

Preparation of Barium Strontium Titanate Powder from Citrate Precursor

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TiCl₄ or titanium isopropoxide reacted with citric acid to form a titanyl citrate precipitate. Barium strontium citrate solutions were then added to the titanyl citrate reaction to form gels. These gels were dried and calcined to (Ba,Sr)-TiO₃ powders. The gels and powders were characterized by DSC/TGA, IR, SEM and XRD analyses. These results showed that, at 500 °C, the gels decomposed to Ba,Sr carbonate and TiO₂, followed by the formation of (Ba,Sr)-TiO₃. The onset of perovskite formation occurred at 600 °C, and was nearly complete at 1000 °C. Traces of SrCO₃ were still present.

The cation ratios of the titanate powder prepared in the pH range 5–6 were closest to the original stoichiometry. Only 0.1 mol% of the free cations remained in solution. The titanyl citrates were precipitated in either ethanol or acetone. The acetone-derived precipitates were always viscous, but those with a sufficient quantity of alcohol were powdery.

The specific surface areas of the ceramic powders obtained by air-, vacuum- and freeze-drying methods were 8.3×10^3 , 10.2×10^3 and $12.5 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$, respectively. The powder obtained by freeze-drying had the lowest degree of agglomeration. The precipitated powders of titanyl citrate which were freeze-dried and calcined at 1100 °C were compacted and sintered at 1300 °C to obtain dense ceramic bodies with 95% of the theoretical density. Copyright © 1999 John Wiley & Sons, Ltd.

Keywords: barium strontium titanate; citrate method; titanyl citrate precursor

INTRODUCTION

BaTiO₃ is ferroelectric and piezoelectric and has extensive applications as an electronic material. It can be used as a capacitor, thermistor, transducer, accelerometer or degausser of colour television. BaTiO₃ doped with strontium retains its original characteristics but has a lower Curie temperature for positive temperature coefficient devices under various conditions.

Besides solid-state reactions, chemical reactions have also been used to prepare BaTiO₃ powder. Among them the hydrolysis of metal alkoxide¹, oxalate precipitation in ethanol², and alcoholic dehydration of citrate solution³ are among the more attractive methods. In 1956 Clabaugh *et al.*⁴ described the preparation of barium titanyl oxalate tetrahydrate for conversion to high-purity barium titanate. Kudaka *et al.*⁵ also prepared stoichiometric barium titanyl oxalate tetrahydrate. Many elements are quite soluble in citric acid,⁶ so a citrate precursor appeared to be useful for preparing titanate powders. Indeed, barium titanyl citrate precursors have become a very important route to prepare BaTiO₃.

In this study, barium strontium titanyl citrate gels were used to produce (Ba,Sr)TiO₃ powders. Besides investigating the effect of the water content and pH of the starting solutions, and the Ba/Sr stoichiometry needed to obtain optimum reaction conditions, we also studied the chemistry and thermogravimetric behaviour of the precursors during calcining, in order to understand the crystal and microstructure changes.

The BaTiO₃ phase transformations⁷ are shown in Scheme 1.

120°C 0°C -90°C
cubic → tetragonal → monoclinic → rhombohedral

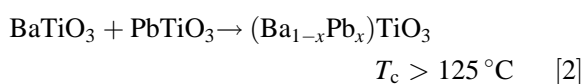
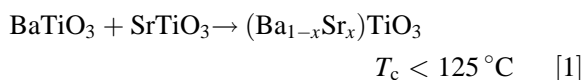
Scheme 1 BaTiO₃ phase transformations.

The addition of Ca, Sr and Pb dopant permits one to change the Curie temperature of BaTiO₃;⁸ the change can be calculated, depending on how much dopant is added. Andrich⁹ reported that each

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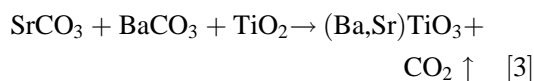
mole% SrTiO₃ added lowered the Curie temperature of BaTiO₃ from 125 °C by -3% and each mole% PbTiO₃ added raised the Curie temperature by +5%. Hence (Ba_{1-x}Sr_x)TiO₃ and (Ba_{1-x}Pb_x)TiO₃ can be tailored so that a given positive temperature coefficient device can operate either above or below 125 °C (Eqns [1] and [2]).



Synthesis of (Ba,Sr)TiO₃ powder

Solid-state reaction

BaCO₃, SrCO₃ and TiO₂ can be mixed and calcined at 1100–1200 °C to give (Ba,Sr)TiO₃ powders (Eqn [3]).



The advantages are simplicity and low cost, but the disadvantages are that the high calcining temperature results in very large grain sizes and therefore cannot be used to obtain materials with a high dielectric constant;¹⁰ if we want fine powder, grinding is required, leading to pollution problems; moreover, the mixing of large amounts of starting materials is not easy and can produce mixtures of Ba₂TiO₄, Ba₆Ti₁₇O₁₀ and BaTi₄O₉ phases as side-products.

Chemical reaction methods

To obtain BaTiO₃ particles smaller than 0.7 μm, with dielectric constants of 5000–6000, chemical reaction methods have been developed to control both phase formation and grain growth, leading to uniform fine particles.

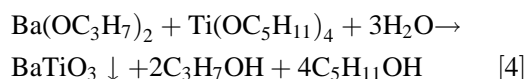
The chemical reaction methods currently used to prepare BaTiO₃ can be classified as follows.

Spray drying and roasting techniques

Ba²⁺, Sr²⁺ and Ti⁴⁺ solutions are mixed at high temperature and then converted to (Ba,Sr)TiO₃ through thermal decomposition.¹⁰ The advantage of this process is the low deviation from stoichiometry. The disadvantages are: (a) agglomeration which requires grinding and (b) hundreds of parts per million of Cl⁻ that remain to occupy the positions of the oxygen atoms in BaTiO₃.

Metal alkoxide hydrolysis (sol-gel method)

As there are many alkoxides which can be used in sol-gel methods, controlling the powder uniformity, better chemical stoichiometry and high purity can be attained than when using conventional ceramic powder processing.¹¹ The method involves dissolving alkoxides of titanium and barium in organic solvent and adding water at appropriate temperatures to hydrolyse these alkoxides to precipitate the mixed oxides. The reaction can be described by Eqn [4].



The shortcomings of this approach are chemical instability of the metal alkoxides, the complexity of the process and the high cost. Therefore this method is unsuitable for mass production.

Hydrothermal synthesis

This method can be used at very low temperatures to prepare multicomponent perovskite powders.¹² For example, at 120–130 °C and 5–50 bar, one can synthesize BaTiO₃ and SrTiO₃ powders from titanium hydroxide and barium and strontium solutions.¹² BaTiO₃ can be easily obtained from TiOCl₂ and BaCl₂ in NaOH solution to prepare uniform-size, spherical grains of ultrafine powder. In hydrothermal synthesis, however, incomplete reactions and inappropriate Ba/Ti ratios make it necessary to supplement the mixture with an excess barium or titanium ions to maintain chemical stoichiometry, as precipitation leads to loss of metal ions.

Synthesis from a complex precursor

Clabaugh⁴ prepared barium titanate tetrahydrate for conversion to high-purity barium titanate, but the disadvantage is that barium titanate does not exist in neutral solution. To obtain appropriate cation ratios, one must control the precipitation process carefully.¹⁰ Kudaka *et al.*⁵ indicated that the Ba²⁺/Ti⁴⁺/C₂O₄²⁻ ratio should be 1.05:1:2.2 to obtain a product with Ba/Ti = 1.0. Because BaCO₃ is very stable and not easily decomposed, BaTiO(C₂O₄)₂·4H₂O is calcined in air, not to BaTiO₃, but to the intermediate Ba₂Ti₂O₅·CO₃, and only over 700 °C does the intermediate decompose to form BaTiO₃ powder.¹³ Consequently, atomically mixed BaTiO₃ from this oxalate complex precipitate precursor is not obtained easily.

