

Preparation and Sintering Characteristics of Y-doped SrZrO₃ by Citrate Gel Method

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Proton-conductive SrZr_{0.95}Y_{0.05}O_{2.975} powder was prepared by citrate gel method and its characteristics and sinterability were investigated. Amorphous gel could be obtained from a citric acid solution that SrCO₃ and metal nitrates were dissolved. The initial decomposition of the gel proceeded up to 250°C, followed by combustion of its decomposition products in the temperature range from 250°C to 500°C. A well-crystallized perovskite phase appeared at 600°C with a small amount of SrCO₃. The powder exhibited a single perovskite phase with a stoichiometric composition after calcination at 1000°C. Sintering green compacts of this powder for 6 h showed a considerable densification to start at 1200°C and resulted in 86.8% and 96.5% relative densities at 1400°C and 1600°C, respectively. Whereas, the powder compacts prepared by solid state reaction had much lower relative densities, 73% at 1400°C and 92% at 1600°C.

Key words : Citrate Gel, Powder Synthesis, Proton Conductor, Perovskite, Sinterability

I. Introduction

Perovskite-type oxides of cerates and zirconates (ABO₃; A=Ba, Sr, B=Ce, Zr) exhibit high proton conductivity in an atmosphere containing hydrogen or water vapor at elevated temperature.^{1,2)} Substitution of B ions by lower valency cations generates oxygen ion vacancies, which react with hydrogen or water vapor to form protons that migrate by hopping from an oxygen to an adjacent one with a relatively low activation energy. High-temperature proton conductors (HTPCs) have been extensively studied due to their potential applications in solid oxide fuel cells, hydrogen sensors and steam electrolyzers. Particularly, zirconates are interesting since they have lower proton conductivity but better mechanical and thermal stability than cerates. Strontium zirconates, for example, are more stable in CO₂-containing atmosphere than strontium cerates which decompose to SrCO₃ and CeO₂.³⁻⁵⁾

Strontium zirconates as well as other HTPCs are fabricated by solid state reaction that carbonates and oxides of the constituents are mixed, followed by calcination and sintering at high temperatures.⁴⁻⁶⁾ Due to a slow solid state reaction between the oxide powders, calcination is carried out at temperature as high as 1450°C and repeated several times to obtain a single perovskite phase. Such heat treatments can cause agglomerates to form and particle size to increase and make it difficult to achieve a high density and homogeneous microstructure. As a result, sintering has to be performed up to 1650°C to attain ≥95% of the theoretical density. Therefore, fine, agglomerate-free powders having a single perovskite phase and good sinter-

ability are essential in fabricating dense HTPCs. Recently, HTPC powders have been prepared by chemical methods, allowing low powder synthesis and sintering temperatures, such as oxalate coprecipitation⁹⁻¹²⁾ and precipitation of hydroxides.¹¹⁾ However, inhomogeneous precipitation occurs and undesirable second phases result in when the solubilities of metal ions considerably differ one another.

Citrate gel method has advantages of a tight control of stoichiometry and homogeneous incorporation of low level dopants. In this method, a citrate solution containing metal ions is heated to convert into a gel, which is decomposed and subsequently calcined to obtain oxide powders. During the evaporation, citrates in the precursor solution are believed to form stable chelate complexes with metal ions, which prevent metal ions from precipitation. Thus, the uniform distribution of metal ions in the precursor solution can be maintained throughout decomposition. Metal nitrates are preferred as starting materials because of their high solubilities in water. However, in preparing Sr-containing perovskite powders, Sr nitrate has been found to exist in a gel state, suggesting that chemical homogeneity can be lost during heat treatments.¹³⁾

In this study, Y-doped SrZrO₃ powder with a nominal composition of SrZr_{0.95}Y_{0.05}O_{2.975} was prepared by citrate gel method. Thermal behavior of the gel and characteristics and sinterability of the calcined powder were investigated and compared with the powder obtained by solid state reaction.

II. Experimental Procedure

An appropriate amount of SrCO₃ (first grade, Shinyo

Pure Chemical Co.) was dissolved in a 0.2 M citric acid (99.5%, $C_6H_8O_7$, Aldrich) solution in a 1:5 molar ratios of Sr: citric acid and a completely transparent Sr citrate solution was obtained. $SrCO_3$ could be dissolved in a 1:4 molar ratio of Sr: citric acid, but Sr citrate was found to precipitate in the solution after aging at room temperature. Whereas, no precipitation was observed in the solution prepared in a 1:5 molar ratio of Sr: citric acid.

