

## Synthesis of SrTiO<sub>3</sub> from Aqueous Solution Using Lactate Titanium Complex

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Lactate-titanium complex that is stable in neutral water was newly synthesized. Using this complex, SrTiO<sub>3</sub> was synthesized from aqueous solution. Ti powder was added to an ice-cold solution of H<sub>2</sub>O<sub>2</sub> and NH<sub>3</sub>. After Ti powder was dissolved, lactic acid was added to obtain lactate-Ti complex followed by addition of Sr(CH<sub>3</sub>COO)<sub>2</sub>·0.5H<sub>2</sub>O. SrTiO<sub>3</sub> powders were synthesized by heating of the precursor obtained by evaporation of the solution. SrTiO<sub>3</sub> films were synthesized by heating of the glass plates coated with the solution by spin-coater. XRD measurements revealed that there is crystallization of SrTiO<sub>3</sub> in the powder heat-treated over 500°C, and pure SrTiO<sub>3</sub> powder were obtained at heating temperature over 700°C. Large specific surface areas were obtained compared with solid-state reaction measured by BET method. It was confirmed from XRD measurements and SEM observations that SrTiO<sub>3</sub> film on glass plate without crack was prepared by heating at 600°C.

Key words: synthesis from aqueous solution, lactate-titanium complex, strontium titanate, film, increase of specific surface area

### 1. INTRODUCTION

Titanium has lots of uses and is used commonly as metal, oxide, and complex oxide. There are number of methods which have been used for the synthesis of Ti based complex oxides which includes the solid-state reaction<sup>1</sup>, and solution methods<sup>2-5</sup>. There are several advantages of the solution methods over solid-state reaction. One of them is the possibility for making of film on a substrate by coating with the solution. The other is reduction of the particle size and increase of specific surface area because the heat-treatment temperature can be reduced. In sol-gel method and polymerizable complex method, Ti alkoxides such as Ti tetraisopropoxide is used as source of Ti and organic solvent is used as solvent<sup>2,3</sup>. In coprecipitation method, TiCl<sub>4</sub> is used as source of Ti and to maintain the pH of the solution HCl is used<sup>4</sup>. However, there are some limitations associated with these methods which includes the high inflammability, relatively high cost and moisture sensitivity of alkoxides and with chlorides there is always a possibility of emission of HCl gas and degradation of electronic properties of the ceramics material if even a small amount of chloride is present in the final product<sup>6</sup>. From environmental point of view and from the economic side, it is more suitable and convenient to use neutral water as a solvent than to use either acid or organic solvent. However, it is difficult to dissolve titanium in neutral water. But, we had succeeded in dissolving Ti into neutral aqueous solution using citric acid as complexant<sup>7</sup>, and to synthesize BaTi<sub>4</sub>O<sub>9</sub> from aqueous solution using it<sup>8</sup>. Recently, we have found that lactate-titanium complex is also stable in aqueous solution (details about this complex will be published).

SrTiO<sub>3</sub> is one of industrially important electroceramics that finds a wide range of applications

especially as grain boundary barrier-layer capacitors and photocatalysis electrode materials<sup>9-13</sup>. In this paper, we report the synthesis of SrTiO<sub>3</sub> from aqueous solution using lactate-Ti complex. SrTiO<sub>3</sub> powders were synthesized and were compared with the sample prepared by solid-state reaction by XRD, SEM, and BET. SrTiO<sub>3</sub> films were synthesized on glass plates by spin-coating and were characterized by XRD and SEM.

### 2. EXPERIMENTAL

#### 2.1 Sample Preparation

To an ice-cold solution of 40ml of 30% H<sub>2</sub>O<sub>2</sub> (Kanto Chemicals Co., Inc. Tokyo, Japan) and 10ml of 28% NH<sub>3</sub> (Kanto Chemicals Co., Inc. Tokyo, Japan), 10mmol of Ti powder (Furuuchi Chemical Co., Tokyo, Japan) was added. Two hours later, a clear solution of Ti-peroxo acid was obtained. 50mmol of lactic acid (CH<sub>3</sub>CHOHCOOH; Wako Pure Chemical Industries, Ltd. Osaka, Japan) was added into this solution to obtain lactate-Ti complex stable in aqueous solution, followed by addition of 10mmol of Sr(CH<sub>3</sub>COO)<sub>2</sub>·0.5H<sub>2</sub>O (Kanto Chemicals Co., Inc. Tokyo, Japan).

