Study of mass transport kinetics in co-doped $Ba_{0.9}Sr_{0.1}Ce_{0.85}Y_{0.15}O_{3-\delta}$ by electrical conductivity relaxation

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ABSTRACT

In this work, Sr^{2+} and Y^{3+} co-doped $BaCeO_3$-based perovskite $Ba_{0.9}Sr_{0.1}Ce_{0.85}Y_{0.15}O_{3-\delta}$ (BSCY) was synthesized by solid-state reaction method, and its mass transport behavior was studied using electrical conductivity relaxation (ECR) measurements in 600–800 °C range with respect to variations in oxygen partial pressure (pO_2) and water vapor pressure (pH_2O). During oxidation/reduction process, the electrical conductivity showed a monotonic relaxation behavior and in $-2.65 \le \log(pO_2/atm) \le -0.67$ range the values of oxygen chemical diffusivity ($\tilde{D}_{vO}$) and surface exchange coefficient (κ_{vO}) varied in 10^{-6}–10^{-4} $cm^2 \cdot s^{-1}$ and 10^{-4}–10^{-2} $cm \cdot s^{-1}$ range, respectively. However, during hydration/dehydration process, the electrical conductivity showed a non-monotonic twofold relaxation behavior, and hydrogen, and oxygen chemical diffusivities ($\tilde{D}_{iH}$) and ($\tilde{D}_{vH}$) values were in 10^{-5}–10^{-3} and 10^{-6}–10^{-4} $cm^2 \cdot s^{-1}$ range, respectively, whereas hydrogen and oxygen surface exchange coefficient (κ_{iH}) and (κ_{vH}) values were in 10^{-3}–10^{-2} and ~10^{-4}–10^{-2} $cm \cdot s^{-1}$ range, respectively. The comparison of H and O diffusivities of BSCY with $BaCe_{0.85}Y_{0.15}O_{3-\delta}$ (BCY) showed that during hydration/dehydration the diffusivities of BSCY were lower than that of BCY. The long-term electrical conductivity measurement for ~800 h in humidified conditions showed a gradual decrease, which might be due to the gradual appearance of rhombohedral phase in otherwise orthorhombic BSCY, as confirmed by the X-ray diffraction (XRD) measurements.

1. Introduction

$BaCeO_3$ and $SrCeO_3$-based perovskites have shown high proton conductivity at intermediate temperatures (~500–800 °C) and are being utilized in a number of proton-conducting electrochemical devices [1]. Doped $SrCeO_3$ although offer lower level of proton conductivity in comparison to the Ba-containing analogues, they have higher proton transport number [2] and as a result these have been extensively employed in high temperature proton conductor-based sensor, fuel cell, and membrane applications [3–5]. There are many reports on $BaCeO_3$ and $SrCeO_3$ with the dopants on B-site; however, only a few attempts have been made with A-site dopants [6,7]. Chokkha et al. [8] reported the synthesis of $BaCeO_3$ doped on A-site with Sr, Na, and Li. Similarly, Lee et al. [9,10] synthesized $Ba_{1-x}K_xCe_{0.6}Zr_{0.2}Y_{0.2}O_{3-\delta}$ ($x = 0.025$–0.075) ceramics by using a combination of citrate-EDTA complexing sol-gel process and the composition-exchange method and investigated its electrical and nano-mechanical properties and fracture behavior for the application as proton-conducting electrolyte.

Since the chemical stability of $SrCeO_3$ against CO_2 is thermodynamically higher than that of $BaCeO_3$ [11], a few attempts have been made to partially replace Ba with Sr in barium cerate-based compounds [12,13]. Also, the incorporation of Sr was found to apparently suppress the formation of CeO_2-like second phase and enhance the grain growth in sintered oxides [12]. Kilner and Brook [14] used lattice simulation techniques to model ionic conduction in perovskites and concluded that the transport properties of perovskites were strongly influenced by the ionic radii of dopants. The partial substitution of Ba^{2+} ion (ionic radius = 0.161 nm) with smaller Sr^{2+} ion (ionic radius = 0.144 nm) [15] in Y^{3+}-doped barium cerate would affect the oxygen sub-lattice and may cause tilting of the CeO_6 octahedron relative to each other [16]. The ABO_3 perovskite structure exhibits larger tilts when either A-site has smaller size ion or B-site is doped with increasing content of Y dopant. Therefore, those effect of different cations makes larger distortions of the $(Ce/Y)O_6$ octahedra in $Ba_{0.9}Sr_{0.1}Ce_{0.85}Y_{0.15}O_{3-\delta}$ (BSCY). The effect of the tilting causes a decline in the symmetry, which in turn may affect the migration of various charge carriers [6,16–19]. However, the detailed information about the transport properties in such co-doped proton-conducting $BaCeO_3$-based perovskite systems is so far lacking. In the present work, we have synthesized BSCY, where barium cerate is doped with 0.1 mole Sr^{2+} at the A-site and 0.15 mole

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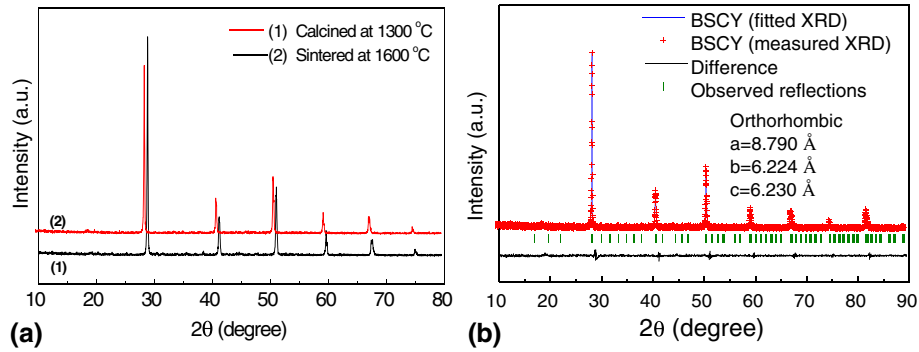E-mail address: song@chonnam.ac.kr (S.-J. Song).

