Kinetics of Barium Titanate Formation from Wet Chemically Derived Precursor

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In a series of studies of fundamental study on the kinetics of electroceramics processing by wet chemical methods, change in composition with temperature and reaction time for barium titanyl oxalates tetrahydrates in the calcination were characterized. Rapid formation of barium titanate was observed above 823 K, which resulted from the reaction between titania and barium carbonate or barium oxide(s). A kinetic model was proposed based on the experimental results. Thermogravimetric change of barium titanyl oxalates tetrahydrates during calcination could be reproduced and dynamics of barium titanate formation was successfully simulated using these kinetic parameters.

Key Word : Barium titanate, Calcination, Electroceramics, Kinetics, Wet chemical method

1. Introduction

Barium titanate (BaTiO_3) is a typical dielectric ceramic widely utilized for multilayer ceramic capacitors, PTC thermistors and electro-optic components. Conventional processing of barium titanate depends on solid-state reaction between barium carbonate and titanium oxide powders¹⁾. However, problems arise with this conventional method because raw materials and ball-milling operations introduce undesirable impurities such as alumina, silica and phosphorous. These impurities cause extraordinary crystalline growth, inhomogeneous microstructure and poor dielectric properties of sintered barium titanate²⁾.

Wet chemical route is one of promising methods for electroceramic preparation to yield low temperature sintering and high purity, homogeneous and ultrafine powders with stoichiometric precision which contributes to stable electric characteristics³⁻⁷⁾. 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. In Japan, 200 ton/month of barium titanyl oxalate is now utilizing for manufacturing 120 billion of multilayer capacitors per month.

Barium titanate is formed by calcination and firing of the precursor. Heat treatment condition (temperature history and atmosphere etc.) of oxalate precursor affects particle size distribution, compact and sintering behavior of high grade barium titanate powder. While there have been many studies of pyrolysis behavior of precursors reported, there have not been any quantitative and kinetic investigations carried out.

In a series of the fundamental kinetic studies of electroceramic processing by wet chemical methods⁸⁾, calcination of barium

titanyl oxalates ($\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$) was investigated. Change in composition with temperature and reaction time for the barium titanyl oxalates in the calcination were characterized by Fourier transform infrared spectroscopy, thermogravimetry with differential thermal analysis, X-ray diffraction, and an acid extraction. Thermogravimetric change of barium titanyl oxalates and formation behavior of barium titanate in the calcination process were successfully simulated assuming a reaction scheme based on experimental results.

Figure. 1 Acid extraction method

2. Experimental

Barium titanyl oxalates tetrahydrates $\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ (Jun-sei Kagaku, JT-1) was used without further purification. The agglomerated sample was crushed to -200 mesh and then supplied to analysis and experiments.

The sample was calcined at various final temperatures up to 1473 K with a heat-up rate of 5 K/min in air. The calcination process of the sample was characterized by Fourier transform infrared spectroscopy (Bomem DA3), thermogravimetry with differential thermal analysis (Rigaku TAS 200) and X-ray diffraction (Rigaku CN155D6). The content of barium titanate in the calcined sample was determined after extraction with acetic and hydrochloric acids shown in Fig. 1. 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 acid⁹⁾. 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.

3. Results and Discussion

3.1 Change in composition with calcination

Figure 2 shows the change in FT-IR spectra of barium titanyl

Figure. 2 Change of FTIR-PA spectra of $\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ with calcined temperature (Heating rate ; 5 K/min, holding time ; 2 h)

oxalates tetrahydrates with calcination temperature. The sample was calcined with TG-DTA apparatus by heating up at a rate of 5 K/min, followed by 2h of holding time at a specified terminal temperature from 673 to 1273 K in air. The spectrum of raw sample shows the peaks at 1270 cm^{-1} , 1420 cm^{-1} and 1640 cm^{-1} which resulted from CO and COO groups. These peaks and a peak at 3200 cm^{-1} attributable to hydroxyl group disappeared in the sample calcined at 673 K. The spectrum of the sample calcined at 673 K showed the three peaks of 870 cm^{-1} , 1060 cm^{-1} and 1420 cm^{-1} attributable to barium carbonate. Barium titanyl oxalates tetrahydrates was changed to barium carbonate while dehydration and pyrolysis of oxalate group were occurred. Formation of barium oxide(s) and barium titanate was observed from the peaks at 1430 cm^{-1} and 680 cm^{-1} , respectively.

The results of thermogravimetric and thermal differential analyses of barium titanyl oxalates tetrahydrates is shown in Fig. 3. The thermogravimetric curve indicates large three-steps weight loss¹⁰⁾. The first large weight loss with endothermic peak corresponded to dehydration while the sample was heated up to 473 K. The second

Figure. 3 TG-DTA curves of $\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ (Heating rate ; 5 K/min)

Figure. 4 XRD patterns of calcined samples (Heating rate ; 5 K/min, holding time ; 2 h)

weight loss with exothermic peak from 573 K to 673 K resulted from decomposition of barium titanyl oxalates to barium carbonate, barium oxide(s) and titanium oxide. The formation of barium titanate caused the third weight loss with endothermic peak in the temperature range from 873 K to 973 K.

In Figure 4, the change of XRD patterns with temperature is shown for barium titanyl oxalates tetrahydrates calcined at 5 K/min up to 1273 K. Three 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.

