RELATIONSHIP OF CRYSTAL STRUCTURE, LATTICE PARAMETERS AND THERMAL EXPANSION TO NONSTOICHIOMETRY IN La$_{1-x}$MnO$_{3+d}$ AND La$_{1-x}$Sr$_x$MnO$_{3+d}$ DETERMINED BY HIGH-TEMPERATURE X-RAY DIFFRACTION UNDER CONTROLLED OXYGEN PARTIAL PRESSURES

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To elucidate the phase change and volume variation of SOFC cathode materials, La$_{1-y}$MnO$_{3+d}$ (y=0, 0.05) and La$_{1-x}$Sr$_x$MnO$_{3+d}$, with temperature and oxygen nonstoichiometry, high temperature X-ray diffraction analysis was made in the atmosphere of the controlled oxygen partial pressure. The structure above 800°C was found to be rhombohedral R3C for the composition with x=0 and 0.1, irrespective of the oxygen content. Both the lattice volume and thermal expansion coefficient increase with decreasing the oxygen content. For x>0.3, the structure above 800°C was essentially cubic. The variation in the lattice parameter with P(O$_2$) at P(O$_2$) > 10$^{-4}$ atm became smaller with the increase in Sr content, x, due to the smaller oxygen excess nonstoichiometry for the larger x in La$_{1-x}$Sr$_x$MnO$_{3+d}$.

INTRODUCTION

During the long time operation of solid oxide fuel cells (SOFC), the cathode materials experience variations of both temperature, T, between room temperature and about 1000°C and oxygen partial pressure, P(O$_2$), between 1 and about 10$^{-4}$-10$^{-5}$ atm. Here, the P(O$_2$) variation is caused both by the consumption of gas phase oxygen due to the electrochemical reaction and by the cathodic overpotential. As the authors have already pointed out, the cathodic overpotential at the interface of oxide electrode / oxide electrolyte is attributed to the deviation of oxygen activity at the interface from that in the gas phase outside the electrodes (1,2). That is, the overpotential, $\eta$, is given by

$$2F\eta = RT \ln \left[\frac{a_0(\text{EL/SE})}{a_0(\text{gas})}\right]$$

[1]

Here, F is the Faraday constant, R is the gas constant, $a_0(\text{EL/SE})$ and $a_0(\text{gas})$ are the oxygen activity, $a_0$, at the electrode / solid electrolyte interface and that in the gas phase, respectively. The $a_0$ variation in the oxide electrode accompanies the variation

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of nonstoichiometric oxygen content in the oxide (3).

Thus, in order to maintain the dimensional matching between the oxide electrode and the electrolyte during the SOFC operation, consideration is required not only for the thermal expansion but also for the variation of volume due to the variation in the oxygen nonstoichiometry. In this paper, interest is focused on the high temperature X-ray diffraction (XRD) analysis of the perovskite-type La$_{1-y}$MnO$_{3+d}$ and La$_{1-x}$Sr$_x$MnO$_{3+d}$ under controlled P(O$_2$) up to 1000°C. Discussion is made on the variation of lattice parameters of the La-Sr-Mn-O SOFC cathode materials with the variation in metallic composition, T, P(O$_2$) and oxygen nonstoichiometry.

EXPERIMENTAL

**Samples.** Precursors for La$_{1-y}$MnO$_{3+d}$ (y=0, 0.05) and La$_{1-x}$Sr$_x$MnO$_{3+d}$ (x=0 — 0.5) were prepared by a freeze–drying method from the mixtures of aqueous La-, Sr- and Mn-acetate solutions (4). The precursors of homogeneous acetate mixtures were calcined at 1200 — 1400°C. Metallic ratio in the samples was confirmed by ICP.

**High Temperature XRD and P(O$_2$) Controlling System.** A vacuum–tight chamber of sample heating element (Rigaku Denki Co.) was attached to the Geigerflex–type XRD apparatus (type RAD–1R, Rigaku Denki Co.). Sample powders were mounted on a platinum flat holder. Temperature of the sample was measured by an R–type thermocouple attached to the holder. Gas–mixtures of O$_2$–N$_2$ and H$_2$–H$_2$O–N$_2$ with desired mixing ratios were let flow through the chamber to control the P(O$_2$) around the sample. The P(O$_2$) in the O$_2$–N$_2$ mixtures and the P(H$_2$O)/P(H$_2$) ratio in the H$_2$–H$_2$O–N$_2$ mixtures were confirmed by means of a zirconia sensor: From the EMF and temperature (~750°C) of a zirconia oxygen concentration cell between air and the outlet gas, the P(O$_2$) in the outlet gas at the temperature of the zirconia cell was evaluated, and from the P(O$_2$) value and the temperature of the zirconia cell, P(H$_2$O)/P(H$_2$) ratio in the outlet gas was calculated. The H$_2$O–H$_2$–N$_2$ gas–mixing system employed in this work was essentially the same as that described elsewhere (5).

