— Technical Paper —

Shrinkage Behavior of $\text{La}_{1-x}\text{MnO}_{3+\delta}$ Perovskites ($0 \leq x \leq 0.1$) by Phase Change during Thermal Cycling in Air

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The shrinkage mechanism of nondoped lanthanum manganite perovskites, $\text{La}_{1-x}\text{MnO}_{3+\delta}$ ($0 \leq x \leq 0.1$), during a thermal cycling in air has been investigated. For the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ samples annealed at 600°C , they shrank during a thermal cycle measurement in the temperature range from 600 to 1100°C , and a decrease of their linear thermal expansion coefficients at temperatures $>$ around 940°C was observed. It was found during the thermal cycle measurement in the temperature range from 50 to 800°C that the $\text{LaMnO}_{3+\delta}$ sample quenched from 1000°C exhibited a large shrinkage at around 700°C by phase change from the orthorhombic into the hexagonal perovskite. For the $\text{La}_{0.95}\text{MnO}_{3+\delta}$ and $\text{La}_{0.9}\text{MnO}_{3+\delta}$ perovskite samples without the phase change, no shrinkage behavior was observed.

Key Words : Lanthanum Manganite, Thermal Expansion, Thermal Cycle, Shrinkage Behavior, SOFC, Cathode

1 Introduction

Alkaline earth metal (AE = Ca and Sr)-doped lanthanum manganite perovskites are considered to be the most promising candidate for cathode materials in high-temperature solid oxide fuel cells (SOFC) with Y_2O_3 stabilized ZrO_2 (YSZ) electrolyte. The application to the cathode for the materials requires to have good thermal expansion match with the YSZ electrolyte,^{1, 2)} high electronic and oxide-ion conductivity,^{3, 4)} high chemical stability with the electrolyte,^{5, 6)} and excellent catalytic activity of oxygen reduction ($\text{O}_2 + 4\text{e}^- \rightarrow 2\text{O}^{2-}$) in air.^{7, 8)} Additionally, they must be capable of being fabricated in a form of a porous layer. Over the past few decades, a considerable number of studies have been conducted on the properties of AE-doped $\text{LaMnO}_{3+\delta}$ perovskites, and it is widely recognized that the perovskites fulfill the requirements of SOFC cathode.

During operation, the SOFC generator undergoes many thermal cycles between room temperature and the operating temperature $\sim 1000^\circ\text{C}$. Since an excellent compatibility of the thermal expansion behaviors of the cell components under each atmosphere is indispensable for giving the least thermal stress in the SOFC stack, the concern with their thermal expansion behaviors between room temperature and the operating temperature has been growing in recent years.^{9–11)} Since the average linear thermal expansion coefficient (TEC) of YSZ electrolyte (whose TEC in the temperature range from 50 to 1000°C shows $10.3 \times 10^{-6}/^\circ\text{C}$) is constant regardless of oxygen partial pressure and Y_2O_3 content,¹⁰⁾ the other cell components should have the same TEC. In the case of LaMnO_3 -based cathodes, it can be achieved by controlling their compositions. From the viewpoint of thermal expansion compatibility among the cell components, $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_{3+\delta}$ and $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_{3+\delta}$ (whose TECs in the temperature range from 1000 to 50°C show $10.0 \times 10^{-6}/^\circ\text{C}$

and $11.2 \times 10^{-6}/^\circ\text{C}$, respectively) have an appropriate composition for SOFC cathodes.²⁾

Quite recently, it has been reported that $\text{La}_{1-x}\text{AE}_x\text{MnO}_{3+\delta}$ with an AE content of $0 \leq x < 0.4$ perovskites show a shrinkage of the sintered samples during a thermal cycling between 600 and 1100°C under the oxidizing atmosphere.²⁾ The shrinkage of the cathode by thermal cycling is quite serious, because of a generation of thermal stress in the SOFC stack. Taking into account LaMnO_3 -based perovskites with an AE content of $0 \leq x < 0.4$ releasing and absorbing oxygen between 600 and 1100°C , the shrinkage of the perovskite samples seems to relate to the phase change and the release and absorption of oxygen.

