

Synthesis and characterization of tetragonal barium titanate powders by an ion-exchange and hydrothermal process

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Tetragonal barium titanate (BaTiO₃) powder with a uniform size distribution was successfully prepared by an ion-exchange treatment followed by hydrothermal process, and with a high precursor concentration. Ion-exchange treatment of the barium-titanium chloride led to the formation of the homogeneous Ba-Ti hydroxide sol. Then, hydrothermal (240 °C for 7 h) led to the preparation of BaTiO₃ powders with a very narrow size distribution (90 ± 3 nm) and a very high tetragonal content (90%), which were confirmed respectively by scanning electron microscopy and differential scanning calorimetry. Further, using the regenerated resin to ion-exchange, the BaTiO₃ yield reached 99%.

Key words: BaTiO₃, Ion-exchange, Hydrothermal, Tetragonal, Powder technology, Electronic materials.

Introduction

The recent development of thinner multilayer ceramic capacitors (MLCCs) has tremendously increased the demand for smaller-sized dielectric ceramic particles. When the thickness of a single ceramic layer decreases to < 1 μm, uniformly distributed, nano-sized particles are required to produce defect-free layers. In the case of BaTiO₃, a tetragonal phase is required as opposed to a cubic one for obtaining better dielectric properties, and this observation is supported by several experimental studies, even though the reason for this phenomena is still being debated [1, 2].

Traditionally, tetragonal- BaTiO₃ is prepared using a solid-state reaction that involves ball milling BaCO₃ and TiO₂. The mixture is then calcined at a high temperature of about 1300 °C [3]. However, BaTiO₃ prepared at a high temperature exhibits some drawbacks such as a large particle size (2-5 μm) and a high impurity content, the high impurity being caused by repetitive calcinations and grinding treatments. Therefore, the resultant BaTiO₃ powders are unsuitable for enhancing the dielectric properties of ceramics for high-performance uses. At present, various other low-temperature chemical methods, such as spray pyrolysis [4], sol-gel processing [5, 6], chemical solution deposition [7], and hydrothermal processing [8-10], are used to prepare tetragonal-BaTiO₃ powders. Of these methods, the hydrothermal method is especially attractive for synthesizing the tetragonal-

BaTiO₃ powders of good dispersion, because the combined effects of the solvent used, and temperature, and pressure on the ionic reaction equilibria can stabilize desirable products while inhibiting the formation of undesirable compounds. However, the as-prepared BaTiO₃ particles have a wide and uncontrollable size distribution, which is not desirable. This is because heterogeneous (non-uniform) barium and titanium hydroxide powders or sols formed from direct precipitation of metal salt with sodium hydroxide or ammonia have wide size distributions, but still they are being used as the hydrothermal precursor. It can be argued that based on the dissolution-precipitation mechanism during the hydrothermal process, the uniform-sized tetragonal-BaTiO₃ powders with nanometer or submicrometer size may be prepared but the hydrothermal process must be carried out at a higher temperature for a longer period of time.⁸ Therefore, there is a need to develop a new method to overcome this problem to obtain a homogenous precipitate with a controllable particle size and narrow size distribution, so that it can be used as the hydrothermal precursor in the process. Meanwhile, to make such preparation attractive to the chemical industry, engineers must focus on developing processes that operate with a high precursor concentration.

In the present study, the possibilities of obtaining tetragonal-BaTiO₃ powders with a uniform particle size distribution was examined by using an aqueous solution of BaCl₂ and TiCl₄ in an ion-exchange and hydrothermal process; the BaCl₂ and TiCl₄ solutions were mixed in advance with an anion-exchange resin converted into homogeneous Ba-Ti hydroxide sol. This method is a modification of the basification method, but may be more advantageous because the nucleation is more homogeneous and no chloride salt is left in the products.

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Experimental

A commercial anion-exchange resin (Diaion SA 10A, Mitsubishi Chemical Co.) was immersed in a basic solution (NaOH) for 1 h to convert it from Cl^- type to OH^- type. After washing with distilled water five times to make the pH closer to 7, the resin was transferred to a plastic container and stirred mildly.

