Oxygen sorption-desorption properties and order–disorder transitions on La–Sr–Co–Fe perovskite-type oxides

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The oxygen non-stoichiometry (δ) and structural properties of a brownmillerite-type oxide of La₀.₁Sr₀.₉Co₀.₉–Fe₀.₁O₃–δ (LSCF1991) during oxygen sorption/desorption were investigated by simultaneously applying a temperature-programmed technique and high-temperature X-ray diffraction. The structural changes of perovskite-type (P-type) to brownmillerite-type (B-type) and B-type to P-type occurred within limited p(O₂) ranges, and a B-type phase-stable region was observed in the presence of oxygen at high temperature. Moreover, P-type LSCF1991 changed into B-type LSCF1991 through tetragonal P-type LSCF1991 as an intermediate phase. B-type LSCF1991 showed repeating structural changes with a certain limited p(O₂), which is 0.5% < p(O₂) < 1.0%, whereas such changes could not be observed at p(O₂) > 1.0%. These behaviors correspond with the temperature programmed desorption of oxygen profiles, as well as the amount of lattice oxygen (3–δ). The p(O₂) dependence of the structural change will provide a basis for a further investigation into the durability of an oxygen-permeated membrane by predicting the strain across the membrane under practical conditions.

Key-words : Perovskite-type oxide, Oxygen permeation, Phase transition, Partial pressure of oxygen

1. Introduction

La₁₋ₓSrₓCo₁₋ₓFeₓO₃₋δ perovskite-type oxides (referred to as LSCF) are promising materials as solid oxide fuel cell cathodes, oxygen permeation membranes, and catalysts.¹–⁵ Their oxygen non-stoichiometry (δ) and crystalline structure are ones of the most important parameters in determining such properties of perovskites. Therefore, the relations of δ on the structure and temperature of perovskites have been reported in many studies. In addition, another parameter, the partial pressure of oxygen p(O₂), is also important when applying LSCF materials under practical conditions. For example, oxygen-permeated membranes are clearly exposed to a wide range of p(O₂) in daily start-stop or cyclic operations. Nevertheless, there have been few reports on the p(O₂) dependence of δ and the crystalline structure against the temperature because of a difficulty in the precise control of p(O₂).⁵,⁶,⁷

We previously reported the oxygen desorption properties of La₀.₁Sr₀.₉Co₀.₉Fe₀.₁O₃₋δ (LSCF1991) under varying p(O₂) conditions using a home-made fixed-bed flow reactor equipped with an yttria-stabilized Zirconia (YSZ) oxygen sensor as a detector.⁸ The results showed that β oxygen desorption was closely related to the oxygen vacancy order–disorder transitions from perovskite-type (P-type) to brownmillerite-type (B-type) phases. However, backward transitions from B-type to P-type phases have yet to be examined in detail. In this study, the p(O₂) dependence of the oxygen sorption/desorption properties during a structural change from B-type to P-type LSCF1991 was investigated to provide guidance for the material design under practical conditions.

2. Material and methods

The chemical composition was fixed at LSCF1991. P-type LSCF1991 was obtained through final calcination at 1,050°C for 5 h using the nitrates of the constituent metals as the starting chemicals. Next, B-type LSCF1991 prepared through the annealing of P-type LSCF1991 under a N₂ atmosphere.

