Preparation of Agglomerate-Free and Highly Crystalline (Ba$_{0.5}$, Sr$_{0.5}$)TiO$_3$
Nanoparticles by Salt-Assisted Spray Pyrolysis

Yoshifumi ITOH and Kikuo OKUYAMA
Department of Chemical Engineering, Graduate School of Engineering, Hiroshima University, 1-4-1, Kagamiyama, Higashi-Hiroshima-shi 739–8527

Optimum conditions for the synthesis of non-agglomerated barium strontium titanate (BST) nanoparticles were examined. The effects of salt concentration, operating temperature, and droplet/particle residence time in the hot zone as a function of carrier gas flow rate and heating zones on particle size, crystallinity, and chemical composition of BST nanoparticles were investigated. Highly crystalline, dense BST nanoparticles in a size range of 17–160 nm were obtained by controlling initial excess of barium and strontium in the solution, relative to titanium. The particle size decreased with decreasing salt concentration, operating temperature and droplet/particle residence time in the hot zones. The chemical homogeneity of the resulting particles was analyzed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The chemical composition of the resulting powder completely reflected the initial solution composition. SASP can be used to produce highly crystalline (Ba$_{1-x}$, Sr$_x$)TiO$_3$ (x=0.5) nanoparticles in sizes as small as 30 nm in a single step.

[Received July 11, 2003; Accepted August 29, 2003]

Key-words: Fine ceramics, Nanoparticle, Crystal growth, Barium strontium titanate, Salt-assisted, Spray pyrolysis

1. Introduction

Nanoparticles and nanostructured materials comprised of metals and semiconductors which exhibit size dependent optical, magnetic, electronic and catalytic properties have been heralded as the next generation of electronic devices in the design of advanced materials. Recently, electronic devices such as multilayer ceramics (MLCs) have been miniaturized. High dielectric constant materials such as barium titanate (BaTiO$_3$) and related compounds with ultra-fine grains (below 50 nm) are required in order to achieve a thinner dielectric layer and to reduce the firing temperature.\(^{1}\) BaTiO$_3$ is seldom used in its pure form, but, rather, is combined with special additives to modify and enhance its dielectric properties.\(^{2}\) Additives such as Sr$^{2+}$ and Zr$^{4+}$ for BaTiO$_3$ are usually used to reduce the $T_c$ (Curie temperature) down to 120°C. Other additives such as Ca$^{2+}$ and Mg$^{2+}$ are used for stabilizing the temperature dependence of its basic properties. (Ba$_{1-x}$, Sr$_x$)TiO$_3$ (BST) represent some of the most extensively studied ferroelectric materials due to their size and composition dependence of the dielectric constants and Curie temperatures. BST has been found to applications in tunable filter, oscillators and phase elements for directional phase array antennas. Due to their high dielectric constants, BSTs have potential for use in large-scale integrated circuits (VLSI), such as dynamic and non-volatile random access memories (DRAMs). Thus, BST compounds are currently being investigated with regard to various electronic applications. Highly pure, highly crystalline, and agglomerate-free particles are required for the manufacturing of reliable electronic devices.

Several routes for the synthesis of BST particles have been reported. These include hydrothermal\(^ {3}\) and solid state processes\(^ {4,5}\) which are used commercially for BaTiO$_3$ powder synthesis, because of their low cost and simplicity. However, several hours are required to produce homogeneous and highly crystalline particles. In the hydrothermal synthesis, powders are proceeded with a small excess of barium and strontium, relative to titanium to obtain BST particles as a pure phase.

It is well known that spray pyrolysis represents a continuous and single-step method for the preparation of fine homogeneous and multi-component powders. Conventional spray pyrolysis (CSP)\(^ {6,7}\) results in multiple nanosized crystallites that are virtually inseparable, since they form a three-dimensional network. Salt-Assisted Spray Pyrolysis (SASP) has been developed as a novel route to the preparation of nanoparticles (below 100 nm).\(^ {8}\) The presence of a salt in the precursor solution inhibits the agglomeration of nanocrystallites resulting in the formation of nanogglomerated nanoparticles. This route requires no further thermal treatment of the product, such as calcination or annealing, because metal salts enhance both the homogeneity of the crystals and crystal growth.

