Thermal Decomposition of Barium Titanate Precursor Prepared by a Wet Chemical Method

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As a part of fundamental study on the kinetics of electroceramics processing by wet chemical methods, barium titanate precursor gel was prepared using barium acetate and titanium tetra-isopropapoxide as starting materials. Experimental results indicated that barium acetate was distributed uniformly in the gel matrix formed by hydrolysis and polymerization of titanium tetra-isopropoxide. In the subsequent calcination of the gel, rapid formation of barium titanate was observed above 823 K, which resulted from the reaction between titania and barium carbonate or barium oxide(s). The dynamics of barium titanate formation under different heat-up programs was successfully simulated based on a proposed reaction model that incorporates a specified reactive portion of barium acetate in the gel matrix.

Introduction

The prominent dielectric ceramic, barium titanate ($BaTiO_3$), is produced commercially by firing a mixture of barium carbonate and titanium oxide powders at temperatures above 1,473 K in order to accelerate solid-state diffusion (Beauger et al., 1983a,b; Kubo and Shinriki, 1952). However, problems arise with this conventional method because the raw-material powders are frequently inhomogeneous and coarse and contain undesirable impurities that affect dielectric properties of sintered barium titanate (Nelson and Cook, 1959). Serious defects can be observed in multilayer capacitors in which the distance between electrodes is the order of 10 μm (Utsumi, 1989). On the other hand, a liquid-phase preparation can provide a high degree of mixing with stoichiometric precision at a nanometer scale, and lowering of the sintering temperature. Various wet-chemical methods, including alkoxide hydrolysis and coprecipitation, have been applied to the synthesis of barium titanate in attempts to obtain chemically pure, stoichiometric products with lower sintering temperatures (Gallagher et al., 1963; Swilam and Gadalla, 1973; Kirby, 1988; Kasai et al., 1987; Kajiyoshi et al., 1991; Stockenhuber et al., 1993). Homogeneous grain growth with narrow size distribution has been reported for the preparation of barium titanate from oxalate though the powders from wet-chemical methods generally have low compact density at low calcination temperature (Kudaka, 1982).

When alkoxide solutions are used, it is necessary to control the hydrolysis rate in order to obtain chemically and physically homogeneous ceramics. This is difficult because metal alkoxides are very reactive with water and hydrolyze at different rates (Sakka and Kamiya, 1982). Diethanol amine and ethylene glycol are known to be effective additives for control of hydrolysis rates of metal alkoxides (Sakka and Kamiya, 1982). Acetic acid and acetyl acetone have also been reported recently to be effective for such control (Phule and Risbud, 1990). In general, however, it is not clear what influence such additives may have on formation of intermediates and final product in barium titanate preparation via the metal alkoxide route.

Barium titanate product is formed by calcination and firing of the precursor obtained from the wet chemical methods. While there have been many studies of the decomposition behavior of precursors reported (Swilam et al., 1973; Gallagher and Thomson, 1965; van de Velde and Oranje, 1976; Chaput and Boilot, 1990), there have not been any quantitative and kinetic investigations carried out because of the complicated reaction routes and numerous intermediates involved in the formation of barium titanate in the calcination step.

The objective of the present work was to carry out a fundamental kinetic study of electroceramics processing by wet chemical methods. The focus of this study is on the calcination of barium titanate precursor gel prepared using barium acetate and titanium tetra-isopropoxide as starting materials, and using acetic acid as the hydrolysis controlling agent. Changes in composition with temperature and reaction time for the precursor gel in the calcination were characterized by Fourier transform infrared spectroscopy, thermogravimetry with differential thermal analysis, X-ray diffraction, and an acid extraction. Thermogravimetric change and formation behavior of barium titanate in the calcination process were successfully simulated assuming a reaction scheme based on experimental results and volume reaction model.

Experimental Studies

Sample preparation

Titanium tetra-isopropoxide, barium acetate, acetic acid, and methanol of commercial GR grade (Nakarai Tesuku Co. Ltd.) were used without further purification. Titanium tetra-isopropoxide was mixed with an equimolar amount of acetic acid in methanol (Chaput and Boilot, 1987). The methanol was dehydrated with the use of a molecular sieve 3A prior to sample preparation. The resulting solution was then mixed with an aqueous solution of barium acetate that was equimolar to titanium tetra-isopropoxide. After gelation at room temperature, the sample was aged at 313 K for 12 h. The resulting wet gel was then dried at 453 K to remove the solvents, and then the dry gel of barium titanate precursor (BT gel) was calcined at various final temperatures up to 1,473 K with a heat-up rate of 300 K/h in air.

