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Temperature Dependence of Hall Coefficient of $La_{1-x}Sr_xMnO_3$

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Temperature dependence of Hall coefficients of $La_{1-x}Sr_xMnO_3$ with x = 0.20, 0.30, 0.31, 0.32, 0.33, 0.34, 0.35 and 0.40 have been measured above 100℃. The results on the effect of Sr on Hall coefficient of $LaMnO_3$ were investigated. It was found that Hall coefficient at x = 0.20 and 0.30 was positive and decreased with an increasing temperature in the temperature range of 100 - 800 °C while that at x = 0.34, 0.35 and 0.40 was negative and decreased with an increasing temperature. Assuming one carrier, hole or electron, is dominant in the electrical conduction, $La_{1-x}Sr_xMnO_3$ is a *p*-type conductor at x = 0.20 and 0.30 and an *n*-type conductor at x = 0.34, 0.35 and 0.40. On the other hand, Hall coefficient at x = 0.31, 0.32 and 0.33 in the whole temperature range was zero, which showed that two carriers were dominant in the electrical conduction. It was suggested that the ratio of hole to electron concentration equals to square of that of electron to hole mobility between x = 0.31 and 0.33.

Key words: Hall coefficient, SOFC, $La_{1-x}Sr_xMnO_3$, LSM

1. INTRODUCTION

The fuel cell attracts a great deal of attention with regard to solution of a global energy problem due to high efficiency electric power obtained from hydrogen and oxygen, and a solution of global environmental problem because waste is not exhausted.[1] The solid oxide fuel cell (SOFC) exhibits the highest power and efficiency in the fuel cells.[1] Moreover, sending-end output efficiency of 70% is expected for SOFC.[1]

SOFC is operated in a temperature range of 700 to 1000℃. Sr doped lanthanum manganites (La(Sr)MnO_3s) are used as an air electrode material of the practical SOFC because the thermal expansion coefficient of La(Sr)MnO_3s fits with that of 8 mole % yttria-stabilized-zirconia (8YSZ) that is adopted as an electrolyte of SOFC. In the meantime, high permeability of gasses and high electrical conductivity are required for the air electrode material. Electrical conductivity relates to the behavior of carriers. Carrier conduction mechanism of La(Sr)MnO_3s for the air electrode material must be explained in order to improve the electrical property of SOFC. A phase diagram of $La_{1-x}Sr_xMnO_3$ is shown in Fig.1.[2] The FM domain in the diagram is Ferromagnetic Metal. In the region, the Hall coefficient R_H and magnetic resistance have been investigated in detail.[3] Magnetic factor, for instance the anomalous R_H, may be neglected above the Currier temperature T_c since $La_{1-x}Sr_xMnO_3$ shows paramagnetic in all composition range. Therefore, in the present study temperature dependence of R_H above 373.15K (100℃) has been investigated to make the type of carriers of $La_{1-x}Sr_xMnO_3$ clear.

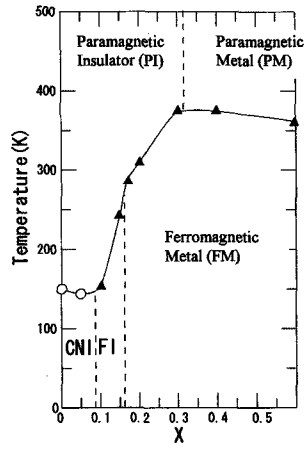

Fig.1 Phase diagram of $La_{1-x}Sr_xMnO_3$. [2]

2. EXPERIMENTAL PROCEDURE

<2. 1> Preparation of specimens

La_2O_3 (3N), SrO (3N) and Mn_2O_3 (3N) powders have been used as starting materials for $La_{1-x}Sr_xMnO_3$ of the SOFC's air electrode material. They were weighed out at composition ratios of x = 0.20, 0.30, 0.31, 0.32, 0.33, 0.34, 0.35, 0.40 and mixed, then sintered in the electric furnace in the atmosphere at 1350 ℃ for 24 hours. The obtained La(Sr)MnO_3s were ground into powder and they were sieved under a particle size of 38 μm. XRD patterns of all of the sintered powders were compared with the JCPDS cards to confirm the formation of the crystalline structures.

