

Preparation of $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ Particles by Vapor Phase Hydrolysis of Precursors Formed through Alkoxide-Hydroxide Route

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Crystalline $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (BZT) particles were successfully prepared at 100°C through alkoxide-hydroxide route. Methanol solution of Ba hydroxide was mixed and reacted with Zr-butoxide and Ti-isopropoxide at room temperature, and then dried under reduced pressure at $\leq 40^\circ\text{C}$ to form powder precursors. The powder precursors were hydrolyzed by introducing nitrogen gas containing water vapor at 100°C . As-hydrolyzed products were crystalline nano size powders of BZT solid solutions with specific surface areas of $50\text{-}80\text{ m}^2/\text{g}$. By increasing Zr content in the BZT, the XRD peaks shifted to lower angles and the Curie temperatures shifted to lower temperatures. $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ bodies sintered at 1300°C exhibited a dielectric constant of approximately 5000 and a $\tan \delta$ of approximately 2 % at room temperature.

Key words: barium zirconate titanate, vapor-phase hydrolysis, nanosize powder, dielectric constant, low-temperature process

1. Introduction

BaTiO_3 and related materials are widely employed in main electronic components such as multilayer ceramic capacitors (MLCCs), positive temperature coefficient (PTC) thermistor and piezoelectric transducers. In general, such materials have been prepared by a number of wet chemical processes such as coprecipitation, oxalate, sol-gel and hydrothermal synthesis. Chemically prepared powders have high purity, submicron particle sizes and much better compositional uniformity than those made by the conventional mixing method. In the fabrication of MLCCs,^{1,2)} chemically prepared powders allow thinner dielectric layers to be used, resulting in the increase of volumetric efficiency.

Dielectric constants of BaTiO_3 ceramics can be increased by using additives which shift the Curie temperature of 130°C closer to room temperature. For example, $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ceramics are reported to have higher dielectric constants over 10000 at room temperature.

Our objective is to develop a simple and economical low temperature preparation process for $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ powders using alkoxide-hydroxide

method, which has been reported³⁾ for the chemical preparation of $(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3$ powders.

2. Experimental

$\text{Ba}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ ($n \approx 1$) obtained by heating $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ at 300°C was dissolved in methanol, and filtered through ultra-filter membranes to remove undissolved hydroxides. After filtration, the concentration of Ba hydroxide in the methanol solution was determined using the titration technique. The concentration of $\text{Ba}(\text{OH})_2$ in methanol was adjusted to 0.5 mol/l .

The methanol solution of Ba hydroxide was mixed with a stoichiometric amount of Ti-isopropoxide and Zr-butoxide with a desired composition ratio. The mixture was allowed to react under conditions of stirring for 24h at room temperature. After the reaction, methanol was evaporated under reduced pressure at $\leq 40^\circ\text{C}$ using a rotary evaporator, whereupon the precursors were obtained as free-flowing white powders.

The powder precursors were slowly hydrolyzed at 100°C by introducing N_2 gas containing water vapor into the rotary evaporator rotating at 60rpm.

The precursors and the hydrolyzed products were examined by thermogravimetric analysis (TGA)/differential thermal analysis (DTA), specific surface area (SSA), scanning electron microscope (SEM) and X-ray diffraction (XRD). The entire process is schematically depicted in Fig. 1.

In this work, our efforts were focused on the chemical preparation and characterization of $Ba(Zr_xTi_{1-x})O_3$ powders. Some of the hydrolyzed powders were calcined at 900 °C for 2h. The calcined powders were ball-milled overnight in alcohol, and then pressed into disks and sintered at 1250, 1300 and 1350 °C for 2h. The dielectric properties of BZT sintered bodies were measured using an impedance analyzer at 1kHz.

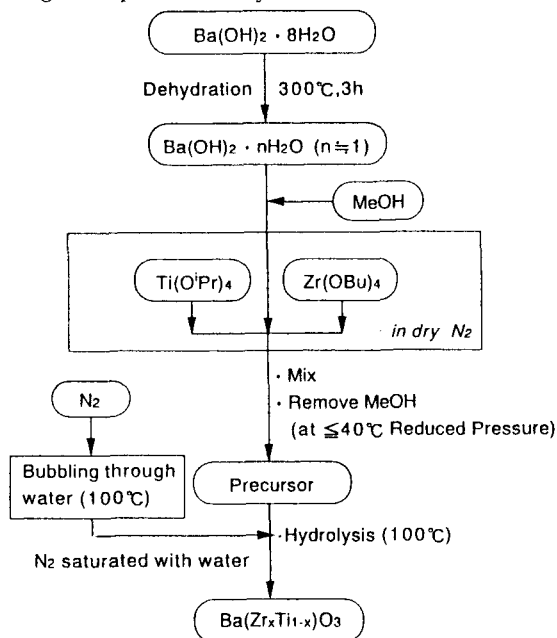


Fig.1 Flow chart preparation of $Ba(Zr_xTi_{1-x})O_3$ particles by vapor-phase hydrolysis.

