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Preparation and dielectric properties of semiconducting lanthanum-doped strontium titanate ceramics from titanyl citrate precursors

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Abstract

This study deals with the preparation of titanyl citrate precursors using the citrate method and titanium isopropoxide as a starting material. After drying and calcining, the titanyl citrate gels were converted into powders of lanthanum oxide doped strontium titanate. The cation ratios of the titanate powder prepared at pH 5–6 were very close to the original one. Only less than 0.1% of free cations remained in the solution. The titanyl citrates were precipitated using either ethanol or acetone. The precipitates obtained using acetone were always of a slimy consistency whereas those obtained using a sufficient quantity of alcohol were powdery. The powder obtained at pH 5–6 consisted of fine particle with a diameter of 0.3–0.5 μm and sintered readily between 1250 and 1350°C. The dielectric constants of the semiconducting La_2O_3-doped strontium titanates were determined. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: Titanyl citrate precursor; Citrate method; La_2O_3-doped strontium titanate

1. Introduction

Strontium titanate is a ceramic material with important electronic properties. It can crystallize as a mixed barium strontium titanate with barium titanate or a mixed calcium strontium titanate, and can be doped with La^{3+} [1,2] or Nb^{5+} [3,4] as a heterovalent dopant. Applying its semiconducting [5,6], and dielectric properties [7] by controlling the grain boundary [8], it is widely used in photoelectronics [9] and electric capacitor elements. For the development of VLSIs a high purity submicron powder with good homogeneity is required for the manufacturing of the high density electronic elements.

Strontium titanate powder can be obtained by solid-state reaction [10], using TiO_2 and $SrCO_3$ as starting materials and calcination at high temperatures. This process has the advantages of being simple and cheap, and it can easily be applied for mass production. But the obtained powders are coarse, chemically inhomogeneous and usually contain some other phases, all of which prevent the powder's use for advanced electronic materials [11]. It is therefore important to study the processes that lead to compositional homogeneity and fine particle sizes of the powder.

In a liquid system several methods are available to obtain strontium titanate, i.e. hydrolysis of a metal alkoxide [12], precipitation of oxalic salts [13,14], and precipitation of citrate salts [15–18], all of which are respected by scholars. Recently, the hydrolysis of metal alkoxides [19,20] to obtain ceramics became very popular. The powder properties (particle size, homogeneity and purity) of strontium titanate prepared by this route are excellent, but the chemically unstable nature and high cost of the metal alkoxides are the main disadvantages.

Citric acid can function as a ligand for many elements [21,22]. In the citrate method, a citrate precursor containing Sr and Ti is prepared, then dried, and calcined, so $SrTiO_3$ powder can be obtained. This is an important method for preparing a high quality $SrTiO_3$ powder.

In this study, we prepared La_2O_3-doped $SrTiO_3$ powders from citrate precursors. We discuss the effects of the solvent amount and pH-value on the (La + Sr)/Ti ratios in the obtained powders, as well as investigate the chemical and thermogravical behavior during the precursor calcination. Additionally, the crystallinity and microstructure of the obtained (La,Sr)TiO_3 ceramics were studied.

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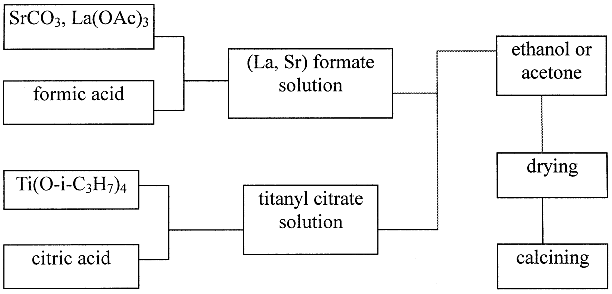


Fig. 1. Schematic illustration of the preparation of (La, Sr)TiO_3 powders using the citrate method.

Table 1
Preparatory conditions for the titanyl citrate precursors prepared at pH 5–6 and sprayed into absolute ethanol or acetone

Solvent	Solvent/precursor (volume ratio)	Precipitate properties	Cation concentration (%) in filtered mother liquor		
			La	Sr	Ti
Ethanol	8	Wet gel	0.02	3.22	2.82
	10	Gel	0.01	1.81	1.42
	13	Powder	<0.01	0.22	0.20
	15	Powder	<0.01	0.08	0.08
	20	Powder	<0.01	0.07	0.08
Acetone	8	Wet gel	0.02	3.48	4.07
	10	Wet gel	0.01	2.41	2.46
	13	Gel	<0.01	0.57	0.58
	15	Powder	<0.01	0.21	0.12

2. Experimental

2.1. Preparation of (La, Sr)TiO_3 ceramic

Strontium carbonate was mixed with 0.5% mol $La(OAc)_3$ as a heterovalent dopant, and added into a 80% formic acid solution to form a 0.1 M Sr-formate solution. A stoichiometric amount of titanium isopropoxide was dissolved in a 0.2 M citrate solution at 60°C so that a citrate solution containing Ti was obtained. Mixing equal volumes of the above two solutions, a clear citrate precursor was obtained and the molar ratio of (La + Sr)/Ti was 1.00. During the mixing process, NH_3 gas was added to adjust the pH-value of the solution as shown in Fig. 1.

The citrate precursor solution was sprayed into a chamber 8–20 times its own volume containing absolute ethanol or acetone, and then a white precipitate formed. After filtering, the precipitate was washed with ethanol several times.

The citrate precursors were dried in a freeze-dryer for 24 h. The dried precursor precipitates were calcined at 1100°C for 8 h, and a white ($La_{0.05}$, $Sr_{0.995}$)TiO_3 powder was obtained.

