

Synthesis of Barium titanate powder by Sol-Gel and Ion-Exchange method

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Spherical Ba-TiO₂ amorphous powders (BT powder) were prepared to obtain mono-dispersed spherical powders that are suitable to the starting materials as BaTiO₃ or BaTi₂O₅ ceramics. BT powder was prepared using Na-TiO₂ amorphous powder (NT powder) as a starting powder. NT powder was first prepared through the emulsion process by the Sol-Gel and Ion-Exchange method. The obtained NT powder was relatively spherical as compared with the powder prepared through the modified Stöber process. The Na/Ti ratio in NT powder (up to Na/Ti=0.8) was controlled by changing the ratio of NaOH to TEOT. BT powder was then synthesized by conducting the exchange between barium ion and sodium in NT powder. The Ba/Ti and Na/Ti ratio depended on the ratio of ethanol to water in the suspension and the concentration of barium in the Ba solution. BT powder fired at 700°C showed crystal phases of BaTi₂O₅ with slight amount of BaTiO₃, and the phases were corresponded to Ba/Ti ratio in BT powder.

Key words: Sol-Gel method, Ion-Exchange, mono-dispersed powder, Ba-TiO₂ amorphous powder

1. INTRODUCTION

Mono-dispersed spheres are an ideal starting powder for ceramics, and the use of the spherical powder would result in homogeneous ceramics that exhibit sophisticated properties. Sol-Gel method is one of the most promising processes for preparing spherical powders because the powder obtained by this method is a sphere in shape and has small distribution of particle sizes [1-4]. We can also obtain spherical powder by this method inexpensively, because the method requires no special and large instruments. The obtained powders are almost gel powder, which is amorphous, and the use of the spherical gel powders as starting materials for ceramics

would lead to both increase homogeneity of ceramic microstructure and lower sintering temperature.

However, it is difficult to prepare mono-dispersed spherical powders that are composed of several metal-oxides by Sol-Gel method because the rates of hydrolysis and condensation are much different among metal-oxides. The difference of the rates leads to be heterogeneous nucleation and the heterogeneous nucleation often results in aggregation.

We previously revealed that the ion exchange between alkali ion and proton of silanol that was produced by the hydrolysis of Si alkoxide occurred under adequate conditions [5-7]. We then prepared Na-SiO₂ amorphous powder by exchanging proton of silanol for sodium (Sol-Gel and Ion-Exchange method), and the silicate spherical powder that contained alkaline-earth metal oxide was also obtained by exchanging sodium in Na-SiO₂ amorphous spheres for alkaline earth ions [8, 9].

The preparation of amorphous titanate spherical powders has investigated in order to fabricate starting powder for highly functional ceramics. Na-TiO₂ amorphous powder (NT powder) was previously prepared by Sol-Gel and Ion-Exchange method. Ethanol was then used as a solvent [10], and the condensation and the exchange between protons of Ti-OH and sodium ion could simultaneously occur after the homogeneous nucleation of titania oligomer (modified Stöber process) [11]. However, we could not find suitable conditions. The powder was aggregated and mono-dispersed spherical powder could not obtained by the modified Stöber process. NT powder was then prepared by using octanol and butanol. Emulsion is formed by mixing octanol, butanol and acetonitrile, and the emulsion process was applied for preparing mono-dispersed NT powder [12, 13]. The effects of synthesis condition on morphology and Na/Ti ratios of NT powder were investigated in order to obtain mono-dispersed spherical

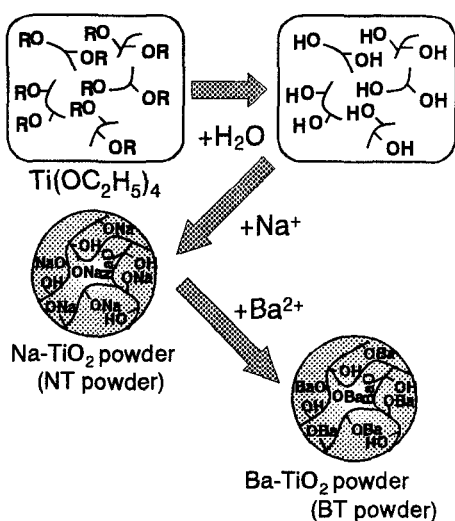


Fig.1 Schematic scheme for preparing Ba-TiO₂ amorphous powder

powder with various compositions.

