Large Magnetoresistance Effect in Polycrystalline Isotropic La-AM-Mn-O Ceramics (AM=Na, K, Rb, Cs)

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Polycrystalline isotropic perovskite-like $\text{La}_{5/6}\text{AM}_{1/6}\text{MnO}_3$ (AM=Na, K, Rb, Cs) partially substituted trivalent La^{3+} for monovalent cations were fabricated by conventional ceramics techniques and their magnetoresistance effects in addition to magnetic/electrical properties were studied. The all studied samples show magnetization as large as about $100\text{--}110 \mu\text{Wb}\cdot\text{m}\cdot\text{kg}^{-1}$ at 77 K and high electrical conductivity of $10^{-3} \Omega\cdot\text{m}$ order at 300 K. At room temperature polycrystalline isotropic $\text{La}_{5/6}\text{K}_{1/6}\text{MnO}_3$ shows large negative magnetoresistance effect $\Delta\rho/\rho_0 \approx -20\%$ when magnetic field of 1.5 T is applied. This value is larger than the previously reported values for $\text{La}_{1-x}\text{Me}_x\text{MnO}_3$ (Me=divalent cations) polycrystalline ceramics.

Keywords: magnetoresistance effect, perovskite structure, manganite, monovalent cation, alkaline-metal, polycrystalline isotropic ceramics

I. Introduction

Recently, giant magnetoresistance (GMR) effects caused by spin dependent scattering in metallic multilayers⁽¹⁾, heterogeneous alloy films⁽²⁾, and spinodally decomposed alloys⁽³⁾ have been interested in view of fundamental physics as well as applications such as magnetic recording heads. Degree of magnetoresistance effect (MR ratio) is ordinarily characterized as $\Delta\rho/\rho_H = (\rho_H - \rho_0)/\rho_H$, where ρ_H is the resistivity when magnetic field of H is applied and ρ_0 is the resistivity when magnetic field is not applied. MR ratio of those GMR materials is typically -5 to -50 %, which is even larger than +3 % for 80%Ni-20%Fe permalloy. Whereas large magnetoresistance effects are also observed in europium chalcogenides⁽⁴⁾⁽⁵⁾, uranium compounds⁽⁶⁾, and perovskite-like manganese oxides⁽⁷⁾⁽⁸⁾⁽⁹⁾ and so on. In recent years, especially, manganites with perovskite structure have been actively investigated for their large magnetoresistance effect and its mechanism. Lately very huge magnetoresistance effects $\Delta\rho/\rho_H = -10^6\%$ in perovskite-like manganites are called as CMR (Colossal Magneto-Resistance) against GMR⁽¹⁰⁾.

Parent compound LaMnO_3 exhibits antiferromagnetism and semiconducting electrical conductivity, but $\text{La}_{1-x}\text{Me}_x\text{MnO}_3$ (Me = Ca, Sr, Ba, Pb, Cd) ceramics partially substituted La^{3+} for divalent cations exhibit ferromagnetism as well as high electrical conductivities below their Curie temperature⁽¹¹⁾. Zener explained their mechanism by the strong ferromagnetic exchange interaction between Mn^{3+} and Mn^{4+} , which is called "double exchange theory"⁽¹²⁾. Afterwards the double exchange interaction is mathematically treated by Anderson and Hasegawa⁽¹³⁾, and

de Gennes⁽¹⁴⁾. In these ferromagnetic manganites, strong correlation between ferromagnetism and electrical conductivity is recognized, such that, the temperature coefficient of resistivity changes from positive to negative near Curie temperature with increasing temperature⁽⁷⁾. Large MR ratio of over -50 %, where the maximum reported value is $10^6\%$ ⁽¹⁰⁾⁽¹⁵⁾⁽¹⁶⁾, is observed in epitaxial or c-axis oriented manganite films grown on a single crystal substrate, such as LaAlO_3 ⁽¹⁰⁾⁽¹⁷⁾⁽¹⁸⁾⁽¹⁹⁾, SrTiO_3 ⁽¹⁵⁾⁽²⁰⁾⁽²¹⁾⁽²²⁾, or MgO ⁽²³⁾, whereas polycrystalline bulk ceramics samples⁽⁹⁾⁽²⁴⁾⁽²⁵⁾⁽²⁶⁾ show small MR ratio in comparison with film samples at the same conditions. The small magnetoresistance effects in polycrystalline bulk ceramics seem to be concerned with the grain boundary. In previous reports, no saturation of magnetoresistance effects was observed in perovskite-like manganites below $\mu_0 H = 8 \text{ T}$ ⁽¹⁵⁾. When absolute value of MR ratio is therefore discussed, it should be paid special attention to check the experimental conditions such as how magnetic field is applied or what temperature measurements are chosen. At room temperature, c-axis oriented $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_x$ film shows $\Delta\rho/\rho_H = -150\%$ at $\mu_0 H = 7 \text{ T}$ ⁽²⁰⁾, which is larger than -40 % in Co/Cu multilayer⁽²⁷⁾ or -10 % in heterogeneous Co/Cu alloys⁽²⁾ at the almost same conditions. Some explanations for the origin of very large magnetoresistance effects in perovskite-like manganites have been proposed⁽²⁰⁾⁽²³⁾⁽²⁸⁾⁽²⁹⁾, but, the mechanism has not been clarified yet.

