Preparation and Characterization of Uniform Submicrometer Lead Titanate Particles[†]

Myung Jin Kim[‡] and Egon Matijević*

Departments of Chemistry and Chemical Engineering, Clarkson University, Potsdam, New York 13676

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Submicrometer size spherical lead titanate particles of narrow size distribution have been prepared by decomposition of complex peroxidic species of titanium in the presence of Pb chelates in alkaline media. The average size and chemical composition of the particles can be controlled by adjusting the concentration of the reacting compounds, aging time, and temperature.

Introduction

Lead-based ferroelectric crystals have been extensively employed as functional ceramic materials. The dielectric, piezoelectric, and pyroelectric properties of lead titanate ($PbTiO_3$) make this material particularly useful for capacitor, ultrasonic transducer, and optoelectric devices.[1-5] This material can be prepared by several liquid-phase reaction techniques including aging of the gels,[6] hydrolysis of mixed alkoxides,[7] and decomposition of mixed salts[4] or metal neodecanoates.[8] The conventional solid-state reaction does not yield small crystallite powders and is a high-temperature process of 850–900 °C.[5] None of the mentioned procedures generates well-defined finely dispersed materials required to fabricate the high-performance devices. High-purity, uniform submicrometer size powders enhance sinterability and yield dense, fine-grained microstructures that tend to be strong and to have more readily controlled physical properties.[5,9]

Recently, it was reported that spherical colloidal barium titanate particles of narrow size distribution can be obtained by homogeneous nucleation and subsequent growth of solids from aqueous solutions containing Ti(IV) and Ba complexes.[10] A modified approach was employed to generate uniform submicrometer lead titanate particles. This technique allows for the preparation of this material at much lower temperatures than reported heretofore.

Experimental Section

Particle Preparation. Materials. All chemicals were of reagent-grade quality. Titanium(IV) isopropoxide (Fluka), disodium salt of nitrilotriacetic acid (Na_2HNTA, Aldrich), lead nitrate (J. T. Baker), hydrogen peroxide (30%, J. T. Baker), hydrochloric acid (37%, J. T. Baker), ammonium hydroxide (VWR), poly(vinylpyrrolidone) (MW = 40 000, General Aniline & Film Co.), poly(vinyl alcohol) (MW = 2500, Polysciences), and sodium dodecyl sulfate (BDH Chemicals Ltd) were used as received. The solutions were made with doubly distilled water from an all-Pyrex apparatus and were filtered on 0.2-μm pore size Nuclepore membranes to remove possible solid contaminants. The following stock solutions were prepared: (A) 0.1 mol dm^{-3} titanium isopropoxide, $Ti(i\text{-}Opr)_4$, 0.4 mol dm^{-3} HCl, and 0.55 mol dm^{-3} H_2O_2; (B) 2.0 mol dm^{-3} NH_4OH; (C) 0.1 mol dm^{-3} disodium salt of nitrilotriacetic acid (Na_2HNTA); (D) 0.1 mol dm^{-3} $Pb(NO_3)_2$. Different volumes of these stock solutions were used to give a range of concentrations of each reaction component.

Mixing Procedures. Two procedures were adopted: (I) The order of mixing was B, A, additional amounts of H_2O_2, C, D, and doubly distilled water to a predetermined final volume.

(II) First, C and D were combined. Next, B, A, and H_2O_2 were premixed. Finally, the two intermediate systems were brought together and water was added to a final volume.

The resulting final systems I and II had quite a different appearance. In case I the solution became turbid, and vigorous gas evolution was observed immediately after the addition of $Pb(NO_3)_2$ (solution D) at room temperature over the pH range between 4 and 9.3. At pH > 9 rapid settling occurred. No obvious turbidity was observed in systems prepared by procedure II, when these were illuminated by a parallel beam light.

Aging. For aging experiments, either system I or II was transferred into 500-cm^3 Pyrex bottles, tightly sealed, and heated in a constant-temperature bath or in an oven at temperatures ranging between 45 and 100 °C for different periods of time (from 1.5 to 48 h).

The precipitates were collected on 0.2-μm pore size Nuclepore membranes and washed with doubly distilled water. The solids were then dried in a desiccator at 60 °C for 12 h under reduced pressure.

Particle Characterization. To examine the morphology of particles by transmission electron microscopy (JEOL JEM-1200EX), the dried powders were first resuspended in water (or NH_4OH solution of pH = 10) in 10-cm^3 Pyrex test tubes, and the systems were treated in an ultrasonic bath for 10 min. The solids were then deposited on collodion-coated 400-mesh copper grids by centrifugation. The particle size histograms were obtained from electron micrographs using the Carl Zeiss TGZ-3 particle size analyzer. In some cases the size distribution of dispersions was determined by photon correlation spectroscopy (PCS), using the Coulter N4MD instrument, which was operated at an angle of 90° and a wavelength of 632.8 nm.

Crystalline properties of dried and calcined powders were elucidated by X-ray diffraction analysis (Philips Norelco diffractometer with Ni-filtered Cu Kα radiation), and the spectra were identified by comparison with the published standards.[11]

[†] Part of a Ph.D. thesis by M.J.K.

* To whom correspondence should be addressed at the Department of Chemistry.