In order to find the prevention technique for the shrinkage of lanthanum manganites during thermal cycling, it is necessary to understand its mechanism. Nondoped $\text{La}_{1-x}\text{MnO}_{3+\delta}$ perovskites ($0 \leq x \leq 0.1$) also show nonstoichiometry of oxygen, depending on temperature. In this perovskite system, Takeda *et al.*¹²⁾ have reported two types of perovskite structures, rhombohedral and orthorhombic, in the temperature range from room temperature to 1100°C . Additionally, the boundary between rhombohedral and orthorhombic phases shifts to higher temperature with increasing La-deficiency. It would be helpful to consider the relationship among the shrinkage, the release and absorption of oxygen, and the phase change for lanthanum manganites during thermal cycling here. The purposes of this study are to clarify the relationship for $\text{La}_{1-x}\text{MnO}_{3+\delta}$ perovskites with a La-deficiency of $0 \leq x \leq 0.1$, during thermal cycling in air.

2 Experimental

Non-doped lanthanum manganites, $\text{La}_{1-x}\text{MnO}_{3+\delta}$ ($x = 0, 0.05$ and 0.1) were prepared using traditional ceramic processing methods. As starting materials, La_2O_3 powder

Table 1 Lattice parameters, cell volumes and symmetries of the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ perovskites after annealing at 600°C in air. (H: hexagonal (rhombohedral)).

Annealed samples	Lattice parameters and cell volumes	Symmetries
$\text{LaMnO}_{3+\delta}$	$a = 5.5237(4) \text{ \AA}$, $c = 13.326(1) \text{ \AA}$, $V = 352.11 \text{ \AA}^3$, $Z = 6$	H
$\text{La}_{0.95}\text{MnO}_{3+\delta}$	$a = 5.5282(5) \text{ \AA}$, $c = 13.347(2) \text{ \AA}$, $V = 353.26 \text{ \AA}^3$, $Z = 6$	H
$\text{La}_{0.9}\text{MnO}_{3+\delta}$	$a = 5.5204(4) \text{ \AA}$, $c = 13.343(1) \text{ \AA}$, $V = 352.16 \text{ \AA}^3$, $Z = 6$	H

(pre-heated at 1500°C for 1 h) (99.9%, High Purity Chem., Japan), and Mn_2O_3 (99.9%, Mitsuwa Chem., Japan) were used. The powders were thoroughly mixed in the desired proportions with ethanol in a ball mill for 10 minutes, where the ball and mill materials used were Y_2O_3 partial stabilized ZrO_2 . After drying, the mixtures were heated at 1200°C for 10 h in air. The milling and heating procedures were repeated twice. The powders with poly-vinyl butyl alcohol and n-butyl phthalate were compacted into tablets at 40 MPa. They were then fired at 1400°C for 20 h in air.

All the samples were analyzed by powder X-ray diffraction (XRD) (18 kW, Mac Science, M 18 XHF²²) using monochromated $\text{CuK}\alpha$ radiation and a scintillation detector. High-temperature XRD measurement was carried out in the temperature range from room temperature to 1100°C in air, and the sample temperatures were maintained for 1 h at selected temperatures. A scanning rate of 0.02°/s was used.

Density of sintered tablets was determined from observed values of size and weight of the tablets. Relative density was derived using the theoretical value determined from the experimental lattice parameters and unit formula.

Although not strictly accurate, the TECs of the perovskite materials in this study are calculated from the following equation:

$$\alpha = (1/L_1)(L_2 - L_1)/(T_2 - T_1) \quad (1)$$

where α is the TEC, T_1 is the starting temperature, T_2 is the terminal temperature of an experiment, L_1 and L_2 are the initial and final gauge lengths, respectively. Thermal expansion behavior during thermal cycles was measured using a Mac Science TD 5000 S system. Samples used were cut into rectangular shapes of approximately 5 mm $\times$ 5 mm $\times$ 20 mm length. A rod of sapphire was used as a reference. Thermal cycle measurements were carried out at a heating/cooling rate of 5°C/min in the temperature range between 600°C and selected temperatures in air, and the sample temperatures were maintained for 30 minutes at 600°C and 800°C, and for 10 minutes at 1100°C. The heating/cooling processes in the thermal cycle measurement were repeated tenth.