Aqueous solutions of zirconyl nitrate ($ZrO(NO_3)_2 \cdot xH_2O$, 98%, Aldrich) and yttrium nitrate ($Y(NO_3)_3 \cdot 5H_2O$, 99.9%, Aldrich) were prepared and each solution was mixed with a 0.2 M citric acid solution in 1:3 and 1:1 molar ratios of Zr: citric acid and Y: citric acid, respectively. The concentrations of Sr citrate solution and zirconyl and yttrium nitrate solutions were determined with an inductively coupled plasma spectrometer and found to be 0.2, 0.38, and 0.1 M, respectively. The citrate solution containing the metal ions were mixed in a 1 : 0.95 : 0.05 molar ratio of Sr : Zr : Y, heated to remove water at 70–80°C and then dried under vacuum at 70°C for 24 h.

The gel was preheated at 300°C for 2 h in air at a heating rate of 3/min and then, further heated to 1000°C for 6 h at a heating rate of 5°C/min. The resulting powder was dispersed in high purity ethanol and milled with zirconia ball for 12 h. The powder was mixed with 0.5 wt% polyvinyl butyral and uniaxially pressed into pellets in 1 cm diameter at 93.5 MPa. The powder compacts were heated at 600°C for 2 h to remove the binder and sintered at temperatures between 1200°C and 1600°C for 6 h in air at a heating rate of 10°C/min. All powders and sintered samples were stored in a vacuum desiccator to avoid contacts with moisture and CO_2 in air.

In addition, powder was prepared by solid state reaction to compare with the powder prepared by citrate gel method. Powders of $SrCO_3$, ZrO_2 (99.9%, Yakuri Purity Chem.) and Y_2O_3 , which had been obtained by calcining yttrium nitrate at 1000°C, were mixed and calcined at 1300°C for 6 h. The powder was milled and used in preparing powder compacts.

Thermal behavior of the gel was studied with a simultaneous TG/DTA (TG-DTA 2000, MAC Science) at a heating rate of 5°C/min up to 1200°C in air. For phase analysis, the gel was heated to temperatures from 300°C to 1000°C at a heating rate of 5°C/min and held for 2 h. Phases presented in the samples were identified by X-ray powder diffraction (CuK α radiation, M03XHF, MAC Science). Some of the decomposition products were examined with an FT-IR spectrometer (FTS-165, Biorad). The samples mixed with dry KBr powder were pressed into pellets and the range of the measured transmission spectra was from 480 to 4000 cm^{-1} .

Precise lattice parameter measurement was carried out based on a pseudocubic perovskite structure using the Nelson-Riley function as described elsewhere.¹²⁾ The powder was prepared from the sample sintered at 1600°C. The measured 2 θ values were calibrated with high purity

Si powder (99.999%) as an external standard and the accuracy of the measurement was within $\pm 0.0003 \text{ \AA}$. The theoretical density of $SrZr_{0.95}Y_{0.05}O_{2.975}$ was determined from the lattice parameter and found to be 5.40 g/cm^3 .

Particle size and apparent density of the calcined powder were measured with a laser diffraction particle size analyzer (SALD-2001, Shimadzu) and a He gas pycnometer (AccuPyc 1330, Micromeritics), respectively. Bulk densities of the sintered samples were determined using the Archimedes method. High purity isopropyl alcohol was used in order to avoid possible hydration of the samples and relative density was calculated from the bulk density divided by the theoretical density. The powders and the sintered samples were examined with SEM (JSM-5410, JOEL). The sintered samples were polished and thermally etched at 50°C below each sintering temperature for 90 min.