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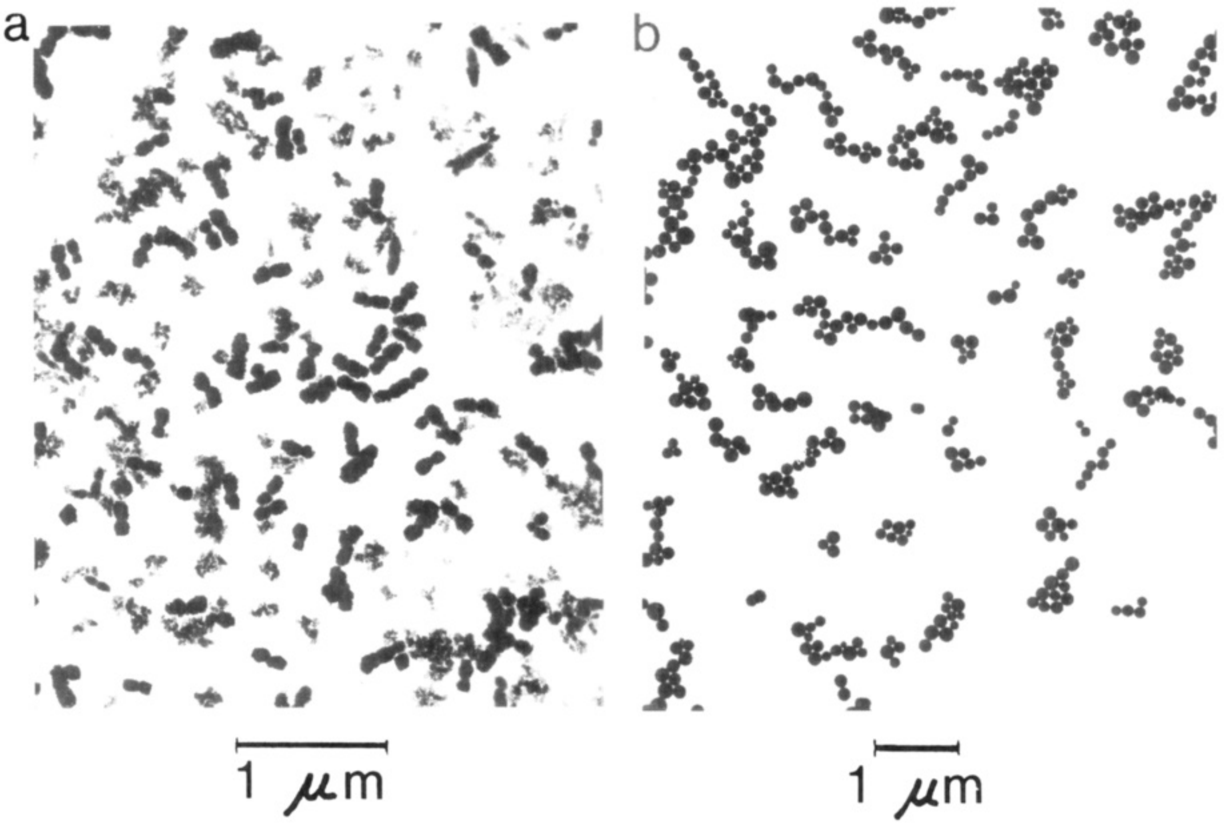

Figure 1. (a) Transmission electron micrograph (TEM) of particles obtained by aging at 60 °C for 4 h a solution prepared by the mixing method I. Concentrations: $[Pb(NO_3)_2] = [Ti(i\text{-}Opr)_4] = 5.0 \times 10^{-3}$ mol dm^{-3}, $[Na_2HNTA] = 1.0 \times 10^{-2}$ mol dm^{-3}, and $[H_2O_2]$ = 0.6 mol dm^{-3}; pH was adjusted to 7.6 by addition of NH_4OH. (b) TEM of particles obtained by aging at 50 °C for 4.5 h a solution prepared by the mixing method II. $[Pb(NO_3)_2] = [Ti(i\text{-}OPr)_4] = 1.0 \times 10^{-2}$ mol dm^{-3}, $[Na_2HNTA] = 2.0 \times 10^{-2}$ mol dm^{-3}, and $[H_2O_2]$ = 0.4 mol dm^{-3}; pH = 9.1.

Calcination was done in air atmosphere using a horizontal tube furnace (Lab-Line). The changes in the solid phase were examined by differential thermal analysis (Perkin Elmer DTA-1700).

To determine the chemical composition of the particles, ~50 mg of the dried solid was dissolved in 10 cm^3 of HCl (37%) and diluted to 500 cm^3 with distilled water, and the lead content was then assayed by flame absorption spectroscopy (Perkin Elmer 5000) at 217.3 nm, by using an air–acetylene mixture.

Titanium content was obtained by measuring the absorbance of acidic titanium(IV) solutions in the presence of hydrogen peroxide at 410 nm[12] (Perkin-Elmer Lamda 3 UV–vis spectrophotometer). The experimental error in determining the chemical composition, in terms of [Pb]/[Ti], was within 5%. The content of peroxidic groups was assayed by the Kingzett iodine method.[13] The possible incorporation of Na in the precipitate was checked by flame absorption spectroscopy at 330.2 nm.

The specific surface area of the powder was obtained by the BET method using a Quantasorb apparatus.

The electrokinetic mobilities of particles were evaluated with the Pen Kem 3000 microelectrophoresis apparatus. The pH of the dispersion was adjusted with either HNO_3 or NaOH, maintaining a constant ionic strength of 1.0×10^{-3} mol dm^{-3} with sodium nitrate.

Results

Particle Precipitation. The solids formed at room temperature on mixing the reaction solutions by method I consisted of elongated particles, which were aggregates of smaller cubic type subunits. Heating these dispersions at 60 °C had little effect on the morphology of the precipitates. Figure 1a illustrates such particles.

Mixing method II was developed to prevent the interaction of H_2O_2 with the Pb^{2+} ion, by first complexing the latter with NTA. Under certain conditions solutions on aging yielded spherical particles as illustrated in Figure 1b. Such uniform stable dispersions were produced when the concentration of $Pb(NO_3)_2$ ranged from 5.0×10^{-3} mol dm^{-3} to 1.0×10^{-2} mol dm^{-3} while keeping $[Ti(i\text{-}Opr)_4] = [Pb(NO_3)_2]$ and $[Na_2HNTA] = 2[Pb(NO_3)_2]$. In addition, the optimum results were obtained at the initial pH = 9.1 ± 0.2 and the total concentration of H_2O_2 that equaled 40 $[Pb(NO_3)_2]$, at aging temperatures of 55–60 °C.