2.2. Testing methods

The dried gels were analyzed by thermogravimetric analysis (TGA), Fourier transfer infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The mean particle

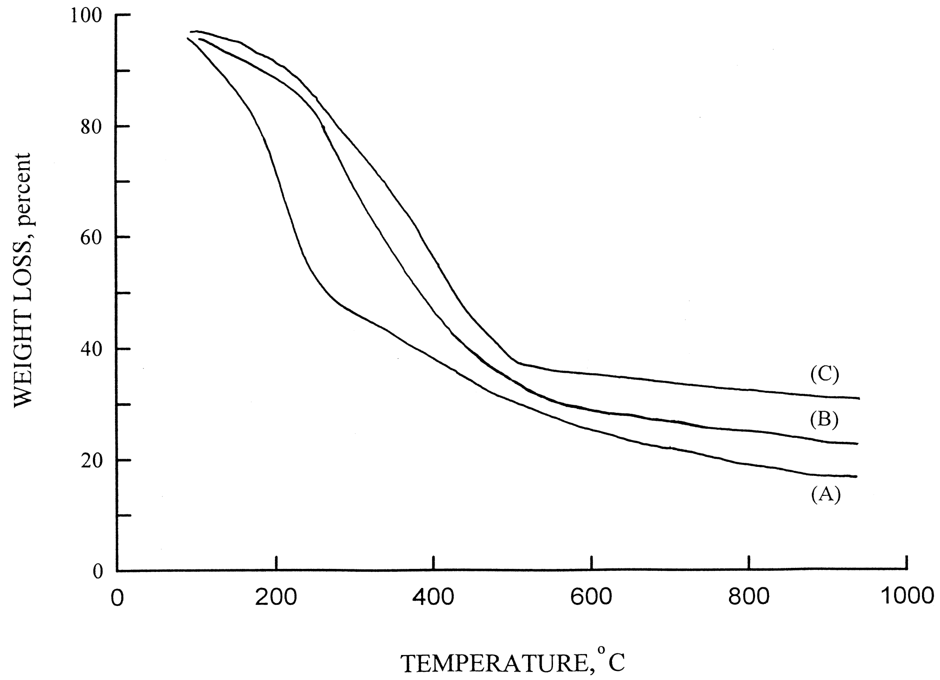


Fig. 2. Results of the TGA analysis of the precursors precipitated at various pH values in absolute ethanol. (A) pH 3–4; (B) pH 4–5, and (C) pH 5–6.

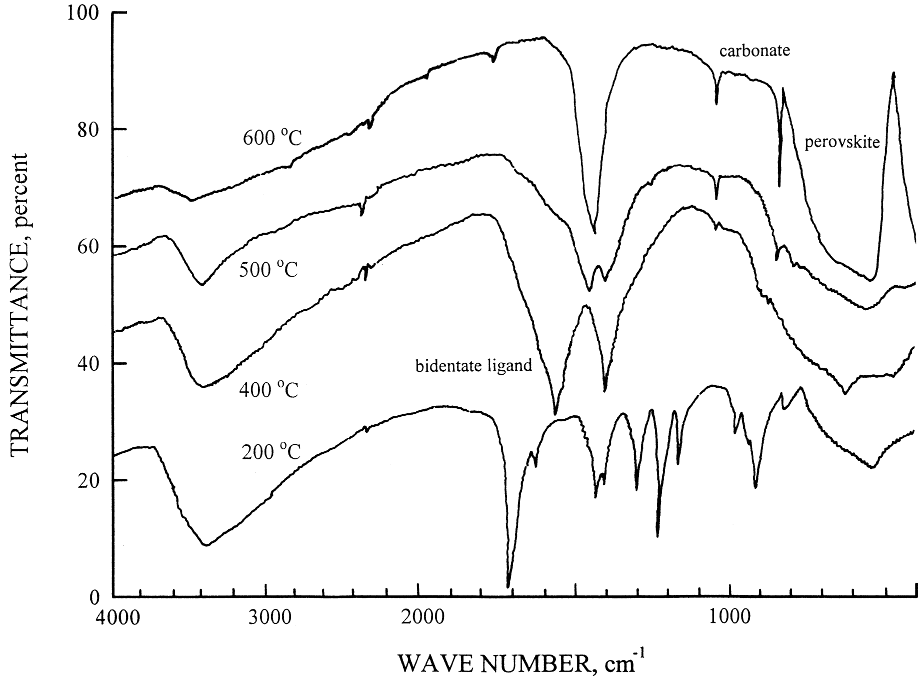


Fig. 3. The FTIR spectra of the dried titanyl citrate precursors at various temperatures.

size of the aggregate powders was measured after freeze-drying, and powder homogeneity (median, mean and standard deviation of aggregates) was determined with a GALAI-CIS-1 laser particle size distribution analyzer. Atomic absorption spectroscopy (AAS) was used to determine the chemical compositions of the ceramic powders. After calcining and grinding through a mesh (< 0.053 mm), the powders were pressed at 110 MPa in a stainless steel mold to form green bodies with a diameter of 13 mm. Scanning electron microscopy (SEM) was used to reveal the microstructures of the powders.

