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Preparation and Electrical Characterisation of Strontium Titanate Ceramic from Titanyl Acylate Precursor in Strong Alkaline Solution

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Abstract: Strontium titanate powder can be obtained from titanyl acylate precursor by using acetic acid chelating with titanium isopropoxide in a strong alkaline solution (pH > 13) at room temperature. Infrared spectroscopy, differential scanning calorimetry/thermogravimetric analysis and X-ray diffraction were used to investigate the effects of the size and properties of the precipitated precursor on the properties of the powder and the sinterability for ceramics. It was found that the strontium ion diffused into the gel made by the hydrolysis of the titanyl acylate precursor to form strontium titanate powder. The reaction rate of forming powder at higher temperature such as 100°C and higher water content (the ratio of water to titanium alkoxide is 20) or higher acetic acid (the ratio of acetic acid to titanium alkoxide is 10), is rapid and the particle size is less than 0·1 μm. Without adding any reagent the density of the sintered strontium titanate at 1300°C from powder after freeze drying was over 95% of its theoretical density. The dielectric constant and dissipation factor of the strontium titanate body sintered at 1250, 1300, 1400 and 1450°C, were also determined at a frequency of 1 kHz to 10 MHz at constant temperature.

1 INTRODUCTION

$SrTiO_3$ belongs to a structure of perovskite and is one of the electronic ceramic materials. Applying the properties of semiconductivity, dielectricity and controlling grain boundary, it is widely used for photoelectrodes[1] and devices of various boundary-layer capacitors.[2-4] From the development of VLSI, high purity submicron powder with stoichiometry is required for manufacturing electronic device of high density up until now.

Recently, various methods of manufacturing ultrafine powder from such as oxalate,[5-6] citrate[7-8] and sol–gel,[9-11] etc. were developed. Among these the sol–gel technique for metal alkoxides as raw material had the advantages of uniform composition and ultrafine powder with stoichiometry and high purity. Kao and Yang[12] studied the preparation and microstructure of silica glass from gels by chemical polymerization with drying control chemical additives. However, the metal alkoxide reacted easily with the moisture to form a gel and decreased the solubility in the solvent thus making the operation inconvenient. Using strontium acetate with titanium alkoxide to produce titanyl acylate precursor, the acetic salt being insensitive to the moisture in air, operated easily and cheaply.[13] Since titanyl acylate could not form hydrous titania[14] as it dissolved into water, it became a developmental potential. Recently a series of papers concerning the processes using acetate as a substitute for an alkoxide of alkaline earth metal[15-18] have been published.

The degree of substituting acetate for alkoxide in the reaction of acetic acid with titanium alkoxide

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is dependent on the ratio of acetate to titanium.[19] Glacial acetic acid in excess for titanium isopropoxide can produce titanyl acylate precursor. This precursor forms the crystalline powder of strontium titanate in a strong alkaline solution (pH >13) at room temperature directly. Until now there is no literature covering investigation and comparison of the mechanism and the properties of forming ceramic powder of perovskite structure from titanyl acylate in a strong alkaline solution.

In this study we investigate the titanyl acylate precursor reacting with the strontium ion to form strontium titanate powder in a strong alkaline solution. Reaction temperature, water content in forming the titanyl acylate precursor, the ratio of water to titanium alkoxide and the ratio of acetic acid to titanium alkoxide have been studied for their effects on the particle size, stoichiometry and sinterability of ceramic powder. The mechanism of forming the powder was investigated to understand relationships among dielectricity, formation process and microstructure of sintered body.

2 EXPERIMENTAL

2.1 Synthesis of strontium titanate powder

The titanyl acylate precursor, formed from titanium isopropoxide with glacial acetic acid in excess, can become a white gel with a little degassed water. To the above-formed precipitate dissolved slightly in water was added water in excess with vigorous stirring to produce completely clear solution. Strontium acetate solution was again added to the above clear solution to prepare the precursor with the ratio of Sr^{2+} to Ti^{4+} as 1:1 to obtain the titanyl acylate precursor containing strontium. This can directly form strontium titanate powder in a strong alkaline solution under an inert gas. The above reactions proceed in the temperature range of 0–100°C. The water content in the precursor is 5–20:1 (water:titanium alkoxide) and of acetic acid:alkoxide is 5–20:1 (ratios in mole: mole).

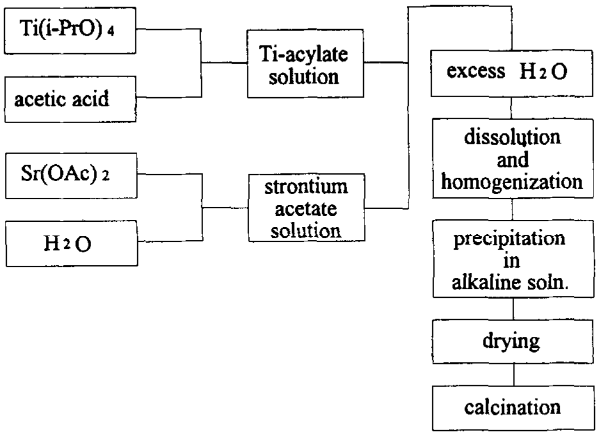

Fig. 1. Schematic illustration of the preparation of $SrTiO_3$ from titanyl acylate precursor.

