THERMAL EXPANSION COEFFICIENT AND ELECTRICAL CONDUCTIVITY OF Mn-BASED PEROVSKITE-TYPE OXIDES

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ABSTRACT

The thermal expansion of AMnO$_{3\pm\delta}$ (A= Y, La, Er, Yb, Ca, Sr) was measured in the temperature range of 25 – 1000 °C. Manganites containing a divalent A-site cation have larger thermal expansion coefficient than those containing a trivalent cation as an A-site ion. This behavior in the thermal expansion was explained in terms of the ionic radius of Mn$^{3+}$ and Mn$^{4+}$. The increase in the thermal expansion of La$_x$Ca$_y$MnO$_{3-\delta}$ by increasing the Ca content was also elucidated. The electrical conductivity of La$_x$Ca$_y$MnO$_{3-\delta}$ was measured.

INTRODUCTION

La$_{1-x}$Sr$_x$MnO$_3$ is known to be one of the most effective cathode materials for Solid Oxide Fuel Cells (SOFC's). However, substitution of Sr for La leads to an increase in the thermal expansion coefficient (TEC) (Table 1) [1].

| Sr-cont.x | 0.00   | 0.05   | 0.10   | 0.20   | 0.30   |
|-----------|--------|--------|--------|--------|--------|
| TEC/K$^{-1}$ | 11.2x10^{-6} | 11.7x10^{-6} | 12.0x10^{-6} | 12.4x10^{-6} | 12.8x10^{-6} |

It has been reported that there are two kinds of Mn cations, Mn$^{3+}$ and Mn$^{4+}$ in LaMnO$_3$ [2]. Hence, substitution of Sr$^{2+}$ for La$^{3+}$ is expected to convert a part of Mn$^{3+}$ to Mn$^{4+}$, which has a smaller ionic radius than that of Mn$^{3+}$. Since the lattice constant of manganites is determined by the bond length of Mn–O, the change of Mn$^{3+}$ to Mn$^{4+}$ is expected to yield larger thermal expansion coefficient [3]. In order to clarify this effect for AMnO$_{3-\delta}$, we studied their thermal expansions by using Y, La, Er, Yb as trivalent A-site cation, and Ca, Sr as divalent cation. We also measured the thermal expansion coefficient and the electrical conductivity of La$_{1-x}$Ca$_x$MnO$_{3-\delta}$. 

EXPERIMENTAL

Solutions of the proper stoichiometry were prepared from single cation nitrate or acetate solutions preanalyzed. Nitrates or acetates were selected because of the high solubility for the cations. The precipitation was carried out by slowly adding ammonium oxalate solution into the solution. The precipitates were dried in a rotary evaporator, and were decomposed to oxides at 450–550 °C for one hour in air. The manganites were obtained by heating the mixed oxides for 12 hours at 1050 °C in air. Phase identification at room temperature was performed by X-ray diffraction (RAD–B, Rigaku Denki).

X-ray diffraction patterns of the samples at elevated temperatures were recorded on In-situ high-temperature XRD apparatus (JEOL JDX–10PA). The measurements were carried out in air by using platinum powders as an internal standard after the diffraction pattern had been settled, i.e. in 30 min after the sample reached a given temperature.

The sample powders were ground in an agate mortar after the solid-state reaction at 1050 °C, and pressed at 400 MPa to a disk of 20 mmφ x 2 mm. A plate of 4 mm x 15 mm x 2 mm was prepared from the disk, and sintered for 12 hours at 1150 °C in air. Platinum paste electrodes connected with platinum wires were attached to the plate. Electrical conductivity of the sample plate was measured at 20 – 1000 °C by the four probe dc method. TGA curves were recorded on TGD–7000 (ULVAC).

RESULTS AND DISCUSSION

Measurements on powder samples of AMnO3±δ showed that the powders for A= Y, La, Er, Yb, Sr were rhombohedrally distorted perovskites at room temperature, and

Table 2 Crystal structure of AMnO3 (A= Y, La, Er, Yb, Ca, Sr) at room temperature.

| Sample       | Ionic radius of A /nm | Crystal system   | Lattice constant* /nm |
|--------------|------------------------|------------------|-----------------------|
| ErMnO3       | 0.096                  | Rhombohedral     | a = 0.6112, c = 1.1389 |
| La0.90MnO3   | 0.117                  | Rhombohedral     | a = 0.5530, c = 1.3365 |
| YMnO3        | 0.099                  | Rhombohedral     | a = 0.6148, c = 1.1382 |
| YbMnO3       | 0.093                  | Rhombohedral     | a = 0.6064, c = 1.1357 |
| Ca0.95MnO3   | 0.114                  | Cubic            | a = 0.7457            |
| SrMnO3       | 0.132                  | Rhombohedral     | a = 0.5453, c = 0.9070 |

*: Hexagonal representation
that \( \text{Ca}_{0.95}\text{MnO}_{3-\delta} \) was cubic. The crystal structures of the samples are shown in Table 2.

Diffraction patterns of \( \text{La}_x\text{Ca}_y\text{MnO}_{3-\delta} \) samples at room temperature showed that these compounds were cubic perovskites for \( 0.32 \leq y \) (Ca content) \( \leq 0.63 \) (Fig. 1). The crystal structures of \( \text{La}_x\text{Ca}_y\text{MnO}_{3-\delta} \) samples are shown in Table 3.