In our previous study\(^ {9,10}\) optimum conditions for the formation of nanogglomerated and dense BaTiO$_3$ nanoparticles were achieved by controlling the salt concentration and operating temperature. Insuffient salt resulted in the formation of agglomerated particles. The primary particle size decreased with decreasing salt concentration and operating temperature. At a salt concentration of 0.75 mol/l and a precursor concentration of 0.05 mol/l, agglomerate-free and dense BaTiO$_3$ nanoparticles in a size range of 30–360 nm with a narrow size distribution were obtained by simply changing the operating temperatures.

In this work, the effect of salt concentration, operating temperature, and droplet/particle residence time in the hot zones on particle morphology, particle size, crystallinity, and chemical homogeneity of SASP prepared (Ba$_{1-x}$, Sr$_x$) \(x=0.5\) TiO$_3$ nanoparticles were investigated without a post-heating treatment.
2. Experimental

Precursor solutions were prepared by dissolving a stoichiometric ratio of barium nitrate (Ba(NO₃)₂) (99.0%), strontium nitrate (Sr(NO₃)₂) (99.0%), and titanium tetraisopropoxide (TTIP) (97.0%) in a solution of 1 mol/l nitric acid. The mixture was heated at 0.05 mol/l of (Ba₁₋ₓ₋ₓ Srₓ)TiO₃ (x = 0.5), BST, while the barium nitrate: strontium nitrate: TTIP ratio used was 1 : 1 : 2. Solutions of KNO₃ (99.0%) and NaN₃O₂ (99.0%) were added to the precursor solution at salt/Ti molar ratios from 15.0 to 30.0. All chemicals were purchased from Kanto Kagaku, Tokyo. The detailed experimental setup has been described elsewhere.⁹ The precursor solution was sprayed by means of an ultrasonic aerosol atomizer (1.7 MHz) into a 1.3 cm inner diameter, 150 cm length Al₂O₃ ceramic tube heated by an electric furnace at various temperatures (550–1000°C) with five independently-controlled heating zones, each of which was 20 cm in length. Nitrogen, at a flow rate of 1 l/min, unless otherwise stated, was used to carry the atomized aerosols into the furnace. The resulting powders were collected by an electrostatic aerosol precipitator operated at 150°C while the gases were dried by passing them through a cold trap and a diffusion dryer, followed by neutralization by passage through a NaOH trap before being evacuated by a vacuum pump. To remove the salt, the collected particles were washed, centrifuged with ultra pure water and dried. The crystalline phases were identified by X-ray diffraction (XRD; Rigaku RINT 2200V) with Cu Kα radiation (λ = 0.154058 nm). The crystallite size of the crystallites was estimated using Scherer’s formula. The grain size and morphology of the particles were characterized by field emission scanning electron microscopy (FE–SEM; Hitachi S5000) operated at 20 kV and transmission electron microscopy (TEM; JEOL JEM–2010). Elemental analysis of the samples was also determined by energy-dispersive spectroscopy (EDS; Thermo NORAN, SERIES II), interfaced with the TEM system. The geometric mean diameter and geometric standard deviation were determined by randomly sampling 200 particles from the SEM/TEM photographs. The Chemical compositions of barium, strontium, and titanium of resulting powders were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES; SII SPS–3000). For the ICP-AES sample, BST powders were dissolved in a solution of 4 g of concentrated HCl and 5 g of ultra pure water in a tightly covered Teflon container at 120°C for 2 h. Thereafter, 0.1 ml of concentrated HNO₃ to stabilize metal ions and ultra pure water were added to adjust the concentration of metal ions.