3. Results and Discussion

3.1 Thermal analysis of precursors and hydrolyzed powders

Figure 2 shows the TG and DTA curves of the precursors and hydrolyzed products. The powder precursors derived from the reaction of hydroxide with alkoxides showed the weight loss of approximately 30 % at 1000 °C. An endothermic peak due to the evaporation of adsorbed water and solvent was observed in the temperature range of 100-180°C. The weight loss at around 650 °C was attributable to decomposition of the barium

carbonate formed during heating, as confirmed by XRD measurement. On the other hand, in the hydrolyzed products, the weight loss at 1000°C was about 6 % as determined by the TG. The gradual weight loss up to 1000°C in TG may be attributable to the evaporation of adsorbed water and solvent, and elimination of OH groups in crystalline powder. Well-defined peaks, however, were not observed in the DTA curve of the hydrolyzed products.

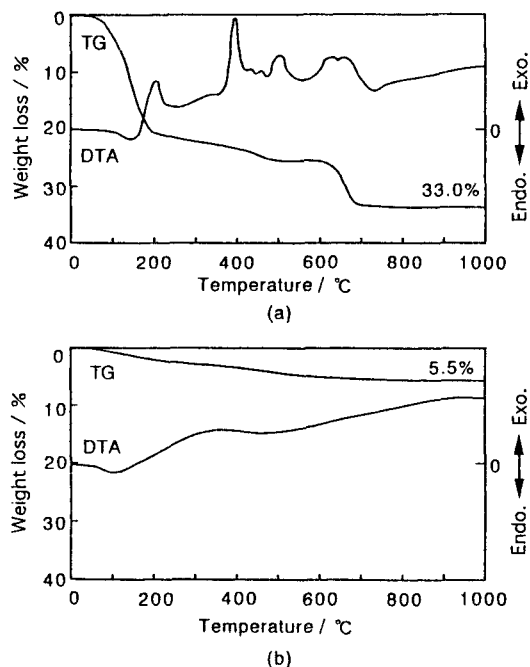


Fig.2 TG/DTA curves of $Ba(Zr_{0.2}Ti_{0.8})O_3$ powders. (a)Precursor, (b)Hydrolyzed product.

3.2 Hydrolyzed $Ba(Zr_xTi_{1-x})O_3$ powders

As-hydrolyzed $Ba(Zr_xTi_{1-x})O_3$ powders showed a relatively high crystallinity with nearly the same compositions as those of the starting reactant solutions. For example, in hydrolyzed $Ba(Zr_{0.2}Ti_{0.8})O_3$ samples, the ratio of Zr/Ti and Ba/(Zr+Ti) were determined to be 0.17/0.84 and 1.01 by inductively coupled plasma atomic emission spectroscopy (ICP) analysis.

The specific surface areas of as-hydrolyzed $Ba(Zr_xTi_{1-x})O_3$ powders are shown in Table I. SEM micrographs of the as-hydrolyzed and calcined $Ba(Zr_xTi_{1-x})O_3$ powders are shown in Fig. 3. The as-hydrolyzed powders were very fine particles of 30-40 nm in diameter with specific surface areas of 50-80 m²/g, and were weakly agglomerated. On the other hand, the calcined powders were hard

agglomerates that could not be broken up by ultrasonication.

Table I Specific surface areas of as-hydrolyzed $Ba(Zr_xTi_{1-x})O_3$ powders.

	SSA(m ² /g)
$Ba(Zr_{0.05}Ti_{0.95})O_3$	56.0
$Ba(Zr_{0.10}Ti_{0.90})O_3$	49.0
$Ba(Zr_{0.15}Ti_{0.85})O_3$	54.0
$Ba(Zr_{0.20}Ti_{0.80})O_3$	56.6
$BaZrO_3$	82.5

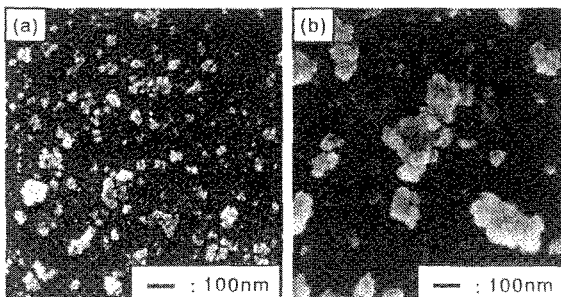


Fig.3 SEM micrographs of $Ba(Zr_{0.2}Ti_{0.8})O_3$ powders. (a) As-hydrolyzed, (b) Calcined at 900°C.

