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Magnetoresistive Properties of Manganite Ceramics Sintered on Various Conditions

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The contribution of microstructure to magnetoresistive properties was studied for perovskite-type manganite ceramics with the chemical composition of $La_{0.6}Sr_{0.4}MnO_3$. The ceramics were sintered at 1500°C for 2 h ~ 48 h and sintered at 1100°C ~ 1500°C for 2 h. Density of the ceramics increased and grain of them grew slightly with increasing sintering time and temperature. All samples showed abrupt increase in magnetoresistance under low magnetic fields, and the abrupt increase became apparent with decreasing measurement temperature. The low-dense ceramics exposed to slight reductive atmosphere above room temperature become to show slight abrupt increase in magnetoresistance of ~1% under a low magnetic field less than ~ 1.6×10^5 Am^{-1}. These results suggest the possibility that magnetoresistive properties of manganite ceramics can be improved by optimizing sintering and/or annealing conditions.

Key words: manganite ceramics, magnetoresistance, microstructure, grain boundary

1. INTRODUCTION

Perovskite-type manganites have been drawn many researchers' interests, because they show giant magnetoresistance (GMR) [1], which is larger than the magnetoresistance of current metal-based materials. Magnetoresistive materials are required to have larger magnetoresistance under lower magnetic field for their applications, such as magnetic sensor. However, large magnetic field is required for the manganites to show the GMR. The perovskite-type manganites have never been applied yet.

Recently, tunneling magnetoresistance (TMR) through ferromagnetic metal - insulator - ferromagnetic metal junction was proposed [2]. The value of TMR is theoretically predicted to depend on the spin polarizations of ferromagnetic metals, *i.e.*, $2P_1P_2/(1-P_1P_2)$, where P_1 and P_2 are the spin polarizations of ferromagnetic metal 1 and 2, respectively. One of typical ferromagnetic metals, Fe, has the spin polarization of 0.44 [3]. Most of perovskite-type manganites show ferromagnetic and metallic properties and have the spin polarizations of 1, because they show ferromagnetism due to double exchange interaction [4]. The value of TMR is calculated to be 'infinite', if the manganites were used as the ferromagnetic metals of the junction.

However, many difficult techniques are required to fabricate the tunnel junctions. Hwang *et al.* [5] reported that abrupt increases in magnetoresistance of tens percent under low magnetic field were found to be apparent when lowering temperature during measurement for the ceramics and not found for single crystal with the chemical composition of $La_{2/3}Sr_{1/3}MnO_3$. They argued that the large change in magnetoresistance is due to the contribution of grain boundary as tunneling barrier. Since their study, many research groups [6-8] have examined manganite ceramics if the grain boundary contributes barrier as the tunneling barrier. However, some of them have not characterized well their ceramics, and have reported that the ceramics, which were sintered at various temperatures, show different ferromagnetic temperatures [6,7]. We guess that these results are due to change in oxygen content.

In the present study, we prepared manganite ceramics on various conditions and we characterized them. We, further, investigated the effect of the microstructure on the magnetoresistive properties of manganite ceramics.

2. EXPERIMENTAL

The manganite ceramics with the chemical composition of $La_{0.6}Sr_{0.4}MnO_3$ were prepared in this work. Stoichiometric mixture of La_2O_3, $SrCO_3$ and Mn_3O_4 as starting materials was calcined at 1000°C for 12 h in O_2 flow. The calcined powder was ground thoroughly in ethanol using a ball mill made of yttrium-stabilized zirconia. After drying, the calcined powder was palletized with 10ϕ×2mm in size by cold isostatic pressing under 1 GPa. The pellets were sintered at 1500°C for 2 ~ 48 h and at 1100°C ~ 1500°C for 2h, and consequently annealed at 700°C for 12h in O_2 flow.

Oxygen contents of the samples were determined by an iodometric titration. Microstructure on fracture surfaces was observed by means of scanning electron microscope (SEM). Electric resistivity was measured by a dc four-probe method below and above room temperature. The samples were cooled at various lower temperatures below room temperature and the magnetic field dependence of electric resistivity was measured in He gas atmosphere. The samples were heated up to 500 K and then temperature dependence of the resistivity was measured down to room temperature. After this measurement, magnetic field dependence of the resistivity was measured at room temperature. These measurements above room temperature were carried out twice under low pressure of 0.5 Pa. In the present study, magnetoresistance is defined as reduction rate of electric resistivity when magnetic field is applied, *i.e.*, $\Delta\rho$ / $\rho(0)\times100(\%)$, where $\Delta\rho$ is the decrease in the electric resistivity when magnetic field is applied and $\rho(0)$ is the electric resistivity under zero magnetic field.

