

## Composition of Spherical Powder Prepared by Ion-exchange and Sol-Gel Process

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Sr-TiO<sub>2</sub> amorphous powders were prepared by ion exchange and sol-gel process, and SrTiO<sub>3</sub> powders were obtained by firing the amorphous powders at relative low temperature in order to utilize the powder as starting materials of ceramics. Na-TiO<sub>2</sub> amorphous powders were first prepared to use as starting powders for preparing Sr-TiO<sub>2</sub> amorphous powders. The use of octanol resulted in dispersed Na-TiO<sub>2</sub> amorphous powder, while the amorphous powders with various concentrations of sodium were obtained by using ethanol. The compositions of Sr-TiO<sub>2</sub> amorphous powders were controlled by controlling concentrations of strontium and ethanol in the suspension during conducting ion exchange between sodium and strontium. Single-phase SrTiO<sub>3</sub> powder was obtained by firing the Sr-TiO<sub>2</sub> amorphous powder at 800°C.

Key words : Sol-gel, Ion-exchange, Mono-dispersed powder, SrTiO<sub>3</sub>, Amorphous powder

### 1. INTRODUCTION

Investigation of starting powders is essential to fabricate homogeneous ceramics that would lead to sophisticated properties. Sol-gel method is one of the most promising processes to obtain mono-dispersed spherical powders utilized as starting powders of ceramics [1-4]. The use of mono-dispersed spherical powders prepared by sol-gel method would lead to both increase homogeneity of ceramics and lower sintering temperature. Sol-gel method is also inexpensive as compared with other processes for preparing mono-dispersed powders, because this method requires no special or large instruments. The fabrication of ceramics by using the mono-dispersed powder thus

needs us no extra cost. However, it is difficult to prepare mono-dispersed spherical powders comprising several metal oxides by sol-gel method, because the rates of hydrolysis and condensation are different among metal alkoxides and the differences of the rates among alkoxides often lead to aggregation.

We have studied on sol-gel processes in multi-component system by NMR, and we previously revealed that ion exchange between alkali ion and proton of silanol that was produced by hydrolysis of Si alkoxides occurred under adequate conditions [5-7]. We have generally known that some properties of dielectric ceramics are influenced by fine structure of ceramics [8-12], and we have then tried to prepare mono-dispersed powders that have the same compositions as dielectrics. We prepared Sr-TiO<sub>2</sub> amorphous powder by sol-gel method and ion exchange, and investigated close control of the composition of Sr-TiO<sub>2</sub> amorphous powder.

Na-TiO<sub>2</sub> amorphous powder (NT powder) was first synthesized by sol-gel method. The synthesis of mono-dispersed powder is much influenced by solvent or suspension during sol-gel reaction. Two kinds of solution were used for preparing NT powder. Sr-TiO<sub>2</sub> amorphous powder (ST powder) was then synthesized by using NT powder as a starting powder, and conducting ion exchange between Sr<sup>2+</sup> and Na<sup>+</sup> in NT powder. Schematic scheme for preparing ST powder is shown in Fig.1. The change in crystal phase of ST powder by sintering at various temperatures was also discussed.

### 2. EXPERIMENTAL

#### 2.1 Preparation of Na-TiO<sub>2</sub> amorphous powder

NT powders were prepared using two kinds of solvents, ethanol [13] and octanol. Figure 2 shows the experimental procedures using ethanol and octanol. When ethanol was used for preparing NT powder, a solution of the water adjusted to pH=3.0,

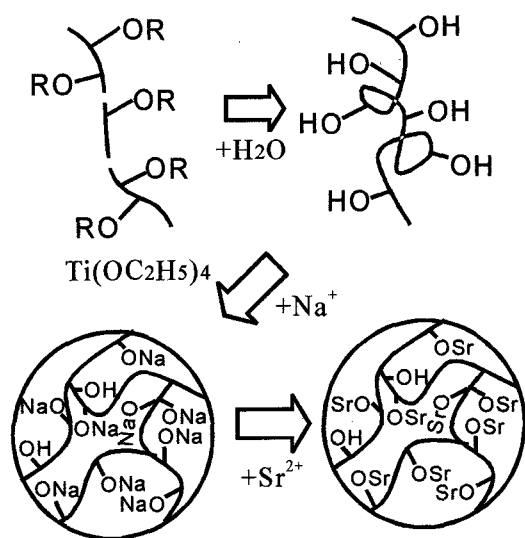


Figure 1 Schematic scheme for preparing Sr-TiO<sub>2</sub> amorphous powder.

