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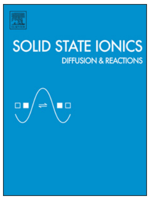

Stabilization of the perovskite structure in Co-based mixed conductors by tri-valent cation substitution

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ABSTRACT

For Co-based perovskite mixed conductors, the substitution of Co by cations with a higher valence than Co has been known to be effective in stabilizing the cubic perovskite structure. Nevertheless, such a substitution may reduce the number of the oxygen vacancies and be unfavorable for increasing oxygen permeability. In order to prepare cubic perovskite mixed conductors with greater oxygen permeability, the effect of substituting the tri-valent cation, In^{3+}, in the Co-based system $(Ba,Sr)(Co,In)O_{3-\delta}$, was investigated and compared to the effect of substituting Y, Al, and Fe. For $(Ba_xSr_{1-x})(Co_{0.9}In_{0.1})O_{3-\delta}$ and $(Ba_xSr_{1-x})(Co_{0.9}Y_{0.1})O_{3-\delta}$, cubic perovskite single phase was found to be attained at high Ba concentrations of $x = 0.9$ and $1.0 \ge x \ge 0.5$. This differed from the cases of $(Ba_xSr_{1-x})(Co_{0.9}Al_{0.1})O_{3-\delta}$ and $(Ba_xSr_{1-x})(Co_{0.9}Fe_{0.1})O_{3-\delta}$ in which pure perovskite appeared in the low Ba concentration ranges of $0.2 \ge x \ge 0$ and $0.5 \ge x \ge 0$, respectively. A disk sample of $(Ba_{0.9}Sr_{0.1})(Co_{0.9}In_{0.1})O_{3-\delta}$ with 1 mm thickness showed high oxygen permeability of 5.69 $cm^3/min/cm^2$ at 900 °C, which was 24% higher than the permeability of $(Ba_{0.5}Sr_{0.5})(Co_{0.8}Fe_{0.2})O_{3-\delta}$.

1. Introduction

Mixed electronic/oxide-ionic conductive perovskite-type oxides have been thoroughly investigated for utilization in oxygen permeating membranes, sensors and cathodes for solid oxide fuel cells (SOFC) due to their high oxygen permeability, which is one or two orders of magnitude greater than the rate of stabilized zirconia under short-circuited conditions [1]. Up to now, a number of perovskite related mixed conductors have been examined [2–17]. According to the literature, mixed conductors with high oxygen permeability are found among perovskites containing cobalt [1,18–22].

Cobalt-based perovskites tend to change to an almost non-oxygen permeable hexagonal polymorph, whose structure consists of columns of face-sharing CoO_6-octahedra, below about 900 °C [3,5]. Typical phases of the hexagonal polymorph are $Sr_6Co_5O_{15}$ [23] and 12H-$BaCoO_{3-\delta}$ [24,25]. Consequently, it is important to control the phase transition to the hexagonal polymorph. The highly permeable perovskite structure must be stabilized by substituting cobalt-based perovskite with the proper cations to form a solid solution. Furthermore, the amount of substitution should be minimized to avoid negatively impacting the oxygen permeability [26]. The stability of the perovskite structure in Sr–Co-based oxides (SC) can be increased by raising the valence of the substitutional cation for SC. Nb was found to be effective as a substitutional cation for SC-based mixed conductors, and $Sr(Co_{0.9}Nb_{0.1})O_{3-\delta}$ showed higher oxygen permeability and higher stability of the cubic perovskite than $SrCoO_{3-\delta}$, $(La_{0.1}Sr_{0.9})CoO_{3-\delta}$, $Sr(Co_{0.9}Fe_{0.1})O_{3-\delta}$ and $Sr(Co_{0.9}Ti_{0.1})O_{3-\delta}$ [27–30].

Assuming as Cu^{2+}, Al^{3+}, La^{3+}, Fe^{3+}, Ti^{4+} and Nb^{+5}, and based on the result of $3-\delta$ at 850 °C in O_2 atmosphere [28], the valence of cobalt in $Sr(Co_{0.9}Cu_{0.1})O_{3-\delta}$ $SrCoO_{3-\delta}$, $Sr(Co_{0.9}Al_{0.1})O_{3-\delta}$, $(La_{0.1}Sr_{0.9})CoO_{3-\delta}$, $Sr(Co_{0.9}Fe_{0.1})O_{3-\delta}$, $Sr(Co_{0.9}Ti_{0.1})O_{3-\delta}$ and $Sr(Co_{0.9}Nb_{0.1})O_{3-\delta}$ can be estimated to be $+3.128 \ge Z \ge +3.038$. Consequently, the substitution of Co by cations with valence of +4 or higher reduces the number of oxygen vacancies in the perovskite solid solution. Since oxygen permeability depends on the number of the vacancies, such a substitution will be unfavorable for increasing the oxygen permeability of the mixed conductor. If the perovskite structure can be stabilized through substitution of the Co-site with a tri-valent cation, the number of the oxygen vacancies will not be sacrificed by the substitution, and, as a result, the oxide ion conductivity in the cobalt-based perovskites may be increased.