Thermogravimetry (TG) measurement was carried out using Mac Science TG-DTA-5000S equipment in the temperature range from room temperature to 1000°C in air. A heating/cooling rate of 5°C/min was used.

3 Results and Discussion

3.1 Shrinkage behavior of $\text{La}_{1-x}\text{MnO}_{3+\delta}$ samples annealed at 600°C during thermal cycling

$\text{LaMnO}_{3+\delta}$ perovskite shows nonstoichiometry of oxy-

Fig. 1 Extension behavior of the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ perovskite samples ($x = 0, 0.05$ and 0.1) annealed at 600°C during a thermal cycle measurement between 600 and 1000°C in air, as a function of temperature. (a) Sapphire, (b) $\text{LaMnO}_{3+\delta}$, (c) $\text{La}_{0.95}\text{MnO}_{3+\delta}$, (d) $\text{La}_{0.9}\text{MnO}_{3+\delta}$.

gen, δ , and its oxygen content has a tendency to decrease with increasing temperature under oxidizing atmospheres. The expression as the formula of $\text{LaMnO}_{3+\delta}$ is often used in the previous papers.¹³⁻¹⁸⁾ Oxygen and A-site metals in lanthanum manganite perovskites show a cubic close packing. From the viewpoint of this close-packed structure, the oxygen contents should be assumed to be 3, and the excess of oxygen is characterized by cation vacancies rather than by interstitial oxygen.^{19,20)} Thus, the perovskites should be strictly expressed as the formula of $\text{La}_{1-x}\text{Mn}_{1-x}\text{O}_3$. However, the formula of $\text{LaMnO}_{3+\delta}$ with the excess of oxygen is adapted in this paper in order to easily understand an expression between A-site and B-site metal contents in the perovskite structures.

Table 1 shows the lattice parameters, cell volumes and symmetries of the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ perovskites after annealing at 600°C in air. The perovskites crystallize in a rhombohedral-hexagonal unit cell. $\text{LaMnO}_{3+\delta}$, $\text{La}_{0.95}\text{MnO}_{3+\delta}$ and $\text{La}_{0.9}\text{MnO}_{3+\delta}$ samples showed a single perovskite phase of hexagonal symmetry and were based on the LaAlO_3 -type (R-3C). The XRD results of these perovskites agree with those by Takeda *et al.*¹²⁾ Figure 1 shows the extension behaviors of the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ perovskite samples during the thermal cycle measurement between 600

Fig. 2 Expansion of the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ perovskites during a thermal cycle, as a function of temperature in air. (a) $\text{LaMnO}_{3+\delta}$, (b) $\text{La}_{0.95}\text{MnO}_{3+\delta}$, (c) $\text{La}_{0.9}\text{MnO}_{3+\delta}$.

and 1100°C in air, as a function of temperature. All the samples were annealed at 600°C. The relative densities of the perovskite samples used for the present measurements were 75% for the $\text{LaMnO}_{3+\delta}$, 74% for $\text{La}_{0.95}\text{MnO}_{3+\delta}$ and 82% for $\text{La}_{0.9}\text{MnO}_{3+\delta}$. It is obvious in these figures that shrinkage behaviors of all the samples were observed in the temperature range from 600 to 1100°C, on the other hand, the sapphire rod showed no shrinkage.