8YSZ powders were sieved under a particle size of 38 μm and pressed into disk shape. Sintering was performed at 1500 ℃ for 20 hours. The $La_{1-x}Sr_xMnO_3$ powders mixed with a PVA solution were spread on the

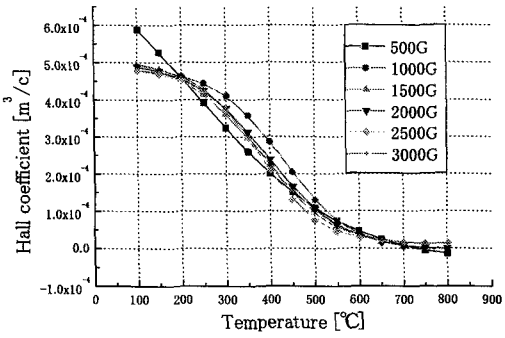

Fig.2 Temperature dependence of Hall coefficient of $La_{0.80}Sr_{0.20}MnO_3$.

8YSZ disk and sintered at 1500 ℃ for 20 hours. The obtained sintered plates were used as the specimens to measure Hall coefficient R_H.

<2. 2> Measurement

Pt wires for the electrode were attached on the specimens using Pt paste. R_H was measured at every 50℃ in the temperature range of 100 to 800℃ and at every 500 G in a magnetic field of 500 to 3000 G. Hall voltage V_H was measured by the Van der Pauw's method. R_H was calculated by

$$R_H = \frac{V_H}{I}\frac{B}{d} \qquad (1)$$

where d is a thickness of specimen, B is a magnetic field, I is a current and V_H is a Hall voltage.

3. RESULT AND DISCUSSION

Figure 2 shows temperature dependence of Hall coefficient R_H at an amount of Sr x = 0.20. The R_H was positive in the whole temperature range. The R_H at x = 0.30 also was positive. It is found that $La_{1-x}Sr_xMnO_3$ at x = 0.20 and 0.30 are p-type conduction from these results. The R_H decreased with temperature. This suggested that the carrier density increased with temperature, because R_H is inverse of carrier density. Temperature dependence of R_H at x = 0.35 is shown in Fig.3. The R_H was negative. Furthermore, the R_H at both x = 0.34 and 0.40 was negative and temperature dependence of the R_H showed

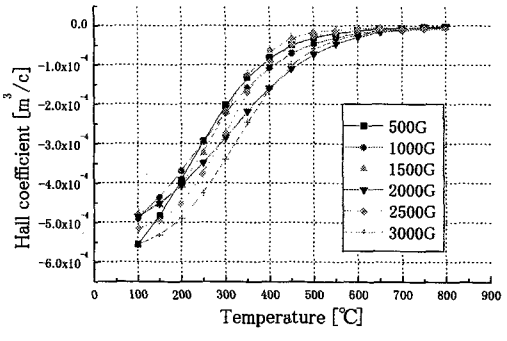

Fig.3 Temperature dependence of Hall coefficient of $La_{0.65}Sr_{0.35}MnO_3$.

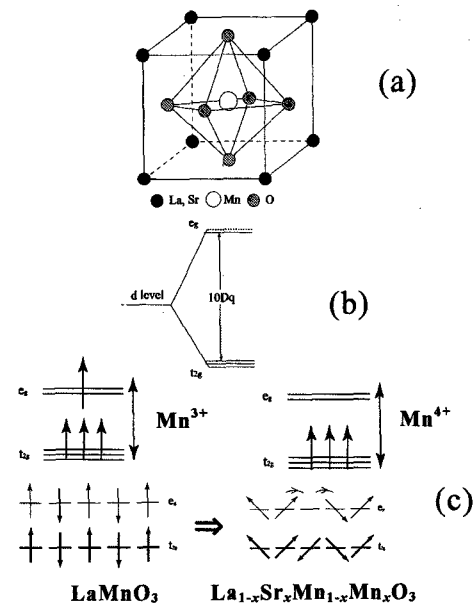

Fig.4 Crystal structure and electron orbit of $La_{1-x}Sr_xMnO_3$. [4]

the same tendency as that at x = 0.35. It was found that these samples were n-type conductors and that carrier density increased with temperature. $La_{1-x}Sr_xMnO_3$ changed the conduction type from p-type to n-type with an increasing x. Here, the p-type conduction mechanism in $La_{1-x}Sr_xMnO_3$ was explained as following: [4]

The perovskite-type crystal structure of $LaMnO_3$ is shown in Fig.4 (a). The 3d orbits of isolated Mn atoms split to eg state where the orbits direct to oxygen sights and t2g site where the orbits direct to avoided oxygen sights. (Fig.4(b)) There are four electrons in 3d orbit of Mn^{3+}. All Mn ions are Mn^{3+} at x = 0. One electron in eg is at each Mn sight due to electron correlation. It is an insulator because the electron does not contribute to conduction. However, an electron in eg of Mn^{3+} is able to move to eg orbit of Mn^{4+} through 2p orbit of O^{2-} by doping Sr, viz., a hole shows a carrier conduction due to the double exchange interaction. (Fig. 4(c)) Therefore, it shows a p-type conduction. It is supposed that the mechanism of changing to an n-type conductor as following: R_H is usually expressed as the following equation using carrier density and mobility:

