The Effects of Dopants and A:B Site Nonstoichiometry on Properties of Perovskite-Type Proton Conductors

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ABSTRACT

Investigations of perovskite-type BaCeO₃ and SrCeO₃ with various dopants (Y, Gd, Nd, and Ni) indicate that their microstructures and electrical properties are strongly influenced by the type and amount of dopants. Grain growth and densification of sintered samples are influenced by dopant level and A:B site nonstoichiometry. The conductivity of BaCe_{1-x}Y_xO_{3-δ} increases with the yttrium content in hydrogen and wet Ar, and exhibits a maximum in oxygen at an yttrium content of 10 to 20%. BaCe_{0.8}Y_{0.2}O_{3-δ} has the highest conductivity in a hydrogen atmosphere: $\sim 1.54 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ at 600°C, and $\sim 4.16 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ at 800°C. The effect of BaO excess depends on the concentration of dopant. Compared with BaCe_{0.95}Y_{0.05}O_{3-δ}, doped BaCeO₃ with BaO excess (BaO·0.90CeO₂·0.025Y₂O₃) has a higher total conductivity in all atmospheres studied (O₂, H₂, and wet Ar), whereas the conductivity of BaCeO₃ with excess BaO (BaO·0.85CeO₂·0.05Y₂O₃) is lower than that of BaCe_{0.9}Y_{0.1}O_{3-δ}. BaCeO₃ based materials have higher conductivities than those of SrCeO₃ based materials, whereas SrCeO₃ based materials show higher proton transference numbers.

Introduction

Mixed ionic electronic conductors (MIECs) are used in many solid-state electrochemical systems such as solid oxide fuel cells (SOFCs), solid-state gas sensors, and membranes for gas separation.^{1,2} Two well-known MIECs are the partially substituted perovskite-type oxides BaCeO₃ and SrCeO₃, in which substitution for Ce by trivalent cations causes the formation of oxygen vacancies and other charged defects and gives rise to mixed conduction in atmospheres containing O₂, H₂, and H₂O vapor. Because much of the charge transport in BaCeO₃ and SrCeO₃ is by protons, these materials are being investigated as possible hydrogen separation membranes. To be suitable for hydrogen separation, a material must have a high selectivity for hydrogen, so its proton transference number must be much higher than its transference number for oxygen ion conduction. To be useful in a nongalvanic mode, the transference number for electronic conduction should be comparable to that for protonic conduction, and the protonic and electronic conductivities should be sufficiently high ($> \sim 5 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$). In addition, the materials must exhibit high catalytic activity for the dissociation and recombination of hydrogen at the gas/solid interfaces.

Transport properties of perovskites are strongly influenced by the ionic radii of dopants. Kilner and Brook³ used lattice simulation techniques to model ionic conduction in perovskites and concluded that the overall activation energy for conduction should be minimal when the host and dopant cations have similar ionic radii. Based on this criterion, Bonanos et al. suggested that Gd would maximize the conductivity of BaCeO₃.⁴ In fact, BaCe_{0.8}Gd_{0.2}O_{3-δ} has been widely studied for SOFCs because of its high conductivity in O₂-containing atmospheres and under fuel cell conditions.⁴⁻⁶ Iwahara et al.⁷ studied the mixed conduction of Yb-, Y-, Dy-, Gd-, Sm-, and Nd-doped BaCeO₃, and reported that the proton transference number decreased while the oxygen ion transference number increased with increasing dopant ionic radius. They reasoned that dopants with large ionic radii made oxygen ion conduction more favorable by enlarging the spacing along the *a* axis.