BT gel was also prepared using ethylene glycol and diethanol amine as controlling agents for the hydrolysis rate. When the BT gels prepared using these controlling agents were calcined at 1,073 K, XRD showed barium carbonate as well as barium titanate peaks. Since only a sharp barium titanate peak was observed for the BT gel prepared using acetic acid, the latter was chosen for all subsequent studies.

For a comparison with BT gel, a dry gel of titanium dioxide precursor (TO gel) was prepared by the same procedure but without barium acetate.

Analyses

The calcination process of BT and TO gels was characterized by Fourier transform infrared spectroscopy (Bomem DA3), thermogravimetry with differential thermal analysis (Rigaku TAS 200) and X-ray diffraction (Rigaku CN155D6). Thermogravimetry was carried out at a heating rate of 300 K/h in air.

The content of barium titanate in the calcined sample was determined after extraction with acetic and hydrochloric acids (Kubo and Shinriki, 1960). The present analysis is based on the fact that barium oxide and barium carbonate dissolve in acetic acid, while barium titanate dissolves in hydrochloric acid but not acetic acid. Preliminary experiments indicated that the extraction could be completed in 2 h with 10 vol. % acetic acid and 4 M hydrochloric acid at 333 K. The barium ion in the filtrate was determined gravimetrically after precipitation of barium sulfate by addition of ammonium sulfate.

Results and Discussion

Composition of dry gel

Figure 1 shows FT-IR spectra of commercial barium titanate and its residue after extraction by acetic acid. While two large peaks were observed for barium titanate at 680 and 1,460 cm^{-1}, the peak at 1,460 cm^{-1} was not present in the residue. Barium ion from barium oxide(s) and barium carbonate was detected in the solution after acetic acid extraction. The peak at 680 cm^{-1} became sharp with calcination temperature above 873 K accompanied with the increment of XRD peak intensity of barium titanate described later. The peak at 680 cm^{-1} is thus due to barium titanate.

Figure 2 shows FT-IR spectra of BT gel, TO gel, and barium acetate reagent. As shown in Figure 1, the spectrum of BT gel was similar to that of barium acetate, but not to that of barium titanate. The doublet observed at 1,420 and 1,580 cm^{-1} is attributable to the stretch vibration of the carboxyl group. No distinct peak was observed in XRD analysis of the BT gel. On the contrary, a barium acetate peak was detected in XRD pattern of BT gel prepared with the use of ethylene glycol and diethanol amine as hydrolysis-controlling additives. These analytical results suggest that barium acetate was distributed uniformly in the gel matrix. The spectrum of TO gel shows a shoulder at 3,200 cm^{-1} and doublet at 1,450 and 1,530 cm^{-1}, which resulted from hydroxyl and acetoxyl groups, respectively, but no peak was observed for the isopropyl group of titanium tetra-isopropoxide. It is speculated that titanium tetra-isopropoxide reacted with acetic acid in the methanol solution to form $Ti(O-i(C_3H_7)_{4-n}-(CH_3COO)_n)$. The peak of the isopropyl group was not observed in FT-IR spectra of TO gel, which was formed by re-

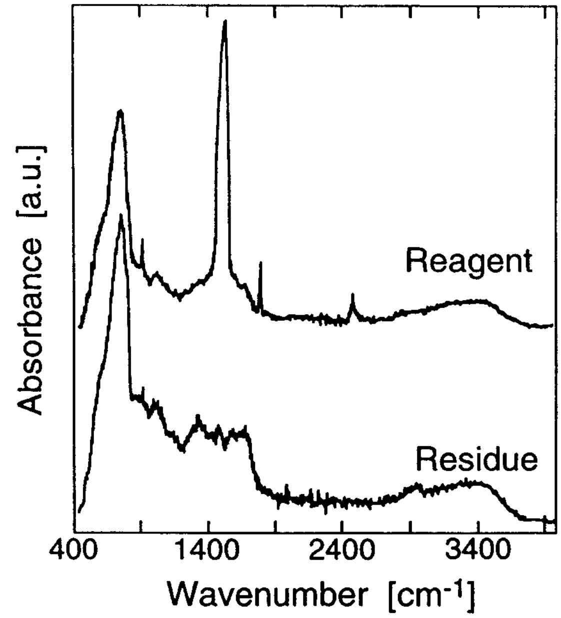

Figure 1. FT-IR spectra of barium titanate reagent and its acetic acid residue.