Particles generated from a solution of $[Pb(NO_3)_2] = [Ti(i\text{-}Opr)_4] = 2.0 \times 10^{-2}$ mol dm^{-3} and $[Na_2HNTA] = 4.0 \times 10^{-2}$ mol dm^{-3}, were extensively coagulated (Figure 2a). To prepare discrete uniform particles at these concentrations, several protective agents were utilized [poly(vinylpyrrolidone) (PVP), poly(vinyl alcohol) (PVA), and sodium dodecyl sulfate (SDS)]. PVP did not help to alleviate coagulation, but SDS in the concentration range of 2.0×10^{-2} mol dm^{-3} and 3.0×10^{-2} mol dm^{-3} did so to a great extent with H_2O_2 concentrations of 0.42–0.47 mol dm^{-3} (Figure 2b). PVA was less efficient than SDS in stabilizing the dispersion.

No difference in resulting particle morphology was observed when lead acetate was substituted for lead nitrate under otherwise the same conditions.

Particle Characterization. X-ray analysis showed that solids as prepared and dried were amorphous. Diffraction patterns of the same powders calcined >500 °C for 10 min or longer were characteristic of either the single-phase tetragonal $PbTiO_3$ or of a mixed phase, such as $PbTiO_3$ and $PbTi_3O_7$ for the powder of $[Pb]/[Ti] < 0.9$ or $PbTiO_3$ and PbO for the powder of $[Pb]/[Ti] > 1.1$.

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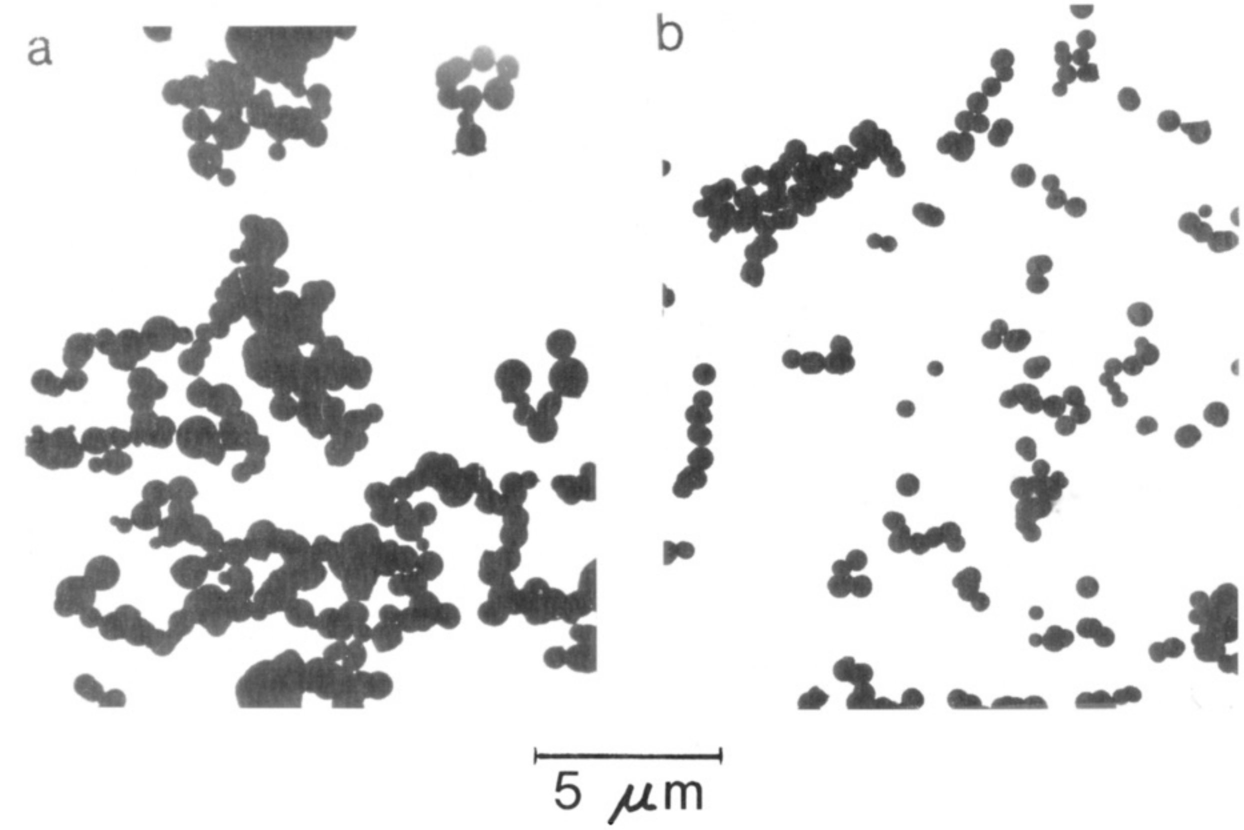

Figure 2. (a) TEM of particles obtained by aging at 60 °C for 8 h a solution prepared by the method II. Concentrations: $[Pb(NO_3)_2] = [Ti(i\text{-}Opr)_4] = 2.0 \times 10^{-2}$ mol dm^{-3}, $[Na_2HNTA] = 4.0 \times 10^{-2}$ mol dm^{-3}, and $[H_2O_2] = 0.8$ mol dm^{-3}; pH = 8.6. (b) TEM of the same system as described in (a) except that $[H_2O_2] = 0.27$ mol dm^{-3} and 2.3×10^{-2} mol dm^{-3} SDS were added at the end of the mixing of reactants. The system was aged at 60 °C for 2.5 h.

