

Effect of rare-earth ions doped in BaCeO₃ on chemical stability, mechanical properties, and conductivity properties

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Abstract

The microstructure, lattice parameters, morphology, mechanical properties, and conductivity of BaCe_{0.9}M_{0.1}O_{2.95} (M=Gd, Nd, Sm, Y) were systematically investigated under different atmospheres (in air and in wet 5%H₂–95%Ar). The XRD results indicated that all of the specimens sintered in air have orthorhombic symmetry, whereas BaCeO₃ and BaCe_{0.9}Gd_{0.1}O_{2.95} decomposed into CeO₂ and BaCO₃ in their specimens. Secondary CeO₂ and BaCO₃ might adversely affect the conductivity of BaCeO₃-based specimens. The maximum conductivity ($\sigma_{\text{total},800\text{ }^{\circ}\text{C}}=6.46 \times 10^{-3}$ S/cm) and minimum activation energy ($E_a=52.3$ kJ/mol) measured in air were observed for BaCe_{0.9}Y_{0.1}O_{2.95} among the BaCeO₃-based specimens. Whereas in wet 5%H₂–95%Ar, the maximum conductivity ($\sigma_{\text{total},800\text{ }^{\circ}\text{C}}=9.20 \times 10^{-3}$ S/cm) and minimum activation energy ($E_a=55.6$ kJ/mol) were measured. The difference in conductivity between the air and wet reducing atmosphere can be explained by the chemical stability. The mechanical properties of BaCe_{0.9}M_{0.1}O_{2.95} significantly depended on the doping element with the rare-earth oxide dopants affecting the structure stability, grain size, conductivity, thermal expansion, and the mechanical properties. Based on a comprehensive evaluation, BaCe_{0.9}Y_{0.1}O_{2.95} revealed good chemical stability and high conductivity and thus it is a promising candidate for a proton-conducting electrolyte for intermediate temperature solid oxide fuel cells (IT-SOFCs).

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1. Introduction

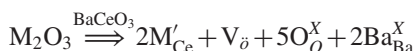
High temperature proton conductors offer advantages over oxide ion conductors when used as electrolytes in SOFCs. When a proton conductor is used instead of an oxide ionic conductor, water vapor is evolved on the cathode side, where it mixes with excess air, which ensures that there is no large change in oxygen concentration resulting from water vapor production at the cathode and which does not significantly reduce the cell voltage [1,2]. Several proton conductors with the perovskite structure (ABO₃) have been intensively investigated due to their potential use for hydrogen separation

membranes, hydrogen sensors, protonic ceramic steam-permeability membranes, etc. [3]. In general, perovskite-type oxides, based on SrCeO₃ or BaCeO₃ and doped with trivalent cations, exhibit high protonic conductivity when exposed to a humidified hydrogen-containing atmosphere at temperatures higher than 300 °C [4]. Acceptor-doped barium cerates have received considerable attention as solid-state proton conductors [5–10]. These materials are particularly promising as electrolytes for intermediate-temperature (400–700 °C) SOFCs, which alleviate many of the materials life time and cyclability challenges that result from the high temperature operation, at 800–1000 °C, of conventional zirconia-based SOFCs [11]. Moreover, in conventional ion-conducting SOFCs, water is formed at the anode, where it dilutes the fuel. In contrast, proton-conducting oxides avoid the dilution of the fuel and water accumulation at the anode, which could interfere with the steam reforming reaction eventually occurring at the anode in hydrocarbon-fueled SOFCs [12].

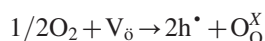
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The increase in proton conductivity with doping is mainly related to the formation of protonic defects in the ABO_3 perovskites due to the dissociative adsorption of water in the presence of oxygen vacancies. Although the factors affecting the conduction properties of this solid electrolyte are very complex, it may be considered that its property is strongly affected by the type and ratio of the dopant and its synthesis method [13–19]. In this study, substituting cations of a rare-earth element M^{3+} ($\text{M}=\text{Gd}, \text{Nd}, \text{Sm}, \text{and Y}$) for Ce^{4+} in barium cerate causes substitution defects M'_{Ce} and oxygen vacancies V_O [20]:



The interaction between V_O and water vapor or the oxygen of a gas phase generates electronic holes h^\bullet and protons localized on oxygen OH_O :



The mechanism of proton migration by a series of jumps from one position to the next position in perovskite oxides has been proposed in the literature [12,21]. Oxygen vacancies are the main defects at the high temperatures at which water molecule desorption occurs together with oxygen migration in the bulk, while the dissolution of protons is favored when decreasing the temperature. Proton conduction becomes predominate at an intermediate temperature near 600 °C [22].