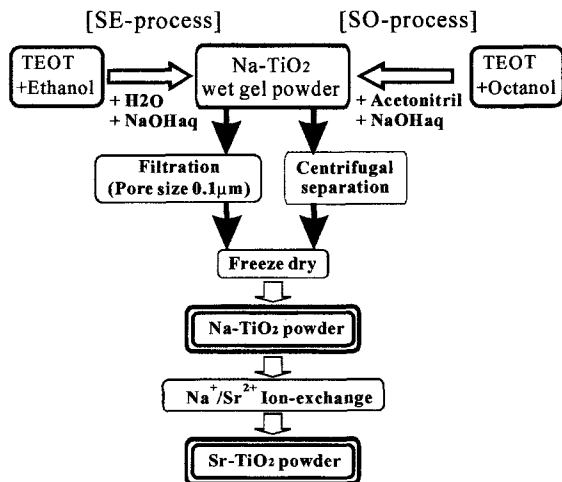


Figure 2 Experimental procedure for preparing Na-TiO<sub>2</sub> and Sr-TiO<sub>2</sub> amorphous powders.

tetraethylorthotitanate (TEOT), ethanol and hydroxypropyl cellulose (HPC) was prepared [14,15]. The solution was stirred at 0°C for 10min in dry N<sub>2</sub>, where conducting hydrolysis and partial condensation of TEOT. Another solution composed of NaOH, water and ethanol was closely controlled as to concentration of proton and sodium ion, and poured into the TEOT solution. After stirred for 40min, wet gel powders resulted through ion exchange between sodium and proton of Ti-OH were separated from the mixed solution by filtration through a membrane filter with 0.1µm. The powders were washed with ethanol several times and dried with a freeze-dryer (SE-process).

NT powders were also synthesized by using octanol as follows [16]. Acetonitril was added into a solution of octanol, TEOT and HPC, and the TEOT solution was stirred at 24°C for 10min in air. The concentration of acetonitril in the TEOT solution was set to 40vol%. Another solution composed of octanol, n-butanol, NaOH, and water was mixed with the TEOT solution, and stirred for 40min. The mixture was allowed to be hydrolysis of TEOT, partial condensation and simultaneous ion-exchange between sodium and proton of OH group. The obtained wet gel powder was separated from the mixed solution with a centrifuge and ultrasonically washed with ethanol for 10min. The separation from ethanol with a centrifuge and the ultrasonic wash were repeated three times, and the powder was dried with a freeze-dryer (SO-process).

## 2.2 Preparation of Sr-TiO<sub>2</sub> amorphous powder

ST powders were prepared by using NT powders as starting materials and conducting ion exchange between strontium ion and sodium. NT powders were added into a suspension of strontium nitrate, water and ethanol, and stirred at 40°C for 24h in air. The exchanged powder was separated from the suspension by filtration through a membrane filter with 0.1µm pores, washed with ethanol several times, and freeze-dried.

Morphologies and particle sizes of NT and ST

powders were investigated by SEM, and the compositions of the powders were by EDS. ST powders were also fired at various temperatures for 5h in air and the crystal phases of the ST powder fired at various temperatures were investigated by XRD in order to estimate the temperature of crystallization as SrTiO<sub>3</sub>.

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Morphologies and particle sizes of NT and ST powders were investigated by SEM, and the compositions of the powders were by EDS. ST powders were also fired at various temperatures for 5h in air and the crystal phases of the fired ST powder were investigated by XRD in order to estimate the temperature of crystallization as SrTiO<sub>3</sub>.

## 3. RESULTS AND DISCUSSION

### 3.1 Composition of Na-TiO<sub>2</sub> amorphous powder

NT powders were prepared using solutions with various concentrations of TEOT and NaOH by SE-process or SO-process, and the molar ratio of sodium to titanium in the obtained NT powder was investigated by EDS. Figure 3 shows the relations between the molar ratio of Na/Ti in the obtained NT powder and the ratio of NaOH to TEOT in the solutions used for preparing NT powder. On preparing NT powders by SO-process, Na/Ti ratio in the NT powder increased with increasing the molar ratio of NaOH to TEOT in the solutions. However, the Na/Ti ratio in the NT powder was saturated by using the solution with the [NaOH]/[TEOT] ratio beyond 0.8. No NT powder containing sodium more than Na/Ti=0.8 was obtained despite solutions with the [NaOH]/[TEOT] ratio more than 0.8 were employed. This saturation would derive simultaneous ion-exchange with hydrolysis and partial condensation. SO-process requires that hydrolysis of TEOT, partial condensation and ion-exchange were almost simultaneously conducted by the addition of the NaOH solution to avoid aggregation. The concentration of Ti-OH, which affords sodium