In order to clarify the effect of the aging time at 600°C and 1100°C in the measurements on the shrinkage, the shrinkage at each aging temperature was calculated. No shrinkage of any of the samples during the aging time at 600°C was observed. Although a very small amount of the aging time dependency on the shrinkage at 1100°C was observed, it was negligible: for the $\text{La}_{0.95}\text{MnO}_{3+\delta}$ sample, the shrinkage during one thermal cycling was 0.14%, and the shrinkage during 10 minutes of aging time at 1100°C was 0.0026%. This shrinkage during the aging time is due to the sintering. It is, therefore, concluded that the shrinkage behavior of these samples is independent of the sintering during the aging time at the highest temperature of 1100°C. When the A-site-deficient $\text{La}_{1-x}\text{MnO}_{3+\delta}$ samples were compared with the $\text{LaMnO}_{3+\delta}$, it showed larger shrinkage. A change in the slope at approximately 850°C and 1000°C was observed in the curve corresponding to $x=0$ and $x=0.05$, respectively. This change should be due to the change from the hexagonal (low-temperature) to the orthorhombic (high-temperature) phase.¹²⁾ The measurement for the $\text{La}_{0.9}\text{MnO}_{3+\delta}$ did not show such a break below 1100°C, because its hexagonal structure is stable until about 1100°C.

In order to make clear the shrinkage process of the lanthanum manganites in the thermal cycle measurement, the expansion of their samples at temperatures $\geq 600^\circ\text{C}$ during the heating and cooling processes is plotted as a function of temperature in Fig. 2, where the open sym-

(a) Heating process

(b) Cooling process

Fig. 3 Differential coefficient of thermal expansion-temperature curve of the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ samples during the heating and cooling processes of thermal cycles, where the TECs are calculated using thermal expansion slopes between 2.5°C above and 2.5°C below a given temperature. (a) Heating process, (b) Cooling process.

bols represent the results during the heating process and the solid-line shows those during the cooling process. No difference in the expansion behaviors between the heating and cooling processes was seen in these figures although the shrinkage of the samples was observed in the extension curves. These results suggest that the shrinkage behavior of the lanthanum manganites occurs during both the heating and cooling processes.

It is quite interesting to discuss what the temperature of the shrinkage starts in the thermal cycle measurement. Figure 3 shows the differential coefficient of thermal expansion-temperature curve of the samples during the thermal cycles, where the TECs are calculated using

Fig. 4 TG curves of the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ perovskite powders annealed at 600°C in air as a function of temperature. (a) $\text{LaMnO}_{3+\delta}$, (b) $\text{La}_{0.95}\text{MnO}_{3+\delta}$, (c) $\text{La}_{0.9}\text{MnO}_{3+\delta}$.

thermal expansion slopes between 2.5°C above and 2.5°C below a given temperature. During the heating processes (Fig. 3(a)), the TEC of the $\text{LaMnO}_{3+\delta}$ sample increased at approximately 840°C and then significantly decreased at approximately 935°C . The TEC of the $\text{La}_{0.95}\text{MnO}_{3+\delta}$ sample showed similar temperature dependence although the increase of the TEC started at approximately 900°C . On the other hand, no remarkable peak on the TEC vs. temperature curves was observed for the $\text{La}_{0.9}\text{MnO}_{3+\delta}$ sample, and its TEC decreased with increasing temperature in the temperature range from 950 to 1100°C . The temperature dependences of the TECs during the cooling process (Fig. 3(b)) were almost similar to those during the heating ones, although there was a temperature shift for the increase of the TECs between the heating and cooling processes. This is related to the difference between releasing and absorbing rates of oxygen in the sintered samples²¹⁾.

In general, the TEC of materials tends to increase monotonically with increasing temperature because of volume expansion due to the formation of point defects at high temperature. For the $\text{La}_{1-x}\text{MnO}_{3+\delta}$, the anomalous peaks at around 900°C on the TEC vs. temperature curves were observed. This indicates two different thermal expansion mechanisms, the increase and decrease of TEC.

