, we used spherical TiO_2 , ZrO_2 , and ZrTiO_4 gel powders to prepare spherical perovskite crystalline powders under hydrothermal conditions. With the reaction between the spherical gel powders and the sources of A-site ions in perovskite oxide (ABO_3) under hydrothermal conditions, we synthesized spherical perovskite oxide powders. For example, using the spherical TiO_2 gel powders with lead acetate trihydrate, barium hydroxide octahydrate, and strontium hydroxide octahydrate as the sources of A-site ions, we hydrothermally synthesized spherical PbTiO_3 , BaTiO_3 , and SrTiO_3 powders, respectively.

II. Experimental Procedure

(1) Preparation of Spherical Gel Powders

Spherical TiO_2 , ZrO_2 , and ZrTiO_4 gel powders were synthesized by the thermal hydrolysis of metal salts in alcohol-water mixed solvent as previously described.²⁰⁻²³ Titanium tetrachloride (98% TiCl_4 , Wako Chemical Industries, Japan) and zirconyl chloride octahydrate (98% $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, Aldrich Chemical, Milwaukee, WI) were dissolved in distilled and deionized water. The concentration of the metal ions was adjusted to 1M. These aqueous solutions were then mixed with alcohols to adjust the volume ratios of alcohol to water (the RH ratio). The compositions of starting solutions for the gel powders are shown in Table I. Homogeneous starting solutions were obtained by stirring for 6 h with a magnetic stirrer at 4°C. All of the reagents were used as received. A long-chained molecule, hydroxypropyl cellulose (HPC) (molecular weight ~100 000, Aldrich Chemical Co., Milwaukee, WI), was used as a steric dispersant.

A 300 mL sample of the starting solution was uniformly heated to the boiling point by an ordinary kitchen microwave oven (2.45 GHz, 650 W) without stirring. In our previous papers,^{20,21} it was demonstrated that microwave heating could be successfully applied to the precipitation of spherical ZrO_2 gel

R. E. Riman—contributing editor

Table I. Compositions of Starting Solutions for Gel Powders

Gel powder	RH ratio [†]	TiCl_4 (M)	$\text{ZrOCl}_2 \cdot 6\text{H}_2\text{O}$ (M)	HPC (g/mL) [‡]
TiO_2 gel powder	3	0.1	0	0.3×10^{-3}
ZrO_2 gel powder	5	0	0.2	1.5×10^{-3}
ZrTiO_4 gel powder	3.5	0.05	0.05	0.3×10^{-3}

[†]RH ratio means the volume ratio of alcohol to water. [‡]Hydroxypropyl cellulose (molecular weight ~100 000).

Manuscript No. 190541. Received November 25, 1997; approved March 5, 1998. Presented at the 99th Annual Meeting of the American Ceramic Society, Cincinnati, OH, May 5, 1997 (Paper No. SX-002-97, Symposium on Interfacial and Colloid Chemistry Related to Ceramic Processing).

Supported by the Korea Science and Engineering Foundation (KOSEF) through the Center for Interface Science and Engineering Materials (CISEM) and the Tong-Yang Central Research Laboratory, Yongin, Korea.

*Member, American Ceramic Society.

Table II. Hydrothermal Synthesis Conditions

Perovskite powder	A/B molar ratio in starting solution [†]	B (M) [†]	KOH (M)	Temp (°C)	Time (h)
PbTiO ₃	1.0	0.15	0.29	220	16
BaTiO ₃	1.1	0.24	0	110	4
SrTiO ₃	1.1	0.24	0	110	4
PbZrO ₃	1.5	0.24	3	220	2
Pb(Zr _{0.5} Ti _{0.5})O ₃	1.0	0.24	0.43	220	30
Ba(Zr _{0.5} Ti _{0.5})O ₃	1.1	0.24	0	130	4

[†]A and B denote ions in A and B sites in perovskite structure ABO₃.

powder. After the precipitation, the mother liquor was neutralized by adding a 4N NH₄OH solution to prevent the precipitates from resolving during cooling. The precipitates obtained from the above procedure were centrifuged repeatedly (at 10 000 rpm for 5-min intervals) and washed in water until no chloride ions could be detected in a supernatant solution. These resulting water-washed gel powders were used for the following hydrothermal synthesis.

