Preparation of Dense $\text{Ba}_{1-x}\text{Sr}_x\text{Zr}_{1-y}\text{Y}_y\text{O}_{3-δ}$ ($y = 0.0, 0.1$) Ceramics by Pechini Method

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ABSTRACT

$\text{Ba}_{1-x}\text{Sr}_x\text{Zr}_y\text{O}_9$, which is the mother phase of proton-conducting $\text{Ba}_{1-x}\text{Sr}_x\text{Zr}_{0.9}\text{Y}_{0.1}\text{O}_{3-δ}$, is prepared by the Pechini method at a sintering temperature of 1500°C. For specimens with $x \geq 0.4$, the sintering densities of the samples prepared by the Pechini method are approximately 90%, whereas those of the samples prepared by the solid-state reaction method are approximately 78%. Although the difference in the mean grain size was small, clear facets are observed around the grains of the $\text{Ba}_6\text{Sr}_{0.4}\text{Zr}_0\text{O}_9$ ceramic prepared by the Pechini method and grain size distribution is less than that of the $\text{Ba}_6\text{Sr}_{0.4}\text{Zr}_0\text{O}_9$ ceramics prepared by the solid-state reaction method. The smaller grain size distribution is attributed to the formation of a $\text{Ba}_6\text{Sr}_{0.4}\text{Zr}_0\text{O}_9$ phase with smaller grains upon calcination at a temperature as low as 800°C by the Pechini method due to the homogeneous cation distribution in the precursor. Not only a decrease in the number of pores but also an increase in the grain size is observed with increasing Sr content in $\text{Ba}_{1-x}\text{Sr}_x\text{Zr}_{0.9}\text{Y}_{0.1}\text{O}_{3-δ}$, resulting in a sintering density as high as 92% for $\text{Ba}_6\text{Sr}_{0.4}\text{Zr}_0\text{O}_{3-δ}$.

Keywords : $\text{Ba}_{1-x}\text{Sr}_x\text{Zr}_y\text{O}_9$, $\text{Ba}_{1-x}\text{Sr}_x\text{Zr}_{0.9}\text{Y}_{0.1}\text{O}_{3-δ}$, Sinterability, Pechini Method

1. Introduction

Materials that act as an ionic conductor between 600°C and 800°C are required for the fabrication of intermediate-temperature solid oxide fuel cells (IT-SOFCs). Candidate materials include proton-conducting perovskite-type oxides such as $\text{Ba}_x\text{Zr}_{1-x}\text{M}_y\text{O}_{3+δ}$, $\text{Sr}_x\text{Zr}_{1-x}\text{M}_y\text{O}_{3+δ}$, $\text{BaCe}_{1-x}\text{M}_y\text{O}_{3+δ}$ and $\text{SrCe}_{1-x}\text{M}_y\text{O}_{3+δ}$, where M is a trivalent cation. Among them, $\text{BaZr}_{1-x}\text{M}_y\text{O}_{3+δ}$ has attracted considerable interest since it exhibits not only high proton conductivity but also higher chemical stability against CO2 than $\text{BaCe}_{1-x}\text{M}_y\text{O}_{3+δ}$ and $\text{SrCe}_{1-x}\text{M}_y\text{O}_{3+δ}$. In addition, a cubic crystal structure is maintained in $\text{BaZr}_{1-x}\text{M}_y\text{O}_{3+δ}$ between room temperature and 800°C, increasing its mechanical stability. However, the poor sinterability of $\text{BaZr}_{1-x}\text{M}_y\text{O}_{3+δ}$ is a severe problem in its application as an electrolyte of IT-SOFCs. It was reported that a sintering temperature as high as 1800°C is necessary to prepare dense $\text{BaZr}_{1-x}\text{Y}_{1-δ}\text{O}_{3+δ}$ ceramics with sufficient density. Since the vapor pressure of Ba is high at such a high temperature, it is possible that the cation composition of the specimen deviated from the stoichiometry and that the properties of the material were affected. To suppress Ba volatilization, the sintering of $\text{BaZr}_{1-x}\text{Y}_{1-δ}\text{O}_{3+δ}$ pellets buried in a powder composed of $\text{BaCO}_3$ and $\text{BaZr}_{1-x}\text{Y}_{1-δ}\text{O}_{3+δ}$ was examined. However, Ba volatilization cannot be completely prevented by sintering at such a high temperature. To prepare materials with sufficient density for use as electrolyte materials and a well-controlled cation composition, it is necessary to decrease the sintering temperature. Also, to reduce the energy required for a preparation, a low-temperature sintering process is required.