There are many works studying ferromagnetic and high electrical conductivities in $\text{La}_{1-x}\text{Me}_x\text{MnO}_3$ ceramics partially substituted trivalent cation La^{3+} for divalent cations Me^{2+} , but there are few reports in which La^{3+} is substituted for monovalent cations such as Na^{+} ⁽³⁰⁾. In present work, polycrystalline bulk samples partially substituted La^{3+} for monovalent cations were fabricated by conventional ceramics technique. The purpose of this work is to study magnetic

and electrical properties, and magnetoresistance effects in polycrystalline isotropic $\text{La}_{5/6}\text{AM}_{1/6}\text{MnO}_3$ (AM=Na, K, Rb, Cs) ceramics without containing divalent cations.

II. Experimental procedure

Nominal composition of the samples is selected as $\text{La}_{5/6}\text{AM}_{1/6}\text{MnO}_3$ (AM=Na, K, Rb, Cs) which is expected to show large magnetization and high electrical conductivity. The samples were prepared by conventional ceramics technique. The mixture of reagent grade La_2O_3 , Na_2CO_3 , K_2CO_3 , Rb_2CO_3 , Cs_2CO_3 , and MnO_2 powders were calcined at 1273 K for 36 ks in air, in following by crashing, forming and sintering at 1473 K for 7.2 ks in air. Short sintering process is due to the prevention from evaporating volatile alkaline metals. Crystalline phases and crystal structures of the samples were analyzed by X-ray diffractometer with Cu-K α ray. Chemical compositions of the prepared samples were determined by inductively-coupled plasma spectroscopy (ICP) and frame emission spectrometry. Magnetization curves and Curie temperature were measured by using a vibration sample magnetometer which has maximum applying magnetic field of 1.5 T, and by a magnetic balance in the temperature range from 77 K to 400 K, respectively. Resistivities and magnetoresistance effects were measured by a four-probe technique between 77 K and 320 K. The size of the samples for electrical measurements was about 10x3.5x2 mm. In this study MR ratio is defined as following equation,

$$\text{MR ratio} = \Delta\rho / \rho_0 = (\rho_H - \rho_0) / \rho_0 \quad (1)$$

where ρ_H is the resistivity when magnetic field H is applied and ρ_0 is the resistivity when magnetic field is not applied. $\Delta\rho/\rho_0$ is smaller than $\Delta\rho/\rho_H$ in these perovskite-like manganites or GMR materials because of $\rho_0 > \rho_H$ (resistivity decreases when magnetic field is applied). The direction of applied magnetic field is parallel to the current flowing through the sample.

III. Results and discussion

Formed crystalline phases and crystal structures of the prepared samples were studied by powder X-ray diffraction analysis. Figure 1 shows X-ray diffraction patterns for $\text{La}_{5/6}\text{AM}_{1/6}\text{MnO}_3$ (AM=Na, K, Rb, Cs) samples sintered at 1473 K for 7.2 ks in air. The X-ray diffraction patterns revealed that the all studied samples consist of a single phase. Crystal symmetry of the samples is the same rhombohedral ($R\bar{3}c$; Z=2) as $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ⁽³¹⁾ and $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ ⁽³²⁾. The X-ray diffraction patterns also suggest that the prepared samples seem to be polycrystalline and isotropic ceramics. Lattice constant (a) of sodium, potassium, rubidium and cesium containing samples is $a=0.5468$, 0.5485 , 0.5490 and 0.5480 nm, respectively, and an angle α (α) is $\alpha=60.49$, 60.46 , 60.51 and 60.59° , respectively. As α (α) increases, distortion of MnO_6 octahedron increases, so that Mn-O-Mn angle decreases. It is known that the Mn-O-Mn angle of the perovskite-like oxides affects their carrier transfer, that is, band width⁽³³⁾. The decrement of Mn-O-Mn angle lead to widening band width.

Chemical compositions of as sintered samples were determined by ICP and frame emission spectrometry. Analyzed