Dilatometry was used to study the sinterability of the green bodies. The green bodies were sintered at 1350 and 1450°C for 2 h, respectively. The cross-section of the sintered body was polished and etched in a 1.5 M nitric acid solution at 70–80°C for 4 h and then subjected to

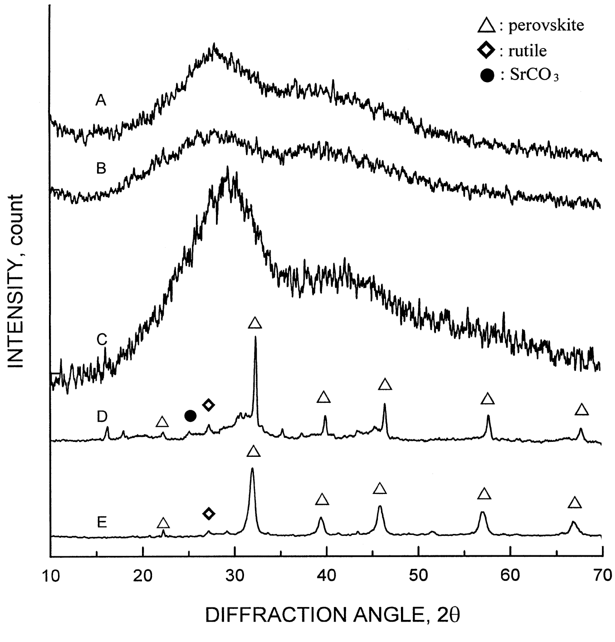


Fig. 4. The XRD patterns of the citrate precursors calcined at various temperatures for 8 h. (A) 200°C; (B) 400°C; (B) 500°C; (C) 600°C; (D) 900°C; and (E) 1000°C.

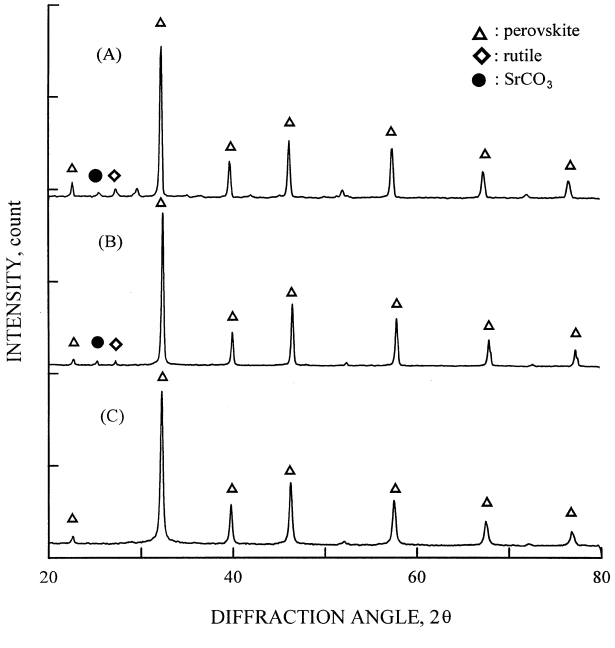


Fig. 5. XRD patterns of the powders obtained at various pH values in absolute ethanol. (A) pH 3–4; (B) pH 4–5; and (C) pH 5–6.

d.c.-sputtered coating. SEM was used to investigate the microstructures of the sintered samples at various sintering temperatures.

The surface of the sintered samples were polished into bodies of 2 mm in thickness and coated with conductive silver paste as an electrode. After baking the electrodes at 700°C, the dielectric constant (*k*) of the ceramic bodies were measured at room temperature with a HP LCR meter 4284 A.

Table 2
Chemical composition of the perovskite powders prepared from the citrate precursors

pH range of preparation	Original La/Ti ratio	Original Sr/Ti ratio	La/Ti ratio in powder	Sr/Ti ratio in powder
2–3	0.005/1.000	0.995/1.000	0.003/1.000	0.845/1.000
3–4	0.005/1.000	0.995/1.000	0.004/1.000	0.943/1.000
4–5	0.005/1.000	0.995/1.000	0.004/1.000	1.026/1.000
5–6	0.005/1.000	0.995/1.000	0.004/1.000	0.985/1.000
7–8	0.005/1.000	0.995/1.000	0.005/1.000	0.694/1.000

3. Results and discussion

3.1. Studies of preparation variables' effects

The citrate precursors can be a clear solution at certain pH-values [23]. The preparation of titanyl citrate precursors of the studies under various pH conditions were investigated. It indicated that the citrate precursors containing La, Sr and Ti formed a clear solution only at pH-values of 3–6, avoiding the premature precipitation of cations that causes the composition of the solution to become inhomogeneous.