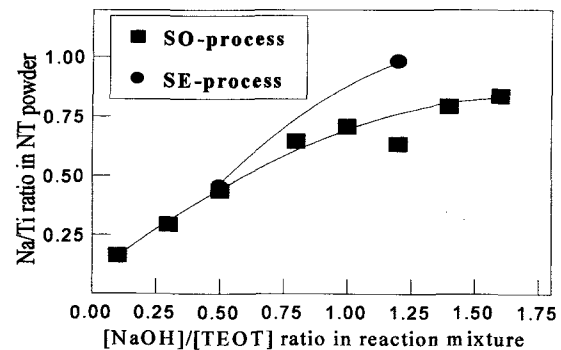


Figure 3 The relationship between [NaOH]/[TEOT] ratio in the reaction mixture and Na/Ti ratio in NT powder

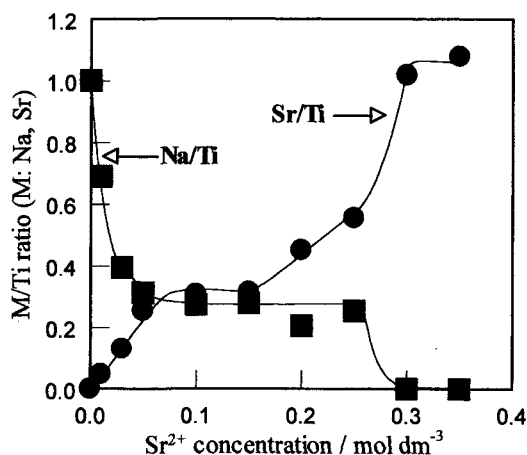


Figure 4 The relationship between Sr<sup>2+</sup> concentrations in suspension and the ratios of Na/Ti and Sr/Ti in ST powders.

ion-exchange, was thus rather small immediately after the addition of the NaOH solution. The concentration of OH group in the oligomer immediately after the addition would be estimated to  $[\text{Ti-OH}]/[\text{Ti}]=0.8$ . SE-process enables the control of Na/Ti ratio up to 1.0 in NT powder. The oligomer obtained by hydrolysis and condensation of TEOT was composed of high concentration of OH group, because the addition of the NaOH solution started ion-exchange between sodium ion and proton ten minutes after hydrolysis of TEOT and partial condensation. In SE-process, changing time interval between the addition of water (pH=3.0) and that of the NaOH solution would easily lead to the control of the composition in NT powder.

Morphologies of NT powders obtained by both SE-process and SO-process were also observed by SEM. The NT powder obtained by SO-process exhibited relatively dispersed particles that were 0.5 $\mu\text{m}$  in average size. However, the NS powder prepared by SE-process was found to be aggregate and showed large distribution of particle size. SE-process is advantageous for the wide control of the composition, and we are then studying improvement of dispersion of NT powder prepared by SE-process.

### 3.2 Preparation of Sr-TiO<sub>2</sub> amorphous powder

ST powder was prepared by using NT powder as a starting material. The used NT powder was prepared by SE-process and contained sodium at the Na/Ti ratio of 1.0. Figure 4 shows the relations between M/Ti (M: Sr and Na) ratios in the ST powder and concentration of strontium in the suspension mixed with the strontium solution and ethanol. The ratio of ethanol to the strontium solution, ethanol/water, in the suspension was set to 5.0. The Sr/Ti ratio increased and accordingly the Na/Ti ratio decreased with increasing concentration of strontium in the suspension. When the suspension containing strontium more than 0.3mol dm<sup>-3</sup> was employed, EDS did not detect sodium in the obtained

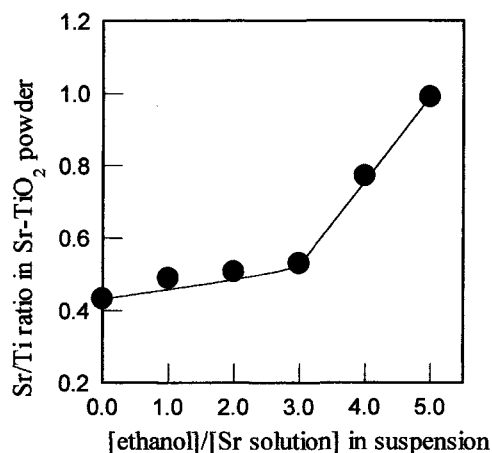


Figure 5 The relationship between the ratio of ethanol to strontium solution in the reaction mixture and Sr/Ti ratio in ST powder.