Ba-TiO₂ amorphous powder (BT powder) was then synthesized by using NT powder as a starting material and conducting the exchange between barium and sodium in NT powder (Fig. 1). The sintering of mono-dispersed BT powder would produce BaTiO₃ and BaTi₂O₅ ceramics that exhibit dielectric or PTC properties [14-18]. The control of composition of BT powder was investigated by using various synthesis conditions, and the change in crystal phase of BT powder by sintering at various temperatures was also discussed to fabricate BT powder suitable to the starting powder as BaTiO₃ or BaTi₂O₅ ceramics.

2. EXPERIMENTS

2.1 Preparation of Na-TiO₂ amorphous powder

NT powders were prepared through the emulsion process by the Sol-Gel and Ion-Exchange method. Acetonitrile was added into a solution of 1-octanol, tetraethylorthotitanate (TEOT) and hydroxypropyl cellulose (HPC), and the TEOT solution was stirred at 40°C for 10 min in dry N₂. The concentration of acetonitrile in the TEOT solution was adjusted to 40 vol%. Another solution composed of 1-octanol, 1-butanol, NaOH, and water was mixed with the TEOT solution. The mixture was stirred for 40 min, and allowed to be hydrolysis of TEOT, condensation and the ion exchange between sodium ion and proton of Ti-OH simultaneously. The obtained gel powder was separated from the mixed solution with a centrifuge, and ultrasonically washed with ethanol for 10 min. The sequence of the separation from ethanol with a centrifuge and the washing with an ultrasonic cleaner was repeated three times, and the powder was finally dried with a freeze-drier.

2.2 Preparation of Ba-TiO₂ amorphous powder

BT powders were prepared by using NT powders as starting materials and conducting the ion exchange

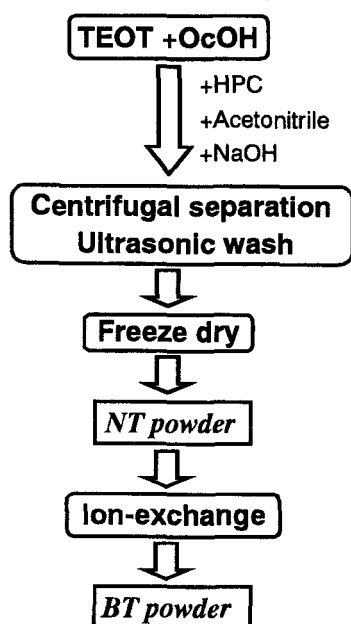


Fig.2 Experimental procedure for preparing NT and BT powder

between barium ion and sodium in NT powder. NT powder was added into a solution of barium chloride, water and ethanol, and dispersed with ultrasonic wave for 5 min. This suspension composed of NT powder and the solution was stirred at 40°C for 24 h. The powder exchanged for barium was separated from the suspension by filtration through a membrane filter with 0.1 μ m pores, washed with ethanol several times and freeze-dried. The flow chart for preparing NT and BT powders was shown in Fig. 2.

2.3 Characterization of Na-TiO₂ and Ba-TiO₂ amorphous powders

Morphologies and particle sizes of NT and BT powders were investigated by scanning electron microscopy (SEM), and compositions of NT and BT powders were analyzed by energy-disperse X-ray spectroscopy (EDS). BT powders were also fired at various temperatures for 5 h in air and the crystal phases of the BT powders were investigated by powder X-ray diffraction (XRD).

3. RESULTS AND DISCUSSION

3.1 Composition of Na-TiO₂ amorphous powder

NT powders were prepared by adding the solution including 1-butanol, NaOH and water into the TEOT solution. This addition was allowed to be simultaneous reactions among the formation of emulsion, the hydrolysis and condensation of TEOT, and the ion exchange between proton and sodium ion. We previously prepared NT powder by adding NaOH solution after the emulsion was already generated, but the Na/Ti ratio of the obtained NT powder was very small and the ion exchange would not effectively occur. The emulsion process requires simultaneous reactions between the formation of emulsion and the ion exchange because the diffusion of sodium in the emulsion would not be fast enough to conduct the ion exchange between proton and sodium in NT powder.