(2) Hydrothermal Synthesis

The resulting water-washed TiO₂, ZrO₂, and ZrTiO₄ gel powders were dispersed in water by stirring for 1 h with a magnetic stirrer (600 rpm). The gel powders were then mixed with lead acetate trihydrate, barium hydroxide octahydrate, or strontium hydroxide octahydrate (Aldrich Chemical, Milwaukee, WI), depending on the final compositions of perovskite. For example, the TiO₂ gel powders were mixed with lead acetate trihydrate, barium hydroxide octahydrate, and strontium hydroxide octahydrate for the synthesis of PbTiO₃, BaTiO₃, and SrTiO₃ powders, respectively. For the synthesis of PbZrO₃, ZrO₂ gel powder and lead acetate trihydrate were used. For Pb(Zr_{0.5}Ti_{0.5})O₃ and Ba(Zr_{0.5}Ti_{0.5})O₃, ZrTiO₄ gel powder and lead acetate trihydrate and barium hydroxide octahydrate, sources of A-site ions, were used. The hydrothermal synthesis conditions for the perovskite oxide powders are shown in Table II. The hydrothermal synthesis was performed in a 1 L 316 stainless steel autoclave with Teflon liner, equipped with a magnetically driven stirring unit (Model DD100SS03AF26D, Autoclave Engineers, Inc., Erie, PA) with a heating rate of 5°C/min and a cooling rate of 10°C/min.

(3) Characterization

The particle size and the morphology of the gel and the perovskite oxide powders were analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). For the particle size analysis, 300 particles in scanning electron micrographs were measured for each sample. The samples for TEM were prepared using a dispersion method. A dilute dispersion of the powder in methanol was homogenized with an ultrasonic probe. Then, a drop of the dispersion was

deposited on a 3 mm diameter microgrid, followed by drying at room temperature. X-ray diffraction (XRD) measurements were used to determine the crystalline phase of the hydrothermally synthesized powders. The XRD patterns were collected with a scan rate of 4°/min for CuKα radiation.

III. Results and Discussion

Figure 1 shows transmission electron micrographs of the synthesized gel powders, TiO₂, ZrO₂, and ZrTiO₄. The powders had a spherical morphology and the average particle sizes of TiO₂, ZrO₂, and ZrTiO₄ were 0.72, 0.43, and 0.85 μm, respectively. The powders had an amorphous phase and they were employed as starting materials for the synthesis of perovskite powders through hydrothermal treatment.

The X-ray diffraction patterns of the hydrothermally synthesized powders are shown in Fig. 2. This shows that the powders consisted of only perovskite phases, except in the case of the powder obtained from ZrO₂ gel and lead acetate trihydrate, which had PbZrO₃ phase with a small portion of cubic ZrO₂.

Figure 3 shows transmission electron micrographs of the perovskite powders synthesized by hydrothermal treatment. The powders consisted of spherical secondary particles composed of small primary particulates. The sizes of the primary particulates were in the range of tens of nanometers. This shows that spherical shapes of powders are retained during hydrothermal treatment. In addition, the sources of A-site ions (lead, barium, or strontium) are incorporated into the gel powders (TiO₂, ZrO₂, or ZrTiO₄) and they are crystallized into the perovskite phases under hydrothermal conditions. It has been reported that gel powders have no solubility at room temperature and very low solubility in water under the hydrothermal conditions in which this experiment was performed.¹⁰ On the other hand, the sources of A-site ions, lead acetate trihydrate, barium hydroxide octahydrate, and strontium hydroxide octahydrate, are soluble in water even at room temperature. It is supposed that this difference in solubility causes the reaction between the elements (Ti or Zr) and the sources of A-site ions to occur only within spherical gel powders, and that this makes it possible to retain the spherical shape of the perovskite powders.