To reduce the sintering temperature to about 1500°C, we regarded the following two types of method as promising. One is preparation by a solution-mixing process, the so-called Pechini method. Using the Pechini method, smaller particles with a more homogeneous cation distribution and improved sinterability can be obtained compared with the solid-state reaction method. So far, the preparation of $\text{BaZr}_{1-x}\text{Y}_{1-δ}\text{O}_{3+δ}$ by solution-mixing methods, such as the oxalate method, citrate method and Pechini method, has been reported. However, there has been no report on the sinterability of specimens prepared by these methods. The other promising method is the partial substitution of Sr for Ba sites. Since $\text{SrZr}_{1-x}\text{Y}_{1-δ}\text{O}_{3+δ}$ shows superior sinterability to $\text{BaZr}_{1-x}\text{Y}_{1-δ}\text{O}_{3+δ}$, we expected that $\text{Ba}_{1-x}\text{Sr}_x\text{Zr}_{1-y}\text{Y}_y\text{O}_{3-δ}$ would possess higher sinterability. On this basis, we prepared a $\text{Ba}_6\text{Sr}_{0.4}\text{Zr}_0\text{Y}_{0.1}\text{O}_{3-δ}$ ceramic specimen at a sintering temperature of 1500°C by the Pechini method. The prepared specimen had a sintering density of approximately 92% with no first-order structural phase transition between room temperature and 600°C. It was observed that the electrical conductivity of $\text{Ba}_6\text{Sr}_{0.4}\text{Zr}_0\text{Y}_{0.1}\text{O}_{3-δ}$ was higher than that of $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-δ}$ prepared at a sintering temperature of about 1500°C, indicating the high potential of $\text{Ba}_6\text{Sr}_{0.4}\text{Zr}_0\text{Y}_{0.1}\text{O}_{3-δ}$ as a new electrolyte.

For the development of superior materials, the origin of the high sinterability of $\text{Ba}_6\text{Sr}_{0.4}\text{Zr}_0\text{Y}_{0.1}\text{O}_{3-δ}$ prepared by the Pechini method should be clarified. The employment of the Pechini method and partial Sr substitution are probable origins. In this study, as the first step toward elucidating the origin, various $\text{Ba}_{1-x}\text{Sr}_x\text{Zr}_y\text{O}_9$ specimens have been prepared by the solid-state reaction method and Pechini method. The density, morphology, structural phase transition behavior and electrical conductivity of the specimens prepared by both methods have been compared. The effect of partial Sr substitution on these properties has also been investigated for each preparation method. Preliminary results for the effect of Sr substitution on the sintering density of $\text{Ba}_{1-x}\text{Sr}_x\text{Zr}_{0.9}\text{Y}_{0.1}\text{O}_{3-δ}$ have also been obtained.

2. Experimental

Ceramic $\text{Ba}_{1-x}\text{Sr}_x\text{Zr}_y\text{O}_9$ specimens were prepared either by the solid-state reaction method or the Pechini method. For the solid-state reaction method, $\text{BaCO}_3$ (99.9%, Furuuchi Chem. Corp.), $\text{SrCO}_3$ (99.9%, Furuuchi Chem. Corp.) and $\text{ZrO}_2$ (99.9%, Furuuchi Chem. Corp.) powders were employed as source materials. Prior to mixing, $\text{BaCO}_3$ and $\text{SrCO}_3$ were dried at 150°C for more than 12 h. They
were a mixed in a stoichiometric ratio using a planetary-type ball mill made of yttria-stabilized zirconia. The obtained mixed powder was pressed into pellets with 20 mm diameter and 5 mm thickness or cylinders with 5 mm diameter and 15 mm height. The pressed samples were heated at 1300°C for 10 h, which was followed by heat treatment at 1500°C for 10 h in air.

For the Pechini method, dried BaCO₃, dried SrCO₃ and ZrOCl₂·8H₂O (99.9%, Wako Pure Chemical Industry, Ltd.) were used as source materials. The purity of ZrOCl₂·8H₂O was calibrated by the weight of ZrO₂ prepared by heating the ZrOCl₂·8H₂O used as source materials. The purity of ZrOCl₂·8H₂O was calibrated by the weight of ZrO₂ prepared by heating the ZrOCl₂·8H₂O specimen in a Pt crucible at 1000°C in air. BaCO₃, SrCO₃ and ZrOCl₂·8H₂O (99.9% to 1300°C for 10 h, followed by heating at 1500°C for 10 h in air.

The obtained powder was pressed into pellets or cylinders with the same dimensions as above. The pellets and cylinders were subjected to heat treatment at 1300°C for 10 h, followed by heating at 1500°C for 10 h in air.