3. Results

Figure 1 shows FE–SEM images of samples, showing the effects of salt concentration and operating temperatures on the morphology of BST particles. All precursor solution concentrations were 0.05 mol/l and salt concentrations were (a) 0 (CSP: Conventional Spray Pyrolysis) and (b)–(f) 0.75 mol/l, respectively. The CSP particles prepared at 1000°C (Fig. 2(a)) were spherical with a rough surface composed of agglomerated small primary particles. Particles prepared at 1000°C with salt (Fig. 2(b)) were hard aggregates of a few crystallites with a smooth surface and well-defined grain boundaries compared to the CSP sample (Fig. 2(a)). By decreasing the operating temperature from 1000°C (Fig. 1(b)) to 900°C (Fig. 1(c)), the degree of agglomeration decreased resulting in particles with a uniform and smooth surface and diameters of around 60 nm. A further decrease in operating temperatures tended to decrease the primary particle size, giving nearly nonagglomerated particles. Agglomeration of the primary particles was controlled not only by increasing the salt concentrations but also by decreasing the operating temperatures. A salt concentration in excess of 0.75 mol/l was required to completely inhibit the agglomeration of BST nanoparticles at temperatures below 900°C.

Figure 2 shows XRD patterns of as-prepared BST particles synthesized by (a) CSP at 1000°C and (b)–(h) SASP at various operating temperatures (550–1000°C). In addition,
Fig. 2. XRD patterns of BST particles prepared with 0.05 mol/l precursor solutions by (a) conventional spray pyrolysis (CSP) at 1000°C and salt-assisted spray pyrolysis (SASP) at salt/Ti ratios of 15 at (b) 1000°C, (c) 900°C, (d) 800°C, (e) 700°C, (f) 600°C and (g) 550°C.

standard XRD patterns for the cubic phase of (Ba0.5, Sr0.5) TiO2 (JCPDS No. 39-1395) are also shown at the bottom of Fig. 2. All particles showed the presence of cubic BST. As will be discussed below, the crystallite sizes, as estimated by Scherer’s formula, are in good agreement with the Feret diameters. Pure phases of BST nanoparticles were obtained in the temperature range from 1000°C to 700°C (Figs. 2(b)–2(e)). Moreover, SASP particles, prepared at temperatures of 1000°C–700°C (Figs. 2(b)–2(e)), showed sharper peaks than the CSP-made particles (Fig. 2(a)) indicating the presence of larger crystallites. The primary particle sizes of the SASP-prepared BST particles, are actually, larger than that of CSP-prepared particles in the operating temperature 1000°C to 800°C evidenced by FE–SEM observations. The use of salt, not only enhanced particle growth and crystallinity and inhibited agglomeration but reducing operating temperatures also resulted in the production of similar primary particle sizes to CSP-made BST particles. Particles prepared at temperatures below 650°C (Figs. 2(f)–2(h)) contained only small amounts of residual components such as TiO2 or amorphous materials. However, XRD peaks corresponding to BaCO3 or SrCO3 were not detected.

Figure 3 shows TEM images of SASP prepared BST particles at various conditions, (a) 700°C and (b) 600°C without any post heat treatment. The carrier flow rate for Figs. 3(a) and 3(b) was 1 l/min. The inset image in Fig. 3(a) shows an enlarged picture of BST particles. The inset values show the geometric mean diameter and standard deviation of the particles. All samples were dense, highly crystalline and nearly nonagglomerated. The use of SASP prevented pore formation inside particle and resulted production of highly crystalline BST nanoparticles, as evidenced by the enlarged TEM image. It is also clear that BST nanoparticles having a size of around 17 nm could be prepared by SASP at an operating temperature of 600°C, but these particles contained TiO2, based on the XRD analysis. As a result, highly crystalline and pure phase BST nanoparticles with diameters as small as 30 nm could be prepared without any compositional control and heat treatment.