The oxygen sorption/desorption behavior of B-type LSCF1991 was examined through the temperature-programmed desorption of oxygen (O₂-TPD), which was conducted using a home-made fixed-bed flow reactor equipped with a YSZ oxygen sensor as a detector.⁹ To
obtain the B-type LSCF1991, a sample of P-type LSCF1991 (200 mg) was fixed in a quartz tube and annealed in N₂ [p(O₂) of 41 ppm] at 700°C for 30 min. After cooling to below 50°C under a N₂ stream, the ambient gas was switched to x %O₂ in N₂ (x = 0–21) with a gas flow rate of 100 mL min⁻¹. The sample was then heated to 950°C at a rate of 10°C min⁻¹. The amount of oxygen sorbed/desorbed into/from LSCF1991 was extracted based on the area of the TPD profile. The detailed information on this measurement system was shown in our previous study.⁶ The crystalline structure and change in lattice parameter were measured using an X-ray diffractometer with elevated temperature (HT-XRD, Cu-Kα radiation, Ultima IV, Rigaku Corporation). The effluent gas p(O₂) was monitored using a commercial oxygen sensor (TB-FI YSZ, Daiichinekkei Co., Ltd.). The gas flow rate was set to 250 mL min⁻¹. To clarify the detailed structural changes between P- and B-type LSCF1991, HT-XRD measurements using synchrotron radiation under operando conditions (operando SR-XRD) were also conducted at BL19B2 in SPring-8, Japan. The measurements were conducted using an incident X-ray energy of 12.4 keV and a 2θ scanning range of 10 to 100° at an incident X-ray angle of 3°, under a N₂ stream [p(O₂) of 41 ppm] of 300 mL min⁻¹ into a 32 mL unsealed cell. Furthermore, both P- and B-type LSCF1991 oxygen contents (3–δ) at room temperature (R.T.) were quantified using an iodometry method proposed by Conder et al.⁹

3. Results and discussion

Figure 1(a) shows the oxygen sorption/desorption profiles of B-type LSCF1991 given based on the difference in oxygen partial pressure between influent and effluent gases under various amounts of p(O₂). The positive and negative signals indicate oxygen desorption and sorption, respectively. In a N₂ atmosphere [including O₂ as a p(O₂) impurity of 41 ppm], B-type LSCF1991 showed no sorption/desorption except for an extremely small amount of desorption appearing at above 750°C caused by a reduction of Co ions from 3+ to 2+.¹⁰ Because the samples were pre-treated in N₂, the oxygen will not sorb/desorb under an exceedingly small p(O₂). In contrast to N₂, the negative Δp(O₂) signal, associated with the oxygen sorption, was observed at a p(O₂) of larger than 0.5% at 50–445°C. This sorption peak was shifted to a lower temperature as p(O₂) increased. Owing to an oxygen desorption pretreatment, the oxygen stoichiometry in the solid phase of B-type LSCF1991 is far from at equilibrium using the gas phase. Note that the profiles were obtained under “temperature-programmed” conditions, and we suppose that a solid and gas cannot equilibrate “perfectly”. This large difference in oxygen chemical potential between a solid and gas resulted in a driving force of the oxygen sorption.¹¹ Therefore, a p(O₂) of 1.5%, which was expected to have the largest chemical potential gradient, exhibited the lowest peak temperature and the highest sorption rate.

Desorption started at 360–425°C depending on p(O₂).

Interestingly, both desorption and re-sorption peaks were observed on only a p(O₂) of 0.50–0.98%. No desorption/sorption peaks of higher than 1.25% could be found on p(O₂). The desorption peak temperatures (Tdes) ranged from 555 to 635°C, whereas the re-sorption temperatures (Tre-sor) were located at higher than 790°C. The difference between Tdes and Tre-sor decreased as p(O₂) increased. This suggests that these positive and negative peaks will disappear by canceling each other out when Tdes equals Tre-sor at a certain p(O₂). This assumption is evidenced by the profiles of p(O₂) of 1.25 and 1.50% in that no peaks exist from 550 to 820°C.

The above-mentioned p(O₂) dependence of the sorption/desorption behaviors can be understood by examining the oxygen stoichiometry in the solid phase. Figure 1(b) shows the lattice oxygen (3–δ) changes under various values of p(O₂), which were derived from the profiles in Fig. 1(a). The 3–δ of the as-prepared B- and P-type LSCF1991 was 2.48 and 2.76, respectively, as determined through iodometry. As might be expected, 3–δ in a N₂ atmosphere maintained a constant value of 2.48 despite the elevated temperature. Although 3–δ under the existence of O₂ increased with the temperature, it decreased at approx-

![Figure 1](image-url)
imately 350–450°C. Above this temperature, the plateau region appeared for a $p(O_2)$ of 0.50–0.98% from 650 to 700°C with a rapid decrease of $\delta$ to 2.5. The plateau in the oxygen stoichiometry ($\delta$ of approximately 2.5) denotes the formation of a stable crystal structure such as a B-type phase. After the plateau region, $\delta$ increases again owing to the oxygen re-sorption. This behavior seems to be different from the $p(O_2)$ of 1.25 and 1.50%, which showed a constant decrease of $\delta$ across the temperature range. To confirm these complicated behaviors of $\delta$, we investigated the change in the crystal structure.