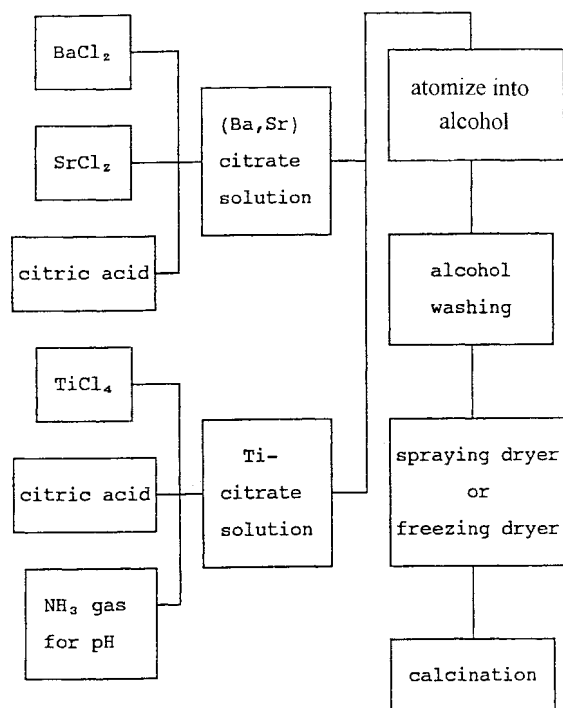


Figure 1 Flowchart for the preparation of $(\text{Ba,Sr})\text{TiO}_3$ powders from citrate.

Citrate process

In this method, tetrabutyl titanate, citric acid and ethylene glycol are mixed to give a solution and then barium carbonate, dissolved in formic acid and water, is added;¹⁰ then the pH is adjusted to induce coprecipitation at $\text{Ba/Ti} = 1:1$ of $\text{BaTi}(\text{C}_6\text{H}_5\text{O}_7)_3 \cdot 4\text{H}_2\text{O}$.¹⁴ Under optimum conditions, one should consider the concentrations of citric acid and ethylene glycol, and the mole ratio of

Table 1. Conditions for precursor coprecipitation with $\text{C}_2\text{H}_5\text{OH}/\text{citrate}$ (13:1) at various pH values

pH	$\text{C}_2\text{H}_5\text{OH}/\text{citrate}$	$\text{Ba}/\text{Sr}/\text{Ti}$ (mol ratio)
2–3	13:1	1:1:2
2–3	13:1	1:0:1
3–4	13:1	1:1:2
4–5	13:1	1:1:2
5–6	13:1	1:1:2
5–6	13:1	0:1:1
7–8	13:1	1:1:2

Table 2. Conditions for precursor coprecipitation at various solvent ratios

Solvent	$\text{Ba}/\text{Sr}/\text{Ti}$ (mol)	Solvent/precursor (volume ratio)
Ethanol	1:1:2	8:1
	1:1:2	10:1
	1:1:2	13:1
	1:1:2	15:1
Acetone	1:1:2	20:1
	1:1:2	8:1
	1:1:2	10:1
	1:1:2	13:1
	1:1:2	15:1

$(\text{Ba}+\text{Ti})/(\text{citric acid} + \text{ethylene glycol})$. The precursor after heat treatment in air produces BaTiO_3 , obtained via a solid-state reaction between intermediate species.¹²

It is noteworthy that the Ba/Ti ratio in solution should be 1:1 at $\text{pH} < 2.6$, and 2:1 at $\text{pH} > 3.2$.

This liquid mixing process has been used to synthesize over one hundred different oxides,¹⁴ including titanates, zirconates and niobates. The advantages of this process are: good control of chemical stoichiometry, low processing temperatures ($< 800^\circ\text{C}$); and easy dopant addition. The disadvantages are the very large mass losses during calcination and agglomeration.

EXPERIMENTAL

Chemicals

Barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, $>99\%$ purity; Ferak), strontium chloride ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, EP; Haya-shi), anhydrous titanium (IV) chloride (TiCl_4 , EP, $>99.5\%$ purity; Shimakyu) and titanium (IV) isopropoxide $\{[(\text{CH}_3)_2\text{CHO}]_4\text{Ti}$, $>98\%$ purity; Janssen} were used as the starting reagents for $\text{Ba}(\text{II})$, $\text{Sr}(\text{II})$ and $\text{Ti}(\text{IV})$, respectively. Citric acid monohydrate $[\text{HOC}(\text{COOH})(\text{CH}_2\text{COOH})_2 \cdot \text{H}_2\text{O}$, EP; Merck] was used as the reagent. Water used was of spectroscopic grade. Ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$, EP, 99.5% ; Shimakyu) or acetone (CH_3COCH_3 , EP; Santoku) was used as the solvent. Polyvinyl alcohol 2000 (PVA; 5 wt%, $>98.5\%$ purity; Showa) was mixed with the calcined powder.

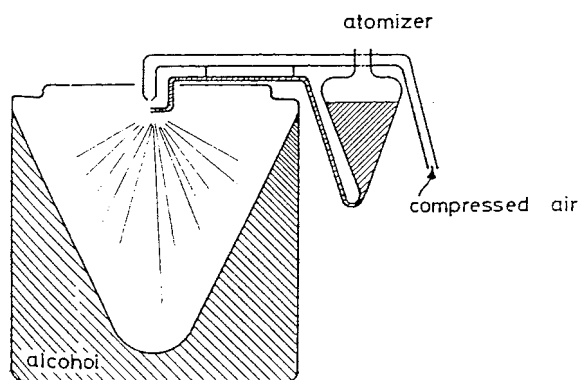


Figure 2 Set-up for coprecipitation.

Procedures

Preparation of citrate precursor

(A) Preparation of barium strontium citrate

$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (6.1070g; 0.025 mol), $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ (6.665g; 0.025 mol) and $\text{HOC}(\text{COOH})(\text{CH}_2\text{COOH})_2 \cdot \text{H}_2\text{O}$ (21.015g; 0.1 mol), were weighed to make the ratio of (Ba + Sr)/(citric acid) 1:2, then 300 ml of water was added to dissolve the mixture and it was diluted to 500 ml with water to make the citric acid concentration 0.2 M.

(B) Preparation of titanium citrate

TiCl_4 was hydrolysed in an ice bath and titanium was precipitated by cupferron.¹⁵ The precipitate was then calcined at 1000 °C for 4 h to form TiO_2 , to determine the extent of the hydrolysis of the TiCl_4 . Citric acid (2 mol/mol titanium ion) was mixed with the hydrolysed TiCl_4 , water was added to adjust the concentration of titanium to 0.2 M, and anhydrous NH_3 gas (Air Products) was added to adjust the pH value during the mixing process.

(C) Preparation of citrate precursor

Barium strontium citrate from (A) was mixed with titanium citrate from (B) with stirring to give a clear citrate precursor. The flowchart for the preparation of citrate precursor is shown in Figure 1. The conditions for precursor coprecipitation at various pH values and solvent ratios are listed in Tables 1 and 2, respectively.

Precipitation of citrate precursor

The solution of citrate precursor was sprayed by compressed air into 8–20 vol. of absolute ethanol or acetone to give a white precipitate (Fig. 2). The

precipitate was then filtered, washed with ethanol and filtered again.

Drying and grinding

The precursor made in step (C) was dried in an air oven, vacuum oven and freeze-dryer, sequentially, and the temperature was maintained at 80 °C for 24 h. Ethanol was added as appropriate and the product was wet-ground in a corneian mortar until the ethanol had evaporated. The sample was then dried for ~8 h to ensure complete removal of ethanol.