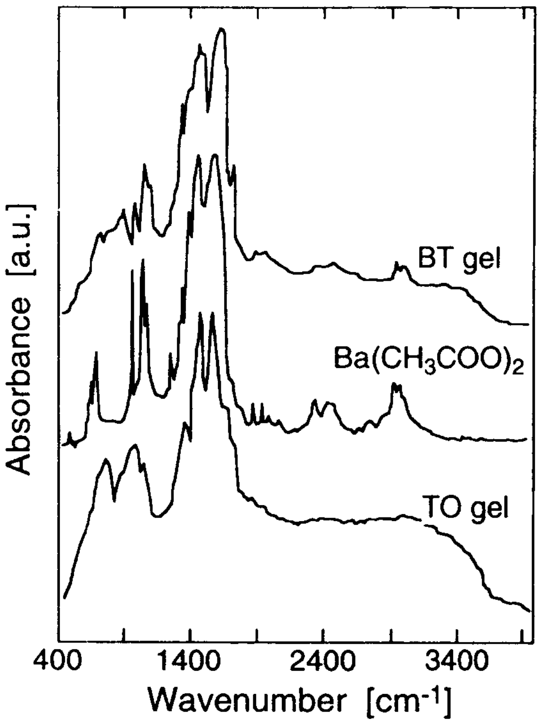

Figure 2. FT-IR spectra of BT gel, TO gel, and barium acetate.

action between Ti(O-i(C_3H_7)$_{4-n}$-(CH_3COO)$_n$) and water, since isopropyl group probably hydrolyzed and polymerized faster than acetoxyl group. Based on the preceding results, it was assumed that BT gel consists of barium acetate and (Ti(CH_3COO)$_x$(OH)$_{2-x}$-O-)$_n$.

Change in composition with calcination

Figure 3 shows the change in FT-IR spectra of BT gel with calcination temperature. BT gel was calcined with TG-DTA apparatus by heating up at a rate of 300 K/h, followed by 2 h of holding time at a specified terminal temperature in air. The spectra of the sample calcined at 673 K showed three peaks at 870, 1,060 and 1,420 cm^{-1} attributable to barium carbonate, but no doublet at 1,420–1,550 cm^{-1} as observed in BT gel. The hydroxyl group peak also disappeared in this sample. Barium acetate, distributed uniformly in BT gel, was apparently changed to barium carbonate, while hydroxyl and acetoxyl groups were pyrolyzed by the heat treatment up to 673 K. For the sample calcined at 873 K, formation of barium oxide(s) and barium titanate was observed from the peaks at 1,430 and 680 cm^{-1}, respectively, while the peaks at 870 and 1,060 cm^{-1} disappeared.

This result indicated that the increased calcination temperature apparently caused the formation of barium oxide(s) from barium carbonate and the formation of barium titanate by the reaction between barium carbonate and titanium oxide. The peak attributable to barium titanate at 680 cm^{-1} became sharper with increase of calcination temperature above 873 K, while the peak of barium oxide(s) at 1,430 cm^{-1} became larger and then decreased above 1,273 K.

Changes in FT-IR spectra of BT gel with holding time at 1,273 K in air are shown in Figure 4. Decrease of the peak at 1,430 cm^{-1} indicates the formation over time of barium titanate by reaction between barium oxide(s) and titanium oxide.

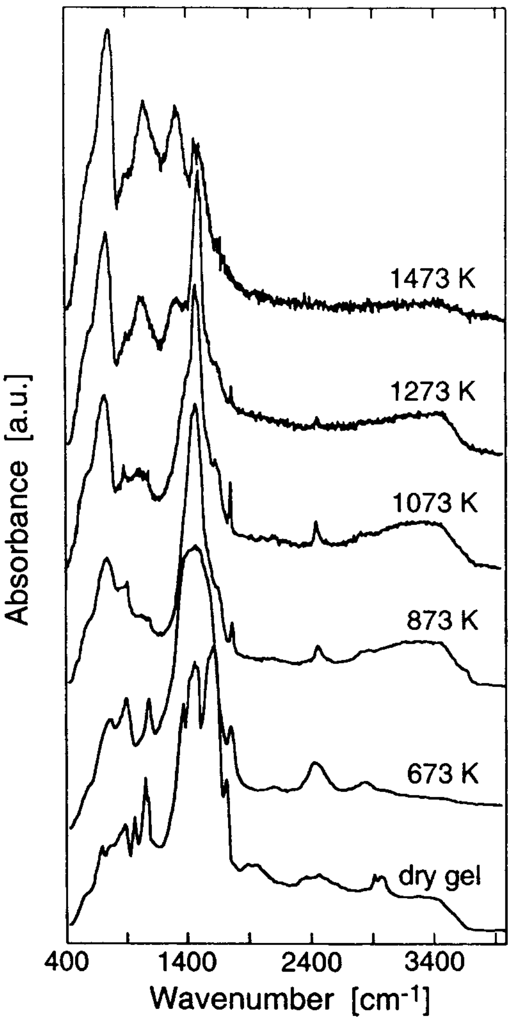

Figure 3. Change in FT-IR spectra of BT gel with temperature.