Ceramic BaₓSrₓZrO₃ (0.0 ≤ x ≤ 1.0) specimens were prepared by the Pechini method. Y₂O₃ (99.9%, Furuchi Chem. Corp.) was used as an additional source material and dissolved in a mixture of dilute HNO₃ and H₂O. After mixing the solutions, citric acid and ethylene glycol were added. The mixed solution was heated to above 300°C and burned to form a resin. The resin was calcined at 800°C in air, resulting in a powder. The obtained powder was pressed into pellets or cylinders with the same dimensions as above. The pellets and cylinders were subjected to heat treatment at 1300°C for 10 h, followed by heating at 1500°C for 10 h in air.

X-ray diffraction (XRD) measurements (CuKα, 50 kV, 250 mA; RINT-2500, Rigaku Co., Ltd.) were carried out to distinguish whether or not the prepared specimens were single-phase. Also, the crystal structure, lattice constant, molar volume and ideal density were evaluated by XRD measurements. The sintering densities of the specimens were calculated by dividing the apparent density of a pellet by the ideal density obtained by XRD measurements to clarify the sinterability of the powders prepared by the Pechini method and solid-state reaction method. The sinterability was evaluated also from the morphology of the prepared specimens observed by scanning electron microscopy (SEM; JCM-5700, JEOL Co., Ltd.).

To clarify the differences between the preparation and sintering mechanism of the two methods, the crystal structure, cation distribution and particle size distribution of the as-mixed and as calcined samples were evaluated by XRD measurements, SEM and energy dispersive X-ray spectroscopy (EDX) measurements (JED-2300; JEOL Co., Ltd.) and laser beam deflection analysis (SALD-3100S; SHIMADZU Co., Ltd.), respectively.

The structural phase transition behavior and thermal expansion of the sintered specimens were measured by dilatometry using a TMA8310 dilatometer (Rigaku Co., Ltd.). SiO₂ was used as a reference material for the sample stage and push rod. The electrical conductivity of the prepared specimens in the temperature range of 300–700°C was measured by the dc four-probe method. Pt wire wound around the specimens and fixed with Pt paste was employed as the electrode. The measurements were carried out in N₂ humidified with saturated water vapor pressure at 18°C (20.65 hPa). The oxygen partial pressure during the measurements was monitored by a zirconia O₂ sensor set downstream of the apparatus.

3. Results and Discussion

3.1 Sinterability of BaₓSrₓZrO₃ prepared by Pechini method and solid-state reaction method

Figure 1 shows XRD patterns of BaₓSrₓZrO₃ prepared by the (a) solid-state reaction and (b) Pechini method. Irrespective of the preparation method, all the XRD peaks of the specimens with...
x = 0.0, x = 0.2–0.4, x = 0.5 and x = 0.6–1.0 can be indexed as cubic (Pm3n), tetragonal (I4/mcm), body-centered orthorhombic (Ihnn) and primitive orthorhombic (Pbnn), respectively. Their difference can mainly be explained by tilt and rotation of [ZrO₆] octahedra and their crystallographic data are presented by Kennedy and coworkers and Howard and coworkers. Figure 2 shows the molar volume of Ba₁₋ₓSrₓZrO₃ at room temperature. The almost linear decrease in the molar volume with increasing Sr content indicates the successful substitution of Sr at Ba sites in single-phase Ba₁₋ₓSrₓZrO₃ after heat treatment at 1500°C in both the Pechini method and solid-state reaction method.

Although the same polycrystalline Ba₁₋ₓSrₓZrO₃ is obtained by both methods, a large difference is observed in the sinterability. Figure 3 shows the sintering density of Ba₁₋ₓSrₓZrO₃ ceramics prepared by the Pechini method and solid-state reaction method. An almost constant sintering density of approximately 77% is observed for the specimens prepared by the solid-state reaction method irrespective of the Sr content. The specimens with x ≤ 0.2 prepared by the Pechini method have almost the same sintering density as those prepared by the solid-state reaction method; however, an improvement in the sintering density to approximately 90% is observed for the specimens with x ≥ 0.4 prepared by the Pechini process.

