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Preparation of Multicomponent Ceramic Powders by Ultrasonic Spray Pyrolysis

Jeong-Han Youn, Byung-Joo Chung and Soo-Man Sim

School of Materials Science and Engineering, Hong-Ik University, Chochiwon 339-701, Korea
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The preparation of Y-doped $SrZrO_3$ powder by ultrasonic spray pyrolysis was investigated as a representative system, in order to produce fine, single phase multicomponent oxide powders. A precursor solution containing metal nitrates, citric acid and ethylene glycol was atomized with an ultrasonic spray nozzle. Gel particles formed by organic functional groups were pyrolyzed and subsequently calcined at 800°C to obtain well-crystallized, single perovskite phase. Most of large particles exhibited macroscopic pores and weak agglomeration between primary particles. However, strong agglomeration was observed in the surfaces of large particles. The effect of the microstructures of these particles on size reduction to submicron particles was described.

Key words: Ultrasonic spray pyrolysis, Y-doped $SrZrO_3$, Proton conductor, Citrate gel, Agglomeration

I. Introduction

Certain perovskite-type oxides, based on alkaline earth cerates doped with rare earth oxides, exhibit proton conduction in an atmosphere containing hydrogen or water vapor at elevated temperatures.[1-3] Doping of lower valency cations generates oxygen vacancies, which react with hydrogen or water vapor to produce protons that migrate with a relatively low activation energy. Owing to high proton conductivity, high-temperature proton conductors (HPTCs) have many potential applications such as solid oxide fuel cells, gas sensors, and steam electrolyzers for hydrogen production.[1,2]

Despite many efforts to understand conduction mechanisms, less attention has been paid to the synthesis of HTPCs. Most HPTCs are prepared by solid state reaction that carbonates and oxides of the constituents are mixed, followed by high temperature calcination and sintering. Calcination is often carried out at temperatures as high as 1400°C in order to obtain a single perovskite phase. Such heat treatments causes agglomerates to form and particle sizes to increase and make it difficult to achieve a dense and homogeneous microstructure. Recently, chemical methods such as oxalate coprecipitation,[4-6] precipitation of hydroxides,[7] citrate gel method[8] have been used to prepare fine, agglomerate-free powders.

Citrate gel method has been employed to prepare Y-doped $SrZrO_3$ powder.[8] The advantages of this method are tight control of stoichiometry and homogeneous incorporation of low level dopants. A solution containing metal ions was heated to form a gel, which was decomposed and subsequently calcined. In order to obtain well-crystallized, single perovskite phase, calcination had to be carried out at 1000°C. As a result, it was found that the primary particles were severely agglomerated. The strong agglomeration could be attributed to high reactivity of the primary particles and heat released during the combustion of the gel. Combustion synthesis technique utilizes combustion heat and a violent release of gases in order to produce fine, agglomerate-free oxide powders. In that method, metal nitrate as an oxidizer and urea, glycine or some carbohydrates as fuels are used.[9-11] However, an extreme care should be given due to an explosive combustion reaction.

In this paper, the feasibility of producing fine, single-phase powders of multicomponent oxides by ultrasonic spray pyrolysis was investigated. Y-doped $SrZrO_3$ powder with a nominal composition of $SrZr_{0.95}Y_{0.05}O_{2.975}$ was chosen as a representative system. A solution containing metal nitrates, citric acid and ethylene glycol was used as a precursor solution. Formation of the particles with macroscopic porosity and break-up of these particles into submic-ron sizes were described.

II. Experimental Procedure

1. Preparation of precursor solution and powder synthesis

Aqueous solutions of 0.35 M zirconyl nitrate ($ZrO(NO_3)_2 \cdot xH_2O$, 98%, Aldrich) and 0.1 M yttrium nitrate ($Y(NO_3)_3 \cdot 5H_2O$, 99.9%, Aldrich) were prepared as stock solutions. These solutions were mixed with 2 M citric acid ($C_6H_7O_8$, 99.5%, Aldrich) solution in a 1:3 molar ratio of Zr:citric acid and a 1:1 molar ratio of Y:citric acid, respectively. An appropriate amount of $SrCO_3$ (99.5%, Cerac) was dissolved in the Zr and Y citrate solution, which had been mixed in a 0.95:0.05 molar ratio of Zr:Y. As a precursor solution for spray pyrolysis, ethylene glycol (99.5%, Junsei Chemical) was added to the metal citrate solution in a 50:50 volume