III. Results and Discussion

Fig. 1 shows TG/DTA curves of citric acid and the citrate gel. In TG/DTA curves of citric acid in Fig. 1(a), a strong and a broad endothermic peaks at 155°C and at 199°C are due to melting and decarboxylation of citric acid, respectively. It has been proposed that decarboxyla-

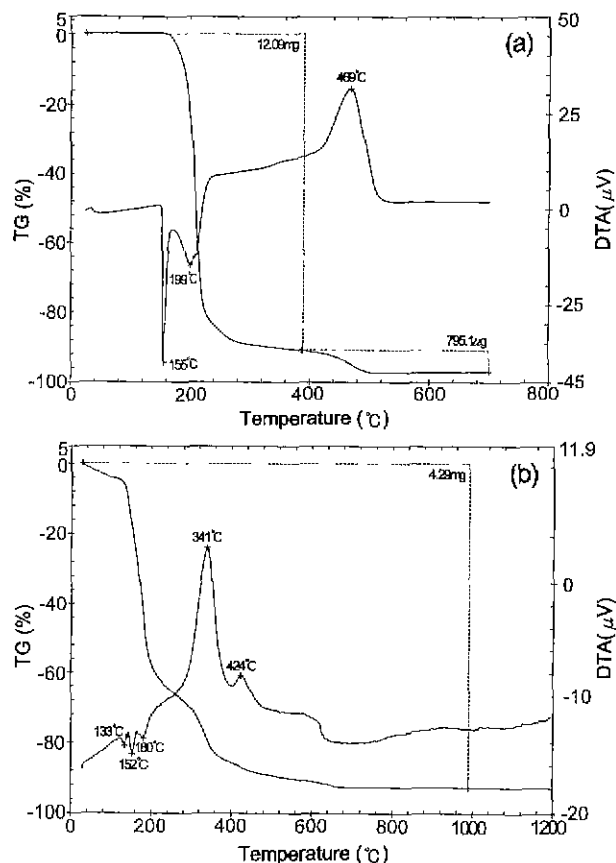


Fig. 1. TG/DTA curves of (a) citric acid and (b) citrate gel in air.

tion occurs in the following sequence at a heating rate of less than 50°C/min: citric acid → aconitic acid (C₆H₆O₆) → itaconic acid (C₅H₆O₄) → itaconic anhydride (C₅H₄O₃).¹⁴ These reactions accompany the evolution of H₂O and CO₂, resulting in a large weight loss. A strong exothermic peak at 469°C is attributed to combustion of the decomposition products.

The citrate gel decomposes in three major stages, dehydration, decomposition of citrate and combustion of the decomposition products, as shown in Fig. 2(b). A weight loss up to 120°C corresponds to dehydration of the gel. The initial decomposition occurs up to 250°C as shown by endothermic peaks between 120°C and 250°C. Peaks owing to melting of citric acid and decomposition of metal nitrates were not observed since most of nitric ions and free citrate in the precursor solution were liberated with water during the evaporation. The combustion of the intermediate decomposition products is indicated by a strong exothermic peak at 341°C and a weak exothermic peak at 424°C. The decomposition of the gel is completed at temperature below 650°C.

IR spectrum of the precursor solution (Fig. 2(b)) exhibits the presence of both free and coordinated carboxylate groups.¹⁵ The absorptions at 1724 cm⁻¹ and 1386 cm⁻¹ arise from the asymmetric and the symmetric stretching vibrations of free carboxylate group (free COO⁻). The absorption at 1634 cm⁻¹ and 1227 cm⁻¹ are due to the asymmetric and the symmetric stretching vibrations of coordinated carboxylate groups (coordinated COO⁻). The decreased intensities

of the absorption peaks due to free COO⁻, as compared to the spectrum (a) of the citric acid solution, indicate that some of citrate functional groups have been chelated with the metal ions.

In the gel decomposed at 250°C, the absorption peaks due to free COO⁻ disappears, while very weak peaks attributing to the decomposition product, itaconic acid, appear at 1767 cm⁻¹ and 1716 cm⁻¹, as shown in spectrum (c).¹⁴ The absorption peaks at 1559 cm⁻¹ and 1397 cm⁻¹ in the gel decomposed at 400°C (spectrum (d)) are likely to be due to intermediate carboxylates, which disappear at 500°C. Note that the absorptions at 706, 867, and 1073 cm⁻¹ arising from CO₃²⁻ ion appear in spectrum (e) and their intensities are increased in spectrum (f).¹⁵ This suggests the formation of SrCO₃ at 500°C and the increase in its amount at 600°C. It has been reported that the formation of Sr or Ba carbonates in a decomposing citrate gels is attributed to the reaction of Sr or Ba species with CO₂ evolved during the decomposition.^{15,16}