The titanyl acylate precursor was slowly added into vigorously stirred sodium hydroxide solution for 2–4 h to form the precipitate. This was washed with water several times to remove the sodium ion to prepare the fine white powder of strontium titanate. The powder was dried in a freeze dryer and then calcined at 1000°C for 24 h to obtain a high purity strontium titanate powder. The flow chart of the preparation of strontium titanate is shown in Fig. 1.

2.2 Testing methods

In order to understand the effect of preparative conditions, such as reaction temperature, water content and the ratio of acetic acid to titanium alkoxide, etc., on the powder formed, a sample of the precipitate of the titanyl acylate precursor containing strontium reacted in a strong alkaline solution for 3 min was removed, cooled on an ice bath and then dried after washing with water. The product was analyzed by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), infrared spectroscopy (IR) and X-ray diffraction (XRD). Scanning electron microscopy (SEM) was used to reveal the microstructures of the powder and sintered body.

After calcining and grinding, the powder, less than 270 mesh, was pressed under 110 MPa in a stainless steel mold to make a green body 13 mm in diameter. The green body was sintered at 1100–1450°C for 4 h.

The cross-section of the sintered body was polished and etched for 1 h and then subjected to sputtered coating. SEM was used to measure the

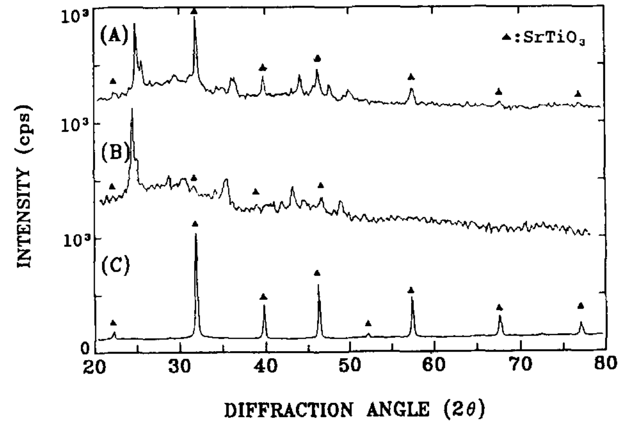

Fig. 2. XRD patterns of the precipitates. (A) strontium titanyl precursor in alkaline solution for 3 min. (B) Product from titanyl acylate precipitate reacted with strontium ion for 3 min. (C) $SrTiO_3$ powder prepared from titanyl acylate precursor for 10 min.

character of its surface. By Archimedes' method the bulk density of the sintered body at various temperatures was determined. The surface of sintered body was polished to a body of 2 mm in thickness and coated with conductive silver paste as the electrode. After baking the electrode at 700°C, the dielectric constant (K) and dielectric loss ($\tan \delta$) of the ceramic body were measured at room temperature in the frequency range of 1 kHz–10 MHz by HP impedance analyzer 4192.

3 RESULTS AND DISCUSSION

3.1 Studies of precursor

3.1.1 Formation mechanism

Titanium isopropoxide was reacted with glacial acetic acid in excess to form the titanyl acylate precursor, $Ti(OAc)_x(OR)_y$, and to this precursor was again added water in excess to give a completely clear aqueous solution of $Ti(OAc)_x(OH)_y$ by the hydrolysis of alkoxide group of the precursor.[19] The aqueous precursor was slowly added to concentrated sodium hydroxide solution (pH >13) to give a white gel, and then was reacted with strontium acetate solution for 2–4 h to form the precipitate, proved as $SrTiO_3$ by XRD analysis after drying. The above result is the same as that proposed by Wilson *et al.*[13] The precipitated $SrTiO_3$ formed directly from the solution of titanyl acylate precursor containing strontium in strong alkaline solution. The reaction temperature in this process is very low, and an ultrafine ceramic powder of perovskite was obtained even at room temperature. The XRD pattern of the precipitate obtained from the strontium titanyl precursor in alkaline solution for 3 min is shown in Fig. 2(A). Figure 2(B) shows that of the product from titanyl acylate precipitate reacted with strontium ion for 3 min. These two patterns are similar to that of Fig. 2(C), and show a small amount of $SrTiO_3$ and presence of other phases. These reacted for 10 min to convert into perovskite nearly completely as shown in Fig. 2(C). The results proved that in the reaction of titanyl acylate precursor in strong alkaline solution the hydrolyzed titanyl acylate gel is first formed and then becomes $SrTiO_3$ with Sr^{2+} diffusion into the gel. The mechanism of this process is the same as that of Diaz-Guemes,[20] in which titanium tetraethoxide reacted with strontium hydroxide, or alkaline earth ion diffused into the gel to form strontium titanate powder. Hence the property of strontium titanate powder formed is controlled by the morphology of titanyl acylate first formed. Therefore the shape and size of the gel of precursor has a very important relationship with the properties of final powder.

In strong alkaline solution according to nucleophilic reaction, four water molecules and two hydroxide ions attack the titanium ion in a titanium compound through electron rearrangement to form $[Ti(OH)_6]^{2-}$ and alcohol as shown in eqn (1). Sr^{2+} combines with $[Ti(OH)_6]^{2-}$ to form strontium titanate powder as in eqn (2).

$$Ti(OR)_4 + 4H_2O + 2OH \rightarrow [Ti(OH)_6]^{2-} + 4ROH \quad (1)$$

$$Sr^{2+} + [Ti(OH)_6]^{2-} \rightarrow SrTiO_3 + 3\,H_2O \quad (2)$$

Flaschen[21] proposed that alkaline earth metal hydroxide is the source of metal ion in the above reaction, but no literature has shown that this could be applied to the reaction of titanyl acylate precursor. Another reaction mechanism could satisfy the experimental results of this study, i.e. that hydroxyl ion was first adsorbed on the surface of the particle of the gel precipitate through hydrolysis of acetic acid chelating with titanium alkoxide. Finally it reacted to lose water through condensation of the gel to take the three-dimensional structure of perovskite.