In the synthesis of SrTiO<sub>3</sub> power, the precursor solution was heated at 150°C on a hot plate with continuous stirring until a 'gel' was obtained (precursor gel), then it was heated for 12 hours at 400°C in a mantle heater resulting in a brown solid mass. It was lightly ground into a powder with an agate mortar (powder precursor). The powder precursor was heat-treated at 500-1000°C for 12 hours in air on an alumina boat followed by natural cooling to room temperature. For comparison, powder of SrTiO<sub>3</sub> was prepared by conventional solid-state reaction using SrCO<sub>3</sub> (Kanto Chemicals Co., Inc. Tokyo, Japan) and TiO<sub>2</sub> (Kanto Chemicals Co., Inc. Tokyo, Japan). They were mixed for 30 minutes in agate mortar and the

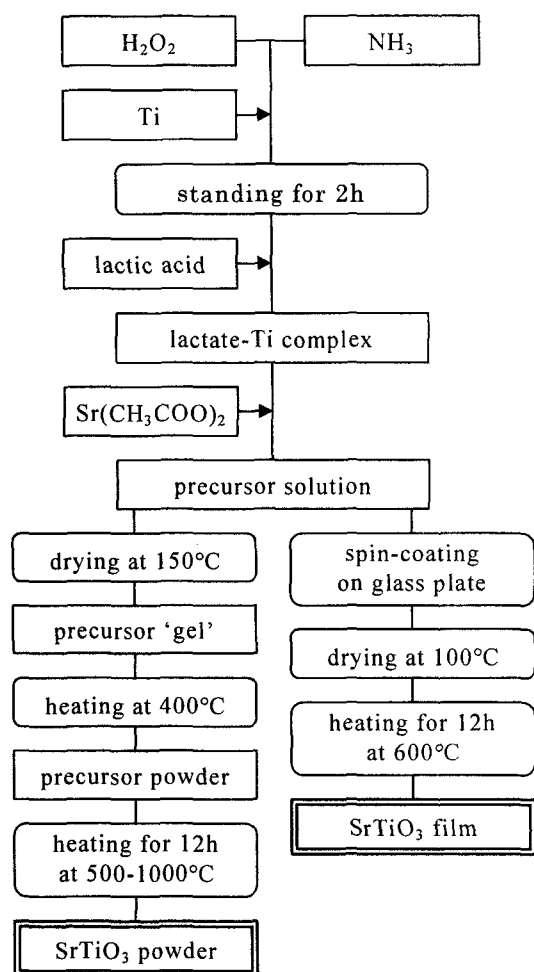


Fig.1 Flow chart for the synthesis of powder and film of SrTiO<sub>3</sub> by the aqueous solution route using lactic acid as complexant.

mixture was heat-treated for 24 hours at 1000°C in air.

In the synthesis of SrTiO<sub>3</sub> film on glass plate, a small amount of polyoxyethylene (23) lauryl ether (Wako Pure Chemical Industries, Ltd. Osaka, Japan) was added to the precursor solution to improve wettability. Coatings were done on the glass plate by spin-coater (2000 rpm, 1 minute). After drying for 1 hour at 100°C, the plate coated with the solution was heat-treated at 600°C for 12 hours in air followed by natural cooling to room temperature.

Flow chart for the synthesis of powder and film of SrTiO<sub>3</sub> is shown in Figure 1.

## 2.2 Characterization

Thermogravimetry-differential thermal analysis (TG-DTA; Type-2020, MAC Science Co., Tokyo, Japan) of the precursor 'gel' was carried out from room temperature to 800°C with heating rate of 5°C min<sup>-1</sup> and data were collected every 5 sec using a Pt crucible. α-Al<sub>2</sub>O<sub>3</sub> was used as a reference.

The powder after heat-treatment between 500-1000°C and the films after heat-treatment at 600°C were characterized by X-ray diffraction (XRD; MXP<sup>3VA</sup>, MAC Science Co., Tokyo, Japan) using Cu Kα radiation of 40kV-40mA with a scan rate of 4° min<sup>-1</sup> (2θ) to

identify SrTiO<sub>3</sub> and impurity phase.

The specific surface areas of the samples were measured by BET method (BET; ASAP 2010, Micromeritics Instrument Co., Georgia, U.S.A. /Shimadzu Co., Kyoto, Japan) using nitrogen gas as absorbent. Approximately 300mg of the samples were used for BET.

The surface morphology of the films prepared by this method was studied by scanning electron microscopy (SEM; S-4500, Hitachi Ltd., Tokyo, Japan). The samples were coated with Pt-Pd by sputtering before observations.