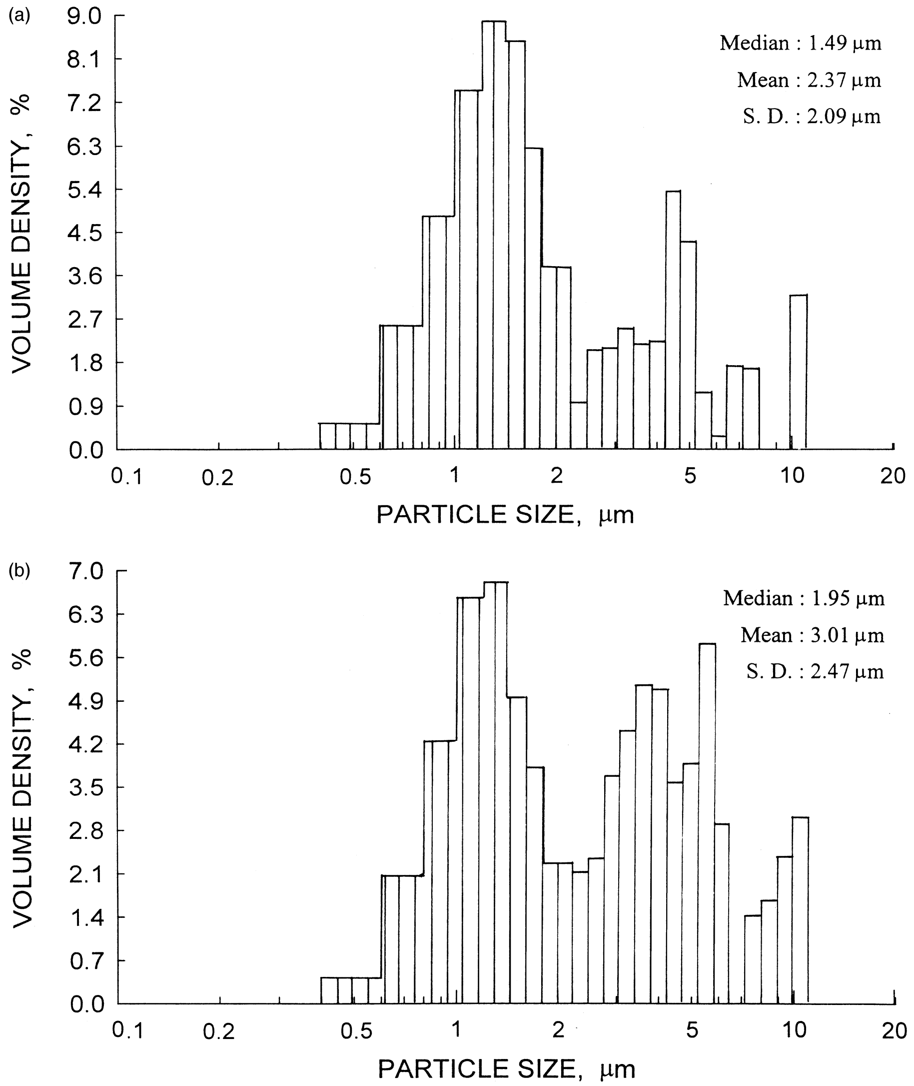


Fig. 6. The laser particle size distributions of (La, Sr)TiO$_3$ calcined at 1100°C for 8 h. (a) Powder prepared by spraying into 15 times its own volume of absolute ethanol and (b) powder prepared by spraying into 15 times its own volume of acetone.

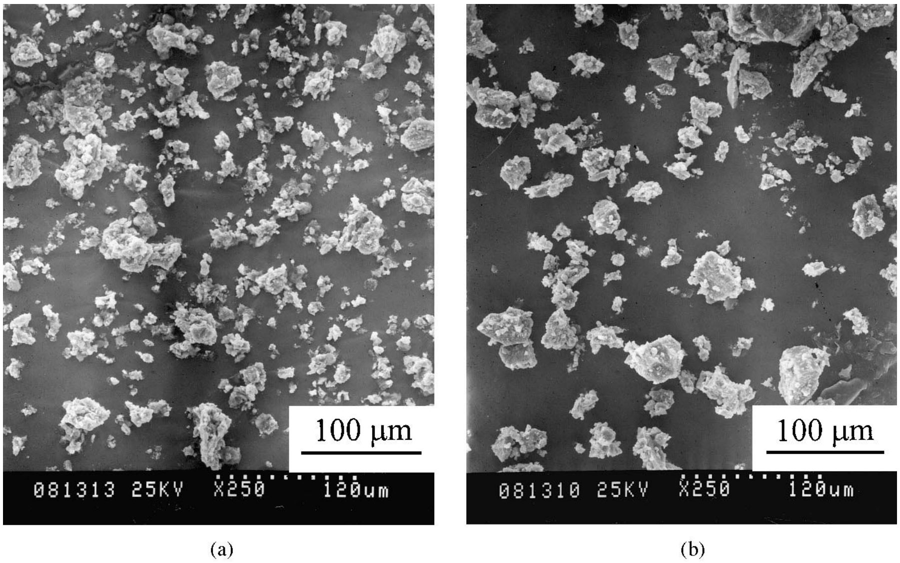


Fig. 7. SEM micrographs of the (La, Sr)TiO_3 powders prepared by the citrate method. (a) Powder prepared by spraying into 15 times its own volume of absolute ethanol, (b) powder prepared by spraying into 15 times its own volume of acetone.

Spraying the citrate precursor solutions into absolute ethanol or acetone has a dehydration effect [24]. Owing to the dehydration effect, the precursor solutions were precipitated. The preparatory conditions of titanyl citrate precursors at pH 5–6 and spraying into absolute ethanol or acetone are shown in Table 1. It contains the solvent/precursor ratio, the precipitate's morphology and cation concentration of the filtered mother liquor. The results indicate that a more moist gel is obtained, due to the incomplete dehydration, when the precursor is sprayed into a smaller volume of the solvent. Additionally, AAS analysis of the mother liquor showed that more cations were still in the mother liquor at smaller solvent volumes.

Spraying the precursor into an ethanol chamber with a solvent volume 15 times the volume of the precursor solution, a white precipitate was obtained. The mother liquor analyzed by AAS showed a lower cation concentration, less than 0.1%. The bigger the solvent volume, the lower the concentration of cations in the mother liquor. In absolute ethanol the dehydration effect was observed to be stronger than in acetone. Comparing the same solvent volumes, the precursor that precipitated from ethanol is drier than the one that precipitated from acetone. Analyzing the mother liquor showed that the ethanol liquor contained fewer cations.

3.2. Calcination of the precursors

3.2.1. TGA analysis

Fig. 2 shows the TGA curves of the citrate precursor precipitates prepared at various pH-values. The TGA curves indicate that the precipitates lose weight as the temperature rises to 100°C, due to the evaporation of water and solvent contained in the precipitates. Additionally, DTA curves show an endothermic peak at 150–200°C (not shown), which indicates the removal of hydrated water in the precursor. Combined FTIR-spectra and DTA/TGA data show that carbon dioxide existed in the gels calcined at 200°C (discussed below). At temperatures of 200–400°C the precursor precipitates exhibited a significant weight loss, revealing that about 50–70% of their weight was constituted by organic groups, which decompose to carbon dioxide in this temperature range.