Figure 4 shows XRD patterns and FE–SEM images of the effects of operating temperatures of (a) 900°C, (b) 800°C, and (c) 700°C, respectively, on the particle sizes and morphologies of SASP-made BST nanoparticles when the salt concentration increased from 0.75 mol/l to 1.5 mol/l. The crystallinity and the primary particle size of SASP-made BST particles increased at the same operating temperature as the salt concentration increased.

Figure 5 shows XRD patterns and FE–SEM images of the effect of droplet/particle residence time in the hot zones on the crystallinity and morphology of SASP-made BST particles as a function of carrier flow rate (Figs. 5(a) and 5(b)) or the furnace length (Fig. 5(c)) through the number of 20-cm heating zones at 700°C. The salt concentration was maintained at 0.75 mol/l. All particles were cubic BST and small amounts of unreacted TiO2 remained in all the samples (marked with ×). When the carrier flow rate was increased from 1 (Fig. 2(e)) to 1.5 (Fig. 4(a)), 2.0 (Fig. 4(b)), and 2.5 (not shown), both the crystallinity and the particle size decreased, respectively. When the furnace length was decreased from 100 cm (Fig. 1(e)) to 20 cm (Fig. 4(c)), the primary particle size decreased. However, increasing the carrier flow rate or decreasing the length of the heating zone resulted in the formation of side reaction products such as TiO2 or amorphous phase. The maximum peak intensity of SASP-made BST prepared using 1 heating zone and a flow rate of 1 l/min (Fig. 4(c)) was higher than that prepared using 5 zones and a 2.0 l/min flow rate (Fig. 4(a)). Regardless of the heating zone length, all particles were cubic BST and had similar primary particle sizes. Thus, the decomposition of the source precursors and diffusion was sufficient to homogenize the intermediates into a single BST phase at temperatures above 700°C with 5 heating zones and a carrier flow rate of 1.0 l/min.

The geometric mean diameters of BST nanoparticles as a function of synthesis temperature are summarized in Fig. 6(a). Particle sizes were determined by measuring the Feret diameter from FE–SEM images. The white and black circles refer to the primary particle sizes as a function of the
Fig. 4. XRD patterns and FE-SEM images of SASP-made BST particles prepared at different temperatures: (a) 900°C, (b) 800°C and (c) 700°C. Precursor solutions 0.05 mol/l and salt/Ti ratio 30. The geometric mean diameter and standard deviation of the primary particles are (a) 41.2 nm and 1.33, (b) 44.2 nm and 1.18, (c) 32.5 nm and 1.22, respectively.

Fig. 5. Effect of the residence time on the crystallinity and morphology of BST particles. (a) 5 zones (100 cm), 1.5 l/min, (b) 5 zones (100 cm), 2.0 l/min, (c) 1 zone (20 cm), 1 l/min. Solution concentration 0.05 mol/l and salt concentration 0.75 mol/l. The geometric mean diameter and standard deviation of the primary particles are (a) 24.3 nm and 1.21, (b) 20.7 nm and 1.23, (c) 20.5 nm and 1.24, respectively (X: unreacted TiO₂ phase).
operating temperature of 5 heating zones and a carrier flow rate of 1.0 l/min using 5 heating zones, at salt concentrations of 0.75 mol/l and 1.5 mol/l, respectively. The white square and triangle symbols refer to the primary particle sizes prepared at an operating temperature of 700°C using 5 heating zones at flow rates of 1.5 l/min and 2.0 l/min, respectively. The gray circle refers to the primary particle size prepared at a temperature of 700°C using 1 heating zone at a flow rate of 1.0 l/min. The primary particle size tended to decrease with decreasing operating temperature and salt concentration. Increasing the carrier flow rate resulted in a decrease in primary particle sizes. However, TiO₂ and/or amorphous phase appeared to be below 25 nm in this study. The correlation of the geometric mean diameters and crystallite sizes, as estimated by Scherer’s formula, are shown in Fig. 6(b). The full-width of the half maximum (FWHM) of (110) diffraction peak has been used for predicting the crystallite size because this peak is very close to (111) peak of standard silicon. Scherer formula is