**Figure 2** shows X-ray diffraction (XRD) patterns of LSCF1991 before and after annealing in N2 measured at ambient temperature. The diffraction patterns of the B-type phase associated with the oxygen-vacancy ordered structure are also illustrated in Fig. 2. The crystal symmetries were indexed using a cubic P-type phase and orthorhombic B-type phase for before and after annealing, respectively, as reported in the literature. The maximum peak of both P- and B-type phases appeared at approximately 32° in 2θ. Hence, diffraction patterns within the 2θ range of 31–34° are focused upon in the following discussion.

**Figure 3** shows the variation in high-temperature XRD peaks of B-type LSCF1991 under a certain $p(O_2)$. In a N2 atmosphere, no structural changes will occur except for a structural change from B-type to P-type phases at over 900°C. This seems to be the re-sorption of oxygen because $p(O_2)$ was relatively higher in the HT-XRD measurement (700 ppm) than in the O2-TPD measurement (41 ppm). The shift in diffraction peaks to a lower angle mainly originated from the pure thermal expansion of the crystal lattice, which was caused by anharmonicity of the interatomic potential. In a $p(O_2)$ of 0.5%, the diffraction peaks showed a three-staged change with an elevated temperature. This structural change can be explained through the change in $\delta$ shown in Fig. 1(b). The first change is observed at 450°C and indicates the phase transition from a B-type to P-type phase, which is caused by oxygen sorption. However, this P-type phase returned to a B-type phase at 600°C by desorbing the oxygen (second transition). From 650 to 800°C, the B-type phase was stable, which corresponds to the plateau region of $\delta$ shown in Fig. 1(b). Finally, the structural change from a B-type to P-type phase was observed at 850°C owing to the re-sorption of oxygen. In a $p(O_2)$ of 1.0%, the change in the diffraction peaks can also be explained similar to that in a $p(O_2)$ of 0.5%, although it includes some peaks that are neither of an orthorhombic B-type nor cubic P-type phase. In a $p(O_2)$ of 1.5% and air, the diffraction patterns no longer change after the structural phase transition of B-type to P-type.

These results suggest that the second (P-type to B-type) and third (B-type to P-type) transitions were caused within

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**Fig. 2.** XRD patterns of LSCF1991 before (top) and after annealing (bottom) in N2. Lattice constants (a, c) and the crystal structure are also shown.

**Fig. 3.** Variation in high-temperature XRD peaks of B-type LSCF1991 under $p(O_2)$ of 0.07% (in N2) to 21% (in air).
a limited $p(O_2)$ range, which has yet to be reported elsewhere. In connection with the results from Fig. 1(b), we successfully found a stable region of the B-type phase with $\delta$ of approximately 2.5 under the existence of oxygen at high temperature.

In contrast, these HT-XRD results included some peaks which are neither an orthorhombic B-type nor a cubic P-type phase between the structural change in the P-type and B-type phases. They are clear under a $p(O_2)$ of 1.0%, and very likely exist in another $p(O_2)$ on N$_2$ annealed (B-type phase) LSCF1991. Then, to confirm whether this unidentified phase appears only for a B-type phase, the same investigation was conducted in air-annealed (P-type phase) LSCF1991. **Figures 4(a) and 4(b) show O$_2$-TPD and HT-XRD patterns of air-annealed LSCF1991 under a N$_2$ stream.**

The first oxygen desorption from 200 to 400°C does not affect the LSCF1991 phase. The following desorption from 400 to 600°C changes the P-type into a B-type phase. Here, uncertain peaks can be found at 500°C. The left peak is located at a lower angle than that of 550°C, although the peaks shift to a higher angle because of thermal expansion. Then, the peaks at 500°C can indicate the same phase as the unidentified phase shown in the B-type phase.