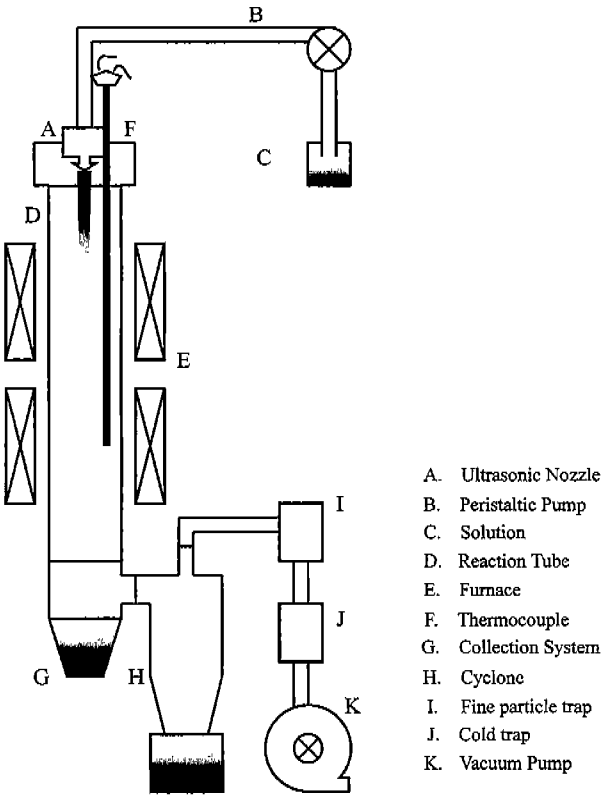

Fig. 1. Schematic diagram of an ultrasonic spray pyrolysis apparatus.

ratio of citric acid:ethylene glycol. The total amount of cations and citric acid was 8.85 mol/L and Sr concentration was 0.5 M. The concentrations of the cations in the precursor solution were determined with an inductively coupled plasma spectrometer and found to coincide with those of $SrZr_{0.95}Y_{0.05}O_{2.975}$.

The powder was prepared using an ultrasonic spray pyrolysis apparatus, as shown in Fig. 1. The precursor solution was continuously fed via a peristaltic pump into an ultrasonic spray nozzle (Sono-Tek Cor.) operating at a frequency of 48 KHz. The median diameter of the liquid droplets generated by the nozzle was estimated to be 38 μm. The droplets were passed through a quartz pyrolysis tube (120 cm long and 6 cm in diameter) in two electrical furnaces held at 500°C and 1000°C, respectively. The resulting powder was collected in a cyclone, dried in a vacuum oven at 120°C for 10 h and kept in a vacuum desiccator. The collected powder had very light grey color.

Calcination was carried out at 800°C for 6 h in air at a heating rate of 5°C/min in order to remove residual carbon and attain a single phase in the as-prepared powder. For particle size reduction, the calcined powder was mixed in isoprophyl alcohol and attrition-milled with zirconia ball (3 mm in diameter) at 450 rpm up to for 6 h.

2. Powder Characterization

Thermal behavior of gel obtained by evaporation of the precursor solution was studied with a simultaneous TG/DTA (TG-DTA2000, MAC Science) at heating rates ranging from 5°C/min to 20°C/min up to 1000°C in air. The powder was calcined at temperatures from 600°C to 1200°C for 2 h and phases were identified by X-ray powder diffractometry (M03XHF, MAC Science) with CuKα radiation. Average crystallite sizes of the as-prepared and the calcined powders were measured using X-ray diffraction line broadening analysis. The crystallite size was determined by the Warren-Averbach method[12] and X-ray diffraction peaks of the powder obtained from a pellet, which had been sintered at 1600°C for 6 h, were used as reference diffraction lines. The crystallite size corresponding to (110) perovskite peak (index based on a pseudo-cubic unit cell) was taken since the peak did not overlap any other phases. The morphology of the particles was examined with SEM (JSM-5410, JEOL). Particle size distribution and apparent density were measured with a laser diffraction particle size analyzer (SALD-2001, Shimadzu) and a He gas pycnometer (Accu-Pyc 1330, Micromeritics), respectively.