Fig. 1. (a) Room temperature XRD patterns of BSCY, (1) calcined at 1300 °C in air for 10 h and (2) sintered at 1600 °C in air for 10 h; (b) Rietveld indexing of XRD data.

Y^{3+} at the B-site, and studied its transport properties in various thermodynamic conditions using electrical conductivity relaxation (ECR) measurements.

In the $BaCeO_3$ system, both Ba^{2+} and Sr^{2+} have same valence state, and therefore, the substitution of Ba^{2+} by Sr^{2+} at A-site would not affect the charge neutrality of the system and as a result would not affect the defect composition. However, the substitution of Ce^{4+} by the lower valence Y^{3+} at the B-site of $BaCeO_3$ would lead to the formation of oxygen vacancies ($V_o^{\bullet\bullet}$), as represented by Eq. (1)

$$Y_2O_3 \xrightarrow{BaCeO_3} Y'_{Ce} + O_o^{\times} + \frac{1}{2}V_o^{\bullet\bullet} \tag{1}$$

where various symbols have their usual Kröger–Vink notation meanings. The oxygen vacancies facilitates oxygen-ion conduction, and in oxidizing conditions leads to the formation of holes, as represented by Eq. (2),

$$\frac{1}{2}O_{2(g)} + V_o^{\bullet\bullet} \leftrightarrow O_o^{\times} + 2h^{\bullet} \tag{2}$$

On the other hand, in hydrogen containing atmosphere the oxygen vacancies can act as proton incorporation sites, as represented by Eq. (3) in humid atmosphere,

$$H_2O_{(g)} + V_o^{\bullet\bullet} + O_o^{\times} \leftrightarrow 2OH_o^{\bullet} \tag{3}$$

Any change in pO_2 during the oxidation/reduction of BSCY affects the overall defect concentration in the material. As the pO_2 increases, e.g., the Eq. (2) proceeds forward to produce more holes but at the same time the proton concentration may decrease due to the loss of available oxygen vacancy sites for water-incorporation reaction, Eq. (3). Obviously, the relative contribution of various charge carriers towards the transient total conductivity can vary depending on the changes in pO_2 and pH_2O. Therefore, the ECR in BSCY with respect to the changes in pO_2 and pH_2O would be dependent upon two external

reactions, Eqs. (2) and (3), affecting the concentrations of various mobile charge carriers ($V_o^{\bullet\bullet}$, $OH_o^{\bullet}$, or equivalent $H_i^{\bullet}$, and $h^{\bullet}$). The application of law of mass action to Eqs. (2) and (3) leads to Eqs. (4) and (5),

$$K_o = \frac{p^2}{[V_o^{\bullet\bullet}](pO_2)^{1/2}} \tag{4}$$

and

$$K_W = \frac{[OH_o^{\bullet}]^2}{[V_o^{\bullet\bullet}](pH_2O)} \tag{5}$$

where K_o is the equilibrium constant for oxygen exchange, p is the concentration of holes, and K_W is the equilibrium constant for the exchange of water.

The electrical conductivity relaxation measurements have been shown to be effective technique in investigating the mass and charge transport properties of mixed conducting oxides [20–22]. The ECR experiments analyze the transient electrical behavior in the re-equilibration process following a sudden change in the thermodynamic conditions, such as oxygen partial pressure (pO_2), water vapor pressure (pH_2O), and temperature, of the surrounding gas, and the relaxation profile is described by a solution to Fick's second law while taking the appropriate boundary conditions into account. A fit to data yields values for the desired material parameters, chemical diffusion coefficient, and surface exchange coefficient [23]. Considering the ease and effectiveness of ECR technique, in the present study, the mass and charge transport properties of BSCY, which are governed by the nature and concentration of various defect species, which, apart from protons, may be oxygen ions, excess electrons, and electron holes, are studied by ECR during the oxidation/reduction process at a fixed pH_2O and during hydration/dehydration process at a fixed pO_2 in 650–800 °C range. The surface exchange coefficients and chemical diffusivities of oxygen and hydrogen are calculated from the Fick's second law by the nonlinear least squares fitting to the conductivity relaxation data [24].
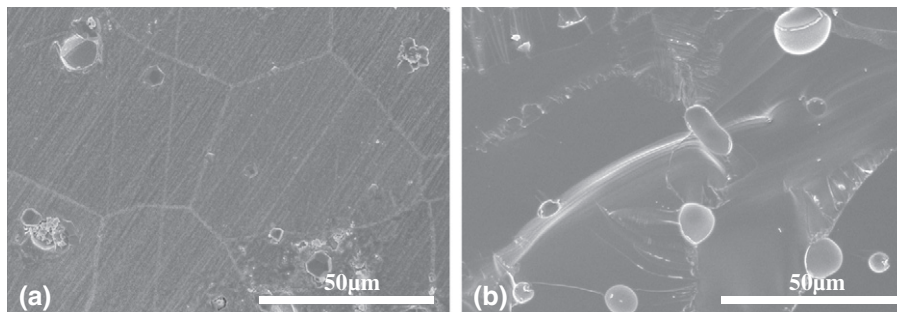

Fig. 2. SEM image of (a) surface and (b) fractured section of BSCY pellet sintered at 1600 °C in air for 10 h.