Table 3 Crystal structure of \( \text{La}_x\text{Ca}_y\text{O}_{3-\delta} \) at room temperature.

| Sample            | Crystal system | Lattice constant /nm |
|-------------------|----------------|----------------------|
| \( \text{La}_{0.60}\text{Ca}_{0.32}\text{Mn}_{0.7715} \) | Cubic          | \( a= 0.7715 \)     |
| \( \text{La}_{0.29}\text{Ca}_{0.63}\text{Mn}_{0.7580} \) | Cubic          | \( a= 0.7580 \)     |

The crystal structures of the manganites employed in this study were not changed at elevated temperatures.

Thermal Expansion of \( \text{AMnO}_{3-\delta} \)

The thermal expansion of \( \text{AMnO}_{3-\delta} \) (A=Y, La, Er, Yb, Ca, Sr) is shown in Fig. 2. By comparing the average thermal expansion coefficients (TEC's) between 25 – 800 °C, it was found that manganites were divided into two classes. One consists of manganites containing a divalent A-site cation, and the other containing a trivalent cation. The former has larger TEC than the latter, and has shorter bond length with an oxide anion than the latter.

In the case of a divalent A-site cation, manganese ion is tetravalent and its diameter is estimated 0.60 Å for octahedral coordination. In the case of a trivalent cation, the diameter of Mn cation which is trivalent is 0.70 Å. Accordingly, the bond length between manganese cation and oxide ion is expected to be shorter for Mn\(^{4+}\) than for Mn\(^{3+}\), which was confirmed by measuring the lattice constants of the compounds. The following relation is obtained from the semi-empirical expression of the thermal expansion coefficient derived by Ruffa [3]:

\[
\beta = \frac{C_V}{a} \left( \frac{r\Delta e}{D} \right)
\]

where \( C_V \) is the heat capacity at constant volume, \( a \) and \( D \) are the parameters appearing in Morse function, and \( r \) the nearest neighbor distance. \( C_V \) is approximately constant at elevated temperatures. The bond energy between a divalent A-site ion and an oxide ion at its nearest is estimated to be half of that for a trivalent A-site ion. The overall formation energy of \( \text{A}^{2+}\text{Mn}^{4+}\text{O}_3 \) is lower than that of \( \text{A}^{3+}\text{Mn}^{3+}\text{O}_3 \) [5] though the bond energy of Mn\(^{4+}-\text{O}^{2-}\) is larger than that of Mn\(^{3+}-\text{O}^{2-}\). Eq. [1] suggests that TEC of
\( \text{A}^{2+} \text{Mn}^{4+} \text{O}_3 \) is larger than that of \( \text{A}^{3+} \text{Mn}^{3+} \text{O}_3 \).

The rapid increase in TEC of \( \text{La}_{0.9} \text{MnO}_3 \) at 800–1000 °C may be due to an increase of the ionic radius from 0.60 Å (Mn\(^{4+}\)) to 0.70 Å (Mn\(^{3+}\)) since the TG measurement showed oxygen desorption in that temperature range (Fig. 3). On the other hand, as shown for manganites containing a trivalent cation, the ionic radius of A-site cations did not affect the thermal expansion. It is suggested that manganites of Mn\(^{4+}\) has larger TEC than those of Mn\(^{3+}\) because of shorter bond length with an oxide ion.

**Thermal Expansion and Electrical Conductivity of \( \text{La}_x \text{Ca}_y \text{MnO}_{3-\delta} \)**

The thermal expansion and the electrical conductivity of \( \text{La}_x \text{Ca}_y \text{MnO}_{3-\delta} \) are shown in Fig. 4 and in Fig. 5, respectively. TEC increased with increasing Ca content, which is due to the change of Mn\(^{3+}\) to Mn\(^{4+}\) by substitution. The electrical conductivity increased with increasing Ca content up to 0.63. However, the conductivities of these samples around 1000 °C were almost the same since the relative density was as low as 77 % for \( y=0.32 \) and 0.63 in contrast to 98% for \( y=0 \). According to Tagawa et al. [4], the conductivity can be expected to double by increasing the relative density to unity. The partial substitution of Ca for La in \( \text{LaMnO}_3 \) yields an increase in the electrical conductivity, accompanying an increase in TEC.

**CONCLUSIONS**

The thermal expansion of \( \text{AMnO}_{3-\delta} \) (A= Y, La, Er, Yb, Ca, Sr) was measured in the temperature range of 25 – 1000 °C. Manganites containing a divalent A–site cation have larger thermal expansion coefficient than those containing a trivalent cation as an A–site ion. This behavior in the thermal expansion was explained in terms of the ionic radius of Mn\(^{3+}\) and Mn\(^{4+}\). The increase in the thermal expansion of \( \text{La}_x \text{Ca}_y \text{MnO}_{3-\delta} \) by increasing the Ca content was also elucidated.

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Fig.1 Diffraction Pattern of La_{0.60}Ca_{0.30}MnO_3-δ.
Fig. 2 Thermal Expansion of $\text{AMnO}_3 \pm \delta$.

Fig. 3 TGA curve of $\text{La}_{0.90}\text{MnO}_3 - \delta$ at 10K/min in air.
Fig. 4 Thermal Expansion of La$_x$Ca$_y$MnO$_{3-\delta}$.

Fig. 5 Electrical Conductivity of La$_x$Ca$_y$MnO$_{3-\delta}$. 

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