Figure 4 shows the XRD patterns of the precursors, as-hydrolyzed and calcined powders of $Ba(Zr_{0.2}Ti_{0.8})O_3$. The precursors were amorphous, while the as-hydrolyzed products showed a single phase of $Ba(Zr_{0.2}Ti_{0.8})O_3$ with good crystallinity. The calcination at 900°C increased the crystallinity of the powders due to the development of grain growth. XRD patterns of BZT powders indicated a shift in the peaks to smaller angles with higher Zr content.

Lattice constants were calculated for the as-hydrolyzed $Ba(Zr_{0.2}Ti_{0.8})O_3$ powders and those calcined at 900°C, and the relation between lattice constants and molar ratios of $Ti/(Zr+Ti)$ is shown in Fig. 5. The values calculated using the joint committee on powder diffraction standards (JCPDS) cards are also shown. The lattice constants of both the powders increased with increase in Zr content. The lattice constants of the calcined powders were in fair agreement with the JCPDS data. However, the lattice constants of the as-hydrolyzed powders were higher slightly than those of the calcined powders. This may suggest that the crystal structure in the as-hydrolyzed powders may be expanded probably due to the presence of OH groups, as reported for $(Ba_{1-x}Sr_x)TiO_3$ powders³⁾

prepared using alkoxide-hydroxide process.

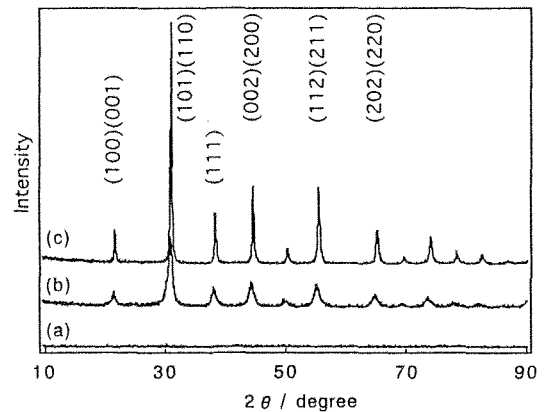


Fig.4 XRD patterns of $Ba(Zr_{0.2}Ti_{0.8})O_3$ powders. (a) Precursor, (b) As-hydrolyzed, (c) Calcined at 900°C.

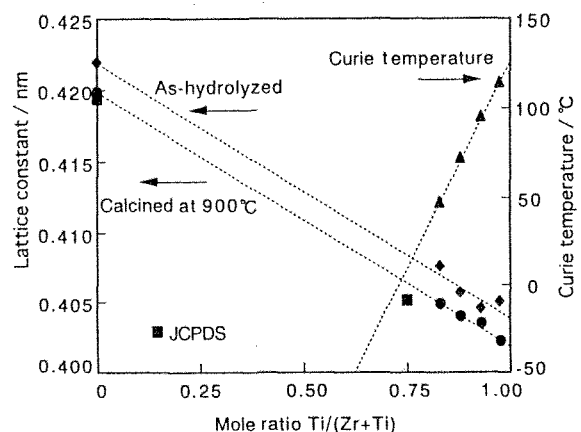


Fig.5 Lattice constant and Curie temperature versus mole ratio $\{Ti/(Zr+Ti)\}$ of $Ba(Zr_xTi_{1-x})O_3$.

3.3 Microstructure and Dielectric Properties

SEM micrographs of $BaTiO_3$ and $Ba(Zr_{0.2}Ti_{0.8})O_3$ bodies sintered at 1300°C are shown in Fig. 6. The grain sizes of BZT sintered bodies were smaller than that of $BaTiO_3$ sintered bodies, suggesting that solid solution of zirconium oxide would suppress the grain growth of BZT. Figure 7 shows the temperature dependence of dielectric constants for $Ba(Zr_{0.2}Ti_{0.8})O_3$ bodies sintered at 1250, 1300 and 1350°C. The dielectric constants of sintered bodies increased with increase in sintering temperature. The Curie temperatures were essentially the same for the samples sintered at different temperatures. Neirman⁴⁾ demonstrated that in BZT ceramics fabricated by conventional oxides mixing method the Curie temperature was a function of the chemical composition of a molecularly homogeneous

BZT powder, but not of the sintering conditions.