Curve (B) shows a pH 5–6 precursor, which had the least weight loss (about 65%). This indicates that the precipitate contained the least amount of organic species, i.e. citrate, which in turn means that in the crystal lattice La^{3+}, Sr^{2+} and Ti^{4+} are located closer to each other. This results in the small particle sizes of the final (La, Sr)TiO_3 ceramic.

3.2.2. FTIR-spectra

The precipitates heat-treated at various temperatures were examined by FTIR-spectroscopy in order to understand the reaction of the organic groups, and to investigate the decomposition mechanism. Spectra are shown in Fig. 3. The gel calcined at 200°C shows a FTIR spectrum similar to itaconic acid [25]. This means that the citrate gel was converted to itaconic acid ($HOOC–CH_2(HOOC)C=CH_2$) at the temperature. In the spectrum of the gel calcined at 400°C, two absorption bands at 1420 and 1560 cm^{-1} indicate bidentate ligand acetate groups [25], revealing that the itaconic acid was still present acetate group (COO) at 400°C. Furthermore, the absorption bands at 860, 1059 and 1460 cm^{-1} in the gel calcined at 500°C reveal the existence of carbonate [26]. The large absorption band found at 575 cm^{-1} in the gel calcined at 600°C represents the formation of perovskite phases, but a considerable amount of carbonate still remains.

3.2.3. XRD analysis

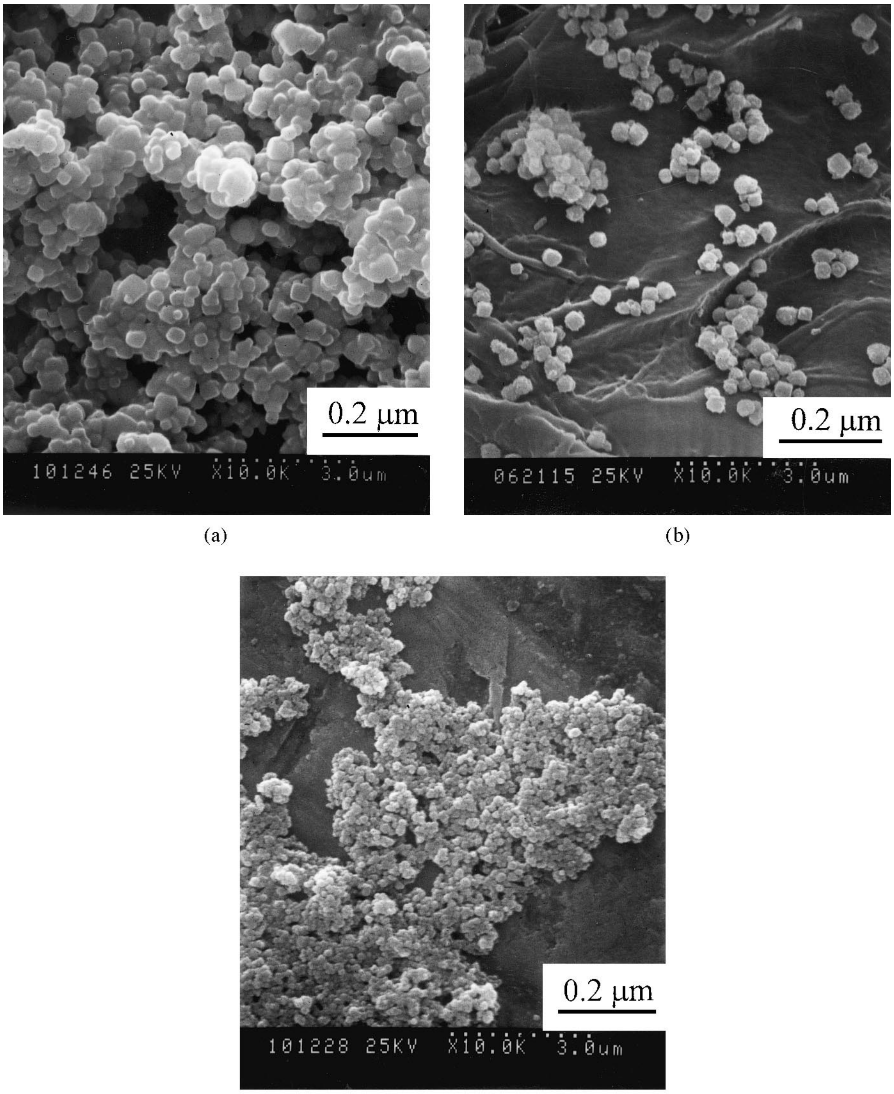
The titanyl citrate precursors prepared at pH 5–6 and calcined at different temperatures for 8 h were characterized by XRD as shown in Fig. 4. The powders were amorphous if calcined at temperatures between 200 and 500°C. Combining the XRD results with the FTIR-spectra study indicates that the precursors were decomposing to carbonate and TiO_2 prior to the formation of $(La,Sr)TiO_3$ at 600°C. The formation of perovskite started at 600°C, but at this temperature a lot of unreacted carbonate and TiO_2 still existed. At 900°C the precursor contained a higher amount of perovskite phases (titanate) and fewer unreacted rutile and carbonate.