**Experimental Conditions and Analysis.** XRD measurements were made using CuKα radiation (40kV 35mA) with step width of 0.04°/2s for 3°<2θ<100° or 0.04°/20s for 60°<2θ<100°. In most measurements, the gas–mixing ratio was kept constant and the sample was equilibrated with the gas at high temperatures, then the temperature was decreased and increased stepwise between room temperature and 1100°C. At T>700°C, samples were kept in the chamber at each temperature under controlled P(O$_2$) more than 8h, so that the samples were equilibrated with the gas phase at each temperature. When T decreases to below ~700°C, the oxygen diffusion in La$_{1-y}$MnO$_{3+d}$ and La$_{1-x}$Sr$_x$MnO$_{3+d}$ becomes very slow (3). Therefore, for T<~700°C, we abandoned the attempt to equilibrate the sample with the gas phase and made XRD analysis immediately after the temperature reached the selected value, so that the composition of the samples was kept at the one equilibrated at ~700°C. Observed diffraction patterns were analyzed by the Rietveld method using a computer program, RIETAN, composed by Izumi (6).

RESULTS AND DISCUSSION

**Structure of LaMnO$_{3+d}$**
**Structural Change with P(O₂) and T.** A typical example of the temperature change of powder XRD pattern is shown in Fig.1. Since the measurement was started from higher temperatures, no line broadening was observed in the lower temperatures. All the patterns in Fig. 1 can be indexed by the rhombohedral R̅3C system.

In the reduced atmospheres attained by H₂O–H₂ gas mixtures, three kind of XRD patterns, R̅3C and two orthorhombic system of Pbnm (Pnma) were observed with varying P(O₂) and T. Here we call two types of Pbnm, Pbnm(II) and Pbnm(III). Typical examples are shown in Fig. 2: Takeda et al. already found these three types at room temperature. They found that the structure changes from R̅3C through Pbnm(II) to Pbnm(III) with decreasing oxygen content (7). The present study revealed that these three types also appear in the samples with nearly stoichiometric or oxygen deficient composition with increasing temperature, from Pbnm(III) through Pbnm(II) to R̅3C.

Figure 3 shows the structure of LaMnO₃₋d at each condition studied in this work. At T≥800°C, the structure belongs to the rhombohedral R̅3C irrespective of the oxygen nonstoichiometry. Pbnm(III) appears only in the reduced conditions at low temperatures. Figure 4 shows the nonstoichiometry of LaMnO₃₋d as a function of P(O₂) (8), on which the boundary of R̅3C and Pbnm(II) is indicated. We see that Pbnm structure appears essentially for the oxygen deficient composition. Using the data in Fig. 4, the P(O₂)–T diagram of Fig. 3 can be converted to the oxygen content, 3+d, vs. T diagram, as shown in Fig. 5. In Fig. 5, room temperature data by Takeda et al. (7) is also plotted. Indicated boundaries between the different crystal symmetries are empirical ones.

**Lattice Parameters of LaMnO₃₋d.** Figure 6 shows the relationship between the cubic perovskite and orthorhombic and rhombohedral unit cells. By the Rietveld analysis, La in Pbnm(II) places on the a₀–c₀ plane in Fig. 6, exactly at the body-center position of the cubic unit cell. While in Pbnm(III), La position deviates alternatively about +0.05 and -0.05 along the b₀ axis in Fig. 6.

Figure 7 shows the temperature dependence of the rhombohedral lattice parameters. At T< 700°C, where the oxygen content in the sample is fixed, the lattice parameters vary almost linearly with temperature. At T>700°C, a and c show positive and negative deviation, respectively, from the straight lines in the lower temperature region. These deviations are due to the decrease in the oxygen content with the increase in temperature (cf. Fig. 4).

In Fig. 8, the variation of the lattice parameters in reduced atmospheres is shown in the extended face centered (FC) orthorhombic sublattice, which is indicated in Fig. 6. In the extended FC lattice, the lattice parameters in R̅3C and Pbnm(II) structure are essentially continuous, while large discrepancies are seen between the Pbnm(II) and the Pbnm(III), in the latter, La displacement is obvious.

**Structural Change with La Deficiency and Sr Replacement**

**Effect of La Deficiency.** Only one composition, La₀.₉₅MnO₃₋d was studied. Contrary to LaMnO₃₋d, La₀.₉₅MnO₃₋d exhibits only the rhombohedral R̅3C structure and no Pbnm pattern was observed. The P(O₂) and T dependencies of the rhombohedral lattice parameters and the absolute value of a₀ are similar to those of LaMnO₃₋d. However, a₀ for La₀.₉₅MnO₃₋d is smaller by 0.5 -- 0.8° than that of LaMnO₃₋d. As reported before (8), in La₁₋yMnO₃₋d a part of Mn ions can enter the A-sites and the ratio of the
ions in A sites and B sites can be kept unity. The predominant defect in the oxygen excess composition is considered to be metal vacancies.