Holding time at a specified terminal temperature of 2 h.

Figure 5 shows the results of thermogravimetric and thermal differential analyses of BT gel heated at 300 K/h up to 1,073 K. The large weight loss with exothermic peak from 473 to 623 K corresponded to the combustion of acetoxyl group coordinated to titanium and barium. The second large weight loss resulted from formation of barium titanate in the temperature range from 873 to 973 K.

In Figure 6, the change of XRD patterns with temperature is shown for BT gel calcined at 300 K/h up to 1,273 K. These XRD patterns were obtained at room temperature for the quenched samples after calcination. While the sample was amorphous below 673 K, peak intensity corresponding to barium titanate increased above 873 K. The only peaks found in XRD analysis were those for barium titanate.

Based on the preceding results, the following apparent reaction scheme is proposed for calcination of BT gel:

$$Ba(CH_3COO)_2 \rightarrow BaCO_3 \quad (1)$$

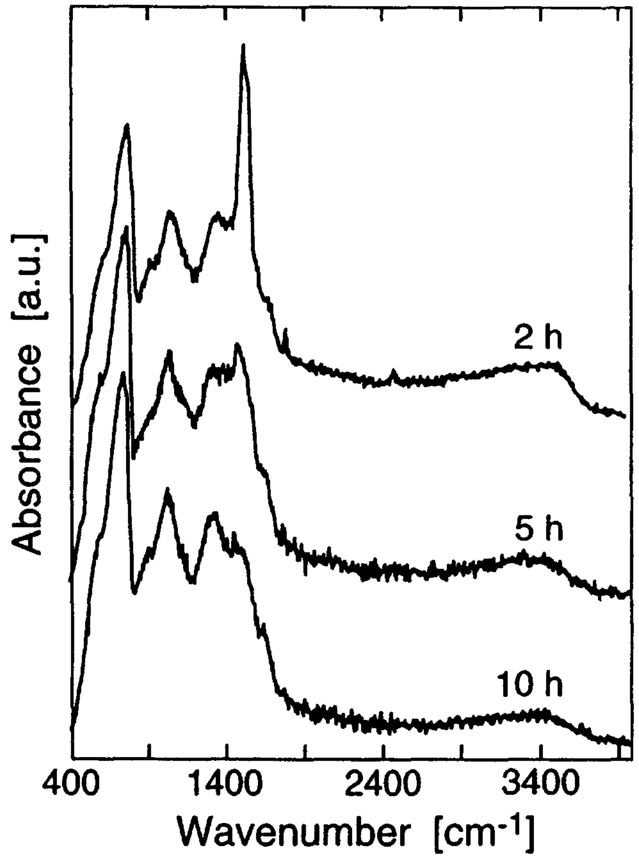

Figure 4. Change in FT-IR spectra of BT gel with holding time at a terminal temperature, 1,273 K.

$$(Ti(CH_3COO)_x(OH)_{2-x}-O-)_n \rightarrow TiO_2 \qquad (2)$$

$$BaCO_3 + TiO_2 \rightarrow BaTiO_3 \qquad (3)$$

Rate analysis

The decomposition behaviors of barium acetate and TO gel were investigated separately using a thermogravimetric analyzer with a constant heating rate of 300 K/h. The observed thermogravimetric change for barium acetate is shown in Figure 7. Decomposition of barium acetate began at 673 K and was completed at 773 K. Now, it is assumed that barium carbonate (BC) is formed from barium acetate (BA) through decomposition, and their formation and decomposition rates are expressed by following first-order kinetic model equations.

$$d[BC]/dt = -d[BA]/dt = k_1[BA]. \qquad (4)$$

An Arrhenius-type temperature dependency is also assumed for the rate constants in this study.

$$k_i = k_{i0}\exp(-E_i/RT). \qquad (5)$$

Temperature history and initial conditions are given by Eqs. 6 and 7.