Fig. 3 shows XRD patterns of the gels heated at various temperatures for 2 h. The gel is amorphous up to 300°C and begins to crystallize at 500°C as seen by the weak and broad peak corresponding to the strongest diffraction peak of perovskite phase. A very weak peak near the broad peak of perovskite phase is due to SrCO₃. It has been observed that SrCO₃ continues to form after a further heating up to for 6 h. At 600°C, a well-crystallized perovskite phase appears with a small amount of SrCO₃, which exists up to 800°C. The appearance of SrCO₃ peak

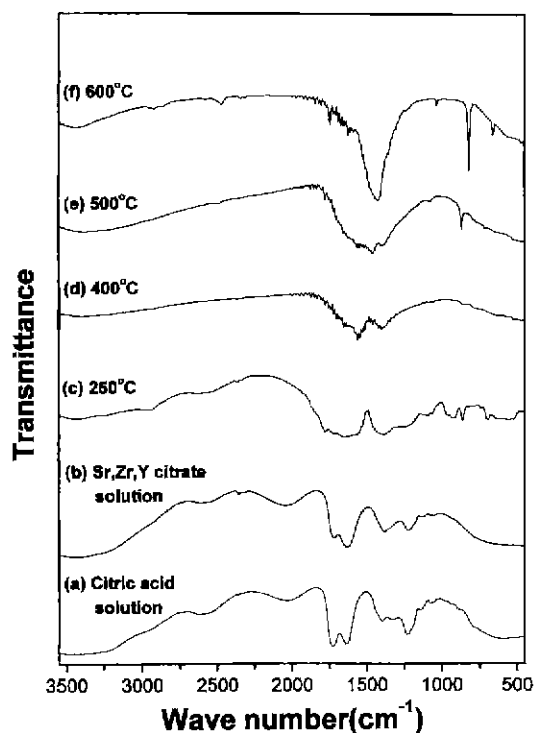


Fig. 2. IR spectra of solutions and gel decomposed at different temperatures.

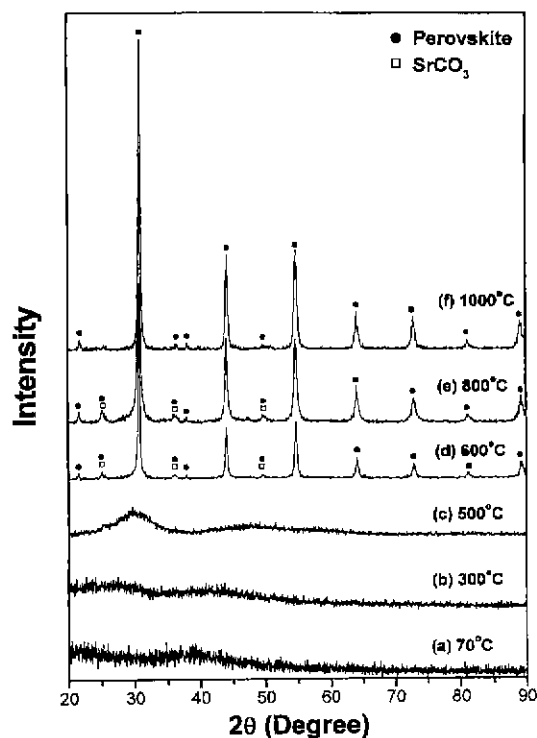


Fig. 3. XRD patterns of the gel heated for 2 h at different temperatures.

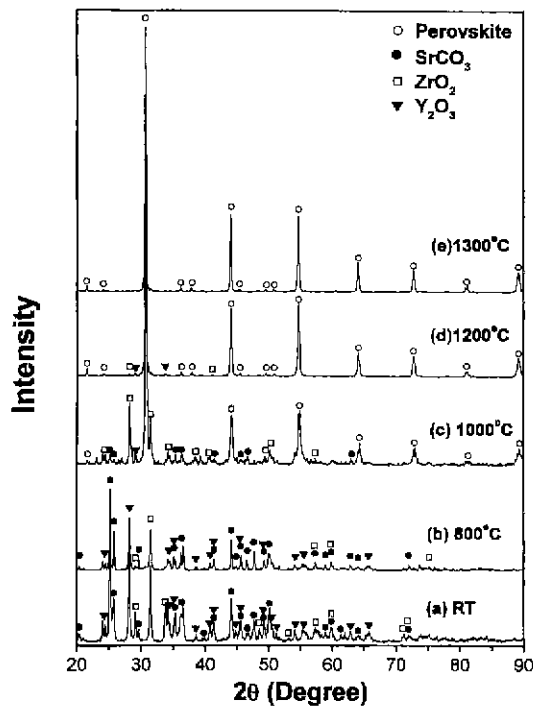


Fig. 4. XRD patterns of the powder prepared by solid state reaction and calcined for 2 h at different temperatures.

in the XRD patterns is consistent with the IR spectra of the gel decomposed at 500°C and 600°C. At 1000°C, a single perovskite $\text{SrZr}_{0.95}\text{Y}_{0.05}\text{O}_{2.975}$ phase develops and SrCO_3 completely disappears.