In atmospheres containing water vapor, protons can be formed through the reaction

Liu and Nowick found that Nd-doped BaCeO₃ was a very good proton conductor when exposed to a water vapor-containing atmosphere⁸ but that Eu-, Yb-, and Gd-doped BaCeO₃ were not.⁹ Proton conduction in moist atmospheres was also studied by Slade and Singh, who showed that Gd-doped BaCeO₃ had the highest conductivity

among compounds doped with Y, Gd, Nd, and La.¹⁰ Stevenson et al. also found that 15% Gd-doped BaCeO₃ had the highest total conductivity among Yb-, Nd-, and Gd-doped samples in wet Ar.¹¹

Formation of protons in alkaline earth cerates occurs readily in hydrogen-containing atmospheres according to

Nagamoto and Yamada have studied the effect of dopants for A and B sites on conductivity in hydrogen.¹² Among BaCeO₃ samples doped with La, Nd, Yb, Er, Tb, and Nb, Nb-doped BaCeO₃ showed the highest conductivity in hydrogen. High conductivity of Nb-doped BaCeO₃ in H₂ was also observed by Rauch and Liu.¹³ However, electromotive force measurements indicated an absence of proton conduction in Nb-doped BaCeO₃.¹² At the same time, Iwahara et al. observed that Y-, Sm-, and Nd-doped BaCeO₃ had high conductivities in hydrogen,^{14,15} and that 20% Sm-doped BaCeO₃ exhibited very high total conductivity in hydrogen, ($\sim 4 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ at 800°C). However, dense samples were difficult to prepare. According to a more recent report,² BaCe_{0.8}Y_{0.2}O_{3-δ} may have the highest conductivity reported to date, $\sim 5.3 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ at 800°C in hydrogen.

SrCeO₃ doped with Yb¹⁶ and Y¹⁷ have also been studied as proton conductors. Compared to BaCeO₃ based materials, SrCeO₃ based materials have lower total conductivities but higher proton transference numbers.¹⁸ Their higher proton transference numbers may make these materials desirable for hydrogen separation due to increased hydrogen selectivity. However, the electronic transference number of Y-doped SrCeO₃ (and BaCeO₃) was < 0.2 at 800°C, based on open-cell voltage measurements on hydrogen concentration cells.^{19,20} Also, the materials exhibited high interfacial polarization during hydrogen permeation tests.²⁰ In order to improve catalytic properties and electronic conductivity, appropriate dopants or a second phase must be introduced. Typically, elements in group VIII, such as Fe, Co, and Ni, are good catalysts, and Ni-oxide cermet has already been used as anode material in SOFCs because of its good catalytic properties and high electronic conductivity.²¹

In addition to stoichiometric alkaline earth cerates, BaCeO₃ containing excess BaO²² and complex perovskites with the formula of A₃B_{1-x}Nb_{2-x}O_{9-δ} (A = Ba, Sr, Ca, and B' = Sr, Ca, Mg)²³ have been studied. After water uptake measurements and conductivity analysis, Kreuer et al.²² concluded that excess BaO formed a grain boundary phase. Recently, Shima and Haile²⁴ reported that excess BaO aids in densification and enhances the conductivity of 15% Gd-doped BaCeO₃ in wet Ar at 500°C, but samples with 4% BaO excess eventually lost mechanical integrity due to reaction with atmospheric CO₂.

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In this study, stoichiometric and nonstoichiometric BaCeO_3 and SrCeO_3 were doped with various materials (Gd, Nd, Y, and Ni) at different dopant levels (5, 10, and 20%), and the effects of these composition variations on sinterability, microstructure, and conductivity were characterized.

Experimental

Sample preparation.— BaCeO_3 and SrCeO_3 based materials were prepared by using solid-state reactions.^{19,20} All powders in this study had a perovskite structure except $\text{SrCe}_{0.8}(\text{Ni}_{0.1}\text{Y}_{0.1})\text{O}_{3-\delta}$, in which CeO_2 was detected by X-ray diffraction (Scintag, XDS 2000). Pellets of doped BaCeO_3 were sintered in air at 1550°C for 10 h. SrCeO_3 based materials without Ni dopant were sintered in air at 1500°C for 10 h, whereas, materials with Ni dopant were sintered in air at 1300°C for 5 h. Both sides of each pellet were then polished with 600 grit SiC polishing paper. Platinum (Heraeus CL11-5100) or silver (Heraeus C1000) paste was painted on the polished surfaces and dried in air at 150°C for 5 h and subsequently fired in air for 12 min at 1200°C (for Pt paste) or at 850°C (for Ag paste) to form porous electrodes for electrochemical measurements.