Spherical perovskite powders are obtained in a limited range of hydrothermal synthesis conditions, low base concentration or no base, in which gel powder has low solubility. Beyond this region, faceted or equiaxed powders are obtained, whose shapes are far from the spherical shape of the starting gel powders. The detailed experimental results and the formation mechanism are in preparation.²⁴

The methodology presented in this work provides a simple method for preparing spherical perovskite oxide powders: preparation of a spherical gel powder composed of B-site ions and crystallization of the powder with sources of A-site ions under hydrothermal conditions. In the wet chemical processes

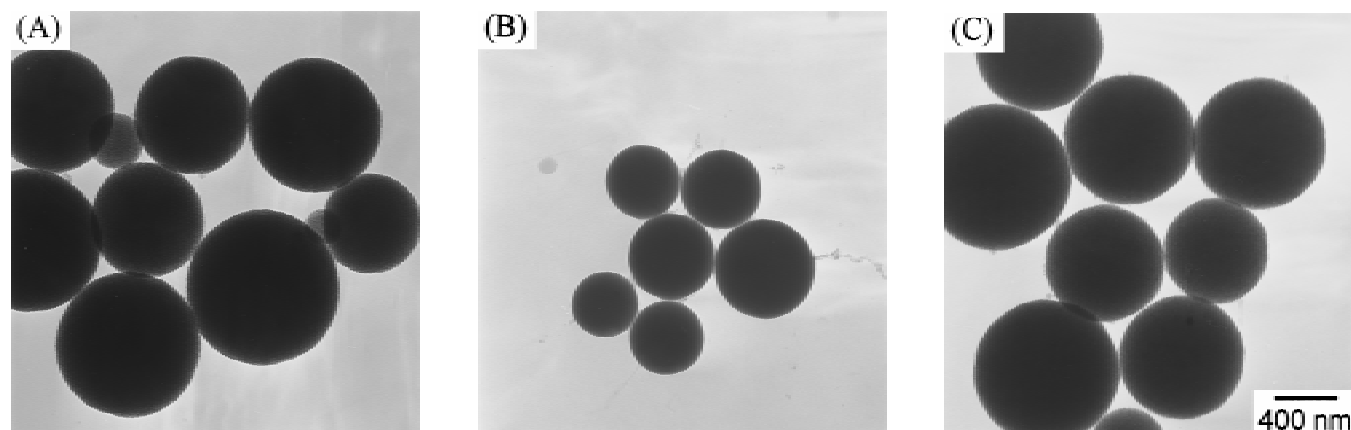


Fig. 1. TEM micrographs of obtained (A) TiO₂, (B) ZrO₂, and (C) ZrTiO₄ gel powders.

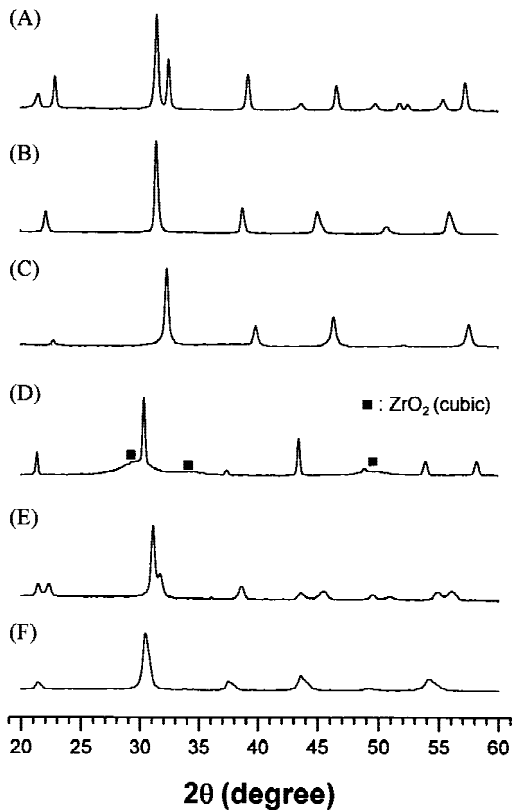


Fig. 2. X-ray diffraction patterns of (A) BaTiO₃, (B) SrTiO₃, (C) PbTiO₃, (D) PbZrO₃, (E) Pb(Zr_{0.5}Ti_{0.5})O₃, and (F) Ba(Zr_{0.5}Ti_{0.5})O₃ powders.

