Influences of A-site Partial Substitution for $BaCo_{0.7}Fe_{0.3}O_3$ Oxide on Perovskite Structure and Oxygen Permeability

Kazuya Kinoshita,* Hajime Kusaba, Go Sakai,† Kengo Shimanoe,† Norio Miura†† and Noboru Yamazoe†
Department of Molecular and Material Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Fukuoka 816-8580, Japan.
†*Department of Materials Science, Faculty of Engineering Sciences, Kyushu University, Fukuoka 816-8580, Japan.*
††*Advanced Science and Technology Center for Cooperative Research, Kyushu University, Fukuoka 816-8580, Japan.*

(Received November 26, 2001; CL-011187)

Oxygen permeation property of A-site partially substituted barium cobaltites, $A'_xBa_{1-x}Co_{0.7}Fe_{0.3}O_{3-\delta}$ ($A' =$ Ba, Pr, Gd, Dy, Y and Yb), were examined. Substitution of Ba by Dy, Y or Yb was found to stabilize cubic perovskite structure even when x remained as small as 0.05. As a result, oxygen permeation through the disks made of these oxides appeared at temperature lower than 500 °C, and reached fairly high levels at elevated temperature.

Perovskite-type oxides with a typical formula of ABO_3 allow total or partial substitution of various cations for A and/or B sites, resulting in interesting effects on physicochemical properties. Among such examples are electronic and oxide-ionic mixed conductors, which have promise in industrial applications to oxygen permeable membrane, solid oxide fuel cell and membrane reactor.[1,2] As for the oxygen permeable membrane, relevant mixed-conductors have been exploited mostly among those perovskite-type oxides which contain Sr and Co at A- and B-site, respectively (cobaltites), finding $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ as the most promising oxygen-permeable oxide in the $La_{1-x}Sr_xCo_yFe_{1-y}O_{3-\delta}$ system.[3] Even with this particular oxide, however, the oxygen permeability attained is not always sufficient for practical applications. Oxides with high oxygen permeability thus need to be explored further covering wider combinations of A- and/or B-site elements. As an effort in this direction we focused attention on $BaCo_{0.7}Fe_{0.3}O_{3-\delta}$ and its A-site partial substituted derivatives. Ba cobaltites have scarcely been investigated for oxygen permeability, because Ba is too large a cation to give cubic perovskite structure for the cobaltites. The relevance of oxygen permeation and cubic perovskite structure has been confirmed clearly with Sr cobaltites-derived oxides, $Sr_{0.9}Ca_{0.1}Co_{1-x}Fe_xO_{2.5+\delta}$ ($0 < x < 0.2$).[4] If the cubic phase can be stabilized at room temperature by partial substitution for A-site, significant oxygen permeability can be expected, because some Ba containing cobaltites exhibited remarkable permeability: $La_{0.6}Ba_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ showed larger oxygen permeability than $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$, and that $Gd_{0.2}Ba_{0.8}Co_{0.7}Cu_{0.2}Fe_{0.1}O_{3-\delta}$ gave extremely high oxygen permeability.[5] It was found in the present study that the Ba cobaltites can in fact exhibit oxygen permeable properties almost comparable to those of the Sr cobaltites, when Ba is replaced only partially by smaller rare earth elements. This paper reports the influences of A-site partial substitution for $BaCo_{0.7}Fe_{0.3}O_{3-\delta}$ on crystal structure and oxygen permeability. The A-site partially substituted oxides selected were $Ba_{0.95}A'_{0.05}Co_{0.7}Fe_{0.3}O_{3-\delta}$ with $A' =$ Ba, Pr, Gd, Dy, Y and Yb. The ionic radii of Ba and the rare earth metal (A′) substituents are in the order: $Ba^{2+}(0.161\,nm) \gg Pr^{3+}(0.118\,nm) > Gd^{3+}(0.111\,nm) > Dy^{3+}(0.108\,nm) > Y^{3+}(0.108\,nm) > Yb^{3+}(0.104\,nm)$.[6] Here the ionic radii of rare earth metal are represented by those of the cations occupying at