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]  

where \( D \) is crystallite size, \( \lambda \) is the wavelength of the X-ray, \( \beta \) is the FWHM, and \( \theta \) is the scattering angle. The geometric mean diameter of the primary particles decreased from 90 nm to 17 nm with decreasing pyrolysis temperature from 900°C to 600°C while the crystallite sizes are in good agreement with the corresponding Peret diameters. These results show that SASP can be used to produce size tunable particles down to 30 nm and dense BST nanoparticles without additional heat treatment, such as post-annealing when temperatures above 700°C and 5 heating zones are used.

High purity is essential for the optimal performance of nanoparticles. The molten salts of the product particles might be removed by a washing process. The energy dispersive spectroscopic (EDS) analysis of BST nanoparticles as a function of characteristic X-ray energy at a temperature of 800°C is shown in Fig. 7 as a typical example. Major peaks, corresponding to barium, strontium, and titanium, are present. Neither a potassium nor a sodium peak was detected in EDS spectra. On the other hand, traces of copper and carbon were detected, probably originating from the TEM sample substrate.

The analytical result of the ICP-AES for as-prepared particles having various particle sizes is given in Table 1. The results showed that the overall stoichiometry of BST particles was achieved even though the particle sizes (operating temperatures) changed. The contents of barium, strontium, and titanium of resulting powders directly reflected the composition of the initial solution. Thus, SASP can be used to produce stoichiometric BST nanoparticles without any stoichiometric control of the initial precursor solutions.

### Table 1. Overall Chemical Composition of (Ba, Sr)/TiO₂ Nanoparticles as a Function of Particle Diameter

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sample No.</th>
<th>( T ) [°C]</th>
<th>( d_0 ) [nm]</th>
<th>Ba [-]</th>
<th>Sr [-]</th>
<th>Ti [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BST02</td>
<td>700</td>
<td>29.5</td>
<td>0.249</td>
<td>0.252</td>
<td>0.499</td>
<td></td>
</tr>
<tr>
<td>BST03</td>
<td>800</td>
<td>41.5</td>
<td>0.248</td>
<td>0.250</td>
<td>0.502</td>
<td></td>
</tr>
<tr>
<td>BST05</td>
<td>900</td>
<td>59.7</td>
<td>0.249</td>
<td>0.248</td>
<td>0.503</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 6.** Correlation of primary particle sizes of BST particles as a function of (a) operating temperature and (b) crystallite size.

**Fig. 7.** Energy dispersive spectra of BST particles prepared at 800°C.
operating temperature and salt concentration. The over all stoichiometry of BST nanoparticles was completely reflect-
ed by the initial solution composition for primary particle
sizes above 30 nm.