3. RESULTS AND DISCUSSION

We sintered the ceramic samples at 1500°C for 2h, 6h, 12h and 48h, and sintered them at 1100°C and 1300°C for 2h. Figure 1 shows the SEM photographs of the fractured surfaces of these samples. The ceramic samples sintered for 2h are porous. For the samples sintered at 1500°C, the density of the sample increases with increasing sintering time. For example, relative densities are 76.7% and 86.6% for the samples sintered for 2h and 48h, respectively. Grain size increases with increasing sintering time, *e.g.*, ~2μm and ~5μm for the samples sintered for 2h and 48h, respectively. For the samples sintered at various temperatures for 2h, the sample sintered at lower temperature has lower relative density and smaller grain, *e.g.*, 52.5% and ~1μm for the sample sintered at 1100°C. The oxygen content of the samples sintered at 1500°C is almost constant within 2.99 ~ 3.02.

Figure 2 indicates the magnetic field dependence of magnetoresistance measured at low temperatures for the samples sintered at 1500°C. The abrupt increase in magnetoresistance under lower magnetic fields was found for all samples. The magnetoresistance at a fixed temperature and under a fixed magnetic field for the sample sintered for 2h is larger than those of the other samples.

Figure 3 also shows the magnetic field dependence of magnetoresistance measured at low temperatures for the samples sintered at 1100°C and 1300°C. The magnetoresistance of these samples at a fixed measuring temperature and under a fixed magnetic field tend to be larger than that of the sample sintered at 1500°C for 2h. Their magnetic field dependences are similar to that for the samples sintered at 1500°C (Figure 2). From figures

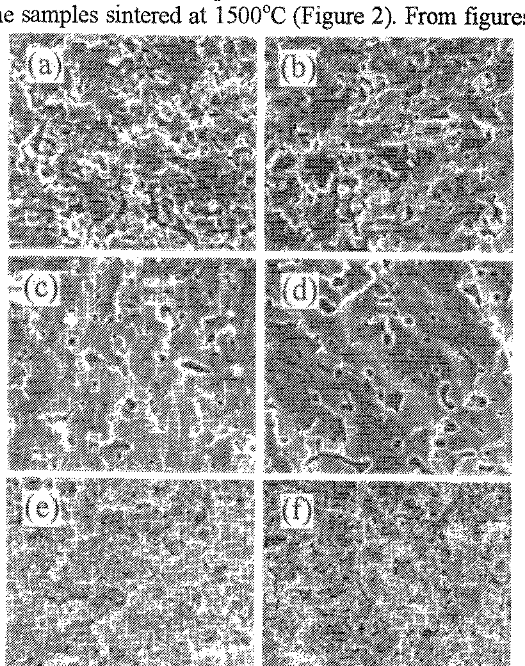

Figure 1 SEM photographs of fractured surfaces of the ceramic samples sintered at 1500°C for (a) 2h, (b) 6h, (c) 12h and (d) 48h, and sintered at (e) 1100°C and (f) 1300°C for 2h.

2 and 3, more porous ceramic samples have larger magnetoresistance at a fixed temperature or under a fixed magnetic field during measurement.

The temperature dependences of the electric resistivity measured above room temperature under no magnetic field are shown for the samples sintered at 1500°C for various time in Figure 4(a). They are also shown in Figure 4(b) for the samples sintered at various temperatures for 2h. The resistivity tends to decrease with increasing sintering time and sintering temperature. The resistivity of the well-sintered samples (sintered at 1500°C for 6h, 12h and 48h) does not change through repeating the measurement above room temperature and under a low pressure of 0.5 Pa. However, the porous samples (sintered at 1100 ~ 1500°C for 2h) show higher