It is well known that, with increasing temperature, a weight decrease, which corresponded to the release of oxygen, is observed for $\text{LaMnO}_{3+\delta}$. Then, the vacancy is formed in the perovskite structure. It has been reported that the TEC is strongly affected by the formation of vacancies.^{2,9)} In order to understand the TEC increase at the high temperature, it is quite important to know the change of oxygen content in the perovskites. Figure 4 shows the TG curves of the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ perovskite powders annealed at 600°C in air. The weight loss started at approximately 800°C for the $\text{La}_{1-x}\text{MnO}_{3+\delta}$. The $\text{LaMnO}_{3+\delta}$ recovered no weight loss at temperatures <

Fig. 5 Cell volume changes of the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ perovskites in air as a function of temperature from the calculation by high-temperature XRD measurement.

approximately 700°C during the cooling process, whereas there remained the weight loss in the A-site deficient samples.

The release of oxygen results in a charge-compensating by reducing of Mn^{4+} to Mn^{3+} ions. Since ionic radius of Mn^{3+} (high-spin, 78.5 pm) and Mn^{2+} ions (low-spin, 81 pm) is larger than that of Mn^{4+} ion (67 pm) on the B-sites in the perovskite structure,²²⁾ the crystal lattice expands by charge compensation. In addition, the formation of oxygen vacancies also reduce Coulombic interactions between cations and anion: accordingly, the crystal lattice expands.²³⁾ It is obvious in Fig. 3(a) that, for the $\text{LaMnO}_{3+\delta}$ and $\text{La}_{0.95}\text{MnO}_{3+\delta}$ perovskites, the temperature of releasing oxygen is similar to that of increasing the TEC. Thus, it should be explained that the increase of the TEC is caused by release of oxygen and formation of oxygen vacancies. Although the $\text{La}_{0.9}\text{MnO}_{3+\delta}$ continues to release the oxygen in the perovskite structure up to 1100°C , the reverse results, namely the decrease of the TEC, were observed in the temperature range from 950 to 1100°C .

Figure 5 shows the cell volume changes of the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ perovskites in air as a function of temperature, where the cell volumes are presented as the same unit cell. The cell volumes of the perovskite structures monotonically increased with increasing temperature. Since no decrease of the perovskite cells in this temperature range is observed for all the perovskites, it is clear that the shrinkage of the materials at the high temperature does not relate to the change of lattice parameters. However, the length of the samples becomes smaller during thermal cycling. This leads to an expectation that the densification of the materials occurs in the temperature range from approximately 940 to 1100°C during thermal cycling. Although details remain uncertain, there is a possibility that the densification of the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ samples might be related to disappear the vacancies of cation and oxygen in the perovskite structure by their excess existence. However, it is not an easy task to measure the

Fig. 6 Thermal expansion behaviors of the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ perovskite samples annealed at 600°C during a thermal cycle measurement.

effect of the vacancy disappearance on lattice parameters from the high-temperature XRD analysis.

It is quite interesting to note why there is the shrinkage behavior of lanthanum manganites during thermal cycling. The previous paper¹²⁾ has reported two kinds of perovskite structures for $\text{LaMnO}_{3+\delta}$ with different oxygen contents in the temperature range from 800 to 1100°C in air: (1) a hexagonal cell of LaAlO_3 -type structure (Space group, $R\bar{3}C$) at temperatures $<$ approximately 800°C , and (2) an orthorhombic of GdFeO_3 -type structure (Space group, $Pbnm$) in the temperature range between 800 and 1100°C . For $\text{La}_{1-x}\text{MnO}_{3+\delta}$ perovskites, the boundary between hexagonal and orthorhombic phases shifted to higher temperature with increasing La-deficiency. It is reported that temperatures of the stable hexagonal phases are at approximately 800°C for $\text{LaMnO}_{3+\delta}$, at approximately 1000°C for $\text{La}_{0.95}\text{MnO}_{3+\delta}$ and at approximately 1100°C for $\text{La}_{0.9}\text{MnO}_{3+\delta}$. This means that all the perovskite samples in the present study show a change between hexagonal and orthorhombic phases during the thermal cycle measurement between 600 and 1100°C .