## 3. RESULTS AND DISCUSSION

### 3.1 Powder

Figure 2 illustrates the TG and DTA curves of the precursor 'gel'. The TG curve indicates a gentle weight loss up to 480°C, a steep weight loss up to 520°C, a plateau between 520-580°C, and a small weight loss up to 600°C. There is no further weight loss up to 800°C. The first weight loss is due to dehydration in the region of ~150°C, and evaporation and decomposition of lactic acid in the region of ~480°C. The steep weight loss between 480°C and 520°C can be ascribed to combustion of organics remained without evaporation. The composition for the small plateau between 520-580°C can be regarded as Sr<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub>CO<sub>3</sub> that was found in the preparation of SrTiO<sub>3</sub> by polymerizable complex method<sup>3</sup>, and the small weight loss about 600°C can be ascribed to decomposition of Sr<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub>CO<sub>3</sub>. There is no further weight loss above 600°C, so it is inferred that the decomposition product at temperatures higher than 600°C contains no carbon. In the DTA result, the exothermic peaks corresponding to the weight loss about 400°C and 500°C can be attributed to the combustion of organics. The shoulder at 590°C can be ascribed to decomposition of Sr<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub>CO<sub>3</sub> from the small weight loss at 600°C.

Figure 3 shows XRD patterns of the powder precursor, the samples heat-treated at 500-1000°C for 12 hours and the sample prepared by solid-state reaction for comparison. The powder precursor was amorphous in structure, as is characterized by the broad continuum (Figure 3 a). The XRD pattern of the sample heat-treated at 500°C (Figure 3 b) shows peaks that correspond to reflections from cubic SrTiO<sub>3</sub>, but there are two extra peaks indicating presence of impurity at 26° and 28°. The peak at 26° disappeared for the pattern of 600°C (Figure 3 c), and there is no peak of impurity for the

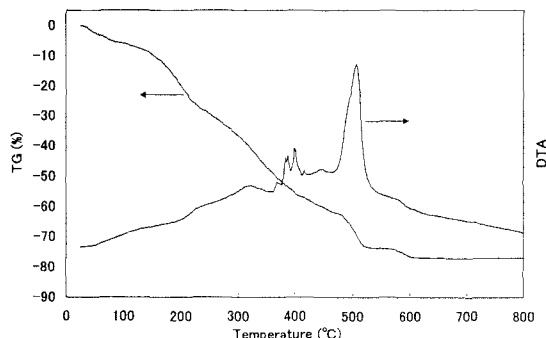


Fig.2 TG-DTA curves of the precursor 'gel' in air with heating rate of 5°C min<sup>-1</sup>.

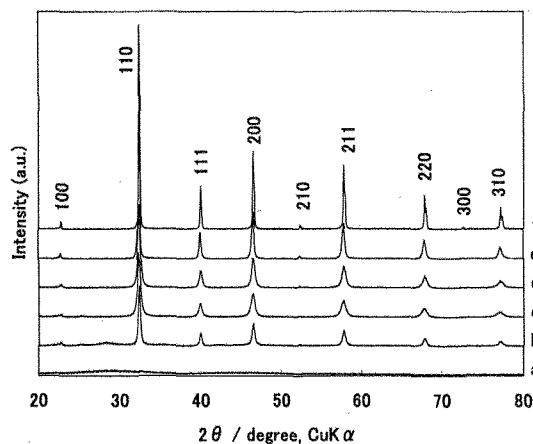


Fig.3 XRD patterns of the precursor for SrTiO<sub>3</sub> (a), and of the products obtained by heating the precursor at 500°C (b), 600°C (c), 700°C (d), 1000°C (e) and of the samples prepared by solid-state reaction at 1000°C (f).

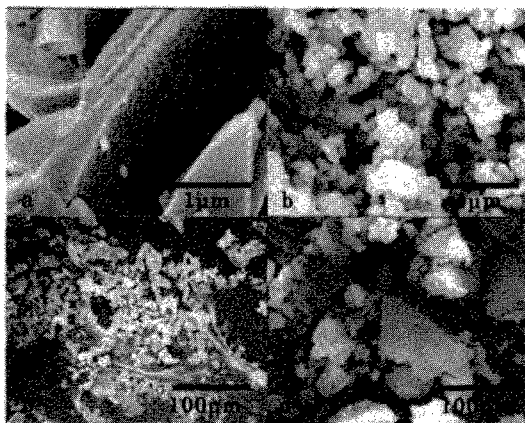


Fig.4 SEM images of the sample heat-treated at 1000°C (a ×30000, c ×300) and the sample prepared by solid-state reaction (b ×30000, d ×300).

pattern at 700°C (Figure 3 d). The overall shape of the XRD patterns remains unchanged from 700°C to 1000°C (Figure 3 e) except that the peaks somewhat sharpens when the heat-treatment temperature is increased. But the peaks for 1000°C were broader than the peaks for solid-state reaction. It can be caused by the particle size (discussed later).

SEM images of the sample heat-treated at 1000°C and the sample prepared by solid-state reaction are shown in Figure 4. Primary particles of the sample heat-treated at 1000°C were small and aggregate, compared with that of solid-state reaction (see Figure 4 a and b). Secondary particles of the sample were small too (see Figure 4 c and d). The sizes of the primary particles were approximately 200nm at solid-state reaction, 100nm at 1000°C, 30nm at 900°C and could not be measured at 500-800°C because those were too small. It is considered that particle growth was suppressed by the decline of the heating temperature.