The rare-earth ions doped on B-sites of BaCeO_3 has a great effect on the properties of its proton conductor. In this study, ionic substitutions were performed on B sites for Gd, Nd, Sm, and Y. The effects of various dopants were substituted for the B sites of BaCeO_3 on the electrical conductivity, were measured in air and in a wet reducing atmosphere, and were systematically investigated. Because the mechanical properties of BaCeO_3 are not ideal, different rare-earth elements doped on BaCeO_3 may likely improve its mechanical strength and ductility. Therefore, the fracture toughness and microhardness of BaCeO_3 -based electrolytes both were investigated. Moreover, the mechanical properties of an electrolyte are very important in a reducing atmosphere; thus, the effect on mechanical properties after exposure to a reducing atmosphere for specimens was also studied. In this research, the Weibull distribution was used to illustrate the strength distribution of a ceramic, which is usually used for calculations of failure probability for small stress. The statistical strength values obtained from the testing of ceramics were analyzed using the cumulative probability parameter, $F(\sigma)$, while the crystal structures and microstructures under different atmospheres (in air and wet 5% H_2 –95%Ar) were also both examined.

2. Experimental

2.1. Sample preparation

The $\text{BaCe}_{0.9}\text{M}_{0.1}\text{O}_{2.95}$ ($\text{M}=\text{Gd}, \text{Nd}, \text{Sm}, \text{and Y}$) powders were prepared using the solid-state technique. Stoichiometric

amounts of high pure barium carbonate (BaCO_3 , 99.9%), cerium oxide (CeO_2 , 99.9%), neodymium oxide (Nd_2O_3 , 99.9%), samarium oxide (Sm_2O_3 , 99.9%), and yttrium oxide (Y_2O_3 , 99.9%) powders (as listed in Table 1) were mixed with distilled water for 12 h and then calcined in air at 1200 °C for 4 h. The powder samples were then pelletized. The pellets were dry pressed at 100 MPa using the as-prepared powder for sintering. The sintering was performed in air at 1400 °C for 6 h with a programmed heating rate of 5 °C/min. The sintered samples were over 90% of the theoretical density in all of the specimens. The densities of sintered ceramics were measured by the Archimedes method.

2.2. Characterization measurements

A computer interface X-ray powder diffractometer (XRD; Model Rigaku D/Max-II, Tokyo, Japan) with $\text{Cu } K_\alpha$ radiation ($\lambda=0.15418$ nm) was used to identify the crystalline phase. The morphological characterization of the $\text{BaCe}_{0.9}\text{M}_{0.1}\text{O}_{2.95}$ ($\text{M}=\text{Gd}, \text{Nd}, \text{Sm}, \text{and Y}$) was performed using a scanning electron microscope (SEM; Hitachi 3500H, Tokyo, Japan). The electrical conductivity of the sintered pellet was measured by A.C. impedance spectroscopy over the 0.1–10⁵ Hz frequency range with a 100 mV applied voltage using a Solartron 1260 impedance analyzer. The conductivity measurements were performed in the 250–850 °C temperature range (50 °C per step) in air and wet 5% H_2 –95%Ar. All the impedance spectra were obtained using a two-electrode cell configuration and analyzed using the Zview modeling software. Arrhenius plots (plots of $\log \sigma T$ vs. $10^3/T$) were constructed, and the activation energies for conduction were computed. The activation energy for conduction was obtained by plotting the ionic conductivity data in an Arrhenius relation for thermally activated conduction. The value was calculated according to: $\sigma T = A \exp(-E_a/kT)$, where E_a is the activation energy for conduction, T is the absolute temperature, and A is a pre-exponential factor [23]. The thermal expansion coefficients (TECs) of the sintered $\text{BaCe}_{0.9}\text{M}_{0.1}\text{O}_{2.95}$ ($\text{M}=\text{Gd}, \text{Nd}, \text{Sm}, \text{and Y}$) pellets were measured using a dilatometer (DIL; Model Netzsch DIL 402 PC, Bavaria, Germany) using a constant heating rate of 10 °C/min in the temperature range of 25–800 °C. To investigate the chemical stability of the BaCeO_3 -based materials, the sintered specimens were exposed to wet 5% H_2 –95%Ar at 800 °C for 16 h. These treated samples were examined by XRD and SEM to determine if their structures were stable in a reducing atmosphere.

Table 1
Composition and abbreviation of $\text{BaCe}_{0.9}\text{M}_{0.1}\text{O}_{2.95}$ ($\text{M}=\text{Gd}, \text{Nd}, \text{Sm}, \text{Y}$) specimens.

Composition	Abbreviation
BaCeO_3	BCO
$\text{BaCe}_{0.9}\text{Gd}_{0.1}\text{O}_{2.95}$	BCO(Gd)
$\text{BaCe}_{0.9}\text{Nd}_{0.1}\text{O}_{2.95}$	BCO(Nd)
$\text{BaCe}_{0.9}\text{Sm}_{0.1}\text{O}_{2.95}$	BCO(Sm)
$\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$	BCO(Y)

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