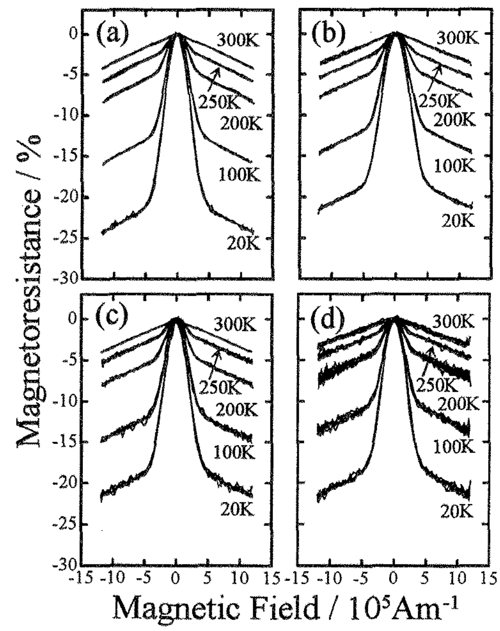

Figure 2 Magnetic field dependence of magnetoresistance measured at various temperatures for the ceramic samples sintered at 1500°C for (a) 2h, (b) 6h, (c) 12h and (d) 48h.

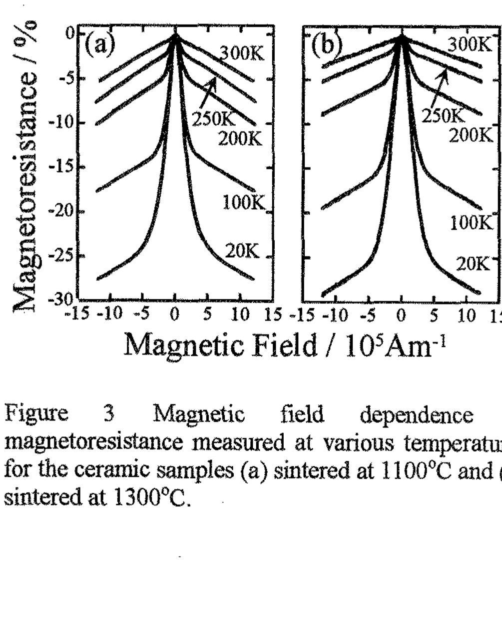

Figure 3 Magnetic field dependence of magnetoresistance measured at various temperatures for the ceramic samples (a) sintered at 1100°C and (b) sintered at 1300°C.

resistivity on the second measurement than that on the first measurement. All samples show an inflection point in their resistivity-temperature curves at ~ 370 K, which is independent of the sintering time and temperature. This temperature also does not change through repeating the measurement. Urushibara *et al.* reported an inflection point at 371 K in the resistivity-temperature curve for the single crystal sample of $La_{0.6}Sr_{0.4}MnO_3$ [9]. They attributed this temperature to the ferromagnetic transition temperature and also reported that this transition temperature strongly depends on the average valence of manganese ions in $La_{1-x}Sr_xMnO_3$. Our results indicate that the average valence of manganese ions of our samples is not changed by the sintering conditions and by the repeating measurement at higher temperature.

Figure 5 indicates the magnetic field dependence of magnetoresistance at room temperature measured after the measurement of temperature dependence of electric resistivity for the samples sintered at 1500°C. For the first measurement, the magnetoresistance increases linearly with increasing magnetic field, and all samples show the magnetoresistance of ~ -4 % under magnetic field of 1.2×10^6 Am^{-1} (~ 15 kOe). For the second measurement, the samples sintered for 6h, 12h and 48h show the similar magnetoresistive properties (Figures (b), (c) and (d)). However, the sample sintered for 2h shows an abrupt increase in the magnetoresistance under a low magnetic field (< 1.6×10^5 Am^{-1}) and subsequently linear increase in magnetoresistance with increasing magnetic field.

Figure 6 also indicates the magnetic field dependence of magnetoresistance at room temperature measured after the measurement of temperature dependence of electric resistivity for the samples sintered at 1100°C, 1300°C for 2h. The magnetoresistance under magnetic field 1.2×10^6 Am^{-1} increases with decreasing sintering temperature. These samples also show the abrupt increase in magnetoresistance under low magnetic field (< 1.6×10^5 Am^{-1}) on the first and the second measurements.