In the previous study, we reported on the stabilization of the perovskite structure through substitution with the tri-valent cation, Y^{3+} [31]. (Ba0.9Sr0.1)$(Co_{0.9}Y_{0.1})O_{3-\delta}$ compound with perovskite single phase showed good oxygen permeability on a level similar to that of

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(Ba0.5Sr0.5)$(Co_{0.8}Fe_{0.2})O_{3-\delta}$. The results seem to support the effectiveness of substitution with a tri-valent cation in Co-based perovskite.

Concerning the substitution of other tri-valent cations into a Co-based system, the phase relations of Ba(Co,In)$O_{3-\delta}$ in which the tri-valent cation, In^{3+}, was substituted in the Co-site was reported on by Istomin et al. [32], Kobayashi et al. [33] and Li et al. [34]. They found the appearance of a perovskite structure in this system. The stabilization of perovskite in Ba(Co,In)$O_{3-\delta}$ seems to be reasonable because $BaInO_{2.5}$ has a brownmillerite structure, which is not a hexagonal polymorph but rather perovskite with oxygen vacancy ordering. In Ba(Co,In)$O_{3-\delta}$, an indium concentration greater than 15% in the B-site was necessary to stabilize the perovskite structure, and the literature tends to be concentrated in the range of high indium concentrations. However, such large substitutions in the B-site are not suitable to attaining higher oxygen permeability [26].

In the present study, the effect of substituting indium for Co was studied in (Ba,Sr)(Co,In)$O_{3-\delta}$ compounds. Cubic perovskite structure was found to be stabilized in the (Ba,Sr)(Co,In)$O_{3-\delta}$-system within a limited range at high Ba concentrations. The stabilization of cubic perovskite through indium substitution was investigated and compared to the effect of substituting Co with the tri-valent cations Y and Al [31], as well as Fe. Furthermore, the oxygen permeability of the cubic perovskites stabilized by the indium substitution was measured. (Ba,Sr)(Co,In)$O_{3-\delta}$ was found to exhibit high oxygen permeability. In particular, (Ba0.9Sr0.1)$(Co_{0.9}In_{0.1})O_{3-\delta}$ with cubic perovskite single phase showed higher permeability than $(Ba_{0.5}Sr_{0.5})(Co_{0.8}Fe_{0.2})O_{3-\delta}$.

2. Experimental

The specimens were prepared by solid reaction and sintering. The synthesized compositions were $(BaxSr_{1-x})(Co_{0.9}In_{0.1})O_{3-\delta}$ and $(Ba_xSr_{1-x})(Co_{0.9}Fe_{0.1})O_{3-\delta}$ where x was 0 to 1.0 with an interval of 0.1 and $Ba(Co_{0.85}In_{0.15})O_{3-\delta}$ and (Ba0.9Sr0.1)$(Co_{0.85}In_{0.15})O_{3-\delta}$. Reagent-grade $BaCO_3$, $SrCO_3$, Co_3O_4, In_2O_3 and Fe_2O_3 were weighed and mixed by ball milling for 3 h with ZrO_2 balls. Ethyl alcohol was used as the medium. The powder mixtures were calcined at 900 °C for 12 h in air and finely ground by ball milling. The calcined and ball milled powders were isostatically pressed into pellets, and the pellets were sintered at 1150 °C for 5 h in air with a heating and cooling rate of 200 °C/h.

After sintering, the ceramic samples were ground and samples of the powder were used for XRD and TG-DTA measurement. X-ray diffraction analysis of the powder was carried out at room temperature using a RIGAKU RINT-1500 diffractometer. Cu-Kα radiation was used as the X-ray source. Thermogravimetric measurement was carried out using a RIGAKU Thermo-plus TG8120 thermogravimetric and differential thermal analyzer (TG-DTA). For the measurements, a powder sample of about 20 mg was heated in air from room temperature to 1100 °C at a rate of 10 °C/min.

For the oxygen permeability measurement, ceramic samples were prepared for $Ba(Co_{0.9}In_{0.1})O_{3-\delta}$, $(Ba_{0.9}Sr_{0.1})(Co_{0.9}In_{0.1})O_{3-\delta}$, $Ba(Co_{0.85}In_{0.15})O_{3-\delta}$, $(Ba_{0.9}Sr_{0.1})(Co_{0.85}In_{0.15})O_{3-\delta}$, $Sr(Co_{0.8}Fe_{0.2})O_{3-\delta}$ and $(Ba_{0.5}Sr_{0.5})(Co_{0.8}Fe_{0.2})O_{3-\delta}$. The calcined and ball milled powders were isostatically pressed into pellets, and the pellets were sintered for 5 h in air. For each composition, the sintering of the ceramic sample was carried at two or three different temperatures between 1050 and 1200 °C, and the densities of the sintered pellets were measured according to Archimedes' method. The sample with the highest density was chosen for the permeability measurement. The sample was sliced and polished into disks of approximately 1 mm in thickness.