Pressing and sintering

The calcined powder was mixed with 5 wt% PVA solution and compacted in a steel die with i.d. 0.013 m, at 110 MPa. The pellets were heated at a rate of 10 °C min^{-1} to 1100, 1200, 1300 and 1450 °C, respectively, for 4 h in air, and furnace-cooled.

Solid-state reaction

The sample was mixed in the mole ratio $\text{SrCO}_3/\text{BaCO}_3/\text{TiO}_2 = 1:1:1$ and then calcined at 1100 °C in an alumina crucible for 8 h. The calcined sample was pressed into the mould, then the material was removed from the mould and sintered at 1450 °C for 4 h. Various properties of this sample were compared with those of the sample made by the citrate precursor route.

Instrumental methods

To understand the influence of the synthesis conditions, such as pH and solvent, on the precursor and final ceramic powder morphology, we freeze-dried the precipitate after washing it with ethanol. Infrared spectroscopy (IR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), X-ray diffraction (XRD) and Brunauer, Emmett and Teller (BET) surface area studies were

Table 3. Preparation of titanyl citrate precursor at various pH values

pH	Ba/Sr/Ti (mol)	Solution character
2–3	1:1:2	Precipitation
2–3	1:0:1	Clear
3–4	1:1:2	Precipitation
4–5	1:1:2	Clear
5–6	1:1:2	Clear
5–6	0:1:1	Clear
7–8	1:1:2	Precipitation

Table 4. Preparation of titanyl citrate precursor in various solvents and at various ratios of solvent/precursor

Solvent	Solvent/precursor (volume ratio)	Properties	Soln concn (%)		
			Ba	Sr	Ti
Ethanol	8:1	Wet gel	3.0	3.5	3.2
	10:1	Gel	1.5	2.2	1.7
	13:1	Powder	0.1	0.2	0.1
	15:1	Powder	0.1	0.1	0.1
	20:1	Powder	—	—	—
Acetone	8:1	Wet gel	4.2	4.0	3.8
	10:1	Gel	2.2	2.3	2.3
	13:1	Gel	0.5	0.6	0.8
	15:1	Powder	0.1	0.2	0.2

used to analyse the precursor and powder. The chemical composition of the filtrate was analysed by atomic absorption spectroscopy (AA). Scanning electron microscopy (SEM) and mapping were used to analyse the microstructures and uniformities of the precursor, powder and sintered bodies. The cross-section of the sintered body was polished with fine diamond grits and etched in 1.5 M nitric acid at 343–353 K for 1 h and then subjected to d.c. sputter-coating. It was investigated for grain growth at various sintering temperatures by SEM.

RESULTS AND DISCUSSION

Precursor studies

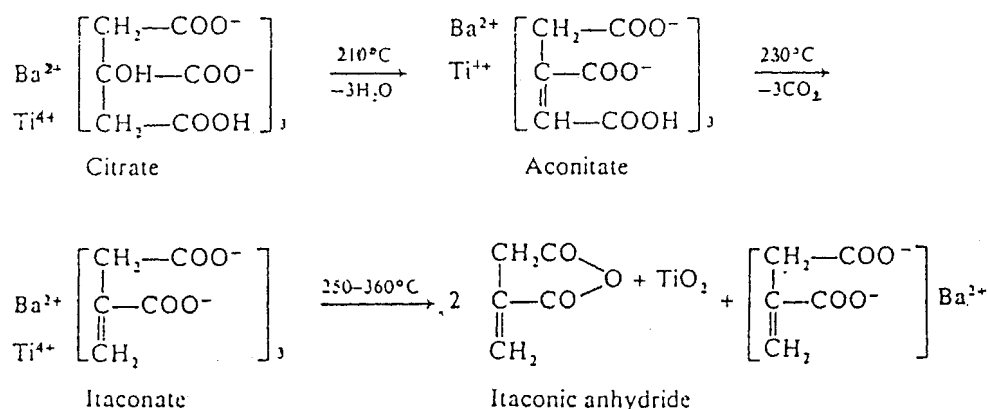
Effect of pH

The barium strontium titanyl citrate precursor is a

clear solution in a specific pH range.¹⁶ Details of the preparation of titanyl citrate precursor at various pH values are listed in Table 3. It is clear from Table 3 that precipitation occurs in neutral or alkaline solutions. Only barium and titanium cations at pH 2–3 result in a clear solution. Strontium and titanium cations at pH 4–6 result a clear solution.

Effect of solvent

A series of titanyl citrate precursor solutions were prepared in various solvents and in varying solvent/precursor ratios as listed in Table 4. When less solvent is used, the precursor forms a wet gel with more cations remaining in solution. When the solvent/precursor ratio is greater than 13, white powders result. The concentration of cation in filtrates, as analysed by AA, is very low, about 0.1%. When more solvent is used, the amount of the



Scheme 2 Reaction of (Ba,Ti) citrate precursor during heating.¹³

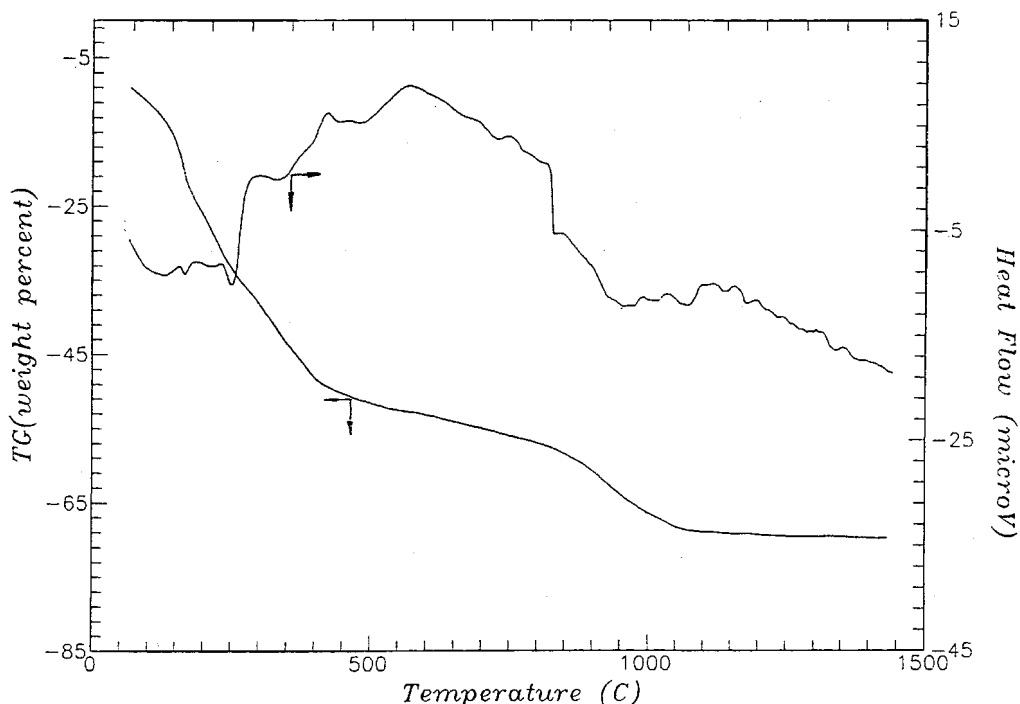


Figure 3 Thermogravimetric analysis (TGA) of the precursor at pH 5-6.

cation in the filtrate is minimized. The effect of ethanol is greater than that of acetone (Table 4).