3.1.2 Infrared spectrum analysis

The infrared spectra of the titanyl acylate precursor before Sr addition calcined at various temperatures for 8 h are shown in Fig. 3. There are two absorption bands in the vicinities of 1420 and 1560 cm^{-1} from chelating of acetate with titanium compound. This is attributed to symmetric and asymmetric vibrations of acetate. When the difference of these two absorptive peaks is larger than 130 cm^{-1}, acetate is the typical chelate bidentate ligand. When it is smaller than 100 cm^{-1}, it is in favour of bridging bidentate ligand. It is indicated that acetate still exists in the structure of the gel formed from acylate precursor in the solution at pH >13. The absorption peaks of Ti–O–R are between 1000 and 1100 cm^{-1}.[19] The structure of the gel in the solution at pH > 13 still has a little Ti–O–R from infrared spectra. Organic substances were vaporized completely at 350°C.

The infrared spectra indicate that the acetate chelating with a titanium compound obtained from the various titanyl acylate precursors with changing preparatory conditions, such as temperature, water content and the ratio of acetic acid to titanium compound, etc., is bidentate whether chelating or bridging and shows no difference.

The gel of precursor reacts with strontium ion to give strontium titanate powder. This can be identified from the large absorptive band of the lower wave number of 580 cm^{-1} in infrared spectra

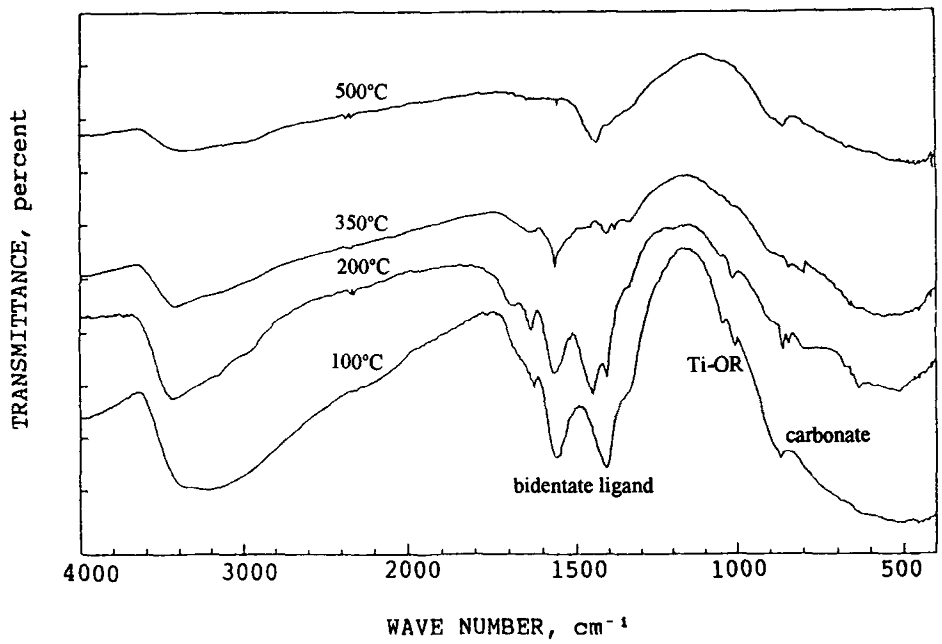

Fig. 3. IR spectra of titanyl acylate precursors calcined at various temperatures for 8 h.

as in Fig. 4 as having the structure of perovskite. From Fig. 4 there is a small amount of carbonate existing as weak absorptive bands of 860, 1059 and 1460 cm^{-1} in the uncalcined powder. Therefore carbonate exists for uncalcined powder in the infrared spectrum. The carbonate disappears at 1000°C for 24 h. There are two absorptive bands for acetate chelating in the vicinity of 1500 cm^{-1} to indicate that acetate exists in the powder.

3.1.3 DSC/TGA analyses

Figure 5 shows the results of DSC analyses of the titanyl acylate precursor before Sr addition prepared from the precipitates in strong alkaline solution at various temperatures. Combining DSC and IR analyses the endothermic peak in the vicinity of 130°C is the vaporization of water and constituents of alcohol. The acetyl group was expelled from the powder over 300°C,[19] and no acetyl group existed through calcining at 500°C in Fig. 3 by IR analysis. Therefore, the exothermic peak at 400°C is the expelling of the acetyl from the gel. Comparing the results of DSC at three different temperatures, at the lower temperature of 10°C there are many more organic substances and acetyl groups. Acetyl groups exist in much higher ratio in the structure of the precipitate gel and the rate of polycondensation is probably lower. On