**Effect of Sr Substitution.** In La$_{1-x}$Sr$_x$MnO$_{3+d}$ (0.5 > x > 0.1), no Pbnm structure was observed. For the samples quenched to room temperature from 700°C at P(O$_2$) = 1 atm, the structure is rhombohedral R3C irrespective of the Sr content, x. Figure 9 shows the room temperature lattice parameters transformed into the orthorhombic perovskite—type unit cell. As x increases, the structure becomes close to cubic.

Figure 10 shows the temperature dependence of the crystal structure of La$_{0.7}$Sr$_{0.3}$MnO$_{3+d}$ as a function of P(O$_2$) at T > 700 °C and that quenched to appropriate temperature from 700°C. At high temperatures, the structure changes from rhombohedral to cubic Pm3m. In the more reduced atmospheres, or in the more oxygen deficient composition region, transformation to cubic structure takes place at the lower temperatures. At P(O$_2$) = 1 atm between room temperature and 1000°C, the cubic structure appears for x > 0.2.

**Lattice Volume Change with P(O$_2$)**

From the lattice parameters, the lattice volume was calculated. Typical examples are shown in Fig. 11 and 12. LaMnO$_{3+d}$ shows large volume variation in the region of -5 < log P(O$_2$)/atm < 0 and the volume variation in the lower P(O$_2$) region is small. On the other hand, La$_{0.7}$Sr$_{0.3}$MnO$_{3+d}$ exhibits small volume variation at log P(O$_2$)/atm > -5 and large volume variation at log P(O$_2$)/atm < -5.

As shown in Fig. 4, LaMnO$_{3+d}$ exhibits the large oxygen excess (metal deficient) nonstoichiometry in the higher P(O$_2$) region, while the oxygen deficient nonstoichiometry in the reduced atmospheres is rather small. The tendency in the variation of nonstoichiometry and that of the lattice volume with P(O$_2$) are essentially similar, suggesting that the variation of volume is due to the variation of nonstoichiometry.

According to the earlier papers (4,9), the oxygen excess nonstoichiometry of La$_{1-x}$Sr$_x$MnO$_{3+d}$ in the high P(O$_2$) atmospheres decreases with increasing x and disappears when x exceeds 0.3 ~ 0.4. While the oxygen deficient nonstoichiometry in the reduced atmospheres becomes larger with increasing x. This P(O$_2$) dependence of nonstoichiometry affects the variation of volume in Fig. 12. At log P(O$_2$)/atm > -5, the variation of nonstoichiometry is very small and the variation of volume is also small. At the lower P(O$_2$) region, the oxygen deficient nonstoichiometry become large with decreasing P(O$_2$) (4,9) and the volume increases.

**Thermal Expansion**

Figure 13 and 14 show the variation of volume with temperature for LaMnO$_{3+d}$ and La$_{0.7}$Sr$_{0.3}$MnO$_{3+d}$, respectively. At T > 700°C at log P(O$_2$)/atm > -5, the thermal expansion of LaMnO$_{3+d}$ under constant P(O$_2$) is much larger than that at T < 700°C because the variation of nonstoichiometry becomes remarkable at the higher temperatures. The volume of La$_{0.7}$Sr$_{0.3}$MnO$_{3+d}$ at log P(O$_2$)/atm > -5 varies linearly with temperature because La$_{0.7}$Sr$_{0.3}$MnO$_{3+d}$ shows essentially no variation of nonstoichiometry at this P(O$_2$) region.

From the slope of the plots, the thermal expansion coefficient is calculated. At log
P(O_2)/atm > -5, the thermal expansion coefficient of LaMnO_{3+d} at T < 700°C is 8.0 \times 10^{-6}/K, while that at T > 700°C is about 23 \times 10^{-6}/K. The thermal expansion coefficient of La_{0.7}Sr_{0.3}MnO_{3+d} at log P(O_2)/atm > -5 is about 12 \times 10^{-6}/K.

**Effect of Volume Variation on the Properties as an SOFC Cathode**

As shown above, the variation of volume with P(O_2) in the cathode atmospheres of SOFC is remarkable for the La_{1-x}Sr_xMnO_{3+d} which exhibits large oxygen excess nonstoichiometry, that is for x < -0.2. This variation is larger for smaller x.