The advantage of citrate gel method over solid state reaction is illustrated by XRD patterns of the powder prepared by solid state reaction in Fig. 4. SrCO_3 , ZrO_2 and Y_2O_3 are present at 800°C, but the peak intensity of SrCO_3 is slightly decreased as SrCO_3 decomposes. Due to a slow solid state reaction, a perovskite phase is detected at 1000°C with unreacted carbonate and oxides. These oxides still remains in very small amounts at 1200°C and

Table 1. X-Ray Diffraction Data^a for $\text{SrZr}_{0.95}\text{Y}_{0.05}\text{O}_{2.975}$ Powder^b

<i>h k l</i>	$d_{\text{obs}}(\text{Å})$	$d_{\text{cal}}(\text{Å})$	$III_0(\text{CuK}\alpha_1)$
1 1 0	2.9133	2.9077	100
2 0 0	2.0586	2.0560	28
2 1 1	1.6806	1.6787	27
2 2 0	1.4548	1.4538	10
3 1 0	1.3012	1.3003	8
2 2 2	1.1883	1.1870	2
3 2 1	1.0994	1.0990	8
4 0 0	1.0283	1.0280	1
3 3 0	0.9694	0.9692	5
4 2 0	0.9197	0.9195	3

^aIndexing based on a pseudocubic unit cell of $a=4.1120\pm 0.0003$ Å.

^bSintered at 1600°C for 6 h.

a single perovskite phase appears at 1300°C. From these results, it is expected that citrate gel method can produce powder with a high reactivity and a single perovskite phase at temperature at least 300°C lower than is required in solid state reaction.

The X-ray diffraction peaks of the sample sintered at 1600°C for 6 h were found to be identical to those of the powder calcined at 1000°C. Although the crystal structure of Y-doped SrZrO_3 is orthorhombic and isostructural with SrZrO_3 ,^{6,7,17)} the diffraction peaks can be indexed based on a pseudocubic structure¹²⁾ and the result is listed in Table 1. Weak diffraction peaks, which belong to an orthorhombic structure, are not indexed. The lattice parameter of $\text{SrZr}_{0.95}\text{Y}_{0.05}\text{O}_{2.975}$ was calculated according to a pseudocu-