The results shown in Figures 2 and 3 have been found in ceramic manganite samples [5-8] but have never been found in single crystal manganite samples [5]. We, therefore, presume that the abrupt increase in magnetoresistance under low magnetic field is the characteristic magnetoresistive property for ceramic manganite. The magnetoresistive properties are affected by the slightly reductive condition above room temperature for the porous ceramic samples sintered at 1100°C ~ 1500°C for 2h, though the average valence of manganese ions of these samples are considered not to be changed from the invariable inflection points as

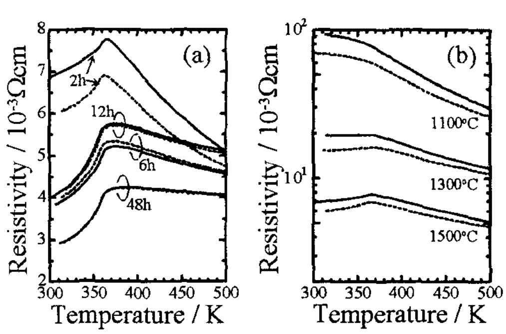

Figure 4 Temperature dependence of electric resistivity measured under zero magnetic field for the manganite ceramics sintered (a) at 1500°C for various time and (b) at 1100°C ~ 1500°C for 2h. Broken lines and solid ones indicate the results of the first measurement and of the second measurement, respectively (see text).

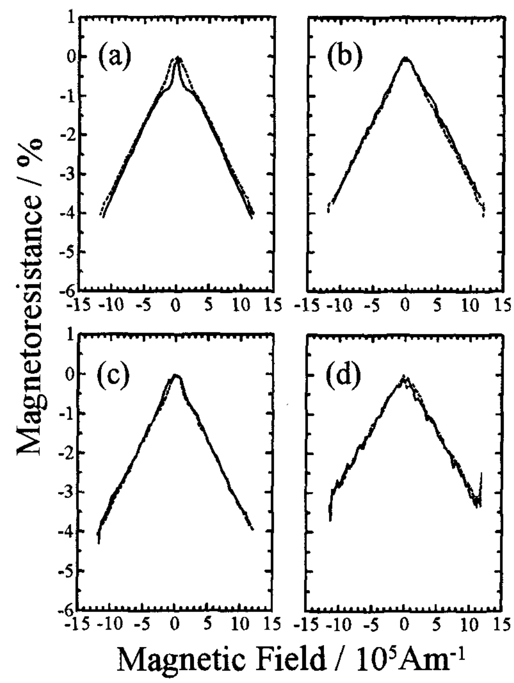

Figure 5 Magnetic field dependence of magnetoresistance measured at room temperature for the ceramic samples sintered at 1500°C for (a) 2h, (b) 6h, (c) 12h and (d) 48h. Broken lines and solid ones indicate the results of the first measurement and of the second one, respectively (see text).

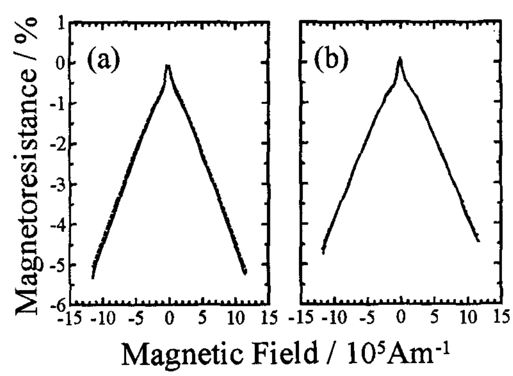

Figure 6 Magnetic field dependence of magnetoresistance measured at room temperature for the ceramic samples (a) sintered at 1100°C and (b) sintered at 1300°C. Broken lines and solid ones indicate the results of the first measurement and of the second one, respectively.

shown in Figure 4(b). Therefore, we consider that the abrupt change in magnetoresistance under low magnetic field is due to partially reduced grain boundary. The grain boundary is easy to be reduced on even slightly reductive condition in porous ceramics. Effect of the grain boundary on the magnetoresistive properties is emphasized with decreasing measurement temperature, because spin fluctuation is suppressed at low temperature. Our results suggest that optimizing sintering conditions and/or annealing conditions improve the magnetoresistive properties of manganite ceramics for their applications, *i.e.* larger magnetoresistance under lower magnetic field.

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