Figure 6 shows the thermal expansion behaviors of the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ perovskite samples, which were annealed at 600°C , during the thermal cycle measurement between 600 and 800°C in air. In this temperature range, all the perovskite samples do not show a change between the hexagonal and orthorhombic phases. From the results of powdered XRD analysis, it was confirmed. It is seen in Fig. 6 that the $\text{LaMnO}_{3+\delta}$ sample showed a very small amount of shrinkage behavior, and no shrinkage in thermal expansion curves was observed for the $\text{La}_{0.95}\text{MnO}_{3+\delta}$

Fig. 7 XRD patterns of the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ perovskite samples quenched from 1000°C in air.

and $\text{La}_{0.9}\text{MnO}_{3+\delta}$. These results support that the shrinkage behavior of the perovskite samples is caused by the phase change in the temperature range higher than 800°C .

3.2 Shrinkage behavior of $\text{La}_{1-x}\text{MnO}_{3+\delta}$ samples quenched from 1000°C during thermal cycling

The lanthanum manganites with high-temperature phase can metastably exist at room temperature by quenching from the high temperatures. Figure 7 shows the XRD patterns of the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ perovskite samples after quenching from 1000°C in air. It is obvious from Fig. 7(a) that the (111) reflection, which is characterized by the orthorhombic phase, is observed in the XRD pattern of the $\text{LaMnO}_{3+\delta}$. As shown in Figs. 7(d-f), it is also observed that the (112) reflection of orthorhombic phase for the $\text{LaMnO}_{3+\delta}$ splits into the (104) and (110) reflections of the hexagonal structure for the $\text{La}_{0.95}\text{MnO}_{3+\delta}$ and $\text{La}_{0.9}\text{MnO}_{3+\delta}$. These results clearly show that after quenching, the $\text{LaMnO}_{3+\delta}$ sample is a single perovskite phase with orthorhombic symmetry, and the $\text{La}_{0.95}\text{MnO}_{3+\delta}$ and $\text{La}_{0.9}\text{MnO}_{3+\delta}$ samples are a single perovskite phase with hexagonal symmetry. Table 2 shows the lattice parameters, cell volumes and symmetries of the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ samples after quenching from 1000°C in air. The XRD results of these $\text{La}_{1-x}\text{MnO}_{3+\delta}$ perovskites agree with those by Takeda *et al.*¹²⁾

Figure 8 shows the thermal expansion behaviors of the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ perovskite samples quenched from 1000°C during the thermal cycle measurement between 600 and 800°C in air. A large anomalous shrinkage behavior during the first heating process was observed for the

Table 2 Lattice parameters, cell volumes and symmetries of the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ perovskites after quenching from 1000°C in air. (O: orthorhombic, H: hexagonal (rhombohedral)).

Quenched samples	Lattice parameters and cell volumes	Symmetries
$\text{LaMnO}_{3+\delta}$	$a = 5.476(2) \text{ \AA}$, $b = 5.533(1)$, $c = 7.789(2) \text{ \AA}$, $V = 235.97 \text{ \AA}^3$, $Z = 4$	O
$\text{La}_{0.95}\text{MnO}_{3+\delta}$	$a = 5.5385(4) \text{ \AA}$, $c = 13.356(1) \text{ \AA}$, $V = 354.81 \text{ \AA}^3$, $Z = 6$	H
$\text{La}_{0.9}\text{MnO}_{3+\delta}$	$a = 5.5358(3) \text{ \AA}$, $c = 13.363(1) \text{ \AA}$, $V = 354.65 \text{ \AA}^3$, $Z = 6$	H

Fig. 8 Thermal expansion behaviors of the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ perovskite samples quenched from 1000°C in air during thermal cycling.