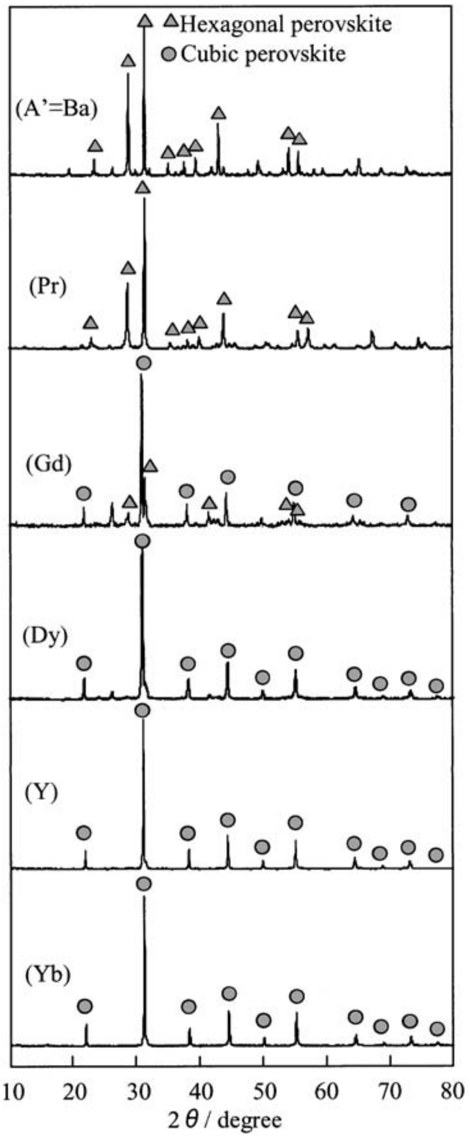

Figure 1. XRD patterns of $A'_{0.05}Ba_{0.95}Co_{0.7}Fe_{0.3}O_{3-\delta}$ ($A' =$ Ba, Pr Gd, Dy, Y and Yb) calcined at 1100 °C for 5 h. (Recorded at room temperature)

the 9 coordination site, because the values at the 12 coordination site have not been reported.

To prepare these oxides, aqueous solutions dissolving acetates or nitrates of the constituent metals to the desired compositions were evaporated to dryness at 350 °C, and then calcined in air first at 850 °C for 5 h and finally at 1100 °C for 5 h. The resulting powder samples were subjected to X-ray (CuKα diffraction analysis at room temperature. As seen from Fig. 1, the structure of crystalline phases formed was different depending on the substituents. A single phase of hexagonal perovskite structure was found for $A' = Ba$ (non-substituted) and Pr, mixed phases of hexagonal and cubic perovskite structures for $A' = Gd$, and a single phase of cubic perovskite structure for $A' = Dy$, Y and Yb. Apparently this change in structure is correlated well with the ionic radii of the substituents. The smallest three substituent (Dy, Y and Yb) could stabilize the cubic phase, while the large ones were not (Pr) or only partially effective (Gd) for the stabilization. The stability of cubic perovskite structure has been discussed based on tolerance factor (*t*). *t* is defined as $(r_A + r_O)/2^{(1/2)}(r_B + r_O)$, where r_A and r_B are the radii of A-site and B-site cations, and r_O is that of oxide ion. When mixed cations occupy A- and/or B-sites, r_A and/or r_B are usually replaced by algebraic mean values. Cubic structure has been considered to be tolerable in case of $0.75 < t < 1.0$. For $BaCo_{0.7}Fe_{0.3}O_{3-\delta}$, *t* is calculated to be 1.073, in accordance with its lattice deformation to the hexagonal structure. The partial substitution of a smaller cation for A is seems to be effective in stabilizing the cubic structure as observed. However, it is also noted that *t* is just a qualitative measure, not applicable for quantitative discussion. For the oxides with $A' = Dy$, Y and Yb, the *t* values are 1.063, 1.063 and 1.064, respectively, all far exceeding unity. Nevertheless, the cubic structure could be stabilized for these oxides as observed. Such remarkable stabilization effects have scarcely been reported so far for the Ba cobaltites. It was confirmed by high temperature X-ray diffraction experiments that these oxides maintained cubic structure upto high temperature. For the oxides with $A' = Ba$, Pr and Gd, phase transformation, hexagonal → cubic, took place at 950 °C on heating, and the reverse transformation did at 900 °C on cooling. In these measurements, XRD patterns were recorded at an interval of 50 °C; each recording took 40 min and 20 min was needed for the next temperature to be settled. To measure the oxygen permeation properties, each of the above powder samples was compacted into a disk, 20 mm in diameter and 1 mm thick under a uniaxial pressure of 100 MPa, and sintered by calcining at 1100 °C in air for 5 h. The disk was polished 0.1–0.2 mm thick from the surface by both sides with emery paper, before it was equipped between the flow of air and that of He to measure the rate of oxygen permeation in between, as described elsewhere.[7] The oxygen permeation was measured by lowering the disk temperature stepwise from 930 °C, because of the convenience for the silver ring sealing used. Figure 2 shows the rate of oxygen permeation for each disk sample as a function of temperature. All the disks exhibited significant oxygen permeation at high temperature (900 °C), although the one with $A' = Pr$ was the smallest of all. For the disks with $A' = Ba$ and Pr, the permeation began to decrease rather abruptly at about 800 °C, reaching very low values at 750 °C. This reflects the occurrence of the cubic → hexagonal transformation in this region. The disks with $A' = Yb$, Y and Dy, for which the cubic structure could be maintained throughout, the permeation showed gradual decreases upon cooling, almost disapearing at 450 °C. This behavior is very similar to one reported for $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$. The disk with $A' = Gd$ gave also similar behavior as indicated, probably because the oxygen permeation property was determined primarily by the cubic perovskite phase dominating in this sample. As mentioned above, the Ba cobaltites ($BaCo_{0.7}Fe_{0.3}O_{3-\delta}$) can be modified to take cubic perovskite structure at room temperature when 5% Ba is replaced by Yb, Y or Dy. As a result, the modified cobaltites can show oxygen permeability in the wide temperature range, like $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$. Although the oxygen permeation rates for the present cobaltites, about 1.3 $cm^3(STP)min^{-1}cm^{-2}$ at 850 °C, are still smaller than those of the Sr cobaltite (3.1 in the same unit at 850 °C), these results suggest that there is plenty of room for discovering new oxygen permeable compounds by materials exploration.