III. Results and Discussion

If a solution containing metal nitrates with different solubilities is used in spray pyrolysis, an inhomogeneous precipitation occurs during dehydration and a second phase can result in. However, in this study, citrate functional groups in the precursor solution prevents the precipitation by chelating the metal ions and converting liquid droplets into gel particles. When heated with ethylene glycol, polyesterifica-

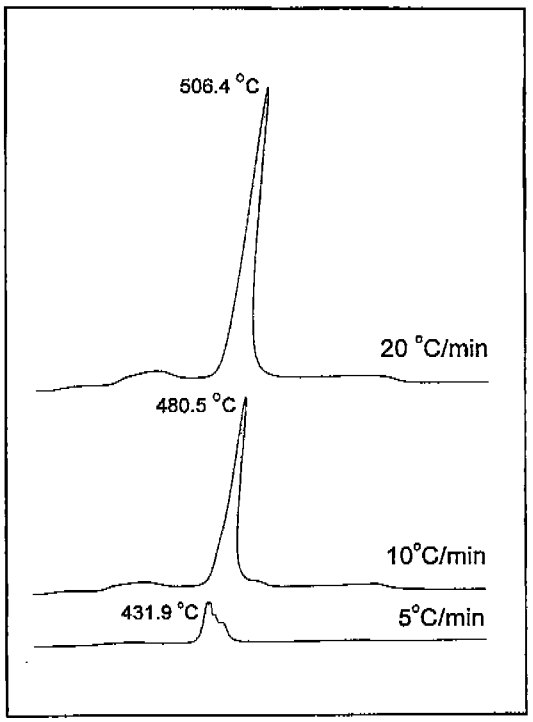

Fig. 2. DTA curves of gels obtained by evaporation of the precursor solution.

tion between citrates and ethylene glycol occurs and gelation is further enhanced.[13] Thus, the uniform distribution of the metal ions in the precursor solution can be maintained throughout pyrolysis. This was confirmed by that the particles obtained at the pyrolysis temperature of 500°C were amorphous and no crystalline phases arising from the precipitation of the metal nitrates were detected.

Thermal decomposition of the gel in air was found to proceed in three major stages, dehydration, decomposition and combustion of the decomposition products.[8] Fig. 2 shows DTA peaks of the gels obtained by evaporating the precursor solution, illustrating the influence of heating rates on exothermicity of the combustion reaction. At a slow heating rate, the combustion reaction occurs in several steps as shown by multiple exothermic peaks at ~432°C. As a heating rate increases, these peaks change into a single peak with increasing peak intensity. The shift of the peak temperature to higher temperature is due to the effect of varying heating rates in the DTA run. Since the gel particles in the pyrolysis tube are heated at a heating rate much greater than in Fig. 2, the combustion reaction is expected to be highly exothermic and occur in a single step at temperature higher than 506°C.

Fig. 3. shows XRD patterns of the powders calcined at various temperatures for 2 h. The as-prepared powder exhibits a perovskite phase with a small amount of $SrCO_3$. $SrCO_3$ is still present at 600°C and disappears at 800°C. As calcination temperature increases to 1200°C, a well-crystallized, single perovskite phase develops as indicated by increasing intensities of the XRD peaks. The presence of $SrCO_3$ is attributed to residual carbon in the particles. Complete decomposition can not take place because of a very short residence time of the particles in the pyrolysis tube, even though the maximum pyrolysis temperature reaches 1000°C. Ba or Sr carbonates have been reported to inevitably form in Ba- or Sr-based perovskite[14-16] and superconducting powders.[11] It seems that the combustion heat evolved from the gel particles is not sufficient to decompose $SrCO_3$ completely.