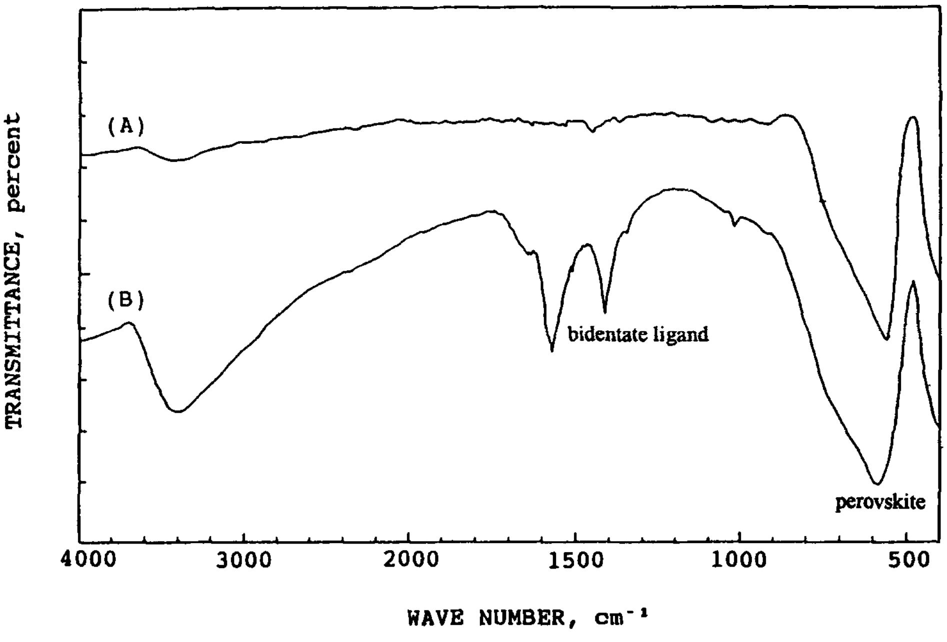

Fig. 4. IR spectra of $SrTiO_3$ powder. (A) dried at 1000°C for 24 h; (B) calcined at 100°C for 24 h.

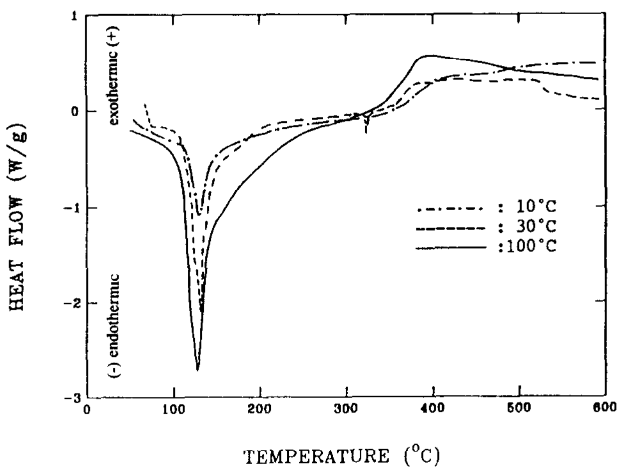

Fig. 5. Results of DSC of titanyl acylate precursor prepared at several different temperatures.

the other hand, at the higher temperature of 100°C, acetyl groups in the structure are easily expelled since the rate of condensation is more rapid at higher temperature.

The DSC/TGA analyses for various compositions of the strontium titanate powder prepared from titanyl acylate precursor reacted with strontium ion at various temperatures were very similar, as shown in Fig. 6. At 200°C an endothermic peak appeared for vaporizing of water and solvent alcohol. In heating up to 1000°C no thermal behaviour occurred. In TGA analyses, weight loss of about 6–7% was thermal decomposition of carbonate. From the studies of IR and DSC/TGA, the precipitate gel obtained from titanyl acylate precursor containing Sr in alkaline solution is the polymer of chelating acylate with titanium compound. The above result is the same as that of acidic titanyl acylate gel investigated by Samuneva *et al.*[18]

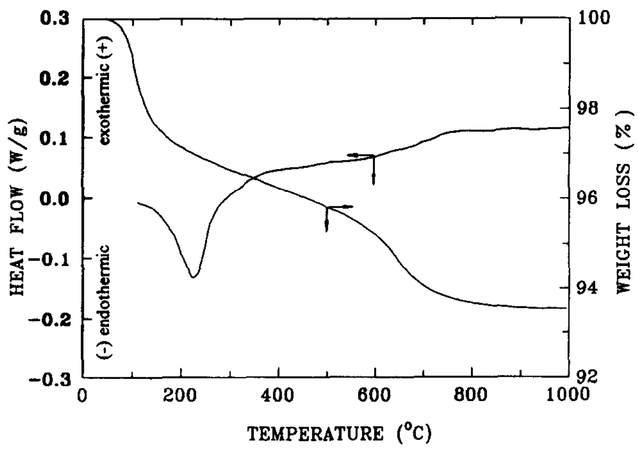

Fig. 6. Result of DSC/TGA of $SrTiO_3$ powder dried at 100°C.