Figure 5 shows change with calcination temperature of barium titanate content determined by the acid-extraction method. A heating rate of 5 K/min was used in these experiments along with a holding time of 2 h at a specified terminal temperature. Barium titanate formed rapidly from 773 K and barium titanate yield reached 80 % at 873 K. A moderate increment in yield was observed above 923 K.

3. 2 Rate analysis

Based on the preceding results, the following reaction scheme is proposed for calculation of barium titanyl oxalates tetrahydrates :

Now it is assumed that decomposition and formation rates are expressed by following first-order kinetic model equations. Dehydration rate of $\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ is expressed by Eq.(6).

$$d[\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}] / dt = -k_1 [\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}] \quad (6)$$

Figure. 5 Change in BaTiO_3 yield with temperature (Heating rate ; 5 K/min, holding time at a specified temperature ; 2 h)

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

$$k_i = k_{i0} \exp(-E_i / RT) \quad (7)$$

Temperature history and initial conditions are given by Eqs.(8) and (9).

$$dT/dt = m \quad (m = 5 \text{ K/min}) \quad (8)$$

$$[\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}] = 1, \quad [\text{BaTiO}(\text{C}_2\text{O}_4)_2] = 0 \quad (9)$$

$$T = T_0 \text{ at } t = 0$$

Formation and decomposition rate of $\text{BaTiO}(\text{C}_2\text{O}_4)_2$ is expressed by Eq.(10).

$$d[\text{BaTiO}(\text{C}_2\text{O}_4)_2] / dt = k_1 [\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}] - (k_2 + k_3) [\text{BaTiO}(\text{C}_2\text{O}_4)_2] \quad (10)$$

Barium titanate is formed by reaction of barium carbonate or barium oxide(s) with titanium oxide. The formation rate of barium titanate is given by Eq.(11).

$$d[\text{BaTiO}_3] / dt = k_4 [\text{BaCO}_3][\text{TiO}_2] + k_5 [\text{BaO(s)}][\text{TiO}_2] \quad (11)$$

Material balances for barium carbonate and barium oxide(s) are given by following equations.

$$d[\text{BaCO}_3] / dt = k_2 [\text{BaTiO}(\text{C}_2\text{O}_4)_2] - k_4 [\text{BaCO}_3][\text{TiO}_2] \quad (12)$$

$$d[\text{BaO(s)}] / dt = k_3 [\text{BaTiO}(\text{C}_2\text{O}_4)_2] - k_5 [\text{BaO}][\text{TiO}_2] \quad (13)$$

$$[\text{BaTiO}(\text{C}_2\text{O}_4)_2] = [\text{BaCO}_3] = [\text{BaO(s)}] = 0 \text{ at } t = 0 \quad (14)$$

Figure 6 shows observed and calculated thermogravimetric

Figure. 6 Observed and simulated TG curves of barium titanyl oxalate

Figure. 7 Observed and simulated values of barium titanate formation (Holding time at a specified terminal temperature of 2 h)

changes of $\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ heated up to 1273 K. As indicated in this figure, the observed thermogravimetric curve of $\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ was successfully simulated. The determined kinetic parameters are :

$$k_{10} = 200 \text{ min}^{-1}, E_1 = 7.1 \text{ kcal} \cdot \text{mol}^{-1}$$

$$k_{20} = 1.5 \times 10^6 \text{ min}^{-1}, E_2 = 22 \text{ kcal} \cdot \text{mol}^{-1}$$

$$k_{30} = 8.0 \times 10^5 \text{ mol}^{-1} \cdot \text{min}^{-1}, E_3 = 22 \text{ kcal} \cdot \text{mol}^{-1}$$

$$k_{40} = 5.0 \times 10^{13} \text{ mol}^{-1} \cdot \text{min}^{-1}, E_4 = 65 \text{ kcal} \cdot \text{mol}^{-1}$$

$$k_{50} = 2.0 \times 10^5 \text{ mol}^{-1} \cdot \text{min}^{-1}, E_5 = 34 \text{ kcal} \cdot \text{mol}^{-1}$$

Figure 7 shows observed and simulated change with calcination temperature of barium titanate content. Solid lines in Fig. 6 indicate simulated changes of barium titanate and other components. Barium titanate formation has been successfully simulated using the kinetic parameters. The simulation indicates that the rapid formation of barium titanate resulted from the reaction between barium carbonate and titanium oxide at the temperatures up to 973 K. On the other hand, the reaction between barium oxide(s) and titanium oxide plays a role of moderate formation of barium titanate without weight loss in thermogravimetric change above 973 K.

4. Conclusions

Changes in composition with temperature for barium titanyl oxalates tetrahydrates in the calcination were characterized by FT-IR, TG-DTA, XRD and acid extraction. Thermogravimetric change and formation behavior of barium titanate were successfully simulated assuming a reaction scheme based on experimental results and volume reaction model. The simulated results indicated that barium titanate formed rapidly by the reaction of barium carbonate and titanium oxide at the temperatures up to 973 K, and moderate formation of barium titanate above 973 K resulted from the reaction between barium oxide(s) and titanium oxide.

Acknowledgments

The authors are grateful to the Electronic Device Division of TDK Corp. for financial support.

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