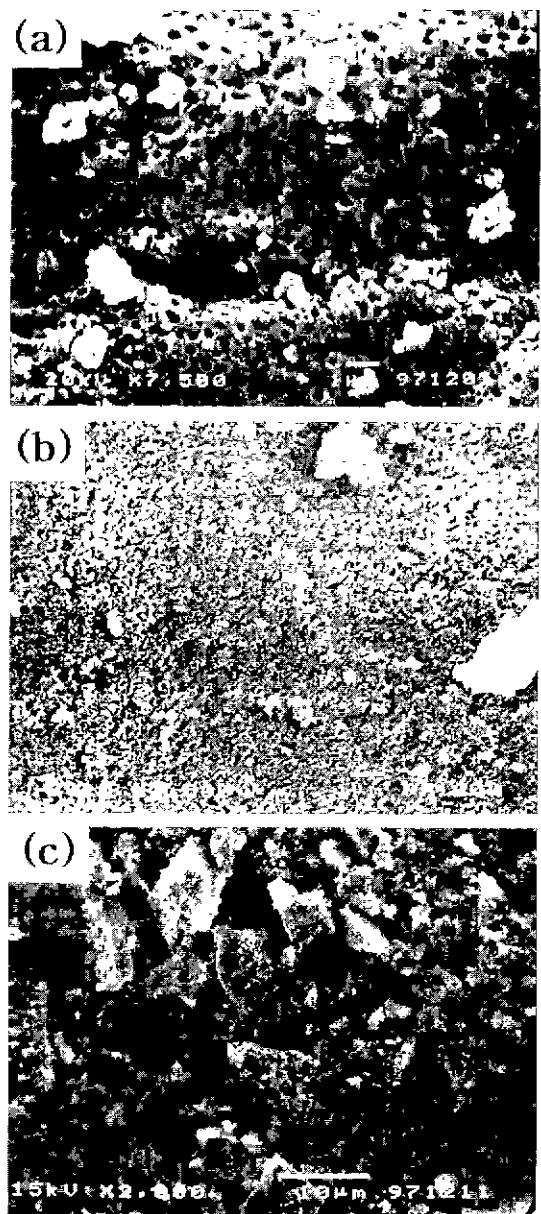


Fig. 5. SEM micrographs of the gel decomposed at (a) 300°C, (b) 500°C and (c) the powder calcined at 1000°C.

bic unit cell ($Z=1$), 1/4 of orthorhombic unit cell ($Z=4$), and found to be 4.1120 ± 0.0003 . The unit cell volume (69.53 \AA^3) is slightly larger than a 1/4 of the orthorhombic unit cell volume (276.0^3) of pure SrZrO₃¹⁷⁾ because of the substitution of larger Y³⁺ ion for Zr⁴⁺ ion.

The gel decomposed at 300°C for 2 h contains macroscopic pores which have been formed due to the evolution of large amounts of H₂O and CO₂ gases during the decom-

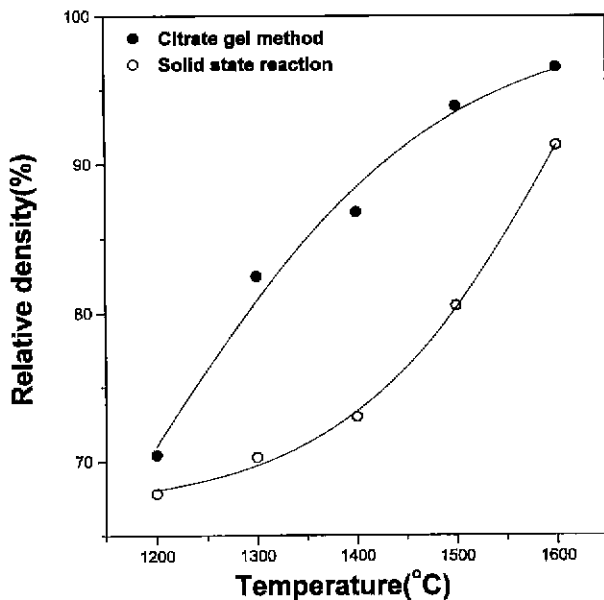


Fig. 6. Relative densities of the sintered samples prepared by citrate gel method and solid state reaction.

position of the citrate, as shown in Fig. 5(a). At 500°C, the particles consist of agglomerated primary particles in sizes smaller than 0.1 μm (Fig. 5(b)). As the decomposition is continued, the macroscopic pores present at 300°C appear to collapse, leaving interagglomerate pores due to the gases evolved during the combustion of intermediate decomposition products. A similar morphological change has been reported in manganite-based perovskite powders.¹³⁾

The powder calcined at 1000°C for 6 h, as shown in Fig. 5(c), reveals the same particle morphology to the powder decomposed at 500°C except that the primary particles have grown. Most particles have irregular shapes because the decomposed gel particles were ground in a mortar and pestle and their shapes were retained after calcination. The calcined powder has an average particle size of 12.3 μm and the particle size was significantly reduced to 1.6 μm after milling. A high macroporosity and weak agglomeration between the particles account for the ease of the size reduction. Apparent density of the calcined powder was 94% of the theoretical density and the composition determined by ICP coincided with that of SrZr_{0.95}Y_{0.05}O_{2.975}.