Table I. Characteristics of the Dried and Calcined Powders (Figure 3)

	dried at 60 °C	calcined at 500 °C
mean diam,[a] μm	0.21	0.19
specific surf. area, m^2 g^{-1}	5.3 [3.8][b]	4.5 [4.2]
chemical anal., wt %		
Pb	58.4	63.1
Ti	13.1	14.3
peroxidic O	6.3	3.8
cryst struct	amorphous	tetragonal

[a] Measurements by photon correlation spectroscopy (Coulter N4). [b] In brackets are specific surface areas calculated by assuming smooth surface spheres.

The morphology was not greatly affected when particles, illustrated in Figure 3a, were calcined at 500 °C for 10 min at the heating rate of 2 °C min^{-1} (Figure 3b).

The calcined product contained the same molar ratio of [Pb]/[Ti] as the dried solid (Table I), and no Na was detected in the latter. The specific surface area of the calcined sample (4.5 m^2 g^{-1}) was smaller than that of the dried powder (5.3 m^2 g^{-1}) owing to particle sintering. The measured specific surface area of the calcined solid is in very good agreement with the calculated value assuming smooth surface and density of 7.5 g cm^{-3}.[14] The crystallite size of calcined particles of 76 nm (100), evaluated from the Scherrer equation,[15] is smaller than the particle diameter, indicating that the calcined powder is polycrystalline. Table I summarizes the characteristics of particles shown in Figure 3.

Figure 4 gives the size distribution of the particles shown in Figure 3a determined by photon correlation spectroscopy (PCS) and compared to the histogram obtained from electron microscopy. In calculating the size distribution by the PCS method, the moments of zero-order log normal distribution were assumed and corrected for polydispersity by the transformation relationship developed by Thomas.[16] The so-obtained number-average diameter is in good agreement with the mean diameter from the electron micrograph.

Typical DTA results obtained with the sample illustrated in Figure 6a, whose chemical composition in terms of [Pb]/[Ti] is 1.1, are shown in Figure 5. Curve A was obtained by heating the amorphous powder to 800 °C. Cooling the resulting crystalline product to room temperature yielded curve B, reheating of the sample gave curve C, and finally cooling again is represented by curve D (with the scanning rate of 10 °C/min in air). The broad exothermic peak between 460 and 570 °C indicated the range where crystallization occurred (curve A). In the crystalline state, the sample undergoes a reversible structure transformation from tetragonal to cubic on heating at 483 °C (curve C) and from cubic to tetragonal on cooling at 464 °C (curves B and D). These transition temperatures are in good agreement with the previously reported results.[17-19] Figure 5b shows that there is no

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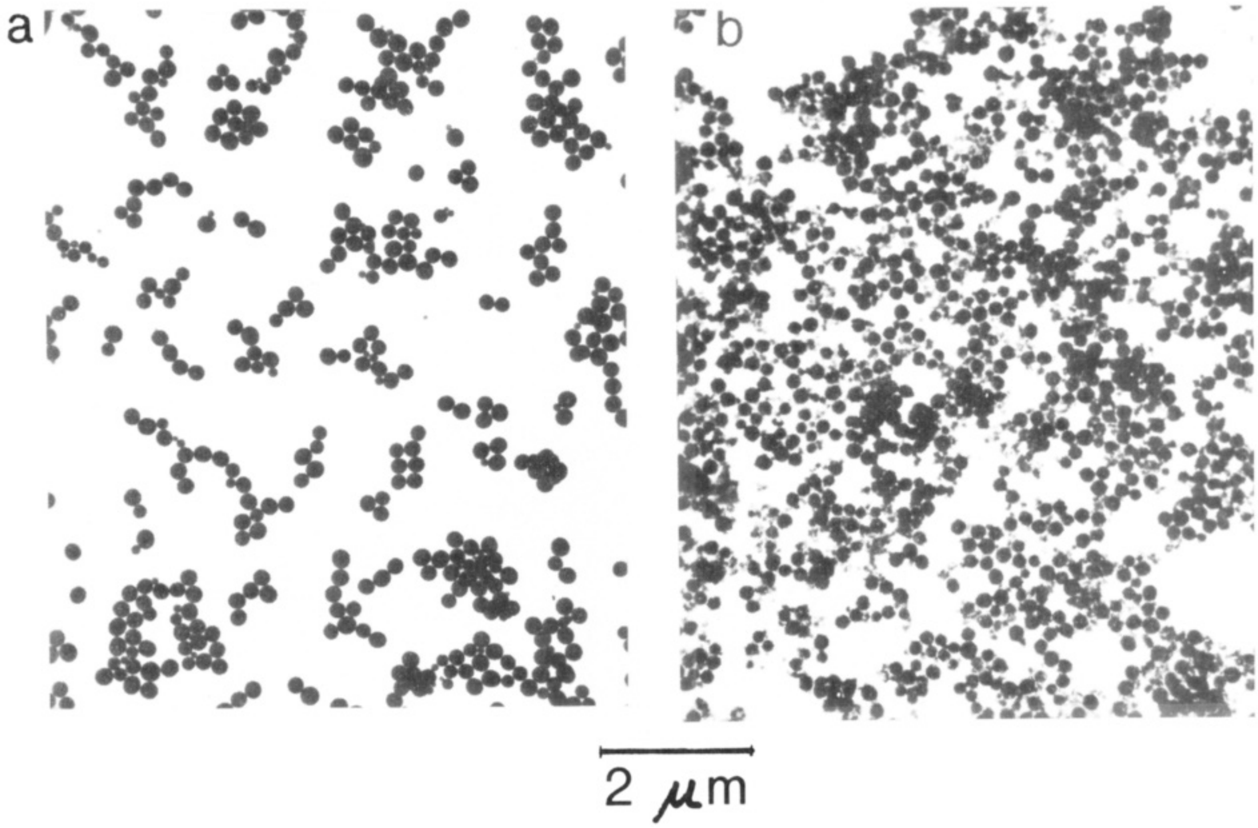

Figure 3. TEM of the particles obtained by aging at 60 °C for 9.5 h a solution prepared by the method II. Concentrations: $[Pb(NO_3)_2] = [Ti(i\text{-}Opr)_4] = 5.0 \times 10^{-3}$ mol dm^{-3}, $[Na_2HNTA] = 1.0 \times 10^{-2}$ mol dm^{-3}; and $[H_2O_2] = 0.2$ mol dm^{-3}; pH = 9.3 (a) as dried and (b) calcined at 500 °C for 10 min at the heating rate of 2 °C min^{-1}.