An aqueous solution of barium and titanium with the Ba/Ti ratio of 1.2/1.0 was obtained by mixing $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (99.6% purity) and TiCl_4 (99.9% purity) in deionized water. The aqueous solution with the concentration of about 3 mol/L was poured into the container to mix with the stirred resin (volume ratio of resin and Ba-Ti chloride solution = 75 : 25) and to obtain the sol. After stirring for 3 h, the colloidal sol was then separated from the resin using a 0.1 mm filter. After washing the resin several times, the final sol was transferred to a 50 ml Teflon-lined stainless steel vessel. The vessel was sealed and heated at 240 °C for 7 h. After the sealed vessel had cooled down to room temperature, the precipitate was centrifuged and finally dried at 80 °C for 12 h in a vacuum oven. Excess Ba^{2+} was removed during washing, and BaCO_3 was not detected in the reaction product by x-ray diffractometry and X-ray fluorescence. The Ba/Ti ratio of the as-prepared powder was 1.000, as analyzed by using a chemical method.

The diffraction pattern of the powder was acquired using a powder x-ray diffractometry (XRD) (Model Geigerflex D/Max 2200, Rigaku Co., Ltd., Tokyo, Japan) with a nickel-filtered $\text{CuK}\alpha$ (1.5405 Å) source. Powder XRD patterns were taken in the continuous mode, over two ranges of 2θ : 20°–70° and 44°–46°. The first range was obtained at a scan speed of 2°/min, with a 0.050° sampling step, and the second range at a scan speed of 0.5°/min, with a 0.010° sampling step. Calorimetric measurement was performed using a thermal analysis system (Model 7 series, Perkin-Elmer, Inc., Norwalk, CT). The particle size and morphology of the prepared powder were also investigated using scanning electron microscopy (SEM; Models XL30 and DX-4I, Philips Electronic Instruments, Mahwah, NJ) and transmission electron microscopy (TEM;

Model JEM-2010, JEOL, Tokyo, Japan). The average particle size was the mean value calculated from the diagonals of about 150 particles. The impurities in the powders, such as Cl^- , were confirmed both by chemical analysis and an inductively- coupled plasma atomic emission spectrometer (ICP-AES; Optima 3000).

Results and Discussion

Fig. 1a showed the SEM photograph of the as-prepared powders prepared by the ion-exchange treatment followed by hydrothermal process. The particles exhibited a good dispersion, and a narrow size distribution (90 ± 3 nm). The XRD pattern of the as-prepared powder is shown in Fig. 1b. Figure 1b shows very sharp X-ray reflections, with well-defined splitting of (002) and (200/020) at 45°. The splitting is characteristic of tetragonal- BaTiO_3 [11]. Clearly, with ion-exchange resin introduced for homogeneous precipitation, the hydrothermal method could be used to synthesize tetragonal- BaTiO_3 powders with a narrow size distribution. The yield of BaTiO_3 was 95% with reference to the starting amount of the raw materials; that is, 5% Ba-Ti hydroxide particles was stored in the inner pores of the resin. However, by using the regenerated resin to mix with Ba-Ti chloride again, the yield of BaTiO_3 could be raised to more than 99%.

By the traditional hydrothermal process, Ba^{2+} and Ti^{4+} cations combined with OH^- to form $\text{Ba}(\text{OH})_2$ and $\text{Ti}(\text{OH})_4$, finally forming hydrous gel-type precipitates. It is well known that controlling the precipitate condition so that homogeneous nucleation would appear easily, is too difficult. Therefore, a heterogeneous gel with a wide and uncontrollable size distribution would usually be formed in the case of the traditional co-precipitation method, and hence, BaTiO_3 powders had a wider size distribution, even if a higher hydrothermal temperature is applied for a longer period of time. In the present work, the ion-exchange method used is a modification of the basification method; however, the precipitate can only be formed slowly because the rate of the adsorption is very slow. The as-prepared sol was dried up and characterized by TEM. The sample showed conglomeration but with a smaller particle size (see

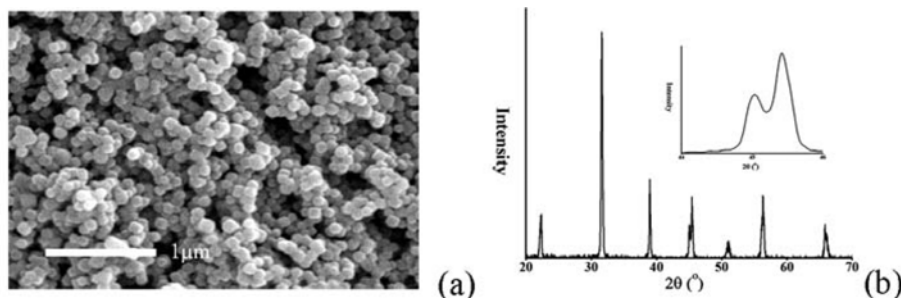


Fig. 1. SEM (a) and XRD (b) of the BaTiO_3 powders prepared by ion-exchange and hydrothermal process.