Fig. 5 shows the XRD pattern of the powders prepared at various pH values, calcined at 1100°C for 8 h. It indicates that the powder obtained from pH 5–6 had an almost pure perovskite structure, and only a trace of unreacted carbonate and rutile was detected. In contrast, powders prepared at other pH-values contained more rutile and carbonate in their microstructures, and therefore had an undesired chemical composition. The results agree with the AAS investigation discussed below.

3.3. Powder characterization

3.3.1. Analysis of chemical composition using atomic absorption spectroscopy (AAS)

The $(La,Sr)TiO_3$ powders made under various conditions were dissolved in conc. HCl and characterized by AAS as shown in Table 2. The cation mol% of the original



(a) (b)

(c)

Fig. 8. SEM micrographs of La_2O_3-doped $SrTiO_3$ powder prepared at different pH ranges by the citrate method and calcined at 1100°C for 8 h. (a) pH 3–4; (b) pH 4–5; and (c) pH 5–6.

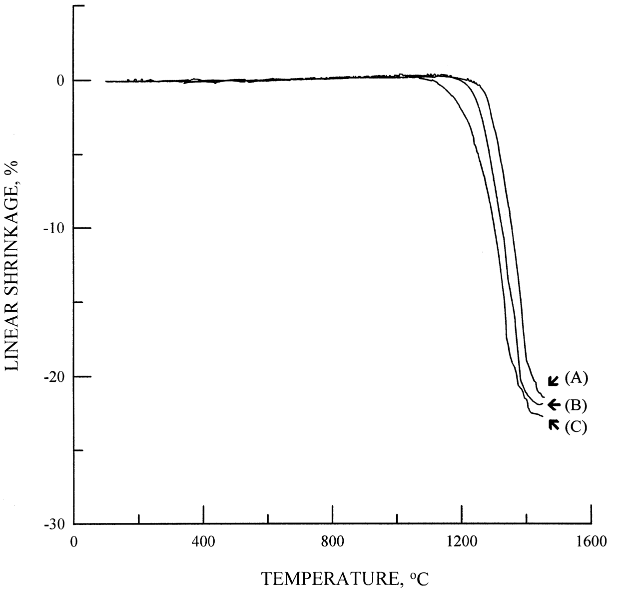


Fig. 9. Dilatometric curves for various (La, Sr)TiO_3 samples: (A) the powder prepared from a precursor at pH 3–4; (B) the powder prepared from a precursor at pH 4–5, (C) the powder prepared from a precursor at pH 5–6.

Table 3
Crystallite sizes of perovskite powders calculated using the Scherrer equation

Calcining temperature	Calcined at 1000°C			Calcined at 1100°C		
	pH 3–4	pH 4–5	pH 5–6	pH 3–4	pH 4–5	pH 5–6
Crystallite size (Å)	125	129	138	190	198	210

precursor design was La:Sr:Ti = 0.005:0.995:1.000. But at different pH-values, the cation mol% of the powders obtained deviated from the mol% in the original precursor solutions. The cation mole ratios of the powder prepared from the precursor at pH 5–6 was closest to the original preparatory conditions. A larger deviation was observed for the Sr concentration in the samples of the lower pH-value precursor solution, i.e. the Sr-citrate precursor precipitated more easily in an acidic solution.

3.3.2. *Powder particle sizes distribution*

The calcined La_2O_3-doped $SrTiO_3$ powders prepared from pH 5–6 and sprayed into absolute ethanol or acetone were characterized by laser particle size distribution (shown in Fig. 6). Comparing the homogeneity of the two unmilled original calcined powders, the powder made by spraying into acetone was found to be less homogeneous, and also consisted of larger aggregate particles. In contrast, the powder prepared from absolute ethanol was more homogeneous, had fewer aggregates and a smaller aggregate particle size was observed. This shows that absolute ethanol had a better dehydration effect, and a drier and more homogeneous powder could be obtained.

The freeze-dried La_2O_3-doped $SrTiO_3$ powders prepared from pH 5–6 in different solvents were characterized by SEM after calcination at 1100°C for 8 h to investigate their morphology (Fig. 7). SEM graphs clearly indicate that the powder obtained from absolute ethanol as a dehydration agent was less aggregated [Fig. 7(A)] as compared to the powder obtained from acetone [Fig. 7(B)]. The SEM results are similar to the laser particle size distribution analysis described above.

The primary particle size of the perovskite powders made at different pH ranges and sprayed into absolute ethanol is shown in Fig. 8. Fig. 8(A) shows the particle size of the perovskite powder made at pH 3–4. It shows the mean particle size to be 0.6–0.8 μm. Fig. 8(B) shows the particle size of the perovskite powder made at pH 4–5. Its mean particle size is about 0.4–0.6 μm. The powder obtained at pH 5–6 has a mean particle size of about 0.3–0.5 μm as shows in Fig. 8(C). The powders obtained at pH 5–6 had smaller particle sizes than powders made at different pH values. The small particle size is beneficial to sintering and results in higher density after the sintering process is completed. The results are in agreement with the above TGA analysis, which found that at pH 5–6, fewer organic groups existed, and finer particles of the final powder could be obtained.

3.3.3. *Sinterability*

The La_2O_3-doped $SrTiO_3$ powders obtained from various pH conditions by spraying in absolute ethanol and calcined at 1100°C for 8 h, were pressed under a pressure of 110 MPa. The relative density of the green bodies was 40–50% of their theoretical density (5.16 g cm^{-1}) [27]. Sinterability and bulk properties were determined by dilatometry. The results are shown in Fig. 9. The samples obtained at pH 5–6 could more readily be sintered than the other samples. Their sintering temperature was about 50–100°C lower than that of the others. Dilatometric curves from the sample prepared at pH 5–6 clearly indicate that sintering of the bulk took place between 1250 and 1350°C. The dilatometric analysis shows that the La_2O_3-doped $SrTiO_3$ powder with the finer particle size (pH 5–6) can more readily be sintered than the coarser powders obtained at other pH values. After sintering at 1450°C for 4 h 94% of the samples' theoretical density was measured by Archimedes' method.