Microstructure.—Microstructures of materials were studied by scanning electron microscopy (SEM; JEOL JSM-5400) on as-sintered surfaces, fracture surfaces, and etched surfaces. To prepare an etched surface, the pellet was first polished with 600 grit SiC polishing paper, then immersed in 1 N HNO_3 solution for 2 min, and finally cleaned in isopropyl alcohol.

Impedance spectroscopy.—An impedance analyzer (HP4192A LF) was used to acquire impedance spectra in the frequency range from 5 Hz to 13 MHz at temperatures between 550 and 800°C. Before the impedance measurements, each cell was first equilibrated at 800°C for 5 h and then cooled to 550°C in the desired atmosphere (O_2 , H_2 , or wet Ar). Water vapor was obtained by bubbling Ar through deionized water at room temperature ($\sim 22^\circ\text{C}$).

H^+/O^{2-} transference number.—The ratios of proton and oxygen ion transference numbers to the total ionic transference numbers were obtained by discharging a fuel cell

with the external circuit shorted. The ratios ($t_{\text{H}^+}/t_{\text{ion}}$ and $t_{\text{O}^{2-}}/t_{\text{ion}}$) were calculated from discharging currents and water vapor evolution rates of the cathode and anode compartments^{4,7,20} using

$$\frac{t_{\text{H}^+}}{t_{\text{ion}}} = \frac{w_c}{w_t} \quad [3a]$$

$$\frac{t_{\text{O}^{2-}}}{t_{\text{ion}}} = \frac{w_a}{w_t} \quad [3b]$$

and

$$t_{\text{ion}} = t_{\text{H}^+} + t_{\text{O}^{2-}} \quad [3c]$$

where w_c and w_a are the rates of water vapor evolution from the cathode side and anode side, respectively, and w_t is the total rate of water vapor evolution from both sides or calculated from the short-circuit currents (using Faraday's law). The rates of water vapor evolution due to electrochemical process were calculated from the flow rates of carrier gas and humidity measurements by a hygrometer (Fisher Scientific) in both sides of the cell under both open-circuit and short-circuit conditions. This procedure provides relative transference numbers only. To measure the absolute transference numbers, a separate experiment would be needed to determine the electronic contribution.

Results and Discussion

Material sintering.—Initially, green pellets were placed directly on an Al_2O_3 setter for sintering. After sintering, the surface areas in contact with alumina were yellowish, while the uncontacted surface areas were brown or dark green, depending on the initial material composition. The

large difference in color suggested a reaction with the setter. As expected, the X-ray diffraction analysis of the contacted surface areas revealed the presence of CeO_2 as the major phase and BaCeO_3 as a minor phase (Fig. 1a). An X-ray diffraction analysis of the uncontacted surface areas (the so-called free surface) showed the perovskite structure of BaCeO_3 , and possibly a trace amount of CeO_2 , due to BaO loss at high temperature (Fig. 1b). Cross-sectional views (Fig. 2a) showed clearly the formation of a reacted

Fig. 1. X-ray diffraction patterns of 20% Gd-doped BaCeO_3 , showing a composition change when contacted by alumina setter during sintering.

Fig. 2. SEM photomicrographs of (a) cross section of contacted surface and (b) cross section of free surface of 20% Gd-doped BaCeO_3 .

Fig. 3. SEM photomicrographs of as-sintered surfaces of (a) SrCeO_3 , (b) 5% Y-SrCeO_3 , (c) 10% Y-SrCeO_3 , and (d) $\text{SrO} \cdot 0.90\text{CeO}_2 \cdot 0.025\text{Y}_2\text{O}_3$. All samples were sintered in air at 1500°C .

layer 10 to $15\text{ }\mu\text{m}$ thick, whereas no such layer was evident in materials that did not contact Al_2O_3 (Fig. 2b). Energy dispersive X-ray (EDX) analysis showed that the molar ratio of Ba over Ce in the reacted layer was $\sim 1:9$. Similar reactions were evident after sintering other doped BaCeO_3 and SrCeO_3 on Al_2O_3 setters, suggesting a reaction such as

Such a reaction between $\text{Ba}(\text{Sr})\text{CeO}_3$ and Al_2O_3 must be considered in fabricating thin films of $\text{Ba}(\text{Sr})\text{CeO}_3$ on alumina substrates.^{25,26} To prevent the reaction in the present study, powders with the same composition as the green pellets were used as a buffer layer between the green pellets and the setter.