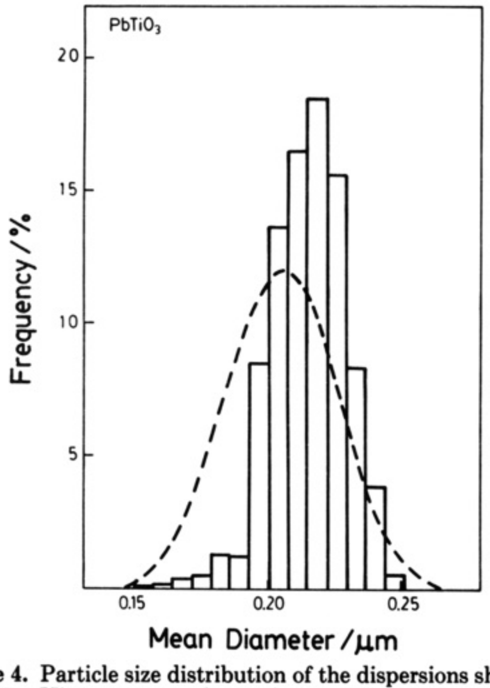

Figure 4. Particle size distribution of the dispersions shown in Figure 3a. Histogram was obtained from TEM, while the dotted line represents the photon correlation spectroscopy measurements with the N4MD instrument (Coulter).

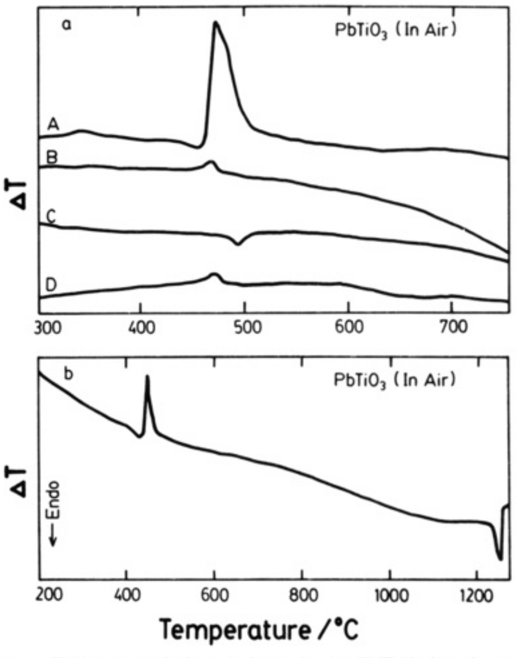

Figure 5. Differential thermal analysis (DTA) for the sample shown in Figure 6a. (a) Cyclic heat treatment from room temperature to 800 °C by heating (curve A), cooling (curve B), heating (curve C), cooling (curve D). (b) Continuous heating to 1400 °C.

other solid phase change on heating dried powder to 1400 °C, except for melting that takes place at 1230 °C.

Figures 7–10 summarize the effect of investigated parameters, varied around the optimum conditions, on the chemical composition of the sols, product yield, and the size of the particles as determined by the PCS. The product yield is defined as the total weight of metals in the solids divided by that in the initial solution (expressed in percent).

These results show that with the aging time at 60 °C the ratio [Pb]/[Ti] in the solids decreased while the particle size and the yield increased (Figure 7). It was also observed

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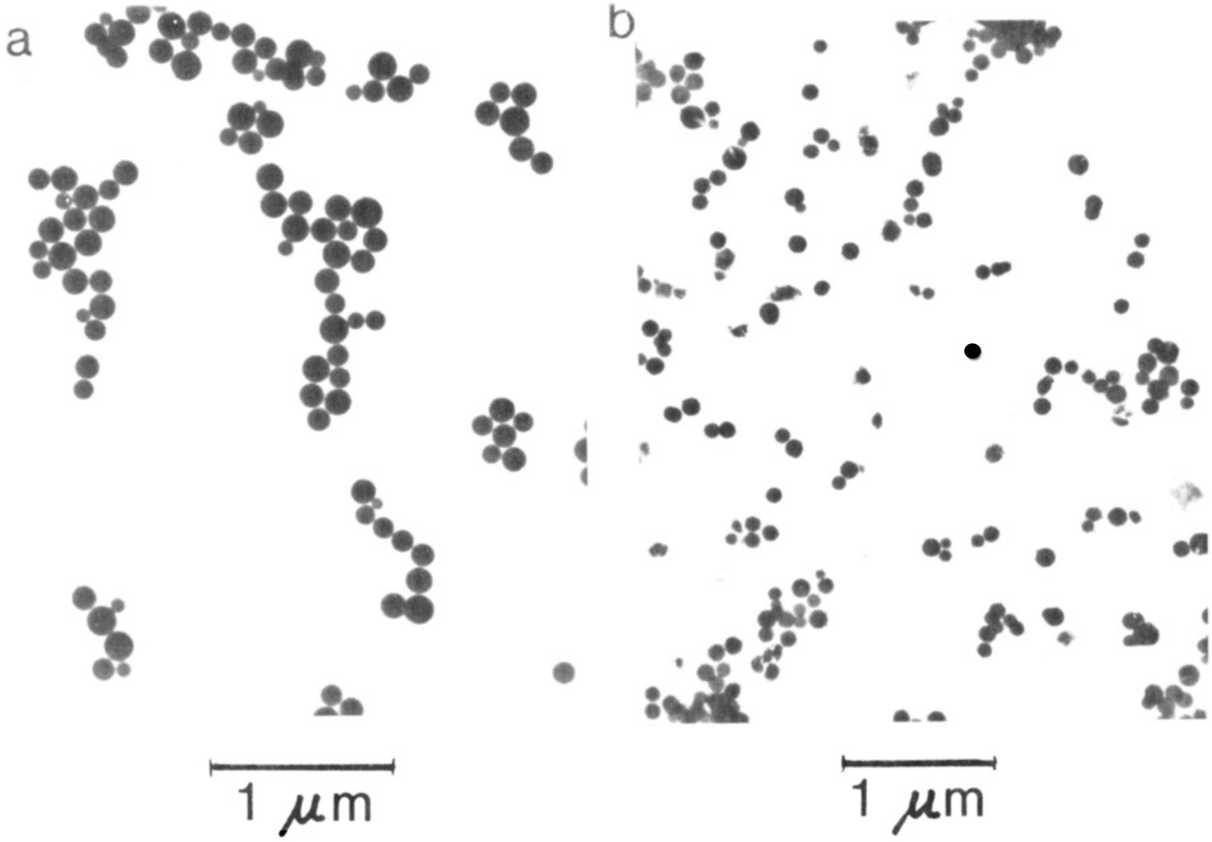