Precursor sintering studies

DSC/TGA analyses

Figure 3 shows plots of heat flow and mass loss versus temperature for precursor formed at pH 5-6. The endotherm at 150-200 °C represents loss of

water of hydration. The associated mass loss at 80 °C is about 8%. DSC/TGA and IR analyses show that the formation of CO₂ occurs at 200 °C. There is a large mass loss at 250-360 °C due to itaconic anhydride from itaconate. The total mass loss is about 70%, owing to the high percentage of organics in the precursor. The mass loss continues until 1000 °C. Therefore we chose 1100 °C as the calcining temperature.

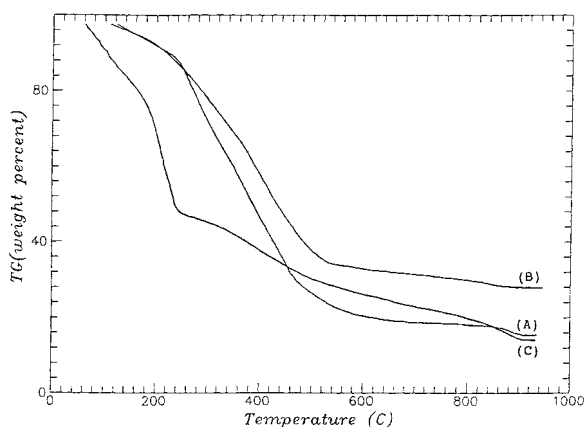


Figure 4 TGA of the precursors at: (A) pH 3-4; (B) pH 5-6; (C) pH 7-8.

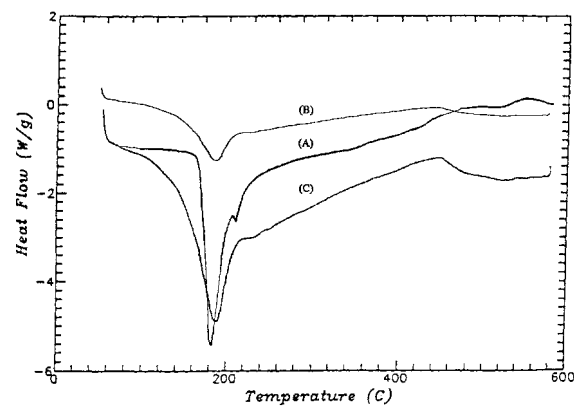


Figure 5 DSC of citrate precursors: (A) barium titanyl citrate; (B) strontium titanyl citrate; (C) barium strontium titanyl citrate.

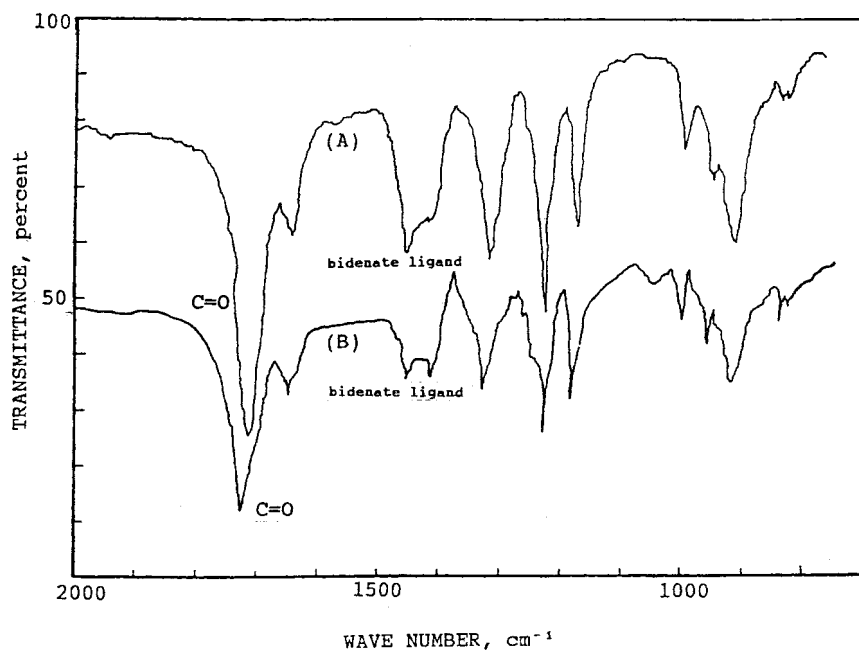


Figure 6 IR spectra of (A) itaconic acid;¹³ and (B) the titanyl citrate precursor, both dried at 200 °C.

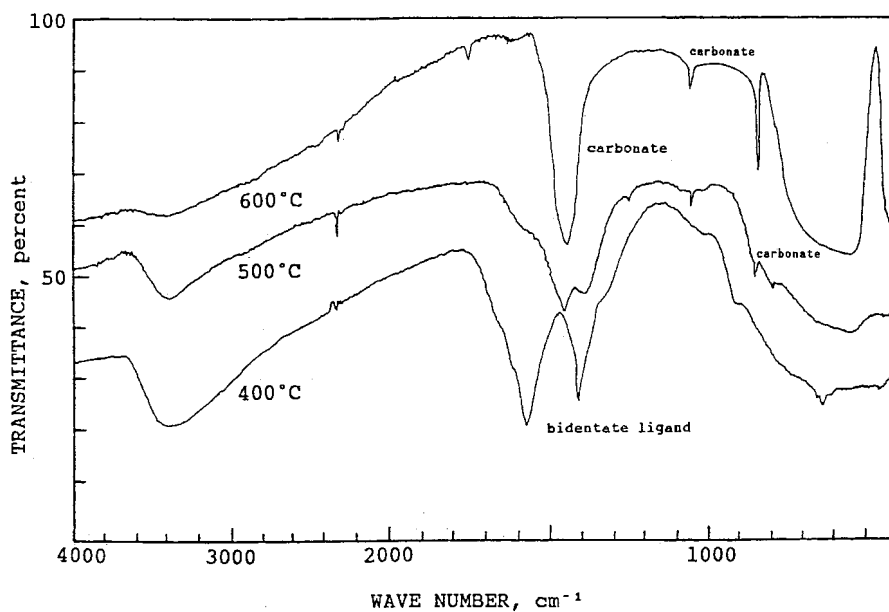


Figure 7 IR spectra of dried barium strontium titanyl citrate precursor at various temperatures.

The result of TGA of the precursor at various pH values is shown in Figure 4. There is a mass loss of 70% for precursor prepared at pH 5–6 and 80–85% at pH 3–4 and 7–8. Therefore, more organics are

present in the latter precursors than in those formulated at pH 5–6. This means that more citrate is incorporated in the precursor at pH 3–4 and 7–8 than at pH 5–6.

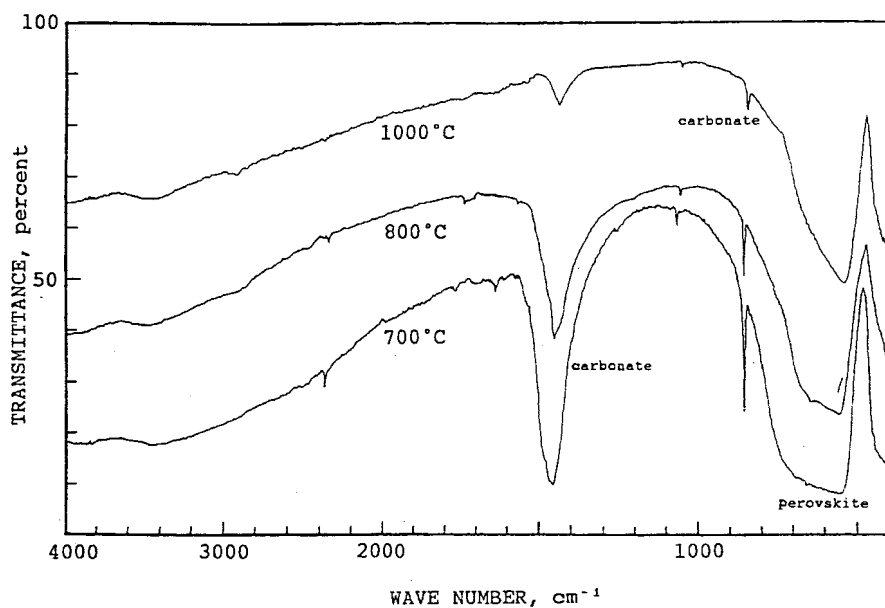


Figure 8 IR spectra of the titanyl precursor calcined at various temperatures for 8 h.