Relative densities of the sintered samples are presented in Fig. 6, showing that the powder prepared by citrate gel method has better sinterability than the powder prepared by solid state reaction. In the sample prepared by citrate gel method a considerable densification occurs at temperatures above 1200°C and the relative density increases from 70.5% at 1200°C to 82.5% at 1300°C. As the densification continues to higher temperatures, the density reaches

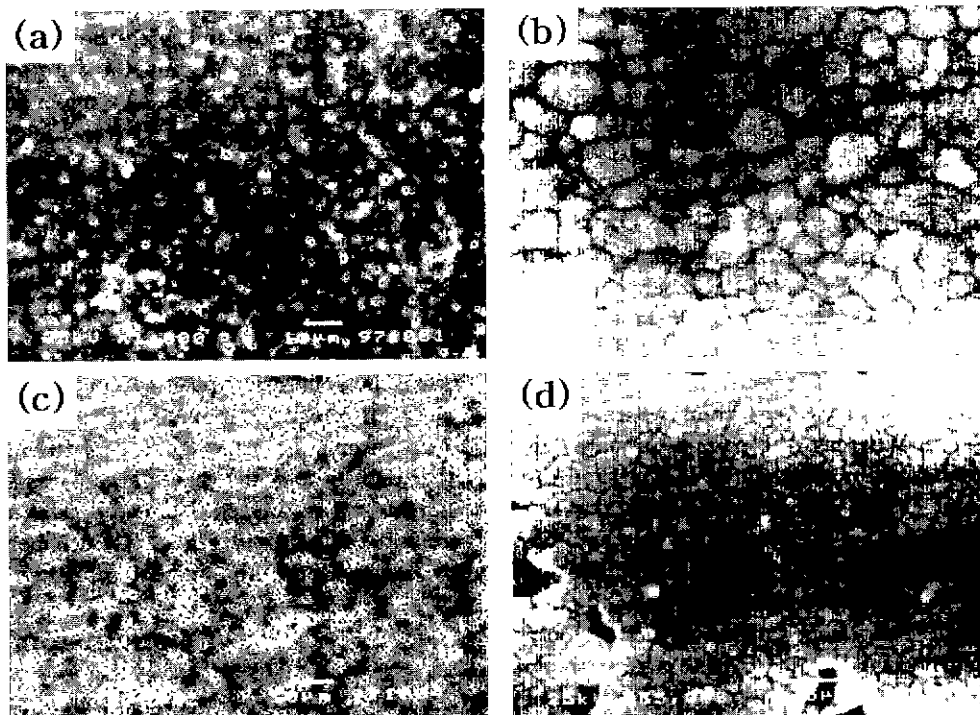


Fig. 7. SEM micrographs of the samples prepared by: (a) and (b) citrate gel method and (c) and (d) solid state reaction (sintered at 1500°C for 6 h).

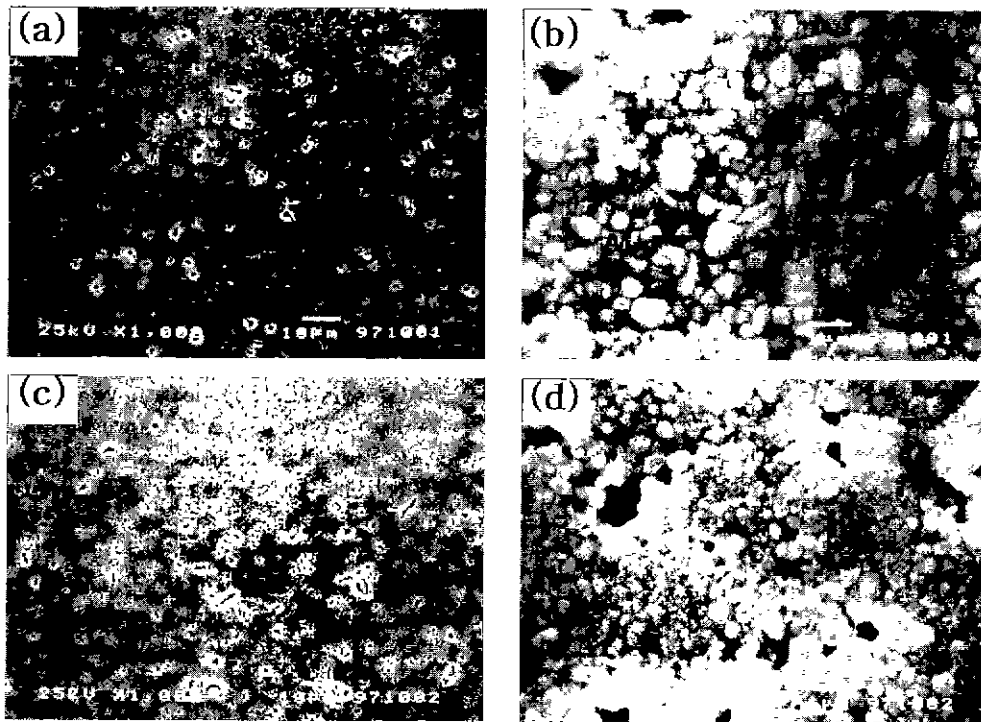


Fig. 8. SEM micrographs of the samples prepared by: (a) and (b) citrate gel method and (c) and (d) solid state reaction (sintered at 1600°C for 6 h).