3.2 Phase transition behavior and electrical conductivity of Ba₀.₆Sr₀.₄ZrO₃ ceramics prepared by Pechini method and solid-state reaction method

For the specimens with x ≥ 0.4, the sinterability is improved by employing the Pechini method as the preparation process. For their application as electrolyte materials, not only high sinterability but also high electrical conductivity is necessary. Information on the phase transition behavior of these specimens is also necessary before their application. Therefore, the electrical conductivity and phase transition behavior of Ba₀.₆Sr₀.₄Zr₀.₉Y₀.₁O₃ prepared by the Pechini method and solid-state reaction method were evaluated and their differences were investigated. In this section, we only consider the specimens with x = 0.4 because it has been reported that Ba₀.₆Sr₀.₄Zr₀.₉Y₀.₁O₃ shows the highest electrical conductivity among ceramics with the formula Ba₁₋ₓSrₓZr₀.₉Y₀.₁O₃.

Figure 4 shows the temperature dependence of the electrical conductivity of Ba₀.₆Sr₀.₄Zr₃O₇ ceramics prepared by the Pechini method and solid-state reaction method in wet N₂ (partial pressure of H₂O: 20.65 hPa). Almost identical dependence of electrical conductivity on temperature is observed regardless of the preparation method. The small difference of logσ in spite of large difference of sinterability by preparation method may be ascribed to lower logσ in the grain due to absence of oxide ion vacancy than those between the grains. Figure 5 shows the temperature dependence of electrical conductivity originating from the second-order structural phase transition from the tetragonal structure to the cubic structure is observed in both specimens. Almost the same thermal expansion coefficient is observed for the specimens prepared by both methods. It can be concluded that there is no difference between the electrical conductivity and thermal expansion behavior of the specimens prepared by both methods, and only a difference is observed in the sinterability as shown in Fig. 3.

3.3 Preparation and sintering mechanism of solid-state reaction process and Pechini process

Figure 6 shows SEM images of fractured Ba₀.₆Sr₀.₄Zr₃O₇ ceramics prepared by (a) the solid-state reaction method and (b) the Pechini method. The mean grain size of the specimens prepared by
the solid-state reaction method is as large as \( \sim 1 \mu m \), which is almost the same as that of the specimens prepared by the Pechini method. However, the distribution of the grain size of the sample prepared by the solid-state reaction method is clearly larger than that of the sample prepared by the Pechini method, resulting in pore formation and lower sintering density. In the SEM image of the specimen prepared by the Pechini method, a facet is observed outside the grains, indicating the progress of uniform crystal growth during sintering at 1300°C and 1500°C, which can also be ascribed to the higher density of the specimens prepared by the Pechini method.

To clarify the origin of the difference in the sintering behavior of the specimens prepared by the solid-state reaction method and Pechini method, the particle size and cation distribution prior to sintering were analyzed using a laser beam particle size analyzer and by SEM-EDX. Figure 7 shows the particle size distribution of (a) the mixture of BaCO\(_3\), SrCO\(_3\) and ZrO\(_2\) powders and (b) the powder obtained by heating the resin at 800°C in the Pechini method. It has been revealed that the mean particle size of the mixture of BaCO\(_3\), SrCO\(_3\) and ZrO\(_2\) powders is of µm order, whereas that obtained by heat treatment of the resin at 800°C in the Pechini method is of 10 µm order. Figure 8 shows the distribution of the cation composition in (a) the mixture of BaCO\(_3\), SrCO\(_3\) and ZrO\(_2\) before heat treatment, (b) the mixture after heating at 800°C in air, (c) the resin obtained by heating the mixed solution at approximately 350°C in the Pechini method and (d) the specimen obtained by calcination of the resin at 800°C in the Pechini method observed by SEM-EDX. In the specimen depicted in Fig. 8(a), an inhomogeneous distribution of Ba, Sr and Zr particles with a size of µm order is clearly observed, in accordance with the particle size distribution detected using the laser particle size analyzer. An inhomogeneous distribution was also observed after heat treatment at 800°C as shown in Fig. 8(b). For the Pechini method, particles with diameter of 10 µm order are mainly observed, consistent with the results shown in Fig. 7. Although the mean particle size obtained by the Pechini method is larger than that obtained by the solid-state reaction method, the color of EDX images depicted in Figs. 8(c) and 8(d) is homogeneous, i.e., the cation distribution in the particles is more homogeneous in the ceramics obtained by the Pechini method.