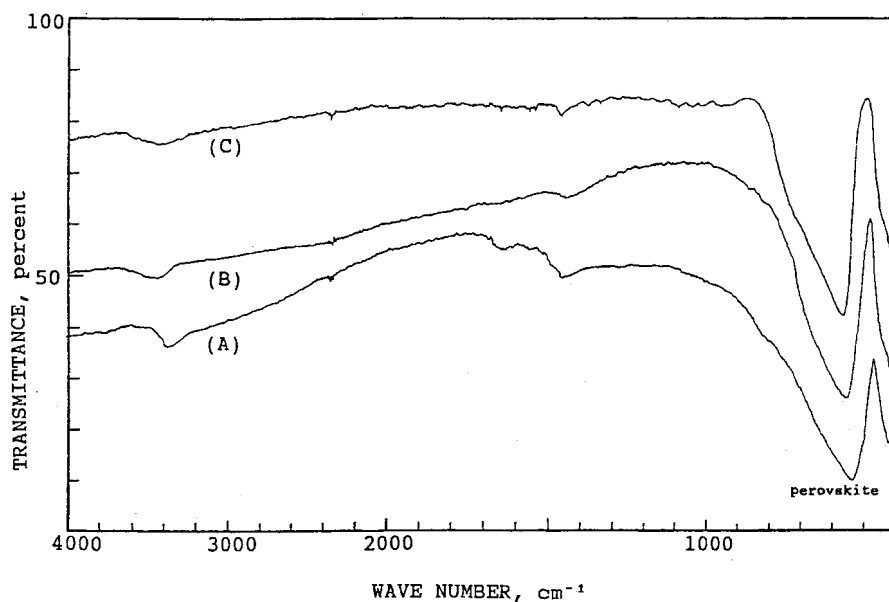


Figure 9 IR spectra of the different perovskite powders calcined at 1000 °C: (A) barium titanate; (B) barium strontium titanate; (C) strontium titanate.

In Figure 5, the (Ba,Ti), (Sr,Ti) and (Ba,Sr,Ti) citrates show similar DSC profiles. This suggests that the three precursors have similar chemical structures. According to a published DSC analysis of (Ba,Ti) citrate,¹³ the reactions shown in scheme 2 occur.

IR analysis

The IR spectra of itaconic acid and the titanyl citrates are shown in Figures 6–9. The IR spectrum of the titanyl citrate precursor dried at 200 °C is similar to that of itaconic acid (Fig. 6).¹³ This suggests that the citrate precursor dried at 200 °C forms itaconic acid.

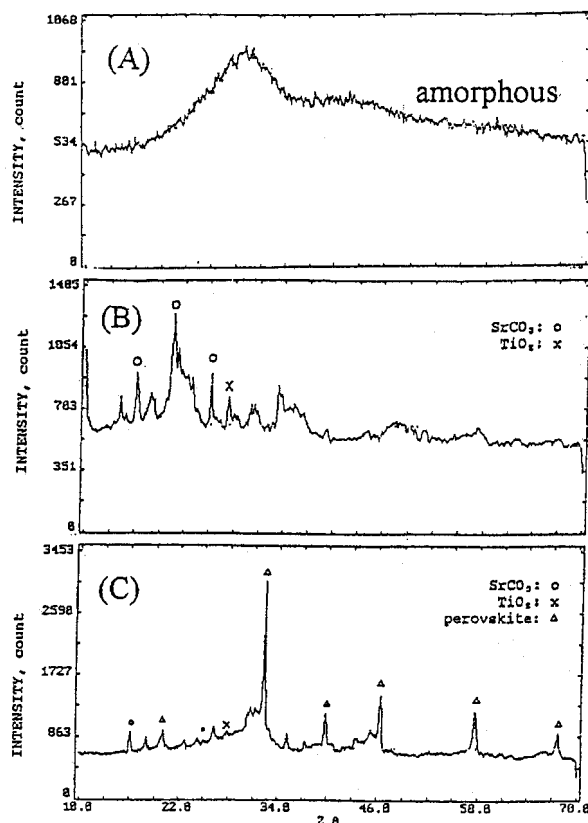


Figure 10 XRD patterns of the citrate precursor calcined for 8 h at (A) 400 °C; (B) 500 °C; (C) 600 °C.

At 400 °C, two absorption peaks appear at 1420 and 1560 cm^{-1} (Fig. 7). These bands are attributed to the bidentate ligand of RCOO^- ,¹⁷ indicating the presence of COO^- . At 500 °C absorption peaks at 860, 1059 and 1460 cm^{-1} appear, indicating carbonate formation.¹⁸ The wide absorption band at 540 cm^{-1} at 600 °C, suggests perovskite formation,¹⁹ even though 20 wt% carbonate is still present. Figure 8 shows the IR spectra of the titanyl citrate precursor heated to 700–1000 °C. At 1000 °C the 1460 cm^{-1} absorption peak decreases, indicating decomposition of carbonate. As shown in Figure 9, there is a perovskite band at 560 cm^{-1} , which is supported by XRD results.

XRD analysis

The XRD patterns of the citrate precursor calcined at various temperatures for 8 h are shown in Figure 10. It is clear from Fig. 10 that the powder calcined below 500 °C is amorphous, and at 500 °C carbonates form as shown in the IR analysis.

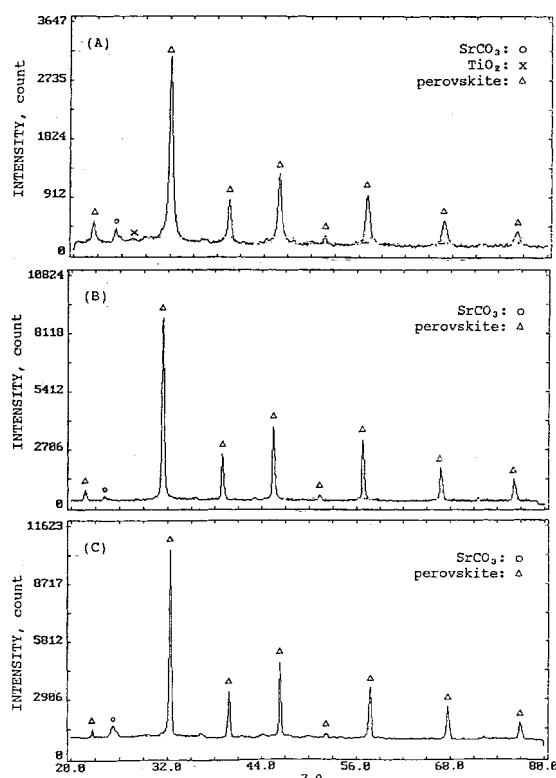


Figure 11 XRD patterns of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ powder prepared by the citrate method at 1000 °C for (A) 2 h; (B) 4 h; (C) 8 h.