3.2 Effect of preparatory conditions on the properties of powder

3.2.1 Effect of water content

The precipitate of gel was formed from titanyl acylate aqueous solution containing Sr in strong alkaline solution at water contents of 5–20 moles per mole titanium alkoxide. The particle size of strontium titanate is different for different water contents. At higher water content (water to titanium isopropoxide is 20 : 1) the particle size of the powder is less than 0·12 μm and at lower water content (water to titanium isopropoxide is 5 : 1) the particle size is about 0·30 μm. The above result suggests the relationship with the morphology of the precursor gel, in that the particle size of the gel is smaller for higher water content and the particle size of powder formed is also finer. The IR spectra of the titanyl acylate precursor prepared at various water contents are shown in Fig. 7. The figure

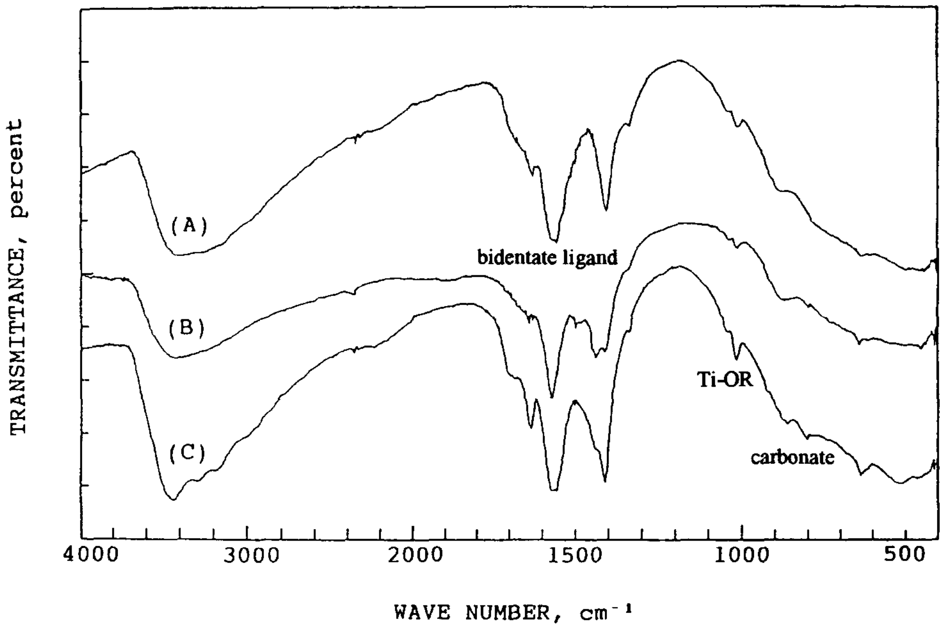

Fig. 7. IR spectra of titanyl acylate precursor containing Sr prepared with different ratios water : titanium alkoxide contents. (A) 5 : 1; (B) 10 :1 ; (C) 20 : 1.

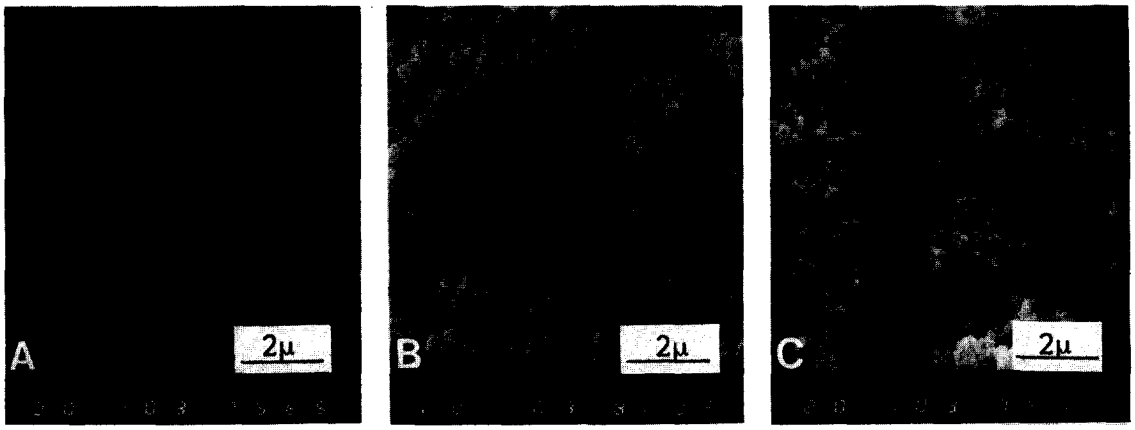

Fig. 8. SEM micrographs of $SrTiO_3$ powders prepared at different temperatures. (A) 30°C; (B) 60°C; (C) 100°C.

shows that the gel of higher water content (water to isopropoxide is 20 : 1) has a lower rate of cross-linking and is of smaller particle size, containing two structures of coordination with bridging and chelating. This higher water content makes it easier to break the bridging coordination down into chelating coordination. Hence the particle size of strontium titanate powder formed from reacting a smaller particle of gel with the strontium ion is smaller, too. On the other hand, the difference of two wave numbers of vibration being 165 cm^{-1} in the IR spectrum for lower water content (water to titanium isopropoxide is 5 : 1) makes chelating bidentate coordination. There are more bridging structures, a higher rate of cross-linking of the gel, and bigger particle size of strontium titanate. For medium water content (water to titanium isopropoxide is 10 : 1) the difference of two wave numbers of vibration is between those for higher and lower water content. There is still an absorption peak at 1000–1100 cm^{-1} in various gels. Therefore there is some quantity of Ti–OR in the gels with different water contents.