$\text{LaMnO}_{3+\delta}$. However, no shrinkage of this sample was observed after the second heating process. The measurements for the $\text{La}_{0.95}\text{MnO}_{3+\delta}$ and $\text{La}_{0.9}\text{MnO}_{3+\delta}$ did not show such a shrinkage behavior. It was observed by the powdered XRD measurement that the $\text{LaMnO}_{3+\delta}$ sample with orthorhombic symmetry changed into the hexagonal phase after the thermal cycle measurement. On the other hand, no phase change of the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ samples with $x = 0.05$ and 0.1 was observed after the thermal cycle measurement. These results suggest that the shrinkage of the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ samples during the thermal cycle measurement is caused by the phase change.

Figure 9 shows the TG curves of the $\text{La}_{1-x}\text{MnO}_3$ powders quenched from 1000°C in air. An absorption of oxygen in the $\text{LaMnO}_{3+\delta}$ powder with orthorhombic symmetry started at approximately 600°C . The oxygen content increased with increasing temperature up to 870°C , and then decreased. An increase of oxygen content in the $\text{La}_{0.95}\text{MnO}_{3+\delta}$ and $\text{La}_{0.9}\text{MnO}_{3+\delta}$ powders was very similar to that in the $\text{LaMnO}_{3+\delta}$. Although the absorption of oxygen was observed for all the sample powders, the $\text{La}_{0.95}\text{MnO}_{3+\delta}$ and $\text{La}_{0.9}\text{MnO}_{3+\delta}$ samples show no shrinkage and no phase change during the thermal cycle measurement between 600 and 800°C . The oxygen content in the lanthanum manganite perovskites is strongly related to the crystal structure.¹²⁾ However, the shrinkage of the samples is irrelevant to release and absorption of oxygen. It is concluded that the phase change by release and absorption of oxygen causes the shrinkage behavior of the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ during the thermal cycle measurement.

3.3 Application to AE-doped lanthanum manganite cathode in SOFC

AE-ions are usually doped in the LaMnO_3 -based SOFC cathode to enhance the electrical conductivity and to obtain the compatibility of thermal expansion behavior among other cell components. Since $\text{La}_{1-x}\text{AE}_x\text{MnO}_{3+\delta}$ perovskites with an AE content of $0 \leq x < 0.4$ also show a shrinkage of the sintered samples during a thermal cycling, to clarify the shrinkage mechanism in the La-AE-

Fig. 9 TG curves of the $\text{La}_{1-x}\text{MnO}_{3+\delta}$ perovskite powders quenched from 1000°C in air as a function of temperature. (a) $\text{LaMnO}_{3+\delta}$, (b) $\text{La}_{0.95}\text{MnO}_{3+\delta}$, (c) $\text{La}_{0.9}\text{MnO}_{3+\delta}$.

Mn-O systems is quite important. However, a relationship among the crystal structure, oxygen content and AE content of the perovskites at high temperature under oxidizing atmospheres is rather complicated, because many perovskite phases with various symmetries appear in the systems in the temperature range $\leq 1100^\circ\text{C}$. It is quite likely that in the $\text{La}_{1-x}\text{AE}_x\text{MnO}_3$ perovskites, the phase change is a cause of the shrinkage behavior. Allowing for the results of this investigation, I will conduct experiments for making clear the relationship between phase change and shrinkage during thermal cycling in AE-doped lanthanum manganite perovskites.

4 Conclusion

The shrinkage behavior of $\text{La}_{1-x}\text{MnO}_{3+\delta}$ perovskites ($0 \leq x \leq 0.1$) during thermal cycling has been investigated. The shrinkage behavior of all the samples was observed in the thermal extension curves. No difference in the thermal expansion curves between the heating and cooling processes indicated that the shrinkage behavior of the samples occurs during both the processes. The TEC decrease at temperatures $\geq 900^\circ\text{C}$ suggested that the shrinkage behavior of the samples occurs in the temperature range from 950 to 1100°C . It was found that the change between the hexagonal (low-temperature) and orthorhombic (high-temperature) phases by release and absorption of oxygen causes the shrinkage behavior of $\text{La}_{1-x}\text{MnO}_{3+\delta}$ perovskites ($0 \leq x \leq 0.1$) during thermal cycling.

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