Table I Hall coefficient, carrier density and conduction type of $La_{1-x}Sr_xMnO_3$.

x	Hall coefficient [m³/C]	Carrier density [1/m³]	Conduction type
0.20	4.8×10^{-4}	1.3×10^{22}	p
0.30	4.3×10^{-3}	1.5×10^{21}	p
0.31	-	-	-
0.32	-	-	-
0.33	-	-	-
0.34	-1.2×10^{-5}	5.1×10^{23}	n
0.35	-4.5×10^{-4}	1.4×10^{22}	n
0.40	-3.2×10^{-3}	2.0×10^{21}	n

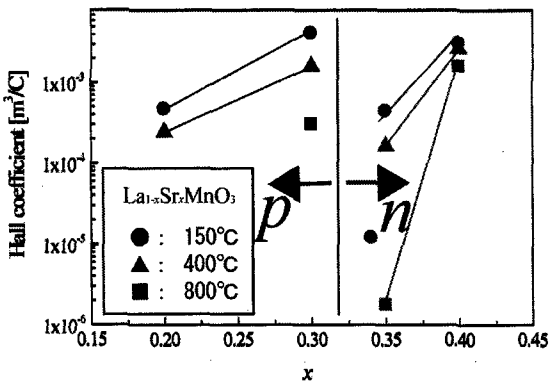

Fig.5 Temperature dependence of Hall coefficient of $La_{1-x}Sr_xMnO_3$.

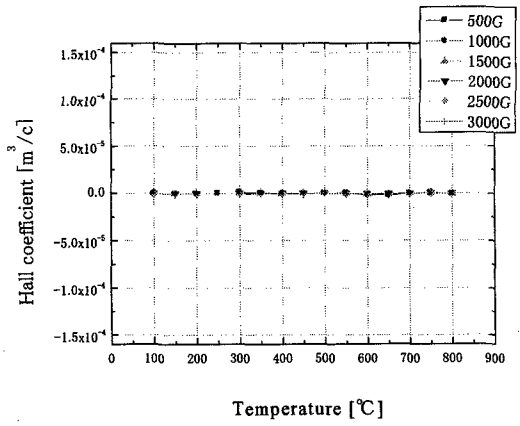

Fig.6 Temperature dependence of Hall coefficient of $La_{0.68}Sr_{0.32}MnO_3$.

$$R_H = \frac{\gamma}{e}\frac{p\mu_h^2 - n\mu_e^2}{(p\mu_h + n\mu_e)^2} \quad (2)$$

γ is a correction factor, e is an elementary electric charge, p is a hole density, n is an electron density, μ_h is a hole mobility and μ_e is an electron mobility. If $n\mu_e^2 > p\mu_h^2$ in equation (2) is satisfied, R_H is negative. In the above mentioned, the hole concentration increases with x. The electron density remarkably does not change from the valance of total ionic charge number. However, it is suggested that electrons provided from Sr^{2+} and Mn^{4+} with doping Sr differ from ones of La^{3+} and Mn^{3+}. Assuming the provided electrons have large μ_e, the condition of $n\mu_e^2 > p\mu_h^2$ is satisfied. Consequently, R_H is negative. R_H, carrier density and conduction type of $La_{1-x}Sr_xMnO_3$ at 150℃ in the magnetic field of 2000 G are listed in Table I. Hall carrier density n_H with the exception of x = 0.31 to 0.33 was calculated by the following equation assuming one carrier is dominant:

$$n_H = \frac{1}{R_H e} \quad (3)$$

The relationship between R_H and x is shown in Fig. 5. R_H decreased and n_H increased with an increasing temperature. However, the conduction type changing point around x = 0.32 was stationary.

Figure 6 shows temperature dependence of R_H at x = 0.32. The value of R_H in the measured temperature ranges were zero. The values at both x = 0.31 and 0.33 were also zero. Then, equation (2) is applied. If R_H equals to zero in equation (2), the following equation is obtained:

$$p\mu_h^2 - n\mu_e^2 = 0 \quad (4)$$

This equation can be expressed as follows:

$$\frac{p}{n} = \left(\frac{\mu_e}{\mu_h}\right)^2 \quad (5)$$

We suggested that R_H equals to zero at x = 0.31, 0.32 and 0.33 because the condition of equation (5) was satisfied.

4. CONCLUSIONS

Temperature dependence of Hall coefficient R_H of $La_{1-x}Sr_xMnO_3$ in high temperature ranges was investigated. It was found that the conduction type changed (p to n-type) around x = 0.32. The conditions of the R_H's sign change and the R_H equals to zero were suggested.

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