for multicomponent powders including perovskite oxide powders, chemicals of different metal ions should be used and these starting sources usually have different chemical reactivities. Thus, various processes for multicomponent powders with controlled morphology, size, and size distribution, against the different chemical reactivities between starting chemicals, have been reported.^{19,25–27} The reported processes, however, required complex synthesis steps and/or low concentrations of the starting chemicals. On the other hand, the hydrothermal process is known to be a method for the preparation of fine, high-purity, and homogeneous powders of various single-component and multicomponent oxide powders. Some hydrothermally synthesized perovskite powders cannot have spherical morphology; it has been reported that hydrothermally synthesized PZT,^{5–10} PbTiO₃,^{11–16} and PbZrO₃⁹ have nonspherical shapes, such as needle, plate, and cubic shapes. It is known that nonspherical powders are not suitable for certain types of ceramic processing, such as forming and sintering. In this work, several perovskite oxide powders with spherical shapes were successfully synthesized by incorporating external sources of A-site ions into spherical gel powders under hydrothermal conditions.

The perovskite powders obtained in this work had spherical secondary particles composed of nanosized primary particulates. This structure is similar to that of TiO₂ and SrTiO₃ powders synthesized by previous researchers.^{16–19} Spherical TiO₂ and SrTiO₃ powders were prepared by crystallizing their spherical hydrous oxide precursors under hydrothermal conditions. The crystallized powders retained their spherical shape and were composed of nanosized primary particulates. When the spherical secondary TiO₂ particles were under ultrasonic treatment, the particles disintegrated into primary particulates, which indicated the weak bond strength between the primary particulates.^{16–18} This powder structure gave enhanced formability and sinterability to spherical TiO₂. The spherical perovskite powders synthesized in this study were disintegrated

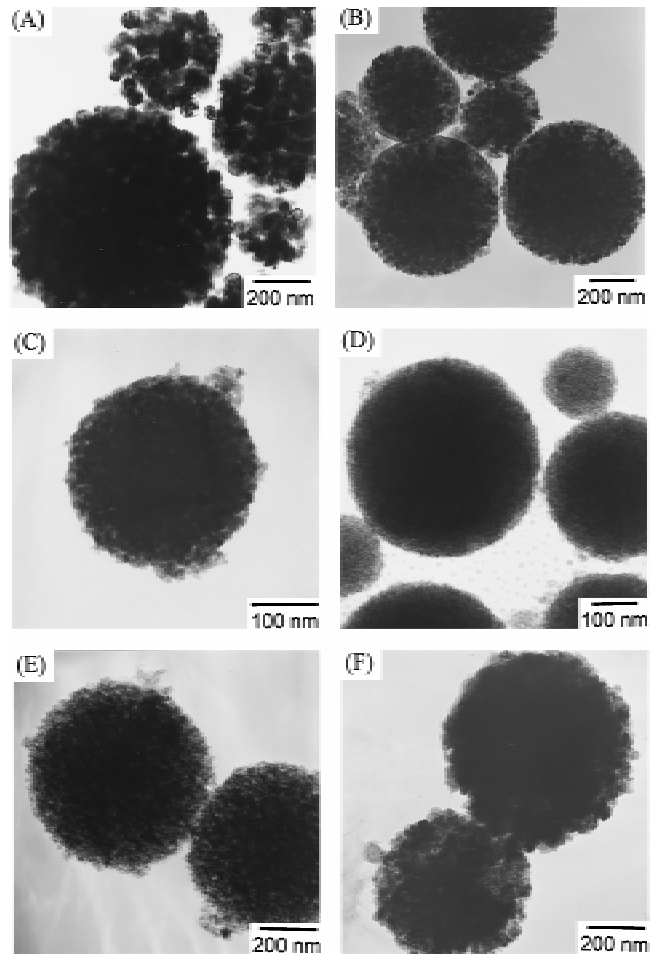


Fig. 3. TEM micrographs of (A) BaTiO₃, (B) SrTiO₃, (C) PbTiO₃, (D) PbZrO₃, (E) Pb(Zr_{0.5}Ti_{0.5})O₃, and (F) Ba(Zr_{0.5}Ti_{0.5})O₃ powders.

into nanosized primary particulates during ultrasonic treatment. It is expected that these unique powder characteristics, the spherical secondary particles composed of weakly bonded nanosized primary particulates, show the excellent behavior of forming and sintering.