Figure 6. TEM of particles obtained by aging at 60 °C for 8 h a solution described in Figure 1b. Age of the intermediate mixed solution of $Pb(NO_3)_2$ and Na_2HNTA (C + D) before making final solution was less than 2 min (a) and 30 min (b).

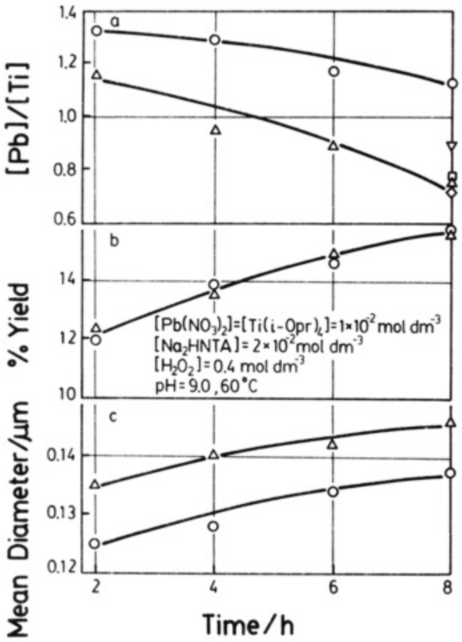

Figure 7. Influence of the aging time at 60 °C on (a) the molar ratio [Pb]/[Ti], (b) product yield, (c) average diameter for lead titanate precipitated by method II. Age of the intermediate mixture (C + D) before adding the second mixture (B + A + H_2O_2): 2 (○), 10 (▽), 20 (□), 30 (△), and 40 min (◇). Concentrations of reactants: $[Pb(NO_3)_2] = [Ti(i\text{-}Opr)_4] = 1.0 \times 10^{-2}$ mol dm^{-3}, $[Na_2HNTA] = 2.0 \times 10^{-2}$ mol dm^{-3}, $[H_2O_2] = 0.4$ mol dm^{-3}; pH = 9.0.

that the aging of the premixed solution of $Pb(NO_3)_2$ and Na_2HNTA (C + D), before adding the other set of reactants, had an appreciable effect on the composition and the size of the resulting particles (Figure 6).

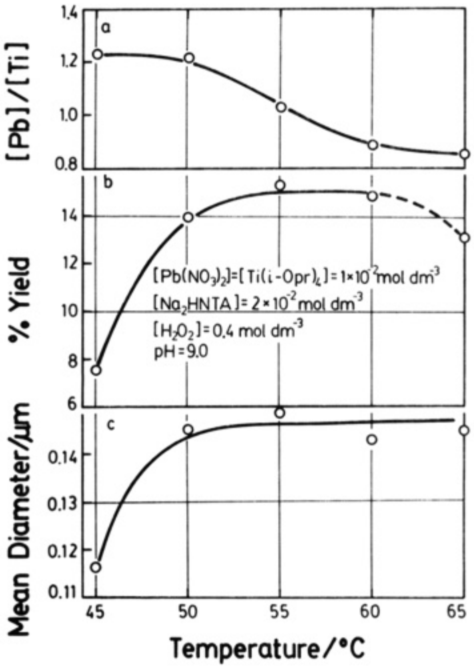

Figure 8. Influence of the aging temperature on the same parameters for the systems shown in Figure 7 heated for 6 h.

Since the molar ratio of [Pb]/[Ti] of the particles depended on the age of the mixture of $Pb(NO_3)_2$ and Na_2HNTA, the storage time before adding the other components was fixed at 30 min in the remaining experiments shown in Figures 8–10.