NT powder were synthesized using the solutions with various concentrations of TEOT and NaOH, and the Na/Ti ratio in the NT powder was investigated by EDS. Fig. 3 shows the relationship between Na/Ti ratio in the

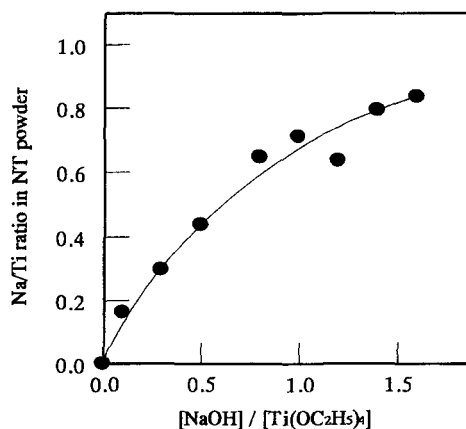


Fig. 3 The relationship between Na/Ti ratio in NT powder and [NaOH]/[Ti(OC₂H₅)₄] ratio in the reaction mixture

obtained NT powders and the molar ratios of NaOH to TEOT in the solution used during the Sol-Gel and Ion-Exchange method, $[\text{NaOH}]/[\text{TEOT}]$. The Na/Ti ratio was increased with an increase in $[\text{NaOH}]/[\text{TEOT}]$ ratio. The Na/Ti ratio would saturate when the concentration of sodium more than $[\text{NaOH}]/[\text{TEOT}]=1.5$ was employed, but the NT powder with the composition less than Na/Ti=0.8 was obtained through the emulsion process and the composition of NT powder was able to control closely by controlling $[\text{NaOH}]/[\text{TEOT}]$ ratio in reaction mixture. The maximum Na/Ti ratio of NT powders prepared through the emulsion process was comparable to that of the powder previously synthesized through the modified Stöber process. The saturation would be ascribed to the simultaneous reactions. The high concentration of Ti-OH generated by the hydrolysis of TEOT was essential to conduct the ion exchange of sodium and produce the NT powder with high Na/Ti ratios. The precise investigation of the formation of emulsion may necessary to obtain mono-dispersed spherical NT powder with Na/Ti ratio higher than Na/Ti=1.0 through the emulsion process by the Sol-Gel and Ion-Exchange method.

The morphology of NT powder was observed by SEM. NT powder obtained through the emulsion process exhibited dispersed sphere, which was 0.3-0.5 μm in particle size, as compared with the NT powder derived from the modified Stöber process.

3.2 Preparation of Ba-TiO₂ amorphous powder

BT powders were prepared by using NT powder as a starting material and conducting exchange between barium and sodium in NT powder. The NT powder was prepared through the emulsion process, and the powder was composed of sodium at the Na/Ti ratio of 0.8. NT powder was added in the solution mixed with ethanol and BaCl₂ water solution, and stirred at 40°C for 24 h. The effects of the ratio of ethanol to the Ba solution and the barium concentration of the Ba solution on Ba/Ti and Na/Ti ratios in BT powder were investigated in order to control compositions of BT powder closely.

Fig. 4 shows the relationship between Ba/Ti and Na/Ti

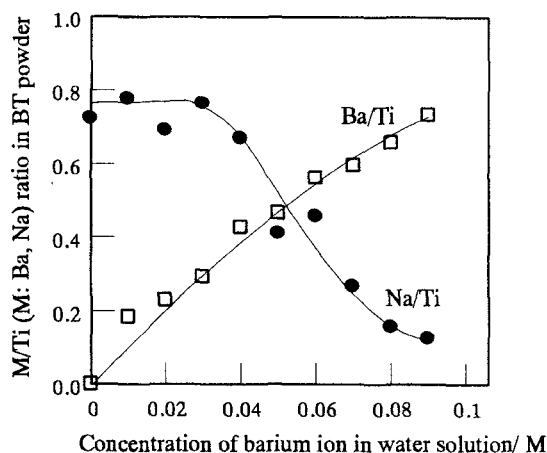


Fig. 4 The relationship between the concentration of barium ion in water solution and M/Ti (M: Ba, Na) Ratios in BT powder ($[\text{EtOH}]/[\text{H}_2\text{O}] = 0.25$)

ratios in BT powders and the Ba concentration in the Ba solutions. The molar ratio of ethanol to H₂O of the Ba solution was set to be 0.25. The Ba/Ti ratio was increased and the Na/Ti ratio was decreased with an increase in Ba concentration. Ba/Ti and Na/Ti ratios in BT powder was controlled by changing Ba concentration in suspension. This change in Ba/Ti and Na/Ti ratios was influenced by the ratio of ethanol in the suspension. The use of the suspension without ethanol often resulted in precipitation of barium salts on the surface of NT powder, and the exchange between barium and sodium would not occur. When the suspension with ethanol was used, the precipitation did not find at the Ba concentration less than 0.1 mol dm⁻³ and the exchange between barium and sodium ions was observed. The exchange would be dependent of dissociation of BaCl₂ in the solution mixed with ethanol and water.