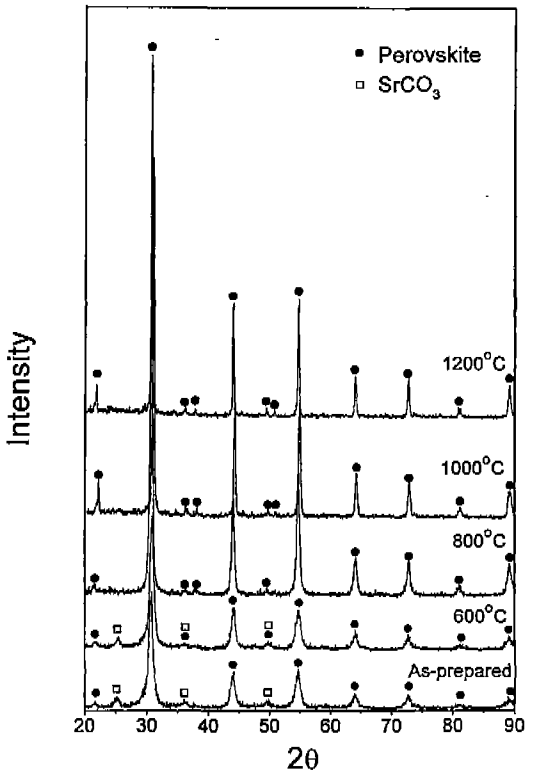

Fig. 3. XRD patterns of powders calcined at various temperatures for 2 h.

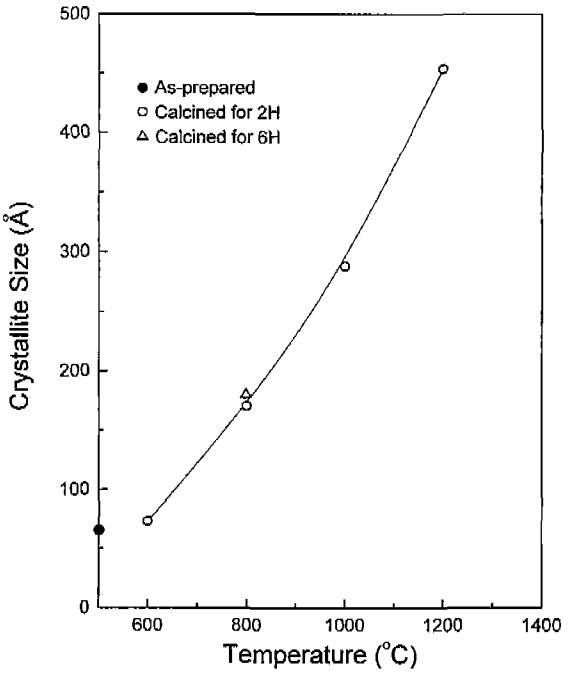

Fig. 4. Average crystallite sizes of powders calcined at various temperatures.

Multicomponent oxide powders prepared by spray pyrolysis have to be calcined to remove residual carbon and form a single phase. However, high calcination temperature results in an increase in crystallite size and strong agglomeration of primary particles. A rapid growth of the crystallites with increasing the calcination temperature is shown in Fig. 4. The crystallite size increased from 67 Å for the as-prepared powder to 454 Å for the powder calcined at 1200°C, indicating that the powder is very reactive. On the other hand, the crystallite size of powder calcined at 800°C little changed after 6 h due to a slow solid state reaction. This suggests that the calcination should be carried out at temperature of at least 800°C for not only removing residual carbon and attaining a single phase but also minimizing the crystallite growth.

The as-prepared powder has a variety of particle morphologies as shown in Fig. 5(a). The same morphologies as in Fig. 5(a) are observed in the powder calcined for 6 h due to low calcination temperature (Fig. 5(c)). Both powders consist of small solid spherical particles, particle frag-