Microstructure.—Photomicrographs of as-sintered surfaces of SrCeO_3 based materials (Fig. 3) show that both stoichiometric and nonstoichiometric (i.e., with excess SrO) SrCeO_3 can be densified at 1500°C . Increasing the temper-

ature to 1550°C caused extra grain growth. Undoped SrCeO_3 showed a rough surface with honeycomblike structure (Fig. 3a). A similar structure was observed by Du and Nowick on a thermally etched $\text{Ba}_3\text{Ca}_{1.15}\text{Nb}_{1.85}\text{O}_{9.8}$ surface.²⁷ Under identical sintering conditions (temperature and dwell time), grain growth increased as dopant level increased (Fig. 3a, b, and c).

Photomicrographs of BaCeO_3 based materials sintered at 1550°C are shown in Fig. 4. In this study, stoichiometric 5% Y-doped BaCeO_3 did not densify well ($\sim 89\%$ dense; Fig. 4a), whereas a sample with 5% excess BaO ($\text{BaO} \cdot 0.90\text{CeO}_2 \cdot 0.025\text{Y}_2\text{O}_3$) had a very dense fracture surface ($\sim 94\%$; Fig. 4b). This suggests that the proper amount of excess BaO promotes sintering for this dopant level (5% Y). At higher dopant concentration (10% Y), however, the stoichiometric material was very dense ($\sim 98\%$; Fig. 4c), whereas, the sample with 5% excess BaO ($\text{BaO} \cdot 0.85\text{CeO}_2 \cdot 0.05\text{Y}_2\text{O}_3$) was not very dense ($\sim 91\%$ dense) and had finer grains (Fig. 4d). The observation of

Fig. 4. SEM photomicrographs of (a) fracture surface of 5% Y-BaCeO_3 , (b) fracture surface of $\text{BaO} \cdot 0.90\text{CeO}_2 \cdot 0.025\text{Y}_2\text{O}_3$, (c) as-sintered surface of 10% Y-BaCeO_3 , and (d) as-sintered surface of $\text{BaO} \cdot 0.85\text{CeO}_2 \cdot 0.05\text{Y}_2\text{O}_3$. All samples were sintered in air at 1550°C .

Kulscar²⁸ that 2 mol % excess BaO in BaTiO₃ acted as a grain size refiner suggests that the excess BaO may inhibit grain growth in the 10% Y-doped sample.

Excess BaO may incorporate into the perovskite up to the solubility limit according to defect reactions^{24,29}

and

At low dopant concentrations, the forward reactions may be favored because the concentration of oxygen vacancies introduced by the dopant is relatively small. As a result, excess BaO can be easily incorporated into the structure to create additional oxygen vacancies, which improve vacancy diffusion and thereby promote sintering. Higher dopant concentrations, however, may saturate the material with oxygen vacancies, in which case the forward reactions in 5a and 5b became less favorable. As a result, Ba-rich phases may segregate at grain boundaries, thus impeding sintering.

Effects of excess BaO on microstructure were also studied by examining 5% Y-doped BaCeO₃ with and without excess BaO after acid etching. After acid etching for 2 min in HNO₃, the sample with 5% excess BaO (BaO·0.90CeO₂·0.025Y₂O₃) showed clearly distinguished grains (Fig. 5a), but the stoichiometric doped BaCeO₃ (BaCe_{0.95}Y_{0.05}O_{3-δ}) was randomly corroded (Fig. 5b) with finer grains. Although excess BaO acted as a grain size refiner in BaO·0.85CeO₂·0.05Y₂O₃ (Fig. 4d), the observation of coarser grains in BaO·0.90CeO₂·0.025Y₂O₃ rather than in BaCe_{0.95}Y_{0.05}O_{3-δ} is exactly opposite. It is possible that most of excess BaO in the sample with low dopant concentration (BaO·0.90CeO₂·0.025Y₂O₃) had already become incorporated into the matrix according to Eq. 5. This incorporation could create more vacancies and thus promote grain growth and densification.³⁰ In the sample with the high dopant concentration (BaO·0.85CeO₂·0.05Y₂O₃), however, most of the excess BaO may exist as grain bound-

ary phases due to oxygen vacancy saturation in the matrix. The existence of excess BaO at grain boundaries in BaO·0.85CeO₂·0.05Y₂O₃, however, could act as a grain-size refiner and impede sintering.²⁸