Specific surface areas of the samples heat-treated between 500-1000°C and the sample prepared by solid-state reaction measured by BET method using nitrogen gas as absorbent are shown in Table I. All of the samples prepared by this method had large specific

Table I Specific surface areas of the products at each heating temperature and the samples prepared by solid-state reaction (SSR).

heating temperature (°C)	specific surface area (m <sup>2</sup> g <sup>-1</sup> )
500	15.13
600	55.42
700	38.64
800	23.00
900	17.38
1000	7.95
1000(SSR)	4.35

surface areas compared with the sample prepared by solid-state reaction. The specific surface area became large as the heating temperature fell except for 500°C. The largest specific surface area was obtained at 600°C. It was more than ten times of solid-state reaction. In this method, it can be regarded that the large specific surface areas were obtained because spaces were made in the particles resulted from volatilization of organics in the precursor particles by heating. The specific surface area of the sample heat-treated at 500°C was relatively small. It can be regarded as that the spaces were occupied by organics remained in the particles as detected by XRD.

### 3.2 Film

XRD pattern of the SrTiO<sub>3</sub> film on glass plate prepared by precursor solution heat-treated at 600°C is shown in Figure 5 a. There are several peaks corresponding to reflection from SrTiO<sub>3</sub> in addition to the continuum of the glass substrate (Figure 5 c) and no peaks due to impurity were observed. XRD pattern of the SrTiO<sub>3</sub> film coated using precursor solution diluted with water is shown in Figure 5 b. There are small peaks that may be considered due to SrTiO<sub>3</sub> on the continuum of the glass substrate.

Figure 6 shows SEM images of the films prepared by heating at 600°C for 12 hours in air of the glass plate coated with the precursor solution and the film prepared using the precursor solution diluted with water. Film of thickness 1.3μm was prepared using the precursor solution and film of thickness 400nm was prepared by dilution of the precursor solution with water. Cracks of about 1μm were found in the film prepared by precursor

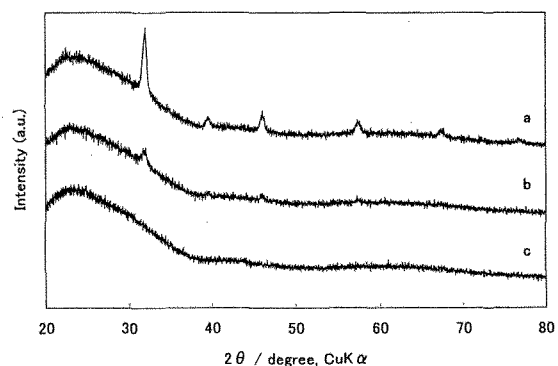


Fig.5 XRD patterns of the film on glass plate prepared by precursor solution (a) and of the film prepared by precursor solution diluted with water (b) and of the glass substrate (c).

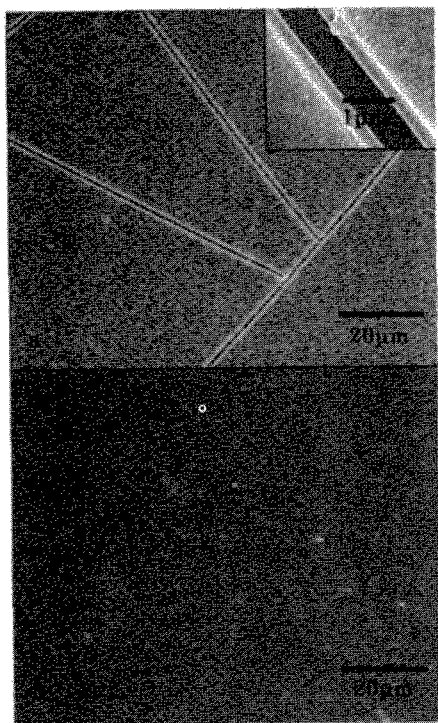


Fig.6 SEM images of the SrTiO<sub>3</sub> film on glass plate prepared by precursor solution (a  $\times 1000$ , inset  $\times 30000$ ) and by precursor solution diluted with water (b  $\times 1000$ ).

solution (Figure 6 a). No crack was found in the film prepared by precursor solution diluted with water (Figure 6 b). With the results of XRD, it was confirmed that SrTiO<sub>3</sub> film was made on the glass plate without crack.

#### 4. CONCLUSION

Powders of SrTiO<sub>3</sub> with large surface areas were successfully synthesized from aqueous solutions using

lactate-Ti complex. A pure SrTiO<sub>3</sub> powder formed by heat-treatment of precursor powder at 700°C for 12 hours in air. A SrTiO<sub>3</sub> film without crack on glass plate was successfully synthesized by spin-coating of the precursor solution and heating at 600°C for 12 hours in air.

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