Figure 8 displays the effect of temperature on the same parameters as in Figure 7 for systems aged for 6 h. While the ratio [Pb]/[Ti] decreases as the temperature becomes higher, the particle size and yield remain essentially con-

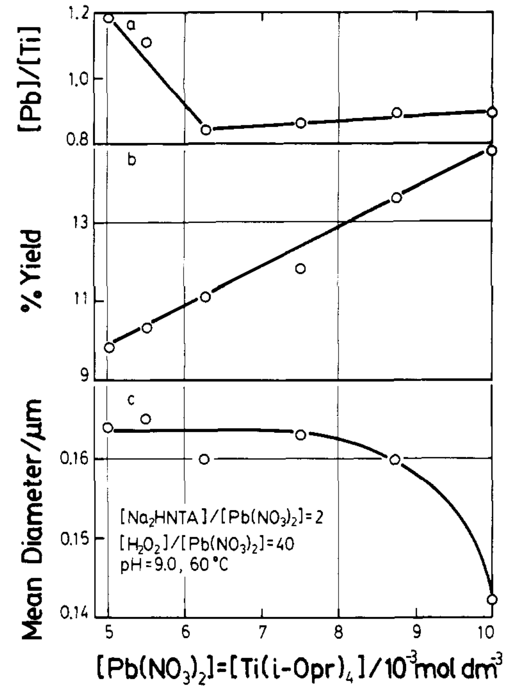

Figure 9. Influence of concentration of $Pb(NO_3)_2$ = [Ti(*i*-Opr)$_4$] on the same parameters as in Figure 7 for systems aged at 60 °C for 6 h. Other concentrations were kept at [Na_2HNTA] = 2.0[$Pb(NO_3)_2$], [H_2O_2] = 40[$Pb(NO_3)_2$]; pH = 9.0.

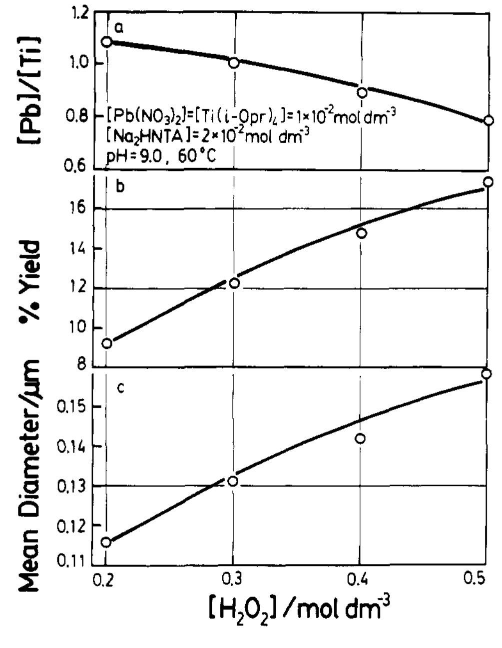

Figure 10. Influence of the total concentration of H_2O_2 on the same parameters for the system described in Figure 7, after 6 h of aging time.

stant at temperatures > 50 °C.

With increasing concentration of [$Pb(NO_3)_2$] = [Ti(*i*-Opr)$_4$] $\leq 9 \times 10^{-3}$ mol dm^{-3}, keeping [Na_2HNTA] = 2.0[$Pb(NO_3)_2$] and [H_2O_2] = 40[$Pb(NO_3)_2$], the ratio [Pb]/[Ti] in the solids decreases at first and then slightly increases while the particle size remains essentially the same (Figure 9).

Finally, the effect of the concentration of H_2O_2 on the same parameters is shown in Figure 10. It is quite apparent that the ratio [Pb]/[Ti] decreases, while the particle size and the yield increase with higher additions of H_2O_2.

By aging solutions containing more hydrogen peroxide than the optimum amount, polydispersed particles were

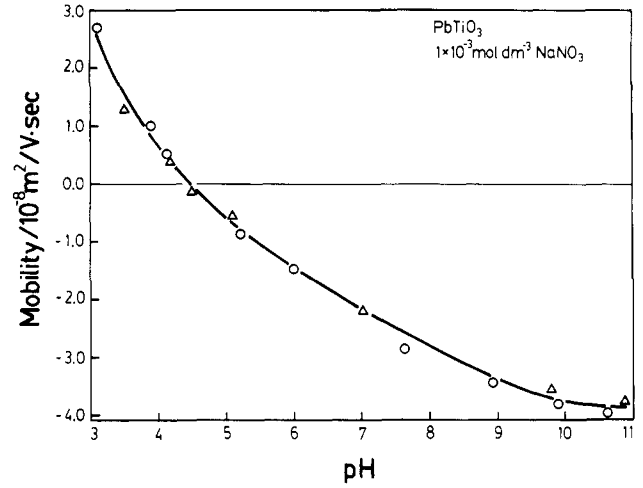

Figure 11. Electrokinetic mobilities as a function of pH of particles shown in Figure 6a (○) and 6b (△), at constant ionic strength of 1.0×10^{-3} mol dm^{-3} ($NaNO_3$).

generated due to the secondary nucleation. To prepare larger particles, i.e., to get a higher yield at the same number concentration, successive addition of hydrogen peroxide was carried out. After heating the solution of [$Pb(NO_3)_2$] = [Ti(*i*-Opr)$_4$] = 5.0×10^{-3} mol dm^{-3}, [Na_2HNTA] = 1.0×10^{-2} mol dm^{-3}, [H_2O_2] = 0.2 mol dm^{-3}, and pH = 9.0 at 60 °C for 6 h (conditions described in Figure 9), more hydrogen peroxide was added to make total [H_2O_2] = 0.3, 0.4, 0.5, and 0.6 mol dm^{-3}. After continuation of aging at 60 °C for 6 h the solids had the molar ratio [Pb]/[Ti] = 1.0, 0.82, 0.71, and 0.67, respectively, with a corresponding yield of 9.9, 11.4, 16.5, and 20.6%, as compared to the original product of [Pb]/[Ti] = 1.2 and a yield of 9.8%. For systems containing [H_2O_2] = 0.5 and 0.6 mol dm^{-3}, the particles appeared to be coated by tiny spheres.

Figure 11 shows the electrokinetic mobilities as a function of pH of the dispersions illustrated in Figure 6. Although the chemical composition and the surface morphology of the particles differed, their electrophoretic behavior was essentially the same.