96.5% at 1600°C. In contrast, the sample prepared by solid state reaction does not show any significant densification up to 1400°C and has much lower relative density (73%) as compared to the sample prepared by citrate gel method (86.8%). After sintering at 1600°C, the sample exhibits only 91.3% of the theoretical density.

It is difficult to make a comparison between the measured densities and reported values since few literature is available for definite density values of doped strontium zirconates. Nevertheless, the densities of both samples prepared in the present study were found to be higher than that of $\text{SrZr}_{0.84}\text{Y}_{0.16}\text{O}_{2.92}$ (64%) sample prepared by solid state reaction and sintering at 1650.⁶⁾ SrZrO_3 and $\text{Sr-Yb}_{0.05}\text{Zr}_{0.95}\text{O}_3$, which were prepared by solid state reaction and sintering at 1600°C and 1680°C, respectively, have been reported to have relative densities over 90%.⁷⁾

Microstructures of the samples sintered at 1500°C are shown in Fig. 7. The sample prepared by citrate gel method exhibits spherical pores and grains with sizes in the range of $\sim 0.5\ \mu\text{m}$. Whereas, the sample prepared by solid state reaction has grain sizes much smaller than the sample prepared by citrate gel method. Large porosity and irregular pore shape in Fig. 7(c) result from the inhomogeneous green microstructure. Strong agglomeration occurs during high temperature calcination for solid state reaction (1300°C) and leads to such a microstructure. Both samples do not clearly reveal grain shapes. In the sample prepared by solid state reaction, the grains consisting of several primary particles suggest that the grain growth occurs by coalescence of the primary particles (Fig. 7(d)).

Fig. 8 shows microstructures of the samples sintered at 1600°C. At this temperature, pore coarsening and grain growth are evident. In the sample prepared by citrate gel method, many grains are in $\sim 1\ \mu\text{m}$ size but grains much smaller than the average size are also present along with a few elongated grains (Fig. 8(b)). Chemical analysis of the calcined powder indicated the presence of liquid forming impurities. Na, Mg and Ca were found to be present as major impurities and Si as a minor impurity. If a small amount of the liquid phase exists, the grains are not completely wet by the liquid. It is believed that, in such a case, clean boundaries having higher mobility than those wet by the liquid move fast and result in elongation of the grains.^{18,19)} Faceted, elongated or platelike Al_2O_3 grains have been observed in Al_2O_3 matrices containing small amounts of liquids.¹⁸⁻²⁰⁾

Pore coarsening is more pronounced in the sample prepared by solid state reaction (Fig. 8(c)). Particularly, the pores in irregular shape, which have been seen in Fig. 7(c), become larger. This arises from the agglomerates that densify fast and leave large pores surrounding them. Large grains formed from the agglomerates are seen around the pores in Fig. 8(d). Such pores are difficult to be removed and thus, impede a further densification.

IV. Conclusion

Y-doped SrZrO_3 powder has been prepared by citrate gel method. Amorphous gel could be obtained from a citric acid solution that SrCO_3 and metal nitrates were dis-

solved. The initial decomposition of the gel proceeded up to 250°C, followed by combustion of its decomposition products in the temperature range from 250°C to 500°C. A well-crystallized perovskite phase appeared at 600°C with a small amount of SrCO₃, which had been formed upon decomposition of the gel. The powder exhibited a single perovskite phase with a stoichiometric composition of SrZr_{0.95}Y_{0.05}O_{2.975} after calcination at 1000°C, that is lower than required for solid state reaction.

The powder prepared by citrate gel method had better sinterability than the powder prepared by solid state reaction. Sintering green compacts of this powder for 6 h showed a considerable densification to start at 1200°C and resulted in 86.8% and 96.5% relative densities at 1400°C and 1600°C, respectively. Whereas, the powder compacts prepared by solid state reaction did not exhibit any significant densification up to 1400°C and had much lower relative densities, 73% at 1400°C and 92% at 1600°C.

Acknowledgments

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