Comparison with JPCDS files indicates that at 500 °C the precursor decomposes to BaCO_3 (11-697), SrCO_3 (5-418) and TiO_2 (29-1360). At 600 °C the product is calcined to $(\text{Ba,Sr})\text{TiO}_3$ (39-1395). The reaction is not complete at 600 °C as seen by XRD, as the spectra contain large amounts of BaCO_3 , SrCO_3 and TiO_2 .

Figure 11 shows the patterns of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ powder prepared by the citrate method and calcined at 1000 °C for 2, 4 and 8 h, respectively. The carbonate and TiO_2 contents (in Fig. 11) in the powder decrease and the crystallinity of perovskite increases with increasing time.

The XRD analysis of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ powder prepared by solid-state reaction at 1000–1200 °C for 24 h is shown in Figure 12. Heating at 1000 °C for 24 h produces powder with large amounts of impurities, including BaCO_3 , SrCO_3 and TiO_2 . Only at 1200 °C do the amounts of impurities decrease significantly. In contrast, much lower reaction temperatures are required in the citrate method. The citrate precursor mix allows stoichio-

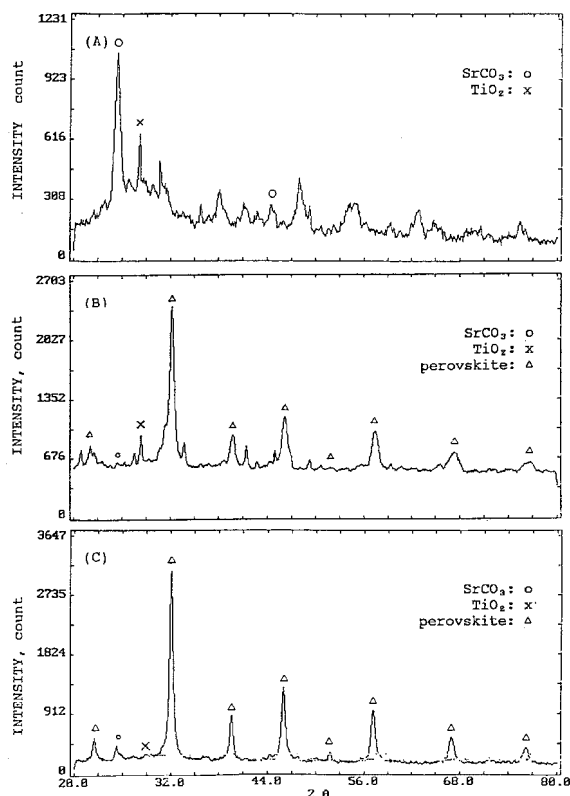


Figure 12 XRD patterns of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ powder prepared by solid-state reaction for 24 h at (A) 1000 °C; (B) 1100 °C; (C) 1200 °C.

metric mixing and finer particle sizes of BaCO_3 , SrCO_3 and TiO_2 , so that a shorter reaction path and larger contact areas occur, thereby decreasing the calcining temperature.²⁰ The XRD patterns of sintered $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ produced by solid-state and citrate methods are shown in Figure 13, from which it is clear that the perovskite structure is very clean only at 1400 °C for the solid-state method, while the citrate method gives a clean material even at 1250 °C. The grain sizes of the body sintered at 1400 °C are larger.

Properties of powder and sintering body

Mapping analysis

Mapping analysis by SEM shows that the mixing of the cations in the ceramic body $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ using the citrate method is more uniform than that obtained by solid-state reaction.

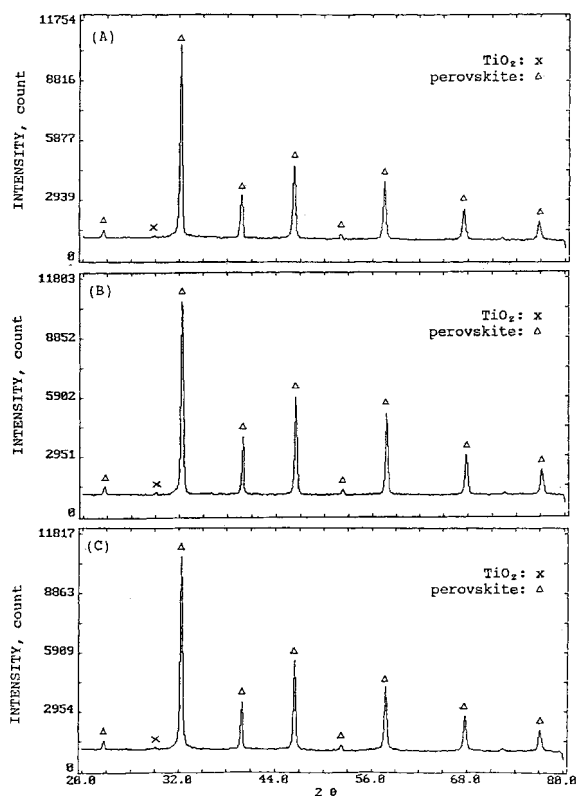


Figure 13 Comparison of XRD patterns of the sintering body of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ prepared, during 24 h, by (A) solid-state reaction at 1400 °C; (B) citrate method at 1250 °C; (C) citrate method at 1400 °C.

SEM analysis

SEM (Fig. 14) of the titanyl citrate precursor, made by precipitating $\text{Ti}(\text{O}-i\text{C}_3\text{H}_7)_4$ or TiCl_4 in acetone or absolute ethanol, shows that the particle size for titanyl citrate made from TiCl_4 is smaller than for that made from $\text{Ti}(\text{O}-i\text{C}_3\text{H}_7)_4$, and the particle size made by precipitating TiCl_4 in absolute ethanol is more uniform than that in acetone. Figure 15 shows the SEM of the perovskite powders prepared by the citrate method, dried in air or vacuum- or freeze-dried, and calcined at 1000 °C for 24 h. The agglomeration of the freeze-dried powder is the lowest, while the oven-dried powder exhibits the greatest degree of agglomeration. The SEM of the perovskite powders of BaTiO_3 , $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ and SrTiO_3 prepared by the citrate method and calcined at 1100 °C for 8 h is shown in Figure 16. The particle sizes for these three powders are close (0.4–0.5 μm).

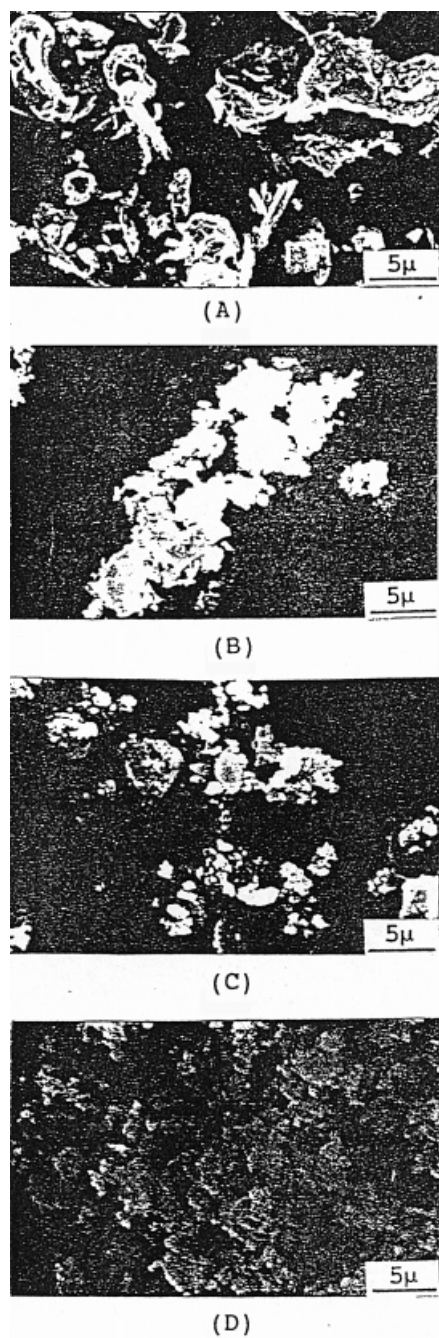


Figure 14 SEM of the titanyl citrate precursor, obtained (A) from $\text{Ti}(\text{O}-i\text{C}_3\text{H}_7)_4$; (B) from TiCl_4 ; (C) by precipitating TiCl_4 in acetone; (D) by precipitating TiCl_4 in absolute ethanol.