3.2.2 Effect of temperature

The structure of the titanyl acylate precursor reacted at a temperature of 0–15°C is amorphous by XRD. The primary particle sizes of the $SrTiO_3$ powders prepared at 30–100°C above room temperature are about 0·1–0·5 μm on SEM micrographs as shown in Fig. 8. The particle size of the powder prepared at room temperature is greater (about 0·5 μm). The production of strontium titanate from strontium ion and the gel is slow at low temperature, although the exothermic heat in the reaction can enhance production of strontium titanate at lower temperatures. Therefore it takes longer to finish the reaction sufficiently to produce cross-linked gels in order to obtain much larger gels. The result is a much larger particle size of the ceramic powder (from SEM). The particle size of the powder prepared at 100°C is smaller than 0·1 μm. The reaction rate of strontium titanate from strontium ion and the gel is fast at high temperature and there is not enough time to form much cross-linked gel (the rate of hydrolysis is very fast and that of condensation is slow). Hence the particle size of the gels is smaller and the particle size of the ceramic powder formed is also smaller.

3.2.3 Effect of the ratio of acetic acid to titanium alkoxide

The morphologies of the gels obtained from strontium titanate prepared at different ratios of acetic

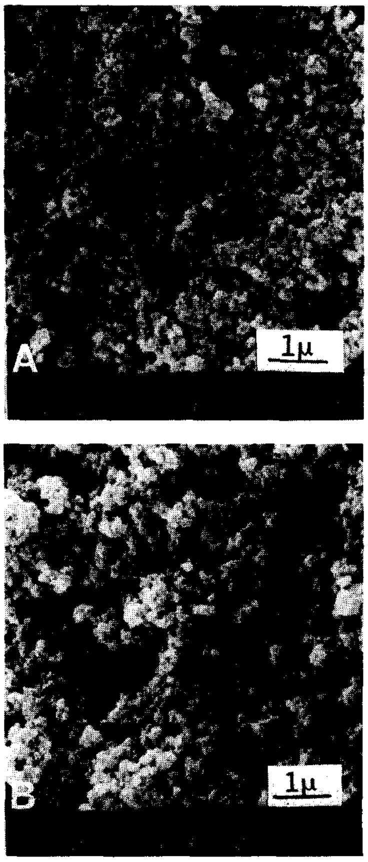

Fig. 9. SEM micrographs of $SrTiO_3$ powders prepared with different ratios of acetic acid/titanium alkoxide. (A) 5 : 1; (B) 20 : 1.

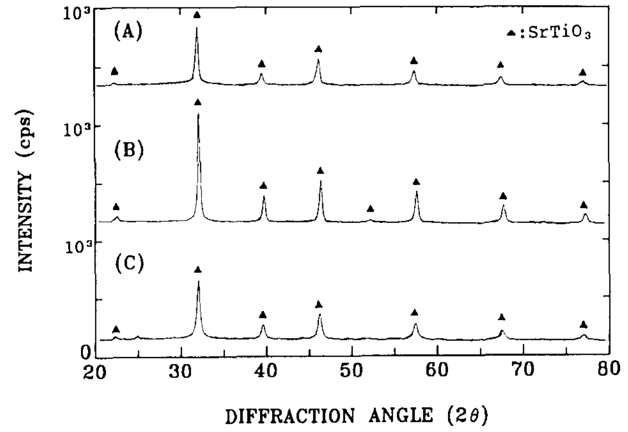

Fig. 10. XRD patterns of $SrTiO_3$ powder prepared at different acetic acid : titanium alkoxide ratios. (A) acetic acid : titanium alkoxide 5 : 1; (B) acetic acid : titanium alkoxide 10 : 1; (C) acetic acid : titanium alkoxide 20 : 1.

acid to titanium alkoxide from 5:1 mole to 20:1 mole, are also different. The gel at high acetic acid ratio (20:1) is the finest in particle size and the particle size of preparatory ceramic powder is the finest, too, as shown in Fig. 9. It is obvious from DSC/TGA analyses (Fig. 5) that the ratio of chelating acetyl group is larger for the gel with high acetic acid ratio. On the other hand, for the gel with low acetic acid ratio (5:1) the ratio of chelating acetyl group is smaller. Therefore the more chelating acetyl group to inhibit polycondensation, the smaller the particle size of the gel and the finer the particle size of ceramic powder of $SrTiO_3$ formed.

Livage *et al.*[22] have shown that the isopropoxide group is much more easily hydrolyzed than the acetic group in condensation and acetic chelating still remains the structure of combining titanium ion from evidence of [^1H], and [^{13}C] NMR and IR spectra. So the acetic group inhibits the process of condensation to prolong the time of gelation. Therefore the rates of hydrolysis and polycondensation of the reaction are slower and the particle size of ceramic powder formed is finer.

The XRD patterns of the strontium titanate powders prepared from different ratios of acetic acid to titanium alkoxide are shown in Fig. 10. When the ratio of acetic acid to titanium alkoxide is as high as 20, the powder contains a large quantity of impure phases to inhibit the formation of strontium titanate. The powder contains unreacted titanium compound and this can be over acetic chelating to make hydroxide ion not easily form strontium titanate. The filtrate separated from the precipitate under the above conditions was found by atomic absorption spectroscopy to contain a large amount of unseparated strontium ion, about 1500 ppm, and a small amount of unseparated titanic ion, less than 1 ppm. It means that it is difficult to prepare stoichiometric strontium titanate powder at such high acetic acid levels.