Discussion

A stable solution of peroxotitanium is produced from the titanium aquo ion and hydrogen peroxide, which may be in excess, according to

$$Ti^{4+} + H_2O_2 + (n-2)H_2O \rightarrow [Ti(O_2)(OH)_{n-2}]^{(4-n)+} + nH^+ \quad (1)$$

Below pH ~1 the peroxotitanium complex is mononuclear, having the composition of $Ti(O_2)OH^+$. The so produced peroxotitanium complex forms a soluble chelate with the quadridentate anion NTA^{3-} of nitrilotriacetic acid.[20]

At pH > 9

$$Ti(O_2)(OH)_4^{2-} + HNTA^{2-} \rightarrow [Ti(O_2)(OH)NTA]^{2-} + 2OH^- + H_2O \quad (2)$$

The addition of Na_2HNTA to the $Pb(NO_3)_2$ solution yields a 1:1 metal chelate, which is negatively charged:[21]

$$Pb^{2+} + HNTA^{2-} \rightarrow [Pb{\cdot}NTA]^- + H^+ \quad (3)$$

A mixture of the above two metal chelates forms a stable aqueous solution at room temperature. At elevated tem-

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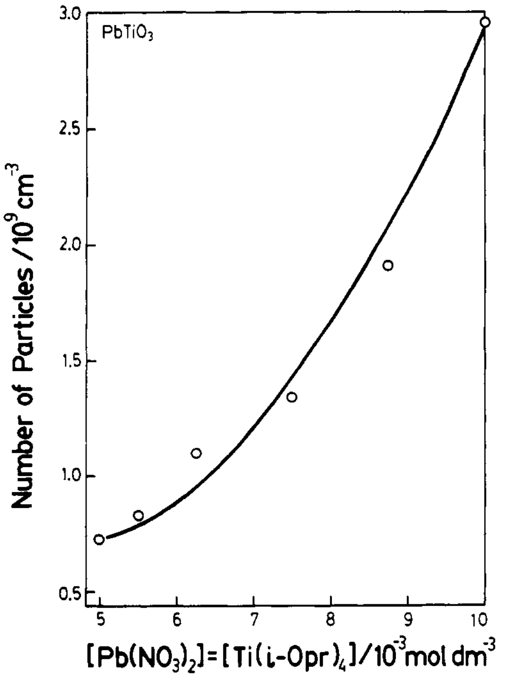

Figure 12. Particle concentration as a function of concentration of $Pb(NO_3)_2$ for systems shown in Figure 9.

peratures, in the presence of excess hydrogen peroxide, decomposition of these chelates results in a controlled release of Pb^{2+} and $Ti(O_2)(OH)_4^{2-}$, which eventually leads to homogeneous nucleation. A quite large value of the particle concentration (10^9 particles cm^{-3}) supports the assumption of homogeneous nucleation (Figure 12). The particle concentration, calculated from the experiments shown in Figure 9 by using the density of lead titanate as 7.5 g cm^{-3},[14] increases rapidly as the concentration of $Pb(NO_3)_2$ becomes higher, while other parameters had little effect on the number density of the dispersion. At still higher metal salt concentration the discrete uniform particles could not be generated without using a protective agent.

The time effect on the particle composition shown in Figure 7a may be explained by kinetic considerations. Although metal chelation is mostly a fast process, the interaction of $Pb(NO_3)_2$ and Na_2HNTA does not go to completion for at least 30 min, which is not unexpected for complexation with NTA. An attempt to establish the degree of chelation by pH measurement proved unsuccessful. On mixing 1 part of $Pb(NO_3)_2$ (0.1 mol dm^{-3}, pH = 4.2) and 2 parts of Na_2HNTA (0.1 mol dm^{-3}, pH = 6.0), the pH of the solution dropped immediately to 2.4 and remained constant. The calculation of the equilibrium concentration in the mixture of $Pb(NO_3)_2$ and Na_2HNTA, using known stability constants,[22] reveals that ~1% of total Pb exists as the free ion at pH = 2.3. However, the actual concentration of Pb^{2+} is higher until the equilibrium has been established. It is the excess concentration of Pb over Ti free cations that affects the composition of the precipitated solids at the earlier stage of reaction.

Table II. Metal Chelates Used for Preparation of Titanates

metal	chelating agent	stability const log *K* (ref 22)	ref
Ba	iminodiacetic acid (IDA)	1.67	10
Ba	ethylenediaminetetraacetic acid (EDTA)	7.78	10
Ba	diethylenetriaminepentaacetic acid (DTPA)	8.62	10
Pb	nitrilotriacetic acid (NTA)	11.39	this work
Pb	ethylenediaminetetraacetic acid (EDTA)	18.30	this work

At longer reaction times and higher H_2O_2 contents the ratio [Pb]/[Ti] decreases, yielding eventually particles richer in Ti than is the stoichiometric requirement for pure $PbTiO_3$. The X-ray analysis showed such solids to also contain $PbTi_3O_7$, which is a known compound.[11] It would seem that under the influence of H_2O_2 the peroxotitanium complex with NTA decomposes more readily than the $PbNTA^-$ solute, causing a change in the composition of the solid phase.

Although the stability of the chelated complexes of peroxotitanium is not known, it may be possible to select an appropriate chelating agent to prepare uniform titanate particles by taking into account the stability of the metal chelates of the divalent metal (Ba, Pb, etc.). Various kinds of chelating agents were tested previously[10] and in this work (Table II). With a weak chelate, such as Ba-IDA, it was not possible to obtain a clear starting solution. With a too strong chelate (e.g., Pb-EDTA) precipitation of TiO_2 ensues even though the starting solution was clear. Metal chelates having a stability constant of ~10^{10} seem to be appropriate to generate uniform titanate particles in the presence of peroxotitanium.

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Registry No. Lead titanium oxide, 12612-48-5.

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(22) Sillén, L. G.; Martell, A. E. Stability Constants of Metal-Ion Complexes. *Chem. Soc. Spec. Publ.* **1964**, *no. 17.*