As for stability, samples with compositions of SrO·0.90CeO₂·0.025Y₂O₃, SrO·0.85CeO₂·0.05Y₂O₃, and 1.05SrO·CeO₂ appeared to be acceptable immediately after sintering, but crumbled into pieces after exposure to air for several days. After exposure to air for many weeks, as-sintered BaO·0.90CeO₂·0.025Y₂O₃ and BaO·0.85CeO₂·0.05Y₂O₃ pellets, however, retained good mechanical integrity. However, if the as-sintered pellets were broken into two pieces and then exposed to air, BaO·0.90CeO₂·0.025Y₂O₃ maintained good integrity while BaO·0.85CeO₂·0.05Y₂O₃ crumbled. The lower stability in air of BaO·0.85CeO₂·0.05Y₂O₃ than that of BaO·0.90CeO₂·0.025Y₂O₃ suggested that the former may have more Ba-rich phases at grain boundaries than the latter. Scanning electron microscopy (SEM) examination on fracture surfaces of BaO·0.90CeO₂·0.025Y₂O₃ showed that the entire fracture surface is dense, as shown in Fig. 4b, and that there was no observable change after the fracture surface was exposed to air for four weeks. However, after exposure of sintered BaO·0.85CeO₂·0.05Y₂O₃ to air for two weeks, examination of the center portion of the fracture surface revealed a Ba-rich phase in the grain boundaries (Fig. 6). EDX analysis showed that the molar ratio of Ba over Ce is ~91:9 in the Ba-rich phase, while neighboring grains had a molar ratio of Ba:Ce:Y ~49:44:7, close to the mixture ratio of Ba:Ce:Y = 100:85:10 when the material was prepared. The observation of a Ba-rich phase in BaO·0.85CeO₂·0.05Y₂O₃ confirmed our assumption that the excess BaO likely exists in the grain boundary area of the sample with high dopant concentration due to the possible saturation of oxygen vacancies. Such a Ba-rich phase was not observed in the surface layer of the sintered pellet because BaO was probably vaporized at high temperature during sintering. As such, the stable surface layer prevented the Ba-rich phase in the center of the sintered body from further reacting with atmospheric CO₂, thereby maintaining the good integrity of the as-sintered pellets. However, after the pellet was broken, the Ba-rich phase inside the sintered body was readily accessed by atmospheric CO₂, forming BaCO₃ and consequently causing the crumbling of the pellet.

Conductivity of BaCeO₃ based materials.—Temperature dependence of stoichiometric doped BaCeO₃—Shown in Fig. 7a are the total conductivities of doped BaCeO₃ in 1 atm oxygen as determined by impedance spectroscopy. The total conductivity of Y-doped BaCeO₃ increased with temperature. The conductivity of BaCe_{0.8}Gd_{0.2}O_{3-δ}⁶ was slightly higher than that of BaCe_{0.9}Y_{0.1}O_{3-δ} and BaCe_{0.8}Y_{0.2}O_{3-δ} in this work at temperatures <700°C, but was almost the same at >700°C.

Fig. 5. SEM photomicrographs of (a) acid-etched surface of BaO·0.90CeO₂·0.025Y₂O₃ and (b) acid-etched surface of 5% Y-BaCeO₃.

Fig. 6. SEM photomicrograph of fracture surface of BaO·0.85CeO₂·0.05Y₂O₃ after exposure to air for 2 weeks.

Fig. 7. Temperature dependence of conductivity of BaCeO₃ based materials in (a) O₂, (b) 4% H₂, and (c) wet Ar.