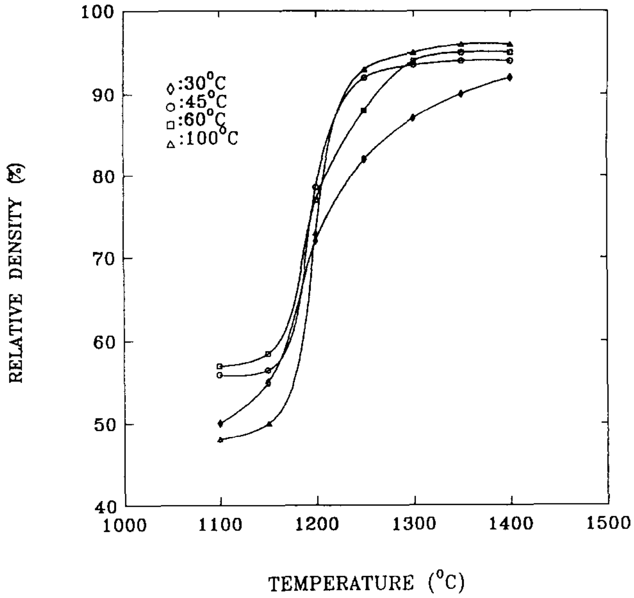

Fig. 11. Change in relative density with increasing sintering temperatures for 4 h for powders obtained from 30 to 100°C.

3.3 Study of sinterability

The powder was calcined at 1000°C for 24 h, ground by ball milling for 24 h and then pressed under a pressure of 110 MPa. The relative density of the green body obtained is 45–55% of its theoretical density. Plots of the relative density of sintered body vs sintering temperature from 1100 to 1400°C are shown in Fig. 11. The particle size of the powder synthesized at high temperature of 100°C was finer and uniform and the body showed better sinterability between 1200°C and 1300°C. The density of the body sintered at 1300°C for 4 h is very high at 95% of its theoretical density. The sinterability of the powder prepared at low temperature of 30°C is at 1300–1400°C.

Figure 12 shows SEM micrographs of the strontium titanate sintered bodies from the powders prepared at 80–100°C and sintered at temperatures of 1250, 1300, 1400 and 1450°C. The grain in the body sintered at 1250°C is fine and uniform and its size is about 1–2 μm. At a sintering temperature of 1400°C the grain size is about 2–3 μm and the density of the body decreases (about 95% of its theoretical density). By SEM, some large holes have been found. It is postulated that some gases existed in the sintered body and the holes were formed from high pressure of the gases at temperatures over 1400°C.

The dielectric constant and dissipation factor of the sintered body after polishing and coating with silver paste on both sides were measured at the frequency of 1 kHz to 10 MHz, as shown in Fig. 13. There are some relationships between the dielectric constant, degree of densification and grain size of the sintered body. The dielectric constant at 1 kHz for the sintered body at 1250°C was the highest at 462, and the dissipation factor of that body is only 0·2. The density of the ceramic body sintered at 1250°C is over 90% and its grain

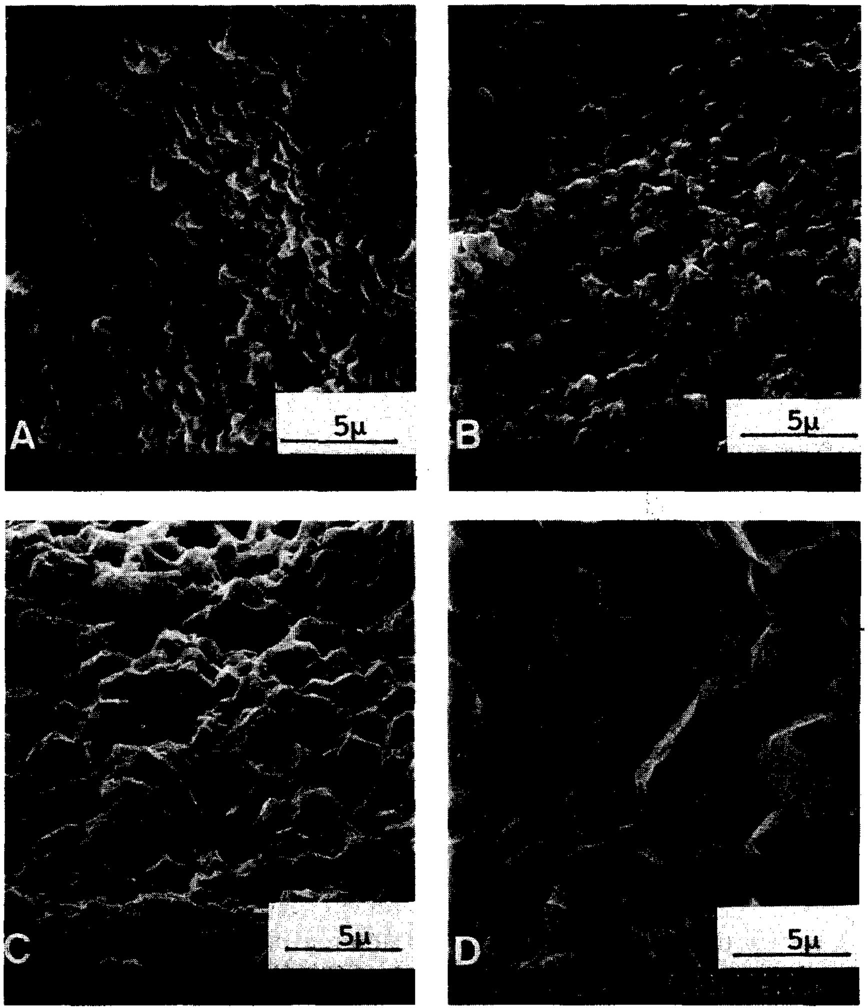

Fig. 12. SEM micrographs of the sintering bodies of $SrTiO_3$ sintered at various temperatures. (A) 1250°C; (B) 1300°C; (C) 1400°C; (D) 1450°C.