IV. Summary

Spherical perovskite oxide powders composed of fine particulates were prepared by using spherical gel powders under hydrothermal conditions. PbTiO₃, BaTiO₃, and SrTiO₃ powders were synthesized hydrothermally from TiO₂ gel powders, PbZrO₃ powder from ZrO₂ gel powder, and Pb(Zr_{0.5}Ti_{0.5})O₃ and Ba(Zr_{0.5}Ti_{0.5})O₃ powders from ZrTiO₄ gel powders with sources of A-site ions in perovskite oxide (ABO₃). Lead acetate trihydrate, barium hydroxide octahydrate, and strontium hydroxide octahydrate were used as the sources of A-site ions, depending on the final composition of the perovskite oxide powders.

During the hydrothermal treatment, the spherical gel powders retained their spherical shape, incorporating sources of A-site ions, and the resulting powders were crystallized to produce spherical perovskite oxide powders, composed of nanometer-sized particulates. Because the reaction elements (Ti and Zr) were confined within the spherical gel powders, limiting the growth space of the crystalline perovskite, it is supposed that the synthesized perovskite powders retained their spherical shape and were composed of fine particulates.

References

- W. J. Dawson, "Hydrothermal Synthesis of Advanced Ceramic Powders," *Am. Ceram. Soc. Bull.*, **67** [10] 1673–78 (1988).