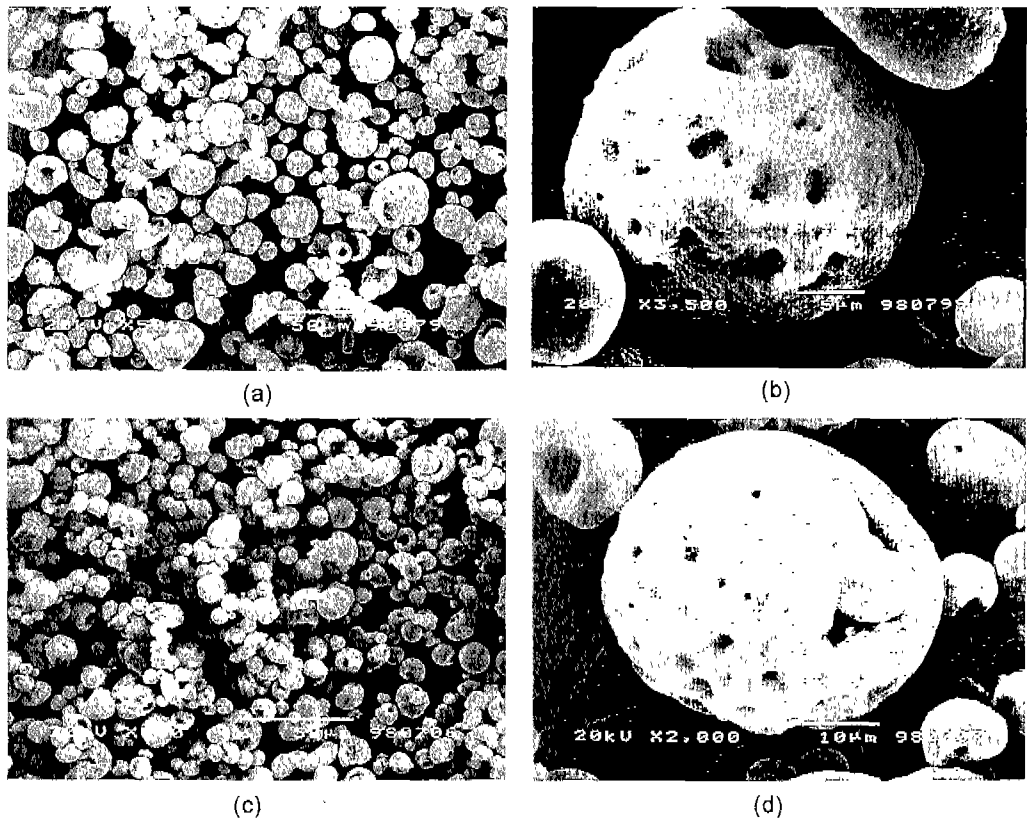

Fig. 5. Particle morphologies of (a) and (b) as-prepared powders and (c) and (d) powder calcined at 800°C for 6 h.

ments, irregular particles, and large particles with open, macroscopic surface pores. The particle fragments are formed by an abrupt evolution of the gases. The liquid droplets passing the pyrolysis tube in a large temperature gradient undergo very rapid gelation and decomposition which occur first in the surface of the particle and result in a dense surface layer. These particles can be fractured when internal gas pressure is build up inside the particles where no pore channels for the release of the gases exist.[17] Macroscopic pores in Figs. 5 (b) and (d) can be attributed to the evolution of large amounts of the gases, such as H_2O and CO_2, during decomposition.[17] It is anticipated that a foamy structure of the particle with a macroscopic porosity can be easily broken.

Fig. 6 shows the particle size distributions of the as-prepared powder and the calcined powder. The as-prepared

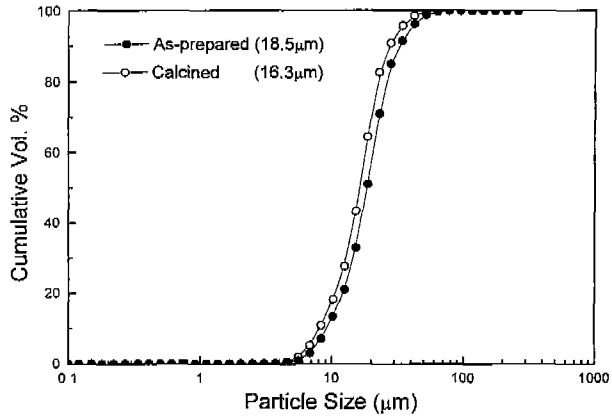

Fig. 6. Particle size distributions of (a) as-prepared powder and (b) calcined powder at 800°C for 6 h.