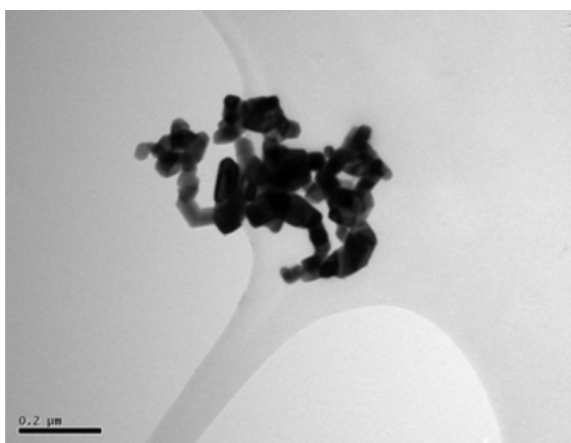


Fig. 2. TEM of the Ba-Ti hydroxide powders prepared by ion-exchange.

Fig. 2). The uniform particles could be grown by the dissolution-precipitation process in the hydrothermal environment with a higher pressure and temperature.

To quantify the tetragonal content of the as-prepared powder, a calibration curve was established (Fig. 3(a)) by measuring the change in enthalpy (ΔH) at the Curie temperature for the samples containing known amounts of tetragonal and metastable cubic forms, which had been prepared using physical mixing according to the method described by Dutta *et al.* [11]. BaTiO₃ powder measuring about 20 nm, in a metastable cubic form, was prepared by the hydrothermal method at 95 °C as reported in the literature [12]; the cubic form was verified using DSC and Raman analysis. BaTiO₃ powder measuring about 2 μm in a pure tetragonal form, was prepared using a solid-state reaction at 1200 °C sustained for 12 h. The ΔH value of the as-prepared BaTiO₃ powder with a 90 nm particle size was in the range 0.80-0.85 J/g, which indicated a 90% tetragonal content (Fig. 3(b)), at the Curie transition of about 130 °C [13].

The dielectric properties of the sintered pellets prepared using the as-prepared BaTiO₃ powder were determined according to the literature.⁹ The dielectric

constants and dielectric losses were measured at a frequency of 1 kHz. The dielectric constant at room temperature reached 8000 with a small dielectric loss of < 0.01. The as-prepared BaTiO₃ powder has so high dielectric constant with low dielectric loss that it is compatible with the requirements of the present MLCCs systems. Hence, the method used in the present work can prepare the nanopowders with a uniform size distribution, higher dielectric constant and lower dielectric loss.

Summary

Barium titanate powder with a uniform size (90 ± 3 nm) and high tetragonal content (90%) was successfully prepared by an ion-exchange treatment followed by hydrothermal process. Moreover, using the regenerated resin to ion-exchange, the BaTiO₃ yield could be raised to above 99%. Therefore, the ion-exchange treatment followed by hydrothermal process offers a simple and effective way for producing uniform BaTiO₃ powders in the materials manufacturing industry.

Acknowledgments

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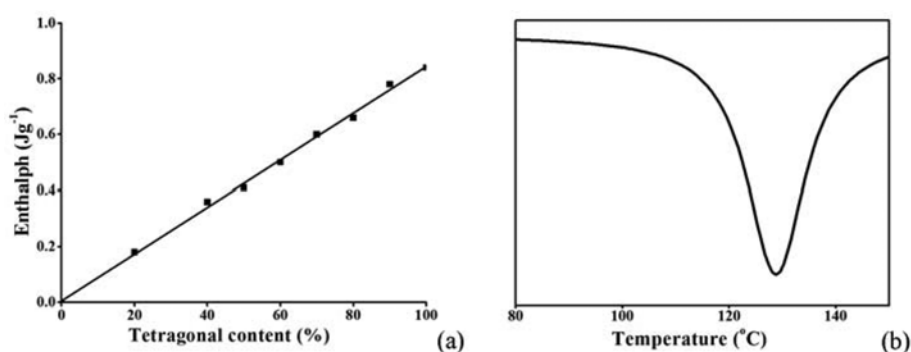


Fig. 3. (a) DSC calibration of the ΔH values for transformation versus tetragonal content, and (b) DSC traces for the as-prepared nanocrystalline tetragonal-BaTiO₃ powder.

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