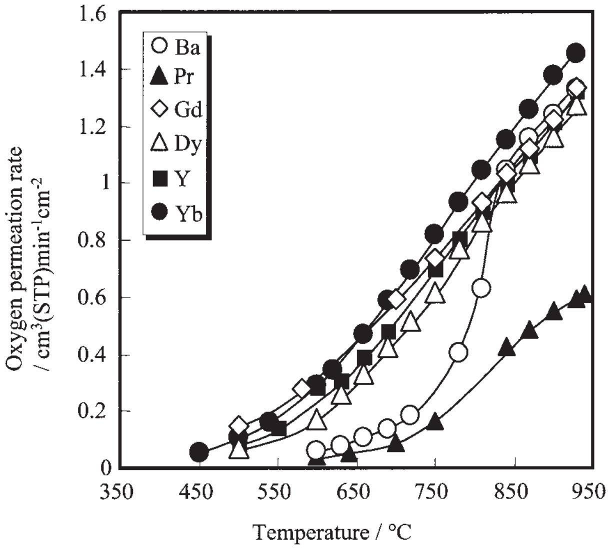

Figure 2. Oxygen permeation rates as a function of temperature for $A'_{0.05}Ba_{0.95}Co_{0.7}Fe_{0.3}O_{3-\delta}$ ($A' = Ba$, Pr Gd, Dy, Y and Yb). (Cooling step)

References

1 W. Jin, S. Li, P. Huang, N. Xu, J. Shi, and Y. S. Lin, *J. Membr. Sci.*, **166**, 13 (2000).
2 S. J. Skinner, *Fuel Cells Bulletin*, **4**, 6 (2001).
3 Y. Teraoka, H.-M. Zhang, S. Furukawa, and N. Yamazoe, *Chem. Lett.*, **1985**, 1743.
4 H. Kusaba, G. Sakai, N. Miura, and N. Yamazoe, *Ionics.*, **6**, 47 (2000).
5 Y. Teraoka, T. Nobunaga, and N. Yamazoe, *Chem. Lett.*, **1988**, 503.
6 R. D. Shannon, Acta. Cryst., **A32**, 751 (1976).
7 N. Miura, H. Murae, H. Kusaba, J. Tamaki, G. Sakai, and N. Yamazoe, *J. Electrochem. Soc.*, **146**(7), 2581 (1999).