Figure 17 shows the SEM of a sintered $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ body prepared by the citrate method at 1100, 1200, 1300 and 1400 °C for 4 h. The pore



Figure 15 SEM of the perovskite powders prepared by the citrate method and calcined at 1000 °C for 24 h, after (A) air-drying; (B) vacuum-drying; (C) freeze-drying.

volume is 16% and 10% for the sintering body at 1100 and 1200 °, respectively, so the body is not dense. At 1300 °C only 6 vol.% porosity remains

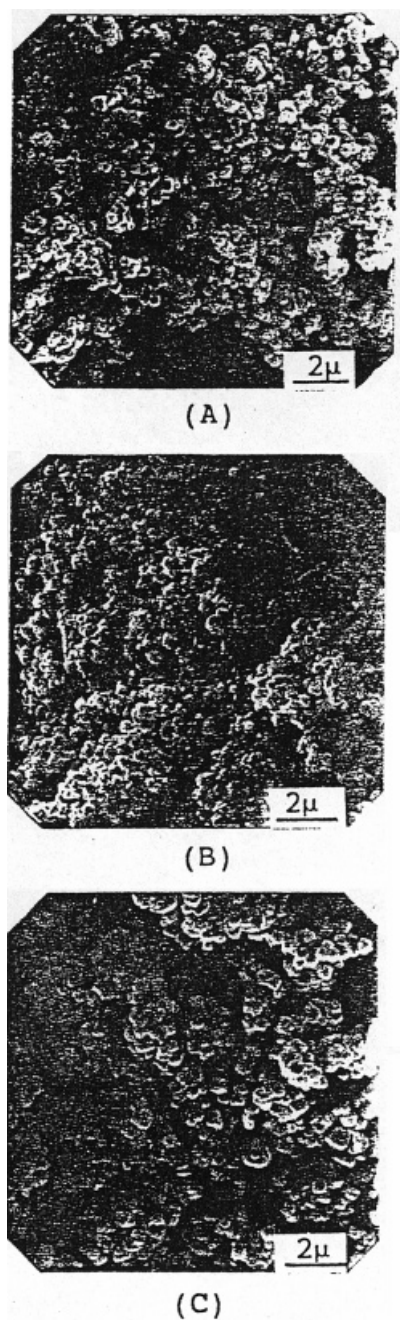


Figure 16 SEM of the perovskite powders prepared by the citrate method and calcined at 1000 °C for 8 h: (A) BaTiO₃; (B) Ba_{0.5}Sr_{0.5}TiO₃; (C) SrTiO₃.

and at 1400 °C only 1 vol.% porosity is found, indicating considerable improvement in density.

Micrographs of the sintered Ba_{0.5}Sr_{0.5}TiO₃ body

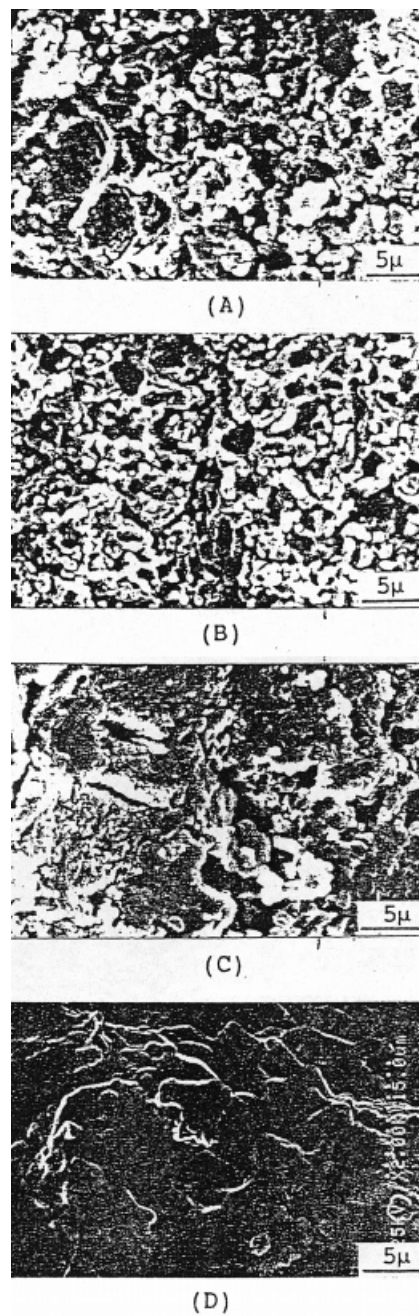


Figure 17 SEM of sintered Ba_{0.5}Sr_{0.5}TiO₃ body prepared by the citrate method during 4 h at (A) 1100 °C; (B) 1200 °C; (C) 1300 °C; (D) 1400 °C.

prepared using the solid-state-derived powders method at 1300, 1400 and 1450 °C for 4 h are shown in Figure 18. The porosity is 13 and 7% at

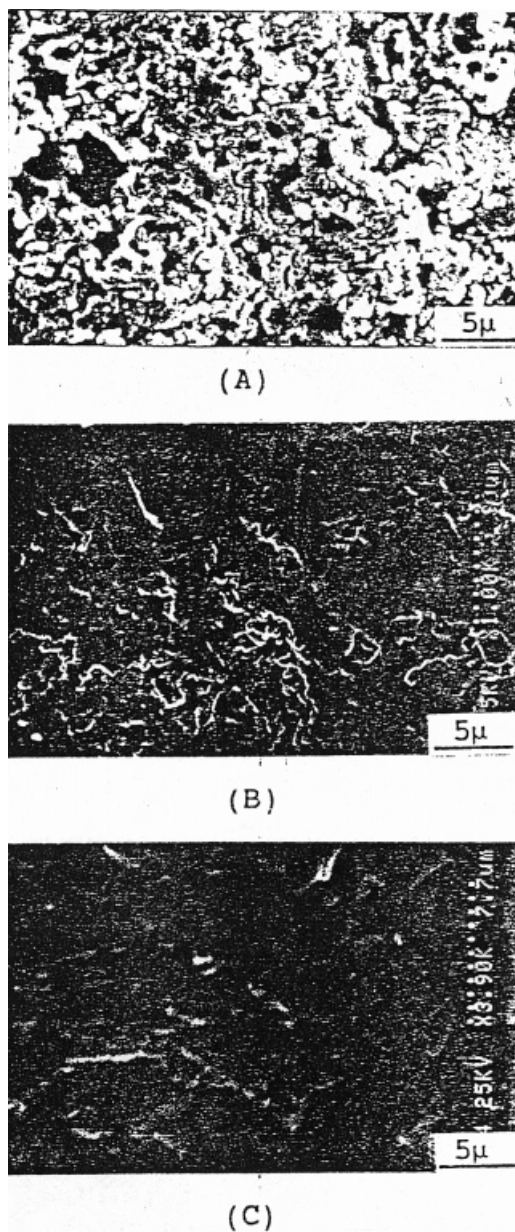


Figure 18 SEM of sintered $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ body prepared by solid-state reaction during 4 h at (A) 1300 °C; (B) 1400 °C; (C) 1450 °C.