ST powder. The control of concentration in the suspension led to the ST powder with various concentrations of strontium and sodium.

The effects of the ratio between ethanol and the strontium solution in the suspension on the compositions of obtained ST powder were also investigated to obtain adequate synthesis conditions. NT powder was introduced in the suspension with the strontium concentration of 0.35mol dm<sup>-3</sup>. Figure 5 shows the relations between the strontium concentration and the composition of the ST powder. The suspension with the ethanol/water ratio less than 3.0 resulted in the ST powder containing relative low concentration of strontium. However, the composition of strontium in ST powder steeply increased with increasing strontium concentration in the suspension with the ratio more than 3.0. The ST powder containing strontium at the Sr/Ti ratio of 1.0 was obtained by employing the suspension with ethanol/water ratio of 5.0. Surrounding of hydrated sodium would be altered by changing the ethanol/water ratio in the suspension and a increase in the ethanol/water ratio would increase susceptibility of being attacked by strontium ion.

### 3.3 Crystallization of sintered ST powder

The amorphous ST powder was prepared by using the suspension containing strontium concentration of 0.35mol dm<sup>-3</sup>, and the composition of the obtained ST powder was estimated to Sr/Ti=1.0. Figure 6 shows XRD patterns for ST powders fired at 600°C and 800°C. The ST powder fired at 600°C showed perovskite structure of SrTiO<sub>3</sub> with slight amount of strontium carbonate, while the ST powder fired at 800°C consisted of single phase of SrTiO<sub>3</sub>. Strontium carbonate in the ST powder fired at 600°C would be attributed to excess strontium in the ST powder and the excess strontium would be solved in the perovskite structure of SrTiO<sub>3</sub> by firing at 800°C. ST powders containing various concentrations of strontium can be obtained by using suspension with various ethanol/water

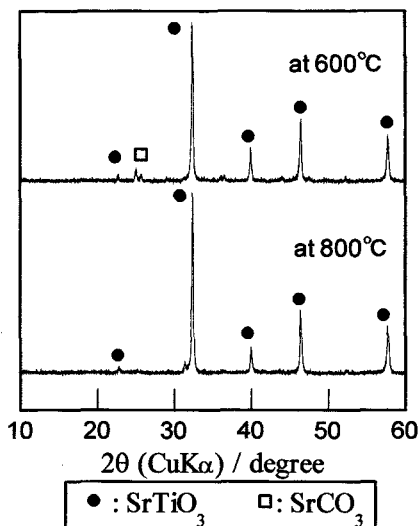


Figure 6 XRD patterns of sintered ST powders.

ratios and concentrations of strontium. Therefore, single-crystal  $\text{SrTiO}_3$  ceramics are supposed to be obtained by firing at temperatures less than  $600^\circ\text{C}$ .

#### 4. SUMMARY

$\text{Sr-TiO}_2$  amorphous powder was prepared by sol-gel method and ion exchange, and the powder composed of perovskite of  $\text{SrTiO}_3$  was obtained by firing the amorphous powder at  $800^\circ\text{C}$ . NT powders were prepared by two kinds of synthesis processes, SE-process and SO-process. Dispersed NT powder was prepared by SO-process, while NT powders with various concentrations of sodium were able to be obtained by SE-process. The NT powder containing sodium at the Na/Ti ratio of 1.0 was thus obtained by SE-process. ST powder was then prepared by using NT Powder as a starting powder. ST powders with various composition of strontium were obtained by the control of strontium concentration in suspension. The composition of ST powder was also much influenced by the amount of ethanol in suspension. The ST powder fired at  $600^\circ\text{C}$  showed perovskite structure of  $\text{SrTiO}_3$  with slight amount of strontium carbonate. Single-crystal  $\text{SrTiO}_3$  powders are therefore supposed to be obtained by firing at temperatures less than  $600^\circ\text{C}$  by controlling the strontium concentration in ST powder.

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