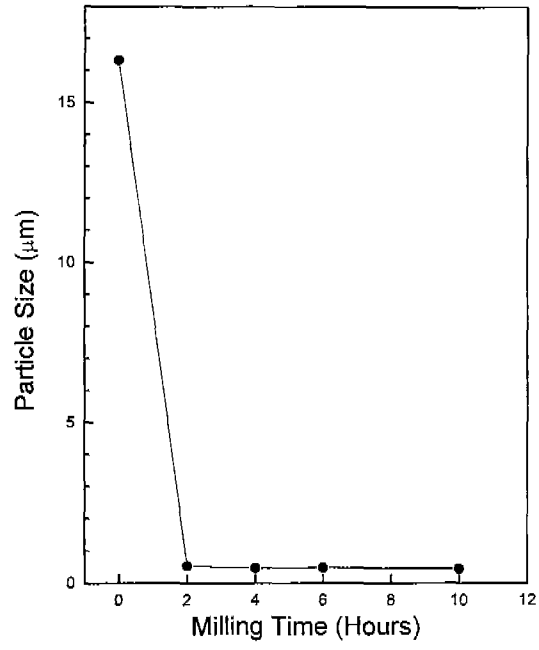

Fig. 7. Particle sizes of powders as a function of milling time.

powder was found to have an average particle size of 18.5 μm and a size range from ~4 μm to ~94 μm. The calcined powder had an average particle size of 16.3 μm, suggesting a slight shrinkage during the calcination. Concurrently, the apparent density of the as-prepared powder was appreciably increased from 81.6% (4.41 g/cm^3) to 95.4% (5.15 g/cm^3) of the theoretical density (5.40 g/cm^3) after calcination. The particle shrinkage and the density increase indicate that a little sintering occurred during calcination and resulted in some agglomeration between primary particles with a corresponding decrease in closed porosity.

Fig. 7 shows average particle sizes of the powder calcined for 6 h as a function of attrition-milling time. A significant particle size reduction from 16.3 μm to 0.53 μm after 2 h milling supports that the particles having a macroporosity and weakly agglomerated primary particles can be milled into submicron size. However, milling for up to 10 h exhibited little change in the particle size. Fig. 8 is the particle size distribution of the powder milled for 6 h, showing a bimodal distribution with an average size of 0.48 μm. The powder contained ~85% of particles smaller than ~2 μm and ~15% of large particles with size ranging from ~2 μm to ~10.5 μm.

The effect of particle microstructure on the size reduction is clearly shown in Fig. 9(a) for the powder milled for 6 h. As compared with Fig. 5, the milled powder does not have any of morphologies of the calcined particles but reveals two distinct particle morphologies. Most particles are sub-

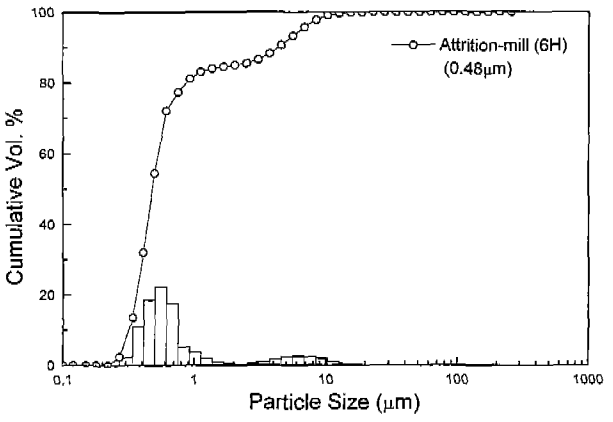

Fig. 8. Particle size distribution of powder attrition-milled for 6 h.

micron-sized particles, in which several primary particles in size smaller than ~0.1 μm are agglomerated (Fig. 9(b)). The flaky particles in size ranges over ~2 μm, as shown in Fig. 9(c), are the surfaces of the large particles that have been fractured during milling. This suggests that the primary particles inside the large particle are weakly agglomerated, whereas the primary particles in the surface region of the large particle are strongly agglomerated. The strong agglomeration is seen in the surface of the flaky particle, which is the inner part of the large particle (Fig. 9(d)). The surface of the particle appears more dense than the inte-