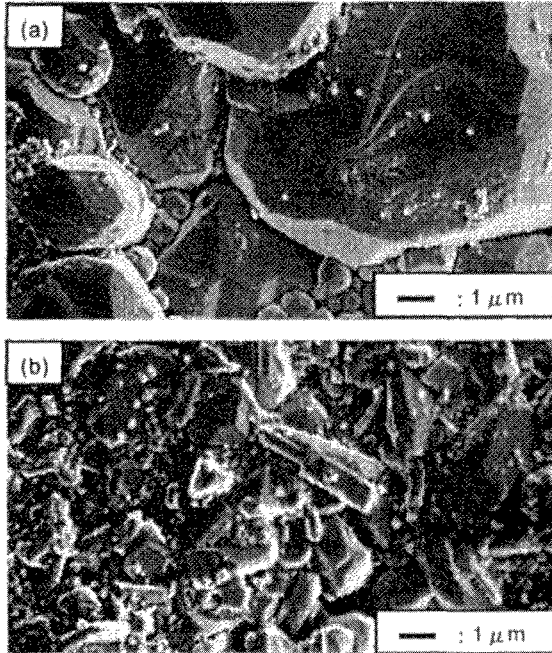


Fig.6 SEM micrographs of (a) $BaTiO_3$ and (b) $Ba(Zr_{0.2}Ti_{0.8})O_3$ bodies sintered at $1300^\circ C$.

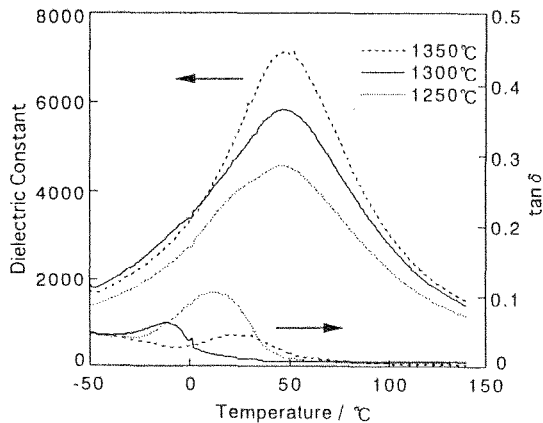


Fig.7 Temperature dependence of the dielectric constants of $Ba(Zr_{0.2}Ti_{0.8})O_3$ sintered bodies.

Figure 8 shows the temperature dependence of dielectric constants for $Ba(Zr_xTi_{1-x})O_3$ ($x=0 \sim 0.2$) bodies sintered at $1300^\circ C$. Zirconium oxide acts as a shifter for $BaTiO_3$, and the Curie temperatures shifted to lower temperatures with increasing Zr content. $Ba(Zr_{0.2}Ti_{0.8})O_3$ sintered bodies exhibited the Curie temperature of around $50^\circ C$. These tendencies agreed well with the results reported by Neirman. $Ba(Zr_{0.2}Ti_{0.8})O_3$ bodies sintered at $1300^\circ C$, which have a relative density of approximately 91 %, exhibited a dielectric constant of approximately

5000 and a $\tan \delta$ of approximately 2 % at room temperature.

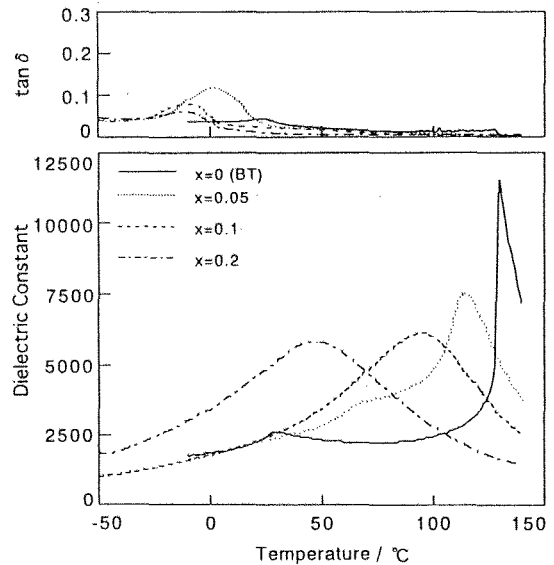


Fig.8 Temperature dependence of the dielectric constants of $Ba(Zr_xTi_{1-x})O_3$ bodies sintered at $1300^\circ C$.

4. Conclusions

The powder precursors of $Ba(Zr_xTi_{1-x})O_3$ powders have been prepared at room temperature by allowing the reaction between methanol solutions of Ba hydroxide and Ti-isopropoxide and Zr-butoxide. By vapor phase hydrolysis of the powder precursors, crystalline nanosize $Ba(Zr_xTi_{1-x})O_3$ powders with homogeneous compositions have been successfully prepared at $100^\circ C$. The lattice constants of the calcined powders were in fair agreement with the JCPDS data. However, the lattice constants of the as-hydrolyzed powders were slightly higher than those of the calcined powders. $Ba(Zr_{0.2}Ti_{0.8})O_3$ bodies sintered at $1300^\circ C$ exhibited the Curie temperature of around $50^\circ C$, a dielectric constant of approximately 5000 and a $\tan \delta$ of approximately 2 % at room temperature.

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