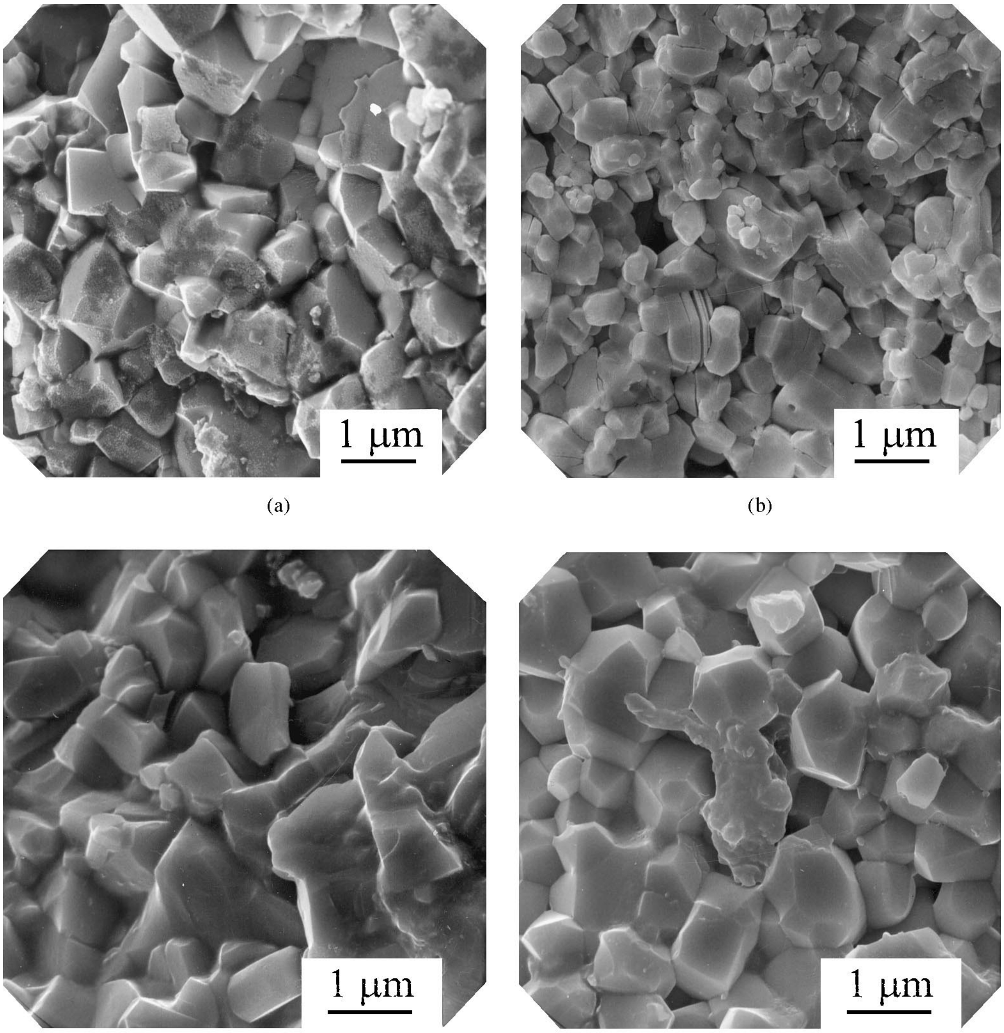
3.4. *Physical characteristics of La_2O_3-doped $SrTiO_3$ specimens*

The La_2O_3-doped $SrTiO_3$ powders obtained by spraying into absolute ethanol and calcination at 1000 or 1100°C for 8 h were characterized by XRD using diffraction angles of 2θ between 31 and 33°. The diffraction angle $2\theta = 32.2°$ represents the (110) plane of perovskite. The average crystallite size ε was determined using the Scherrer equation [28] below:

$$\varepsilon = \frac{\lambda}{\beta_1 \cos\theta}$$

λ is the incident X-ray wave length (in Å, $\lambda_{\mathrm{Cu}} = 1.5418$ Å), β_1 the integral board (rad) of the diffraction pattern at $2\theta = 32.2°$, and θ represents the diffraction angle (in degrees).

The average crystallite sizes of the powders were calculated as listed in Table 3. The average crystallites of the powders prepared at pH 5–6 were larger than the crystallites obtained under other conditions. The cations in the pH 5–6 precursor were more homogeneously mixed and therefore had a shorter path of reaction between them, which resulted in the formation of a



(a) (b) (c) (d)

Fig. 10. SEM images of the (La, Sr)TiO_3 samples that were sintered at various temperatures for 2 h: (a) the precursor sprayed into absolute ethanol and sintered at 1350°C; (b) the precursor sprayed into acetone and sintered at 1350°C; (c) the precursor sprayed into absolute ethanol and sintered at 1450°C; and (d) the precursor sprayed into acetone and sintered at 1450°C.