Owing to the higher cation homogeneity, it can be expected that the Ba\(_{0.6}\)Sr\(_{0.4}\)ZrO\(_3\) perovskite phase can be prepared at a lower temperature by the Pechini method than by the solid-state reaction method. Figure 9 shows XRD patterns of (a) the as-mixed powder of BaCO\(_3\), SrCO\(_3\) and ZrO\(_2\) and (b) the powder after heat treatment of (a) at 800°C. In Fig. 9(a), all the peaks are identified as either BaCO\(_3\), SrCO\(_3\) or ZrO\(_2\). After heat treatment, a trace peak identified...
as the main peak of \( \text{Ba}_{0.6}\text{Sr}_{0.4}\text{ZrO}_3 \) perovskite is observed; however, almost all the peaks can be identified as the raw materials or an unknown phase. XRD patterns of the resin obtained by the Pechini method and the powder after heating the resin at 800°C are shown in Figs. 10(a) and 10(b), respectively. It has been observed that the structure of the resin is amorphous and that single-phase \( \text{Ba}_{0.6}\text{Sr}_{0.4}\text{ZrO}_3 \) perovskite is obtained even at the low heating temperature of 800°C. The large full width at half maximum of the XRD peak indicates that the crystal size of the perovskite phase is small.

Therefore, it can be concluded that preparation involving cation diffusion between the particles with different sizes and the crystal growth of perovskite \( \text{Ba}_{0.6}\text{Sr}_{0.4}\text{ZrO}_3 \) simultaneously occur during sintering at 1300°C and 1500°C in the solid-state reaction method, which can be attributed to the inhomogeneous grain size in the sintered specimens. In contrast, only homogeneous crystal growth from small grains is considered to occur during sintering at 1300°C and 1500°C in the Pechini method, resulting in a homogeneous grain size and high sintering density.

3.4 Effect of Sr substitution on sintering behavior of \( \text{Ba}_{1-x}\text{Sr}_x\text{ZrO}_3 \) and \( \text{Ba}_{1-x}\text{Sr}_x\text{Zr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta} \)

Since it has been revealed that the Pechini method is suitable for the preparation of dense \( \text{Ba}_{1-x}\text{Sr}_x\text{ZrO}_3 \), the effect of Sr substitution on the sinterability has been investigated using the specimens prepared by the Pechini method. As already shown in Fig. 3, the sinterability of \( \text{Ba}_{1-x}\text{Sr}_x\text{ZrO}_3 \) with \( x \geq 0.3 \) is much higher than that of specimens with \( x \leq 0.2 \). Figure 11 shows SEM images of the fractured surfaces of \( \text{Ba}_{1-x}\text{Sr}_x\text{ZrO}_3 \) specimens prepared by the Pechini method. Irrespective of the Sr content, little difference is observed in the grain size of \( \text{Ba}_{1-x}\text{Sr}_x\text{ZrO}_3 \). The number of pores decreases when the Sr content is increased to 0.4 or more, resulting in a high sintering density. Figure 12 shows SEM images of the fractured surfaces of \( \text{Ba}_{1-x}\text{Sr}_x\text{Zr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta} \) specimens prepared by the Pechini method. A difference in the grain size with the Sr content is clearly observed. The grain size of \( \text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta} \) is about 0.25 µm and a number of pores is observed. The grain size increases with increasing Sr content, indicating the enhancement of grain growth by Sr substitution. Facets are clearly observed in the grains of the specimens with \( x = 0.4 \), 0.6 and 1.0, also indicating promotion of grain growth by Sr substitution, resulting in the high sintering density of \( \text{Ba}_{1-x}\text{Sr}_x\text{Zr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta} \) with \( x \geq 0.4 \).
4. Conclusions

The sintering density of Ba$_{1-x}$Sr$_x$ZrO$_3$ with $x \geq 0.4$ is improved from $\sim 77\%$ to $\sim 90\%$ by changing the preparation method from the solid-state reaction method to the Pechini method. No difference is observed between the electrical conductivity nor thermal expansion behavior of the specimens prepared by the Pechini method and solid-state reaction method. It has been observed that polycrystalline Ba$_{0.6}$Sr$_{0.4}$ZrO$_3$ prepared by the Pechini method is composed of grains with clear facets and a more homogeneous size than those obtained by the solid-state reaction method. It has been revealed that single-crystal perovskite with a small grain size is formed by even low-temperature heat treatment at 800°C by the Pechini method. This may originate from the homogeneous cation distribution in the amorphous resin and is ascribed to the preparation of the dense Ba$_{0.6}$Sr$_{0.4}$ZrO$_3$ ceramic with a homogeneous grain size. The partial substitution of Sr at the Ba sites is effective for enhancing the grain growth of Ba$_{1-x}$Sr$_x$Zr$_{0.9}$Y$_{0.1}$O$_{3-\delta}$ prepared by the Pechini method. The grain size of Ba$_{0.6}$Sr$_{0.4}$Zr$_{0.9}$Y$_{0.1}$O$_{3-\delta}$ is about twice that of BaZr$_{0.9}$Y$_{0.1}$O$_{3-\delta}$ resulting in increase in sintering density from 64.5% to 92.4%.

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