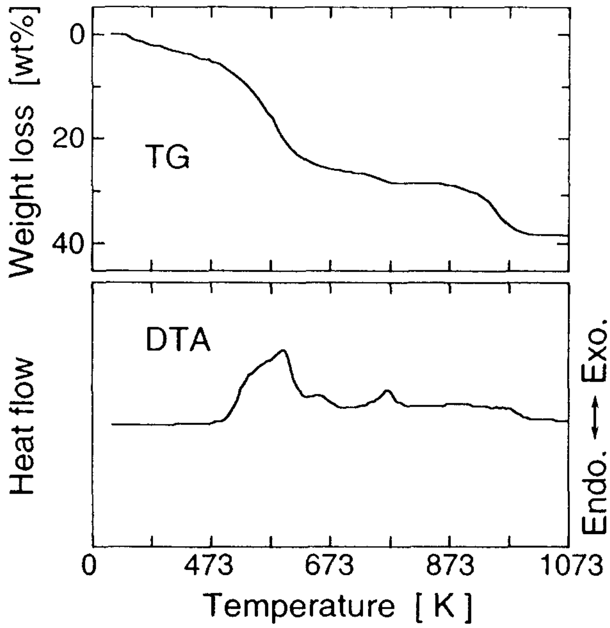

Figure 5. TG-DTA curves of BT gel.

$$dT/dt = m, \quad (m = 300\ \mathrm{K/h}) \qquad (6)$$

$$[BA] = 1, \quad [BC] = 0, \quad T = T_0 \quad \text{at } t = 0. \qquad (7)$$

Equations 4–7 were solved by means of the Runge–Kutta–Gill algorithm. The frequency factor k_{i0} and activation energy E are adjustable parameters that were optimized to fit the experimental results.

The lines labeled BC and BA in Figure 7 indicate simulated changes in the contents of barium acetate and barium carbonate computed from Eqs. 4–7. The calculated value of weight loss is completely consistent with the experimental thermogravimetric curve in Figure 7. Frequency factors and activation energy were determined to be 1×10^{15} min^{-1} and 52 kcal/mol for BA decomposition.

Figure 8 represents observed and calculated thermogravimetric changes for TO gel. The weight loss of TO gel was

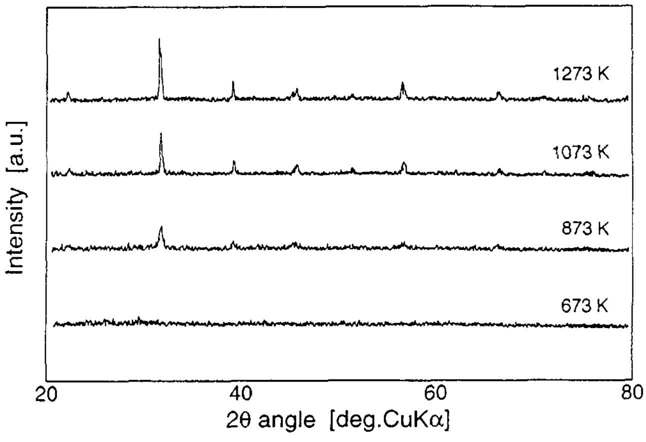

Figure 6. Change in XRD pattern of BT gel with terminal temperature with holding time at a specified terminal temperature of 2 h.

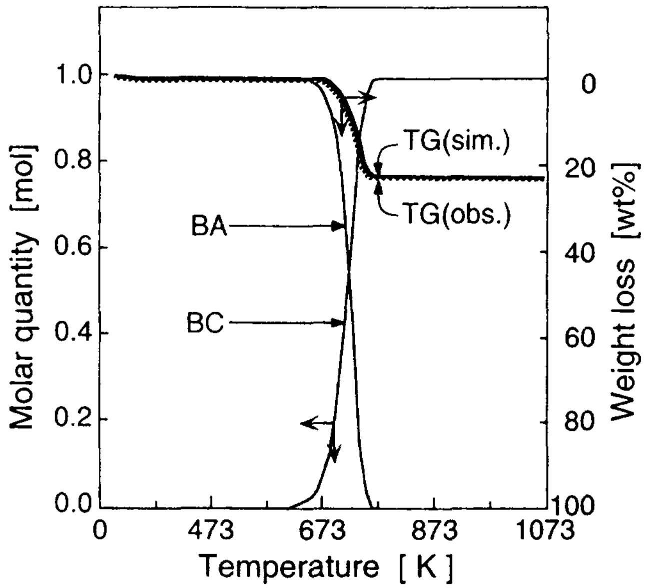

Figure 7. Observed and simulated TG curves of barium acetate reagent (BA: $Ba(CH_3COO)_2$, BC: $BaCO_3$).