The oxygen permeability of the disks was measured by a method similar to that used in previous work [28]. The disk-shaped sample was placed between two concentric Al2O3 tubes. The sealing between the outer Al2O3 tubes and the sample was achieved by glass rings. After forming the glass seals at 700 °C, the sample was heated to 900 °C. The permeability measurements were conducted during the cooling process. The temperature was held at 900, 850, 800 and 750 °C, and the permeability was measured. During the permeability measurements, the upper side of the sample was supplied with a mixture of oxygen with helium as the feeding gas. The oxygen partial pressure of the feeding gas was kept at 0.21 atm, 0.5 atm and 1 atm in order to evaluate the dependence of permeability on $(PO_2)1/n$. The total gas flow rate on the upper side was held steady at 40 cm^3/min. The lower side of the sample was supplied with argon as the sweep gas. The oxygen potential of the outlet gas was monitored using the Toray LC-800 oxygen analyzer. The argon gas flow rate was controlled at 40 cm^3/min using a mass flow controller. The sample was maintained under fixed conditions for more than 1 h until the oxygen potential of the outlet gas reached equilibrium. The permeation of oxygen through the sample was evaluated from the gas flow rate and the oxygen potential of the outlet gas. The leak rate through the sample was estimated from the amount of helium in the outlet gas, which was measured using the ANELVA AQA-100 MPX quadrupole gas analyzer. The oxygen permeability was corrected by subtracting the amount of oxygen due to the leak.

The oxygen permeability was compared under the following constant conditions: the sample thickness was 1 mm and the oxygen partial pressure of the feeding and sweeping gas was 0.21 atm and 0.01 atm. These values were obtained under the assumption that the oxygen permeability of the samples is in inverse proportion to the sample thickness and dependent on the oxygen partial pressure according to the power law, $(P_{o2\text{-high}})^{1/n}$-$(P_{o2\text{-low}})^{1/n}$.

3. Results and discussion

Fig. 1 (a) shows the X-ray diffraction patterns of $(Ba_xSr_{1-x})(Co_{0.9}In_{0.1})O_{3-\delta}$ in which the indium substitution for Co was fixed at 10 mol% and that in which the Ba concentration was varied between $x = 0$ and 1.0. The magnified view of Fig. 1 (a) for $0.5 \geq x \geq 0$ is shown in Fig. 1 (b). The XRD pattern of $Sr(Co_{0.9}In_{0.1})O_{3-\delta}$ at $x = 0$ shows that the sample contains a hexagonal polymorph of $SrCoO_{3-\delta}$, and $SrIn_2O_4$ (JCPDS 33-1336). Position of the diffraction peaks for the hexagonal polymorph agreed better with rhombohedral $Sr_2Co_2O_5$ (JCPDS 40-874) than $Sr_6Co_5O_{15}$ (JCPDS 86-614). Consequently, the hexagonal polymorph in $Sr(Co_{0.9}In_{0.1})O_{3-\delta}$ is described as $Sr_2Co_2O_5$ in this study, though the structure of the hexagonal polymorph in $SrCoO_{3-\delta}$ is usually explained as $Sr_6Co_5O_{15}$ [23]. In Fig. 1 (a) and (b), the peaks corresponding to $Sr_2Co_2O_5$ and $SrIn_2O_4$ are marked with "r" and "i", respectively. For $x = 0.1$ to 0.4, the diffraction patterns can be explained mainly as a hexagonal polymorph with similar structure to rhombohedral $Sr_2Co_2O_5$. The peaks corresponding to the hexagonal polymorph are marked with "R". The results suggest that $(Ba_xSr_{1-x})(Co_{0.9}In_{0.1})O_{3-\delta}$ where $0.4 \geq x \geq 0$ mainly consists of the hexagonal polymorph. The diffraction peaks of the hexagonal polymorph shift to a lower angle with increasing Ba, and the lattice constant of the hexagonal polymorph increases with the increasing content of Ba, which has a larger ion radius than that of Sr. The appearance of the $SrIn_2O_4$ peaks in the pattern for $x = 0$ suggests that the solubility of indium at the B-site of $SrCoO_{3-\delta}$ is less than 10% [28]. As shown in Fig. 1 (b), the peaks for $SrIn_2O_4$ also appear in the diffraction patterns for $x = 0.1$ to 0.5, indicating that the solubility of indium at the B-site of $(Ba_xSr_{1-x})CoO_{3-\delta}$ is less than 10% where $0.5 \geq x \geq 0$.

The XRD patterns where $1.0 \geq x \geq 0.5$ are changed considerably from those of $0.4 \geq x \geq 0$. For $x = 0.5$ to 0.8, the diffraction pattern can be explained as the coexistence of the hexagonal polymorph and cubic perovskite. The peaks corresponding to the cubic perovskite are marked with "p". The traces shown by arrows in Fig. 1 (b) for $x = 0.4$ seem to correspond to cubic perovskite, but the intensity of the peaks is small and the existence of the perovskite phase at $x = 0.4$ seems uncertain. Thus, the appearance of the perovskite was identified to occur where $1.0 \geq x \geq 0.5$. The diffraction pattern at $x = 0.9$ shows that the sample consists only of the cubic perovskite. The Miller indices of the