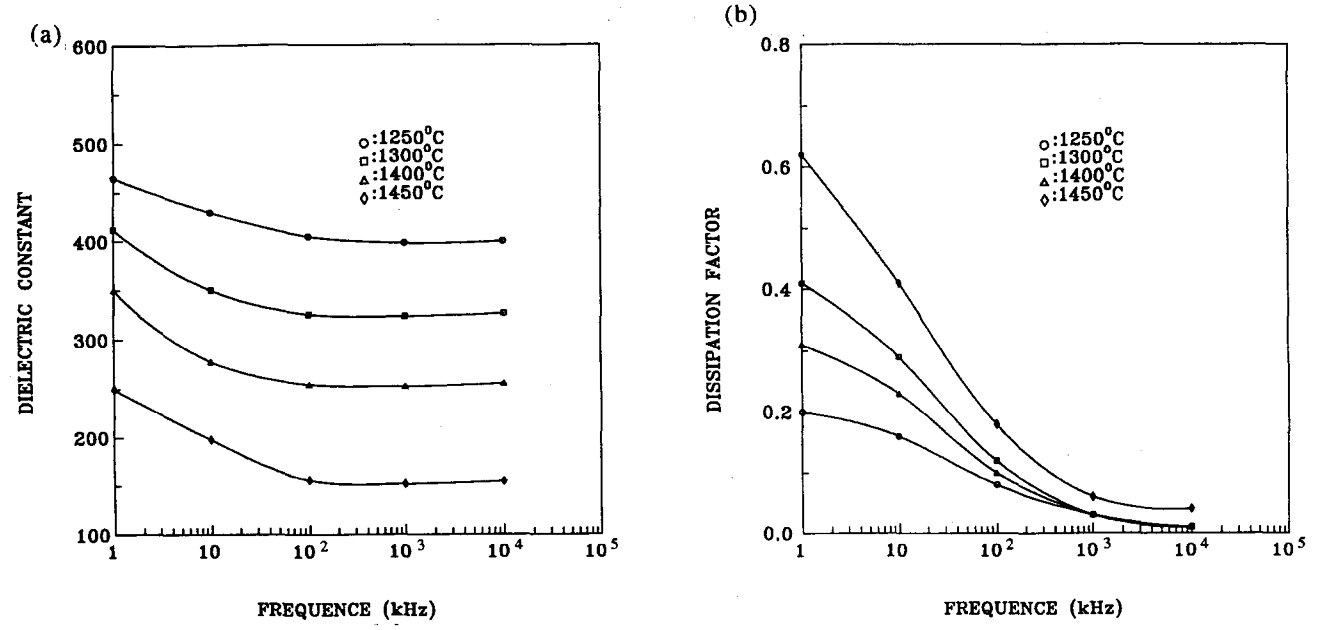

Fig. 13. Dielectric characteristics of $SrTiO_3$ sintered bodies obtained at different sintering temperatures. (a) Dielectric constant; (b) dissipation factor.

Table 1. Comparison of the characteristics of $SrTiO_3$ powders made by several processes

Process Characters	Citric method Refs 26,27	Sol–gel process Ref. 18	Present work
$SrTiO_3$ form. temperature, °C	600–700	600–700	below 100
Ions mixing grade	Not all atomic scale mixing	Not all atomic scale mixing	All atomic scale mixing
Particle size, μm	0·3–0·8	0·1–0·6	0·10–0·15

size is small, hence its dielectric constant is the largest. As sintering temperature is increasing, the growth of the grain size becomes larger, hence dielectric constant decreases.[23] The dissipation factor for a body with small grain is also small and as the grain size becomes large, the dissipation factor increases. Sintering at 1450°C brings abnormal grain growth and more intergranular porosity to reduce dielectric constant.

4 CONCLUSION

It is obvious from the above investigation that preparatory variables affect indirectly the amount of chelating acetate group, change the mode of condensation of the gels and even control the particle size of the powder. The optimum preparatory conditions for better strontium titanate powder are that the drying temperature is over 60°C, the mole ratio of acetic acid to alkoxide is 10 : 1, and the mole ratio of water content to alkoxide is 20 : 1. The distribution of the composition of the better powder is uniform and coincides with chemical stoichiometry, and its particle size is about 0·1 μm.

There are many methods, such as oxalic, citrate, sol–gel process, etc., to prepare ultrafine strontium titanate powder. The oxalic method, in which the strontium and titanium ions cannot be coprecipitated completely to control the chemical composition and the particle size of the powder obtained is large,[24–25] is consequently scarcely studied. The properties of strontium titanate powder prepared from several processes using alkoxide as raw material are listed in Table 1. It is of advantage that this process is all atomic-scale mixing, the chemical composition is uniform, synthesis temperature is lower and the particle size is ultrafine, etc. Therefore a high density of the sintered body of strontium titanate can be obtained at lower temperature of about 1300°C.

ACKNOWLEDGEMENT

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