The Na/Ti ratio was decreased from 0.8 to 0.1 with increasing Ba/Ti ratio from 0.0 to 0.7 in Fig. 4. The ratio of increasing Na/Ti ratio to decreasing Na/Ti would be estimated to be 1.0. This ratio of exchange between univalent Na⁺ and bivalent Ba²⁺ would reveal that Ba²⁺ with OH⁻ is exchanged for Na⁺.

In addition, the obtained BT powders were washed with hot water at 90°C to remove Na remaining in BT powder, because alkali metals often diminish electrical properties of barium titanate ceramics. In case of using the hot water with pH=1.0, Na/Ti ratio was decreased rapidly and simultaneously Ba/Ti ratio was also decreased. The use of the hot water with pH=3.0 led to a decrease in only Na/Ti ratio. Only Na/Ti was able to be decreased by washing BT powders under an adequate condition, and sodium-free BT powder would be applicable to a starting materials for barium titanate ceramics.

3.3 Crystallization of sintered BT powder

Barium titanate ceramics was prepared by sintering BT powder. The amorphous BT powder was prepared with the suspension containing barium at the concentration of 0.10 mol dm⁻³, and the BT powder was washed with hot water (pH=3.0) at 90°C for 30 min. The composition of the obtained BT powder was estimated to Ba/Ti=0.6 and sodium in BT powder was not detected by EDS. However,

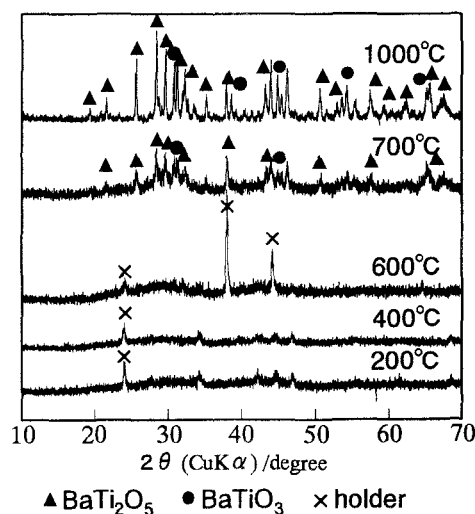


Fig. 5 XRD patterns of sintered BT powder

the measurement of ICP showed that some hundreds ppm of sodium would remain in the BT powder after washing once with hot water (pH=3.0) at 90°C for 30 min.

Fig.6 shows XRD patterns for the BT powders from 200 to 1000°C. The BT powder fired from 200 to 600°C in the crystallization of BaTi₂O₅ and slightly BaTiO₃. Single crystal phase of BaTiO₃ or BaTi₂O₅ was not obtained, but the crystal phase of fired BT powder was corresponded to Ba/Ti ratios in BT powder.

4. SUMMARY

BT powder was synthesized in order to prepare mono-dispersed spherical powders that are suitable to the starting materials as BaTiO₃ or BaTi₂O₅ ceramics.

BT powder was prepared using NT powder as a starting powder. NT powder was first prepared by the emulsion process by the Sol-Gel and Ion-Exchange method. The obtained NT powder was relatively spherical as compared with the powder prepared through the modified Stöber process. The Na/Ti ratio in NT powder was controlled by changing the ratio of NaOH to TEOT, and the spherical NT powder with Na/Ti=0.8 was obtained by using the reaction mixture with [NaOH]/[TEOT]=1.5.

BT powder was synthesized by conducting the exchange between barium ion and sodium in NT powder. The Ba/Ti and Na/Ti ratio depended on the ratio of ethanol to water in the suspension and the concentration of barium in the Ba solution.

BT powder fired at 700°C showed crystal phases of BaTi₂O₅ with slight amount of BaTiO₃, and the phases were corresponded to Ba/Ti ratio in BT powder.

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