When air (P(O_2) = 0.21 atm) is used as cathode gas and cathodic overpotential of 200mV is applied, the \alpha_{EL/SE} at 800 — 1000°C is, from Eq. [1], about 10^{-2}. Then, the effective P(O_2) at the electrode / solid oxide electrolyte is about 10^{-4} atm. When the cathode material is LaMnO_{3+d}, we find from Fig. 11 that the volume of LaMnO_{3+d} at the interface expands about 1.5% from that at the equilibrium with air, or at the electrode / gas interface. (At 1000°C, v = 123.7 \times 10^{-24}cm^3 at P(O_2) = 10^{-4} atm and v = 122.0 \times 10^{-24}cm^3 at P(O_2) = 0.21 atm.) The expansion due to overvoltage along one axis is about (1.5\% / 3 \approx) 0.5%.

So far we use La_{1-x}Sr_xMnO_{3+d} as the cathode and stabilized zirconia as the electrolyte, the mismatching of thermal expansion coefficient is less that 3x10^{-6}/K. Then, the difference in thermal expansion at the interface between room temperature and 1000°C is less than (3x10^{-6} \times 1000 \approx) 0.3%. Thus, the mismatch due to overvoltage expansion describe above is more than the thermal expansion mismatch usually emphasized.

For the selection of SOFC cathode material, it is necessary to examine the volume variation of the cathode material due to P(O_2) and overvoltage variation. When one employs the perovskite-type Ln_{1-x}A_xMnO_{3+d} (Ln: lanthanoid, A: alkali-earth metals) as cathode of SOFC, one must select the materials with x large enough, maybe x > 0.2, to reduce the oxygen excess nonstoichiometry of this oxide.

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Fig. 1. Temperature change of XRD pattern for LaMnO$_{3-d}$. At $T > 673^\circ$C, the sample was in equilibrium with the gas phase of $P(O_2) = 1$ atm. At $\leq 673^\circ$C, the sample was quenched from the equilibrium state at 673°C.

Fig. 2. Typical XRD patterns observed in LaMnO$_{3-d}$. LaMnO$_{2.980}$ at 800°C: indexed by R3C, LaMnO$_{2.983}$ at 700°C: indexed by Pbnm (named Pbnm(II)), LaMnO$_{2.988}$ at 400°C: indexed by Pbnm (named Pbnm(III)). Composition was determined using Fig. 4.
Fig. 3. Crystal structures observed in LaMnO$_{3+d}$. Data shown by closed symbols were obtained under the equilibrium condition indicated on the upper scale. Data points with open symbols were measured for the samples quenched to respective temperatures from the condition around the hatched band.

Fig. 4. Nonstoichiometry of LaMnO$_{3+d}$ (8) on which the boundary between R$\bar{3}$C and Pbnm(II) structure is indicated.
Fig. 5. Regions for R3C, Pbmm (II), and Pbmm(III) structure in LaMnO$_{3+d}$ empirically determined on the $T$ - 3+d diagram. Results by Takeda et al. (7) are indicated by closed symbols.

Fig. 6. Relationship among cubic perovskite, the rhombohedral $R3C$ and the orthorhombic Pbmm unit cells. A face centered sublattice with $z=8$ is also indicated by thin dotted lines.

Fig. 7. Temperature dependence of rhombohedral lattice parameters of LaMnO$_{3+d}$. 

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Fig. 8. Temperature dependence of lattice parameters in a face centered orthorhombic extended cell for LaMnO$_{3+d}$ with d < 0.

Fig. 9. Room temperature lattice parameters of La$_{1-x}$Sr$_x$MnO$_{3+d}$ quenched from 700°C and P(O$_2$) = 1 atm in the orthorhombic perovskite-type unit cell. Actual symmetry is R$3C$.

Fig. 10. Crystal structures observed in La$_{0.7}$Sr$_{0.3}$MnO$_{3+d}$. Data shown by closed symbols were obtained under the equilibrium condition indicated on the upper scale. Data points with open symbols were measured for the samples quenched to respective temperatures from the condition around the hatched band.
Fig. 11. $P(O_2)$ dependence of rhombohedral lattice volume ($z=2$), $v$, for LaMnO$_{3+d}$. Curves are drawn to indicate the rough tendency of $V$ vs. log $P(O_2)$ relationship.

Fig. 12. $P(O_2)$ dependence of rhombohedral lattice volume ($z=2$), $v$, for La$_{0.7}$Sr$_{0.3}$MnO$_{3+d}$. Curves are drawn to indicate the rough tendency of $V$ vs. log $P(O_2)$ relationship.

Fig. 13. Thermal expansion of rhombohedral lattice volume ($z=2$), $v$, for LaMnO$_{3+d}$ under constant $P(O_2)$ for $T > 700^\circ C$ and quenched from $700^\circ C$ for $T < 700^\circ C$.

Fig. 14. Thermal expansion of rhombohedral lattice volume ($z=2$), $v$, for La$_{0.7}$Sr$_{0.3}$MnO$_{3+d}$ under constant $P(O_2)$ for $T > 700^\circ C$ and quenched from $700^\circ C$ for $T < 700^\circ C$. 