composed of two parts, that is, a gradual initial decrease followed by a rapid decrease from 473 K to 673 K. These changes result from the decomposition of titanium coordinated hydroxyl and acetoxyl groups, respectively. These dehydration and decomposition rates in TO gel were then expressed as in Eqs. 8 and 9.

$$d[\text{T-OH}]/dt = -k_2[\text{T-OH}] \tag{8}$$

$$d[\text{T-OAc}]/dt = -k_3[\text{T-OAc}], \tag{9}$$

where [T-OH] and [T-OAc] represent the concentrations of titanium coordinated by hydroxyl and acetoxyl groups, respectively. The formation rate of titania (TO) is expressed by Eq. 10, and the initial conditions are given by Eq. 11.

$$d[\text{TO}]/dt = k_2[\text{T-OH}] + k_3[\text{T-OAc}] \tag{10}$$

$$[\text{T-OH}] = 1 - x, \quad [\text{T-OAc}] = x, \quad [\text{TO}] = 0 \quad \text{at} \quad t = 0, \tag{11}$$

where x indicates coordination ratio ($x < 1$).

Equations 6 and 9–11 were again solved and the best values of the adjustable parameters (frequency factors, activation energies, and coordination ratio x) were determined. The frequency factors and activation energies found were $k_{20} = 1{,}000\ \text{min}^{-1}$ and $E_2 = 7$ kcal/mol for dehydration, and $k_{30} = 7 \times 10^7\ \text{min}^{-1}$ and $E_3 = 24$ kcal/mol for decomposition of acetoxyl group. With the coordination ratio x as taken, 0.22, the thermogravimetric curve for TO gel decomposition was very well simulated, as shown in Figure 8.

Figure 9 shows a comparison of observed and simulated thermogravimetric curves for BT gel heated up to 873 K. It was confirmed that barium titanate formation occurred above 873 K, according to the results of FT-IR and XRD. The same kinetic parameters determined for barium acetate reagent and TO gel were applied separately here to generate the simulated thermogravimetric curves of BT gel. The simulation was carried out by solving Eqs. 4 to 11. Figure 9 indicates, however, a large discrepancy between the observed and simulated curves. The simulation could not reproduce a gradual weight loss up to 473 K and rapid decrease around 673 K. The observed temperature of the onset of barium acetate decomposition was lower than that of simulated curve. This fact implies that barium acetate, distributed in the BT gel, must be considered to be more reactive for decomposition. It was observed in the preliminary experiment that barium titanate only formed effectively from the BT gel that did not exhibit a barium acetate peak. In fact, the possibility of low-temperature formation of barium titanate was reported in alkoxide

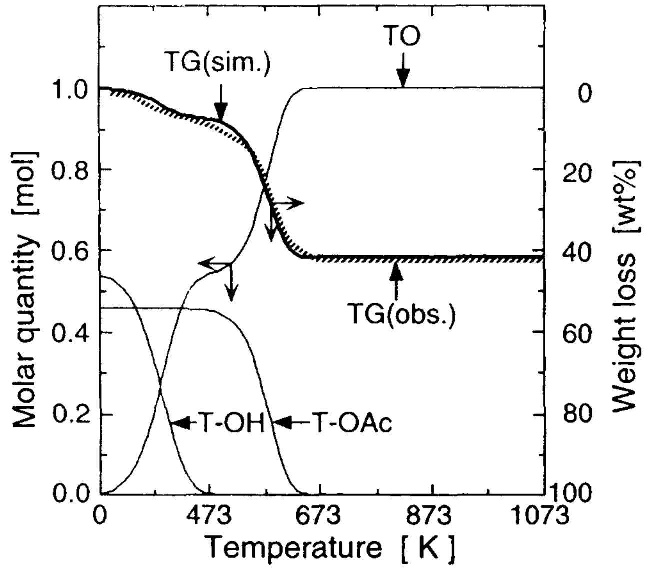

Figure 8. Observed and simulated TG curves of TO gel (T-OH: $-Ti(OH)_2-$, T-OAc: $-Ti(OAC)_2-$, TO: TiO_2).