Table 4
The A.C. electrical resistivity of bulks prepared at various pH range measured in Ω cm at 100 Hz of the bulks (color of sample is given in parentheses)

Sintering temperature	1250°C	1300°C	1350°C	1400°C	1450°C
pH 3–4	6.7×10^{10} (brown)	2.4×10^{9} (brown)	8.7×10^{8} (brown)	4.1×10^{8} (brown)	2.6×10^{6} (gray)
pH 4–5	1.3×10^{10} (brown)	1.5×10^{9} (brown)	7.6×10^{8} (brown)	3.2×10^{8} (brown)	2.3×10^{6} (bluish gray)
pH 5–6	1.1×10^{9} (brown)	9.1×10^{8} (brown)	5.2×10^{8} (brown)	4.3×10^{6} (bluish-gray)	2.7×10^{5} (blue)

more agglomerate crystalline powder. The average crystallite size of La_2O_3-doped $SrTiO_3$ obtained at pH 5–6 and calcined at 1100°C is 210 Å.

Fig. 10 shows the SEM micrographs of the La_2O_3-doped $SrTiO_3$ ceramics from the powders prepared at pH 5–6 in absolute ethanol or acetone and sintered at temperatures of 1350 and 1450°C. The grains in the body sintered at 1350°C are fine and uniform and their average size is less than 1 μm [Fig. 10(A) and (B)]. The grain size of the powder prepared using absolute ethanol, sintered at a temperature of 1450°C, is about 1–2 μm and the density of the body increases to about 94% of its theoretical density [Fig. 10(C)]. The SEM analysis also shows that the specimens obtained from ethanol could more readily be sintered than the ones obtained from acetone.

3.5. The electrical properties

The bulks prepared from different pH ranges were sintered at various temperatures between 1250 and 1450°C for 2 h. The samples prepared at pH 3–4 contained various phases and were buff brown in color. The samples prepared at pH 4–5 and sintered at 1450°C were bluish-gray in color. However, the sample prepared at pH 5–6 sintered at a temperature higher than 1400°C was bluish-gray in color.

The A.C. electrical resistivity of the bulk ceramics measured at a frequency of 100 Hz with an LCR analyzer, are shown in Table 4. Obviously, the bluish-gray samples show semiconducting behaviour, the resistivity was about 10^5–10^7 Ωcm. In contrast, the buff brown samples had a higher resistivity, about 10^9–10^{11} Ωcm. Values for the room temperature dielectric constant in this study only give the real part of the dielectric constant measured at a frequency of 1 kHz with the LCR analyzer. The dielectric dissipation (i.e. imaginary part) of the dielectric constant was relatively small (in the range of 1–5%) and could therefore be neglected. The dielectric constants are shown in Fig. 11. The dielectric constants are reciprocal to the electrical resistivities. If the samples exhibit semiconducting behavior, i.e. have a low electrical resistivity, their dielectric constants are high. The bulk ceramics prepared at pH 5–6 displayed higher dielectric constants, up to 3150 for the sample sintered at 1450°C. Bulks prepared at pH 4–5 sintered above 1400°C showing a higher dielectric constant. Bulks prepared at pH 3–4 were brown in color and highly resistant, i.e. lacking semiconducting behaviour, and had a lower dielectric constant. Their typical dielectric constant was in the range of 300–500.

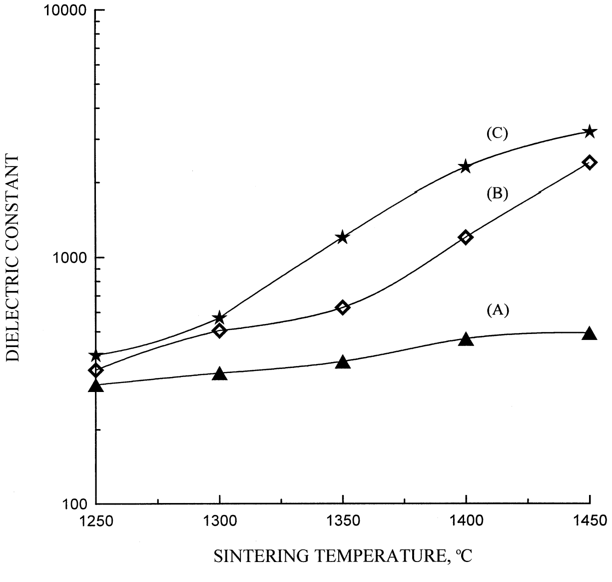


Fig. 11. Dielectric constant of La_2O_3-doped $SrTiO_3$ bulks prepared from different pH ranges. (A) pH 3–4; (B) pH 4–5; and (C) pH 5–6.

4. Conclusion

The studies investigate the citrate process to prepare La_2O_3-doped $SrTiO_3$ ceramics. The influence of different pH-values on the cation ratios in the obtained powders are discussed and the chemical and thermogravical behavior of the precursors during the calcination process are investigated as well. The crystallinity and microstructures of the obtained ceramics were also studied.

Combining data from the TGA, FTIR and XRD analyses, the chemical and thermogravical behavior during the calcination process of the precursors was investigated. The precursors decomposed to carbonate at about 600°C, and then reacted with TiO_2 to form $(Ba,Sr)TiO_3$. The cation ratio of the citrate precursor precipitate was close to that of the original solution at pH 5–6, i.e. close to 1. The concentration of unseparated cations in the mother liquor was less than 0.1%. The precipitate obtained using absolute ethanol as a dehydrating solvent was found to be drier than the precipitate formed using acetone due to a better dehydration effect observed in absolute ethanol.

The powders obtained at pH 5–6 from the citrate process had larger crystallites than powders made under other pH conditions. For the La_2O_3-doped $SrTiO_3$ powder calcined at 1100°C, the crystallite size calculated by the Scherrer equation was 210 Å. The powder obtained at a pH range of 5–6 and sprayed into absolute ethanol had particle sizes of 0.3–0.5 μm, and sintered more readily at 1250–1350°C. The room temperature dielectric constant of La_2O_3-doped $SrTiO_3$ sintered at 1250–1450°C was also determined.

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