The mechanism of uniform nanoparticle formation using
the SASP method, however, is not well understood. The for-\mation of nanoparticles in the molten salt layer is thought
to be one of segregation because of the large differences in
the melting points of salt and product particles. Metal salts
and product particles precipitate in the droplet/particle
during solvent evaporation. The KNO₃ and NaNO₃ mixture
melts to form a liquid phase at temperatures above 230°C.¹¹
The liquid phase promotes self-assembly, crystallization, and
sintering of the product particles, thus preventing the
formation of polycrystalline particles, pores in the primary
due to the elimination of fine bubbles that are
initially present in the solution. As mentioned above, the
primary particle sizes decreased with decreasing salt
concentration. However, insufficient salt concentration
resulted in the formation of agglomerated nanoparticles
because the crystallites readily come into contact with each
other due to the coagulation in the droplet/particle. On the
other hand, sufficient molten salt inhibits aggregation of
primary particles in a droplet/particle.⁹,¹⁰ This implies an
optimum salt concentration exists for forming nonagglomer-
ated nanoparticles. However, at high operating tempera-
tures, even though the BST particles are surrounded by
sufficient molten salt, diffusion, nucleation, chemical
reactions, and the coagulation of primary BST nanoparticles
are promoted to form agglomerated particles (Fig. 1(b)). On
the other hand, at lower operating temperatures (550–
900°C), it is generally thought that particle growth is not
based on the coagulation of primary particles but, rather, is
based on nucleation of the intermediate BST, since crystal
growth and chemical reactions are delayed as the operating
temperature decreases. Thus, it is presumed that the BST
intermediate grows on the primary particle surface and the
salt layer inhibits the aggregation of primary particles at
lowering operating temperatures. Moreover, the presence of
molten salt enhances crystallization, resulting in the
formation of highly crystalline nanoparticles. However,
decreasing the operating temperatures below 650°C or
reducing the droplet/particle residence time at 700°C
resulted in the production of biphasic particles of BST and
TiO₂. Melting points of Ba(NO₃)₂ and Sr(NO₃)₂ are
reported to be 592°C and 570°C, respectively, for bulk
materials and they decompose at around those melting
points. However, TiO₂ is formed at temperature of around
400°C.¹⁰ It is supposed that small amounts of Ba(NO₃)₂ and
Sr(NO₃)₂ did not completely decompose to form BST
nanoparticles, considering the low operating temperature
and short residence time in the hot zone used in this study.
As a result, by increasing the furnace length or decreasing the
carrier flow rate, Ba(NO₃)₂ and Sr(NO₃)₂ decompose to
form BST particles due to longer residence time. The ex-
cess of Ba(NO₃)₂ and Sr(NO₃)₂ and any intermediates are
removed by the washing process.

Further studies will be necessary to obtain a phase pure of

BST nanoparticles below 20 nm by controlling the precursor
composition with an initial excess of barium and strontium
in solution, relative to titanium and to understand the effect
of surface energy between precipitate/crystallite and
molten salt, the solubility of the precipitant in the molten
salt, viscosity of the salt, and the diffusivity in the droplet/
particle.

5. Conclusions

Size tunable (17–60 nm) and dense BST particles were
prepared by changing the operating temperature and salt
concentration without any post heat treatment. The use of
salts leads to an increase in crystallite size and a smoother
surface and contributes to the formation of agglomerate-free
BST nanoparticles. Decreasing the pyrolysis temperature
decreases the crystallite size and gives rise to uniform parti-
cles with a smooth surface and narrow size distribution.
Increasing the concentration of the salt and prolonging the
residence time in the hot zone also resulted in an increase in
crystallite size. Agglomerate-free BST nanoparticles, 30 nm
in size, can be prepared without any control of the initial
precursor concentrations. SASP can be used to produce
monodispersed, nonagglomerated, dense, highly crystalline,
and size tunable particles in a few seconds of heating time.

Acknowledgement The authors thank to Dr. I. W. Lenggoro
for his valuable advices and Mr. Hironaka Fuji for experimental
assistance. Grant-in-Aids and a fellowship sponsored by the
Ministry of Education, Culture, Sports, Science and Technology
of Japan and the Japan Society for the Promotion of Science (JSPS)
are gratefully acknowledged. This work was also supported in part
by the New Energy and Industrial Technology Development
Organization (NEDO)’s “Nanotechnology Materials Program-
Nanotechnology Particle Project” based on funds provided by the
Ministry of Economy, Trade, and Industry (METI), Japan, by
Hosokawa Powder Technology Foundation, and by the Sasakawa
Scientific Research Grant from The Japan Science Society.

References

(1999).
4) Dobal, P. S., Dixit, A., Katuyar, R. S., Garcia, D., Guo, R. and
9) Itoh, Y., Lenggoro, I. W., Pratsinis, S. E. and Okuyama, K., J.
10) Itoh, Y., Lenggoro, I. W., Okuyama, K., Madler, L. and
(2003).