Shown in Fig. 7b is the temperature dependence of conductivity in 4% H₂. The conductivities of samples with 5, 10, and 20% Y increased with dopant concentration. For BaCeO₃ doped with 20% Y, Nd, and Gd, the conductivity increased in the order of Nd, Gd, and Y at a given temperature. Contrary to expectation, the conductivity of 20% Nd-doped BaCeO₃ was not very high. Moreover, 20% Y-doped BaCeO₃ had the highest conductivity in this work, $\sim 1.54 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ at 600°C and $\sim 4.16 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ at 800°C. Compared to the results of Iwahara et al.² for 20% Y-doped BaCeO₃ in H₂, the conductivities in this work are lower, partially because measurements in the present study were made in 4% H₂ instead of 100% pure hydrogen.

Shown in Fig. 7c is the temperature dependence of conductivity in wet Ar. The conductivity of Y-doped BaCeO₃ increased with dopant concentration. Among the samples with 20% dopants, conductivity increased in the order of Nd-, Y-, and Gd-doped BaCeO₃ in the temperature range of 550 to 800°C. The 20% Gd-doped BaCeO₃ had the highest conductivity with the lowest activation energy (~ 0.31 eV) in wet Ar,⁶ whereas the activation energies for other materials were very close to one another, ~ 0.4 eV.

Composition dependence of stoichiometric doped BaCeO₃.—For Y-doped BaCeO₃, at a given temperature, conductivity measured in wet Ar (Fig. 7c) and 4% H₂ (Fig. 8a) which is dominated by ionic conduction, increased monotonically with dopant concentration from 5 to 20%. In O₂, however, there is a significant contribution from electron hole conduction; conductivity increased with dopant concentration from 5 to 10%, and then decreased slightly with dopant concentration up to 20%. The smooth curve in Fig. 8b implies a possible maximum between 10 and 20%. The increase in conductivity with dopant concentration could be related to an increase in charge carrier concentration through the reaction

However, sintered density and defect structure may also affect total conductivities.

Effects of A:B site nonstoichiometry.—As shown in Fig. 9, samples with BaO excess had higher conductivity than the stoichiometric doped samples with 5% Y as the dopant. However, at a higher dopant concentration (10% Y), excess BaO reduced the total conductivity, except at a lower temperature ($<600^\circ\text{C}$), in H₂. This variation of conductivity with BaO excess could be correlated to the density change with BaO excess. At a 5% dopant level, BaO·0.90CeO₂·0.025Y₂O₃ had a greater density ($\sim 94\%$ dense) than BaCe_{0.95}Y_{0.05}O_{3-δ} ($\sim 89\%$ dense), whereas, at the 10% level, BaO·0.85CeO₂·0.05Y₂O₃ had a lesser density ($\sim 91\%$) than BaCe_{0.9}Y_{0.1}O_{3-δ} ($\sim 98\%$; Fig. 4). However, Shima et al. found that 4% excess BaO reduced the conductivity of 15% Gd-doped BaCeO₃ in wet Ar at lower

temperatures (250 to 400°C) and enhanced it at higher temperatures (500°C), even though the sample with excess BaO had increased density. They attributed the reduced conductivity at low temperature to defect association.²⁴ This variation of conductivity with excess BaO may also

Fig. 8. Effects of dopant concentration on conductivity of Y-doped BaCeO₃ in (a) 4% H₂ and (b) O₂.

Fig. 9. Effects of nonstoichiometry on conductivity of BaCeO₃ based materials in (a) O₂, (b) 4% H₂, and (c) wet Ar.

be related to defect structure. At a low dopant concentration (5% Y), incorporation of excess BaO into the perovskite matrix induces high vacancy concentration and increases conductivity, whereas at a high dopant concentration (10% Y), excess BaO tends to reside in grain boundary phases that may inhibit conduction in the temperature range studied.