To clarify the detailed structural changes between P- and B-type LSCF1991, an operando SR-XRD measurement was also conducted in air-annealed LSCF1991 with a P-type structure. **Figures 5(a)–5(c) show synchrotron XRD patterns of P-type LSCF1991 under a N$_2$ stream into the unsealed cell, which $p(O_2)$ of exhaust gas was estimated $\approx$0.1%. At 300°C, a single peak from cubic P-type LSCF1991 200 can be observed. As shown in Fig. 5(c), the diffraction peak splits at 400–450°C, and completely different peaks appear at above 600°C, which correspond to 004 and 220 reflections of B-type LSCF1991. However, the diffraction peaks appearing at 400–450°C correspond to neither P-type nor B-type LSCF1991. According to the previous report on SrCoO$_3$, which has a close compo-

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Fig. 4. P-type LSCF1991: (a) O$_2$-TPD profile under $p(O_2)$ of 0.004% (in N$_2$) and (b) HT-XRD peaks under $p(O_2)$ of 0.07% (in N$_2$).

Fig. 5. (a) Operando synchrotron XRD patterns of P-type LSCF1991 under exhaust $p(O_2)$ of $\approx$0.1%, (b) enlarged view around P-type 110 diffraction peak, and (c) enlarged view around P-type 200 diffraction peak.
sition to LSCF1991, it was indicated that SrCoO$_{3.4}$ changes the crystalline structure from a cubic P-type phase ($3-\delta = 3.0$) into an orthorhombic B-type phase ($2.5 < 3-\delta < 2.75$) through a tetragonal P-type phase ($2.875 < 3-\delta < 3.0$) as an intermediate phase. Therefore, this suggests that P-type LSCF1991 can also change into B-type LSCF1991 through tetragonal P-type LSCF1991 as an intermediate. Although we were unable to conduct a refined analysis from these operando SR-XRD results owing to the use of a qualitative method with a $2\theta$ scan, we believe that the unidentified diffraction peaks at 400–450°C indicate an intermediate phase of LSCF1991.

Figure 6 shows the temperature dependence of the change ratio of the lattice constant ($\Delta a/a_0$) evaluated using HT-XRD. The change ratio of the lattice constant ($\Delta a/a_0$) was calculated as follows:

$$\Delta a/a_0[\%] = 100 \times [a(T) - a_0]/a_0$$

where $a(T)$ and $a_0$ indicate the lattice constant at a temperature of T°C and 50°C, respectively. The monotonic increase in the change ratio of the lattice constant was found for all values of $p(O_2)$ with an elevated temperature, indicating that the thermal expansion mainly dominates the increase in the crystal lattice. The rapid increase of $\Delta a/a_0$ corresponds to the structural change of a P- to B-type phase. However, the change ratio of the lattice constant in a $p(O_2)$ of 0.5% showed a rapid three-fold increase in $\Delta a/a_0$. This suggests that the structure of LSCF1991 changes repeatedly in a $p(O_2)$ of 0.5%.

4. Conclusion

In conclusion, we investigated the $p(O_2)$ dependence of the oxygen sorption/desorption properties during the structural change of B-type to P-type LSCF1991 and revealed two facts regarding LSCF1991. First, an intermediate phase exists between the P-type and B-type LSCF1991. Second, B-type LSCF1991 showed repeating structural changes within a certain limited $p(O_2)$, which is $0.5% < p(O_2) < 1.0%$, although this was not observed at $p(O_2) > 1.0%$. These behaviors correspond with the O$_2$-TPD profiles as well as the amount of lattice oxygen ($3-\delta$). The oxygen permeation membrane is exposed within a wide range of $p(O_2)$, which is covered by the present study. The $p(O_2)$ dependence of the structural change could provide a basis for further examining the durability of the oxygen permeation membrane by predicting the strain across it under practical conditions.

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