Table 5. Specific surface areas for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$

Drying method	Citrate gel			Calcined powder		
	Air-drying	Vacuum-drying	Freeze-drying	Air-drying	Vacuum-drying	Freeze-drying
Surface area ($\text{m}^2 \text{g}^{-1}$)	20.8	25.2	29.8	8.3	10.2	12.5

1300 and 1400 °C, respectively. However, at 1450 °C only 1 vol.% porosity remains and the compact is close to theoretical density.

Measurement of specific surface area

The specific surface areas of the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ citrate precipitate dried in air, vacuum or by freeze-drying and calcined at 1000 °C for 8 h were measured by the BET method. The results are listed in Table 5. The agglomeration of the freeze-dried precursor and of the freeze-dried and calcined powder prepared from citrate are the least; it was hence their specific surfaces were the greatest (Table 5). The specific surface area obtained by air-drying is the lowest, due to a greater degree of agglomeration.²¹

Chemical compositions of the body

The chemical compositions of the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ citrate powder were analysed chemically by AA; Table 6 shows that the cation ratios are nearest those of the original stoichiometry in the pH 5–6 range. When the pH of the preparatory solution is lower, the deviation of Sr^{2+} is greatest (Table 6). This is due to the poor precipitation of the strontium citrate precursor in acid solution.²² At pH 7–8, the deviation of Ba^{2+} is the greatest due to the solubility of the barium citrate precursor in neutral solution.

Determination of bulk density

The changes in bulk density of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$, dried in air or vacuum- or freeze-dried and then calcined at 1000 °C for 8 h, and sintered at various temperatures, are shown in Figure 19. The bulk density increased with increasing sintering temperature, as expected, with the compact obtained by freeze-drying reaching the highest densities at temperatures around 1300 °C. The compact made using air-dried powders requires 1400 °C sintering to reach full density, owing to high initial agglomeration and the large size of the pores after sintering.

Figure 20 shows the changes in the bulk densities of BaTiO_3 , $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ and SrTiO_3 obtained by

Table 6. Chemical compositions of the perovskite powders from citrate precursor

pH range of preparation	Org. chemical composition		Powder chemical composition	
	Ba/Ti ratio	Sr/Ti	Ba/Ti	Sr/Ti
2–3	1:2	1:2	0.44	0.42
2–3	1:1	0	0.99	—
3–4	1:2	1:2	0.46	0.46
4–5	1:2	1:2	0.51	0.52
5–6	1:2	1:2	0.48	0.49
5–6	0	1:1	—	0.98
7–8	1:2	1:2	0.23	0.34

freeze-drying and sintered at various temperatures. The sintering temperature of BaTiO₃ is lower, about 1300 °C, and that of SrTiO₃ is higher, about 1425 °C.

Perovskite powder crystallite sizes

The BaTiO₃, Ba_{0.5}Sr_{0.5}TiO₃ and SrTiO₃ powder grain sizes after calcining at 1100 °C for 8 h were measured using the XRD 31–33 ° (2θ = 32.2 °) peak, which is the (110) face of perovskite by Scherrer's formula (Eqn [5]).

$$\varepsilon = \lambda / (\beta \cos \theta) \quad [5]$$

The calculated grain sizes are listed in Table 7.

The crystallite sizes obtained using the citrate

method are larger than those from the solid-state reaction, because the initial uniform mixing leads to shortening of the diffusion paths, compared with solid-state mixing. Hence grains form faster and grow longer for any given sintering temperature and time.

CONCLUSIONS

The DSC/TGA and IR data provide a clear picture of the thermogravimetric behaviour and chemical changes occurring in the citrate precursor during calcination. The precursor is converted at 500 °C to

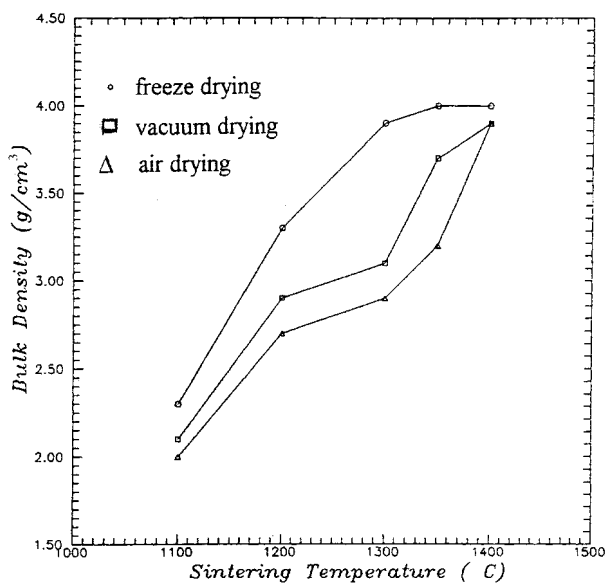


Figure 19 Changes in bulk density with increasing sintering temperature of Ba_{0.5}Sr_{0.5}TiO₃ obtained by various drying modes.

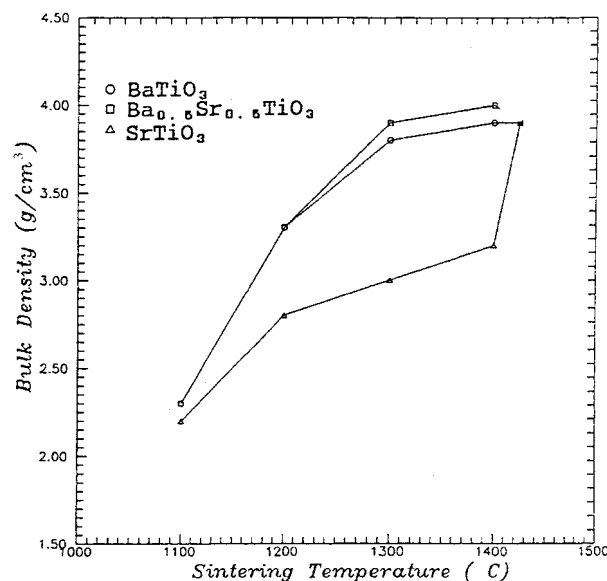


Figure 20 Changes in bulk densities of BaTiO₃, Ba_{0.5}Sr_{0.5}TiO₃ and SrTiO₃ with increasing sintering temperature.

Table 7. Crystallite sizes for perovskite powders calculated by Debye–Scherrer method

Crystallite size (Å)	Preparation method					
	Solid-state reaction			Citrate method		
	BaTiO ₃	SrTiO ₃	(Ba, Sr) TiO ₃	BaTiO ₃	SrTiO ₃	(Ba, Sr) TiO ₃
Crystallite size (Å)	120	140	140	210	230	225

carbonate, which begins to react with TiO₂ to form (Ba,Sr)TiO₃ powders at 600 °C. This powder can finally be transformed to product by calcining at 1100 °C.

The ratios of the cations in the powder are the nearest to the original stoichiometry in the pH 5–6 range, where the concentration of cation in the filtrate is only 0.1 mol%. The effect of absolute ethanol on precipitation is much greater than that of acetone, and one can obtain a completely dry precipitate with ethanol.

The specific surface area of the calcined Ba_{0.5}Sr_{0.5}TiO₃ powder is 12.5 m² g⁻¹ by the BET method, and the crystallite size of the Ba_{0.5}Sr_{0.5}-TiO₃ powder using the citrate method is about 225 Å (2.2 μm) by XRD.

Among the drying modes, freeze-drying is best as it minimizes agglomeration. When the precipitated titanyl citrate powders that had been freeze-dried and calcined at 1100 °C were compacted, and sintered at 1300 °C, densities as high as 95% of theoretical were achieved.

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