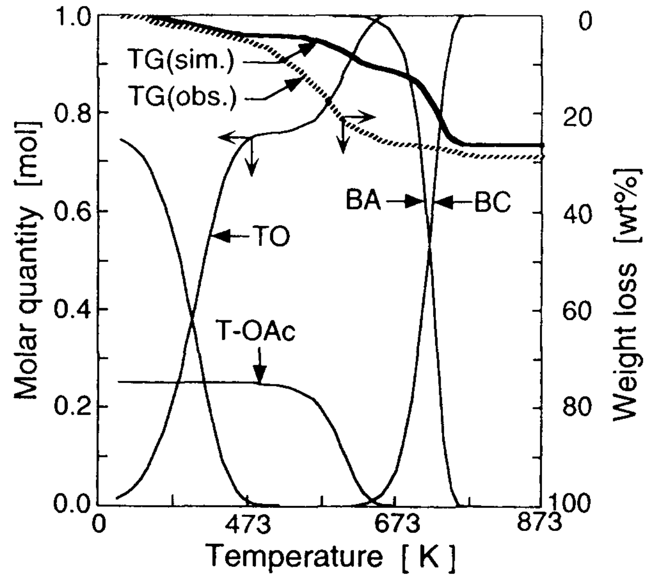

Figure 9. Observed and simulated TG curves of BT gel.

hydrolysis and hydrothermal processing with finely dispersed titania particles and barium hydroxide (Frey and Payne, 1995).

To account for these facts Eq. 1 was replaced by the following three reactions for simulation of the observed thermogravimetry of BT gel:

$$Ba(CH_3COO)_2 \text{ (nonreactive)} \rightarrow BaCO_3 \tag{12}$$

$$Ba(CH_3COO)_2 \text{ (reactive)} \rightarrow BaCO_3 \tag{13}$$

$$Ba(CH_3COO)_2 \text{ (reactive)} \rightarrow BaO \text{ or } BaO_2. \tag{14}$$

Correspondingly, decomposition rates of nonreactive (BAn) and reactive (BAr) barium acetate are expressed by Eqs. 15 and 16:

$$d[\mathrm{BAn}]/dt = -k_1[\mathrm{BAn}] \tag{15}$$

$$d[\mathrm{BAr}]/dt = -(k_4 + k_5)[\mathrm{BAr}]. \tag{16}$$

Barium titanate is formed by reactions of barium carbonate or barium oxide(s) (BO) with titania. The formation rate of barium titanate (BT) is given by Eq. 17:

$$d[\mathrm{BT}]/dt = k_6[\mathrm{BC}][\mathrm{TO}] + k_7[\mathrm{BO}][\mathrm{TO}]. \tag{17}$$

Finally, material balances for barium carbonate and barium oxide(s) (BO) are given by following equations:

$$d[\mathrm{BC}]/dt = k_4[\mathrm{BAr}] + k_1[\mathrm{BAn}] - k_6[\mathrm{BC}][\mathrm{TO}] \tag{18}$$

$$d[\mathrm{BO}]/dt = k_5[\mathrm{BAr}] - k_7[\mathrm{BO}][\mathrm{TO}] \tag{19}$$

$$[\mathrm{BAr}] = y, \quad [\mathrm{BAn}] = 1 - y, \quad (y < 1) \tag{20}$$

$$[\mathrm{BC}] = [\mathrm{BO}] = [\mathrm{BT}] = 0 \quad \text{at} \quad t = 0, \tag{21}$$

where y is content of reactive barium acetate.

Figure 10 shows observed and calculated thermogravimetric changes for BT gel heated up to the temperature range of barium titanate formation. As indicated in the figure, the observed thermogravimetric curve of BT gel was successfully simulated by assuming that 85% of barium acetate was reactive for decomposition, that is, $y = 0.85$. The resulting kinetic parameters are listed in Table 1. It is concluded from the simulation that 80% of barium titanate is formed by the reaction of barium carbonate and titanium oxide, and the remainder is produced by the reaction of barium oxide(s) and titanium oxide.

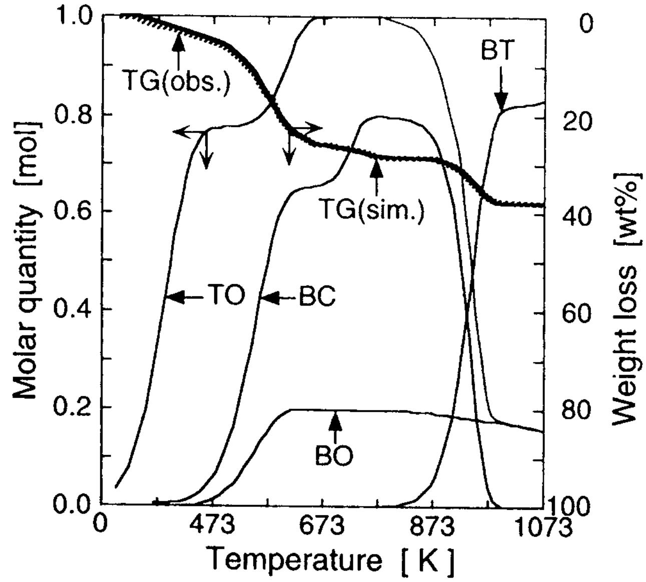

Figure 10. Observed and simulated TG curves of BT gel.