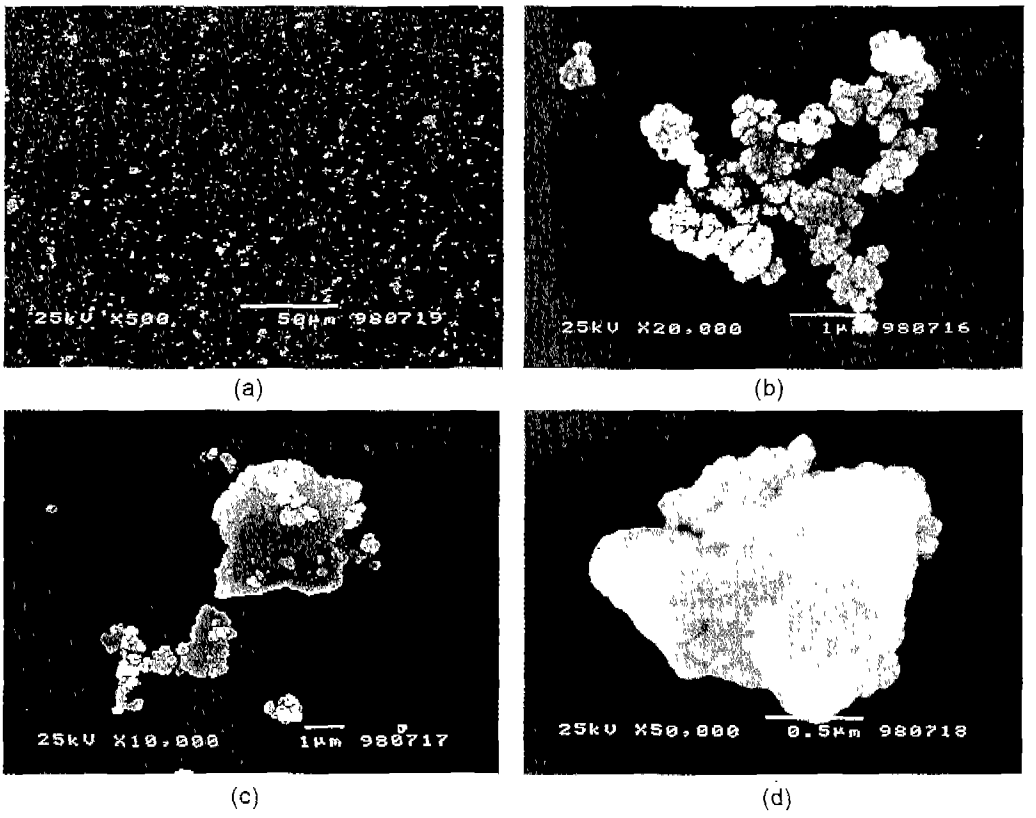

Fig. 9. Particle morphology of powder attrition-milled for 6 h.

rior, because the surface of the particle is sintered faster than the interior when the particles are subjected to heating at a maximum temperature (1000°C) in the pyrolysis tube. Therefore, the strongly agglomerated flaky particles persist during milling and make a further size reduction difficult. This gives rise to the bimodal size distribution.

IV. Summary

In order to produce fine, single phase powder of multicomponent oxide, the preparation of Y-doped $SrZrO_3$ powder was investigated as a representative system. The ultrasonic spray pyrolysis technique employed using the solution containing the metal nitrates, citric acid and ethylene glycol indicates that the production of submicron-sized particles is feasible.

Well-crystallized, single perovskite phase was obtained by pyrolysis of the gel particles formed by organic functional groups and subsequent calcination at 800°C. Most of the calcined particles having macroscopic pores and weakly agglomerated primary particles could be easily broken into submicron sizes. However, the strong agglomeration in the surfaces of the large particles occurred during the pyrolysis and prevented a particle size reduction to submicron size. For a further size reduction, the processing conditions such as pyrolysis and calcination temperatures have to be optimized to minimize the strong agglomeration in the particle surface and obtain a single phase.

Acknowledgments

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