- ²L. E. Cross, "Dielectric, Piezoelectric, and Ferroelectric Components," *Am. Ceram. Soc. Bull.*, **63** [4] 586–90 (1984).
- ³K. S. Mazdiyasi, "Fine Particle Perovskite Processing," *Am. Ceram. Soc. Bull.*, **63** [4] 591–94 (1984).
- ⁴W. H. Rhodes, "Agglomerate and Particle Size Effects on Sintering Yttria-Stabilized Zirconia," *J. Am. Ceram. Soc.*, **64** [1] 19–22 (1981).
- ⁵T. R. N. Kutty and R. Balachandran, "Direct Precipitation of Lead Zirconate Titanate by the Hydrothermal Method," *Mater. Res. Bull.*, **19**, 1479–88 (1984).
- ⁶K. C. Beal, "Precipitation of Lead Zirconate Titanate Solid Solutions under Hydrothermal Conditions"; pp. 33–41 in *Advances in Ceramics*, Vol. 21, *Ceramic Powder Science*. Edited by G. L. Messing, K. S. Mazdiyasi, J. W. McCauley, and R. A. Haber. American Ceramic Society, Westerville, OH, 1987.
- ⁷K. H. Lee, K. Asaga, T. Ichihara, and M. Daimon, "Synthesis of PZT Crystalline Powders by Reaction of Aqueous Solution below 200°C," *J. Ceram. Soc. Jpn.*, **95** [7] 736–40 (1987).
- ⁸M. M. Lencka, A. Anderko, and R. E. Riman, "Hydrothermal Precipitation of Lead Zirconate Titanate Solid Solutions: Thermodynamic Modeling and Experimental Synthesis," *J. Am. Ceram. Soc.*, **78** [10] 2609–18 (1995).
- ⁹H. K. Kim, "Hydrothermal Synthesis of Pb(Zr,Ti)O₃ Powders"; M.S. Thesis. Seoul National University, Seoul, Korea, 1993.
- ¹⁰Y. Ohba, T. Rikitoku, T. Tsurumi, and M. Daimon, "Precipitation of Lead Zirconate Titanate Powders under Hydrothermal Conditions," *J. Ceram. Soc. Jpn.*, **104** [1] 6–10 (1996).
- ¹¹S. Kaneko and F. Imoto, "Reactions between PbO and TiO₂ under Hydrothermal Conditions," *Bull. Chem. Soc. Jpn.*, **51** [6] 1739–42 (1978).
- ¹²K. Takai, S. Shoji, H. Naito, and A. Sawaoka, "Fine Powder PbTiO₃ Obtained by Hydrothermal Technique and Its Sinterability"; pp. 877–85 in *Proceedings of the First International Symposium on Hydrothermal Reactions*. Edited by S. Somiya. Gakujutsu Bunken Fukyu-Kai, Tokyo, Japan, 1982.
- ¹³M. Suzuki, S. Uedaira, H. Masuya, and H. Tamura, "Hydrothermal Synthesis of Lead Titanate Fine Powders"; pp. 163–70 in *Ceramic Transactions*, Vol. 1, *Ceramic Powder Science IIA*. Edited by G. L. Messing, E. R. Fuller, Jr., and H. Hausner. American Ceramic Society, Westerville, OH, 1988.
- ¹⁴D. J. Watson, C. A. Randall, R. E. Newnham, and J. H. Adair, "Hydrothermal Formation Diagram in the Lead Titanate System"; pp. 154–62 in *Ceramic Transactions*, Vol. 1, *Ceramic Powder Science IIA*. Edited by G. L. Messing, E. R. Fuller, Jr., and H. Hausner. American Ceramic Society, Westerville, OH, 1988.
- ¹⁵M. M. Lencka and R. E. Riman, "Synthesis of Lead Titanate: Thermodynamic Modeling and Experimental Verification," *J. Am. Ceram. Soc.*, **76** [10] 2649–59 (1993).
- ¹⁶Y. Oguri, R. E. Riman, and H. K. Bowen, "Processing of Anatase Prepared from Hydrothermally Treated Alkoxy-Derived Hydrous Titania," *J. Mater. Sci.*, **23**, 2897–904 (1988).
- ¹⁷M. Kondo, K. Shinozaki, R. Ooki, and N. Mizutani, "Crystallization Behavior and Microstructure of Hydrothermally Treated Monodispersed Titanium Dioxide Particles," *J. Ceram. Soc. Jpn.*, **102** [8] 742–46 (1994).
- ¹⁸M. Kondo, H. Funakubo, K. Shinozaki, and N. Mizutani, "Formability and Sinterability of Hydrothermally Crystallized Monodispersed Titanium Dioxide Particles," *J. Ceram. Soc. Jpn.*, **103** [6] 552–56 (1995).
- ¹⁹R. E. Riman, R. R. Landham, and H. K. Bowen, "Synthesis of Uniform Titanium and 1:1 Strontium-Titanium Carboxyhydrosols by Controlled Hydrolysis of Alkoxy-metal Carboxylate Precursors," *J. Am. Ceram. Soc.*, **72** [5] 821–26 (1989).
- ²⁰Y. T. Moon, D. K. Kim, and C. H. Kim, "Preparation of Monodisperse ZrO₂ by the Microwave Heating of Zirconyl Chloride Solutions," *J. Am. Ceram. Soc.*, **78** [4] 1103–106 (1995).
- ²¹Y. T. Moon, H. K. Park, D. K. Kim, C. H. Kim, I.-S. Seog, 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).
- ²²H. K. Park, Y. T. Moon, D. K. Kim, and C. H. Kim, "Formation of Monodisperse Spherical TiO₂ Powders by Thermal Hydrolysis of Ti(SO₄)₂," *J. Am. Ceram. Soc.*, **79** [10] 2727–32 (1996).
- ²³H. K. Park, D. K. Kim, and C. H. Kim, "Effect of Solvent on Titania Particle Formation and Morphology in Thermal Hydrolysis of TiCl₄," *J. Am. Ceram. Soc.*, **80** [3] 743–49 (1997).
- ²⁴J. Y. Choi, C. H. Kim, and D. K. Kim, "Formation of Spherical Lead Titanate Powders from Spherical TiO₂ Gel Powders under Hydrothermal Conditions," in preparation.
- ²⁵P. Gheerandi and E. Matijevic, "Homogeneous Precipitation of Spherical Colloidal Barium Titanate Particles," *Colloids Surf.*, **32**, 257–74 (1988).
- ²⁶A. Celikkaya and M. Akinc, "Morphology of Zinc Sulfide Particles Produced from Various Zinc Salts by Homogeneous Precipitation," *J. Am. Ceram. Soc.*, **73** [2] 245–50 (1990).
- ²⁷S. Nishikawa and E. Matijevic, "Preparation of Monodispersed Spherical Silica-Alumina Particles by Hydrolysis of Mixed Alkoxides," *J. Colloid Interface Sci.*, **165**, 141–47 (1994). □