Simulation was conducted by modified reaction path, BO: BaO or BaO_2, BT: $BaTiO_3$.

Figure 11 shows change with calcination temperature of barium titanate content (as shown by the circles) determined by the acid-extraction method. A heating rate of 300 K/h was used in these experiments along with a holding time of 2 h at a specified terminal temperature. Barium titanate formed rapidly around 873 K and barium titanate yield reached 80% at 900 K. A moderate increment in yield was observed above 900 K. Solid lines in Figure 11 indicate simulated changes of barium titanate and other components in BT gel based on the kinetic parameters listed in Table 1. This figure shows clearly that the formation of barium titanate has been successfully simulated using these kinetic parameters.

Conclusion

Barium titanate precursor gel was successfully obtained by alkoxide hydrolysis using barium acetate and titanium tetraisopropoxide as starting materials and acetic acid as a rate-controlling agent. Barium acetate was reactive for decomposition in the gel matrix formed by hydrolysis and polymerization of titanium tetra-isopropoxide. A kinetic model was proposed involving reactive and nonreactive barium acetate, titanium dioxide precursor gel, barium carbonate, barium oxide(s) and barium titanate, and kinetic parameters for the

Table 1. Kinetic Parameters Determined for Decomposition of BT gel*

Reaction Step i		Frequency Factor k_{i0}	Activation Energy E_i
$Ba(CH_3COO)_2$ (nonreactive)	$\rightarrow BaCO_3$	1.0×10^{15}	52
$(Ti(OH)_2\text{-}O\text{-})_{1-x}$	$\rightarrow TiO_2$	1.0×10^{3}	7
$(Ti(CH_3COO)_2\text{-}O\text{-})_x$	$\rightarrow TiO_2$	7.0×10^{7}	24
$Ba(CH_3COO)_2$ (reactive)	$\rightarrow BaCO_3$	2.9×10^{4}	14
$Ba(CH_3COO)_2$ (reactive)	$\rightarrow$ BaO or BaO_2	8.9×10^{3}	14
$BaCO_3 + TiO_2$	$\rightarrow BaTiO_3$	1.1×10^{13}	60
$BaO + TiO_2$	$\rightarrow BaTiO_3$	1.5×10^{4}	27

*k_{i0} (i = 1-5) [min^{-1}]; k_{60} and k_{70} [$\mathrm{mol}^{-1}\cdot\mathrm{min}^{-1}$]; E_i [$\mathrm{kcal}\cdot\mathrm{mol}^{-1}$].

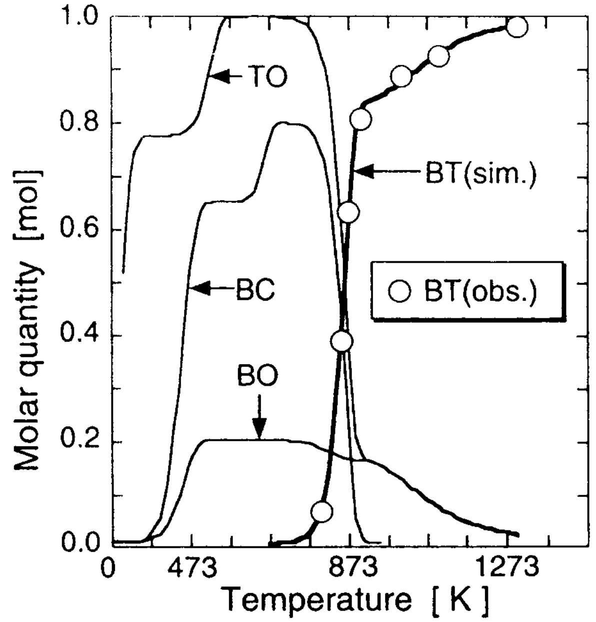

Figure 11. Observed and simulated values of barium titanate formation.

Holding time at a specified terminal temperature of 2h.

model were determined. The thermogravimetric change of barium titanate precursor gel during calcination could be well reproduced using these kinetic parameters. Rapid formation of barium titanate above 823 K was also successfully simulated using these kinetic parameters. The simulation results suggest that 80% of barium titanate is formed by the reaction of barium carbonate and titanium oxide, and the remainder is produced from the reaction of barium oxide(s) and titanium oxide.

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