Conductivity of doped SrCeO₃.—Shown in Fig. 10 are the total conductivities of doped SrCeO₃ in oxygen and hydrogen. The conductivities for BaCe_{0.9}Y_{0.1}O_{3-δ} under comparable conditions are reproduced from Fig. 7 for reference. Obviously, doped SrCeO₃ had lower conductivities in O₂ and H₂ than those of BaCeO₃ based materials. As with BaCeO₃, conductivity increased as dopant concentration increased from 5 to 10% in both O₂ and H₂. The activation energy for conduction in H₂ was lower than that in O₂. Conductivity of SrCe_{0.8}(Ni_{0.1}Y_{0.1})O_{3-δ} was surprisingly low ($\sim 10^{-5} \Omega^{-1} \text{cm}^{-1}$ at 650°C). The Ni was probably not a good dopant in terms of conductivity,^{31,32} although Ni-oxide cermets were reported to have good catalytic properties in SOFC applications.²¹

H⁺/O²⁻ conduction.—Figure 11 shows the relative ionic transference numbers of SrCe_{0.95}Y_{0.05}O_{3-δ} in this work, as well as those of the 10% Y- and 10% Gd-doped BaCeO₃ that were reported by Iwahara et al.⁷ Compared to the results of BaCeO₃ based materials, SrCeO₃ based materials have higher proton transference numbers and lower oxy-

gen ion transference numbers. In SrCe_{0.95}Y_{0.05}O_{3-δ}, more than 85% of the ionic conductivity was carried by protons in the testing temperature range (600–800°C) and oxygen ions contributed to only $\sim 15\%$ of the ionic conductivity. Ionic conduction was completely protonic below 600°C.

Conclusions

Dopant species and concentration strongly affected the microstructures and electrical properties of BaCeO₃ and SrCeO₃. Grain growth and densification of sintered samples were influenced by dopant level and nonstoichiometry on A and B sites. The conductivity of BaCe_{1-x}Y_xO_{3-δ} ($x = 0.05, 0.1$, and 0.2) increased in hydrogen and wet Ar with Y content. Of the doped BaCeO₃, BaCe_{0.8}Y_{0.2}O_{3-δ} showed the highest conductivity in hydrogen ($\sim 1.54 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ at 600°C and $\sim 4.16 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ at 800°C). Although SrCeO₃ based materials had lower conductivities than those of BaCeO₃ based materials, they exhibited higher proton and lower oxygen ion transference numbers than BaCeO₃, which may be useful for improving their selectivity for hydrogen separation.

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Fig. 10. Conductivities of doped SrCeO₃ and 10% Y-doped BaCeO₃ in O₂ and 4% H₂.

Fig. 11. Relative ionic transference numbers under fuel cell condition of 5% Y-SrCeO₃ in this work, and in 10% Y-doped BaCeO₃ and 10% Gd-doped BaCeO₃ by Iwahara et al.⁷

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Determination of the Trap Density in Amorphous Silicon by Quasi-Static Capacitance-Voltage Measurements

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ABSTRACT

A special metal-oxide-semiconductor structure based on hydrogenated amorphous silicon has been fabricated. The quasi-static capacitance-voltage (CV) curves of this device are calculated for various trap densities of the amorphous silicon. Due to the occurrence of punch-through, Poisson's equation cannot be solved analytically. Thus, a finite elements approach has been used to compute the potential distribution and the charge density in the semiconductor. Differentiation of the charge with respect to the applied voltage delivers the low-frequency CV curve. In the last step, this CV curve is fitted to a measured one in order to determine the trap density. We find a trap density of $N_{b0} = 9 \cdot 10^{16} \text{ V}^{-1} \text{ cm}^{-3}$ at midgap.

Introduction

Amorphous silicon (a-Si) is a material widely used in thin film transistors (TFTs) and solar cells. In a large scale manufacturing process routine control is desirable. With respect to the above applications, the control should be based on electrical measurements. The a-Si characterization, however, involves optical methods to a large extent. This is especially true for a characteristic material parameter, namely, the bulk trap density, N_b . It is the purpose of this work to deliver an electrical measurement method for N_b .

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In this method a specially designed metal-oxide-a-Si structure is used¹ and its CV curve is recorded. CV techniques are known from monocrystalline silicon MOS capacitance measurements where they are among the major diagnostic tools used to investigate trap properties. There is a big difference, however, between monocrystalline and amorphous metal-oxide-semiconductor (MOS) structures: in the monocrystalline case, the CV characteristics are controlled by surface states (the bulk states being negligible), while for amorphous silicon, the CV characteristics are controlled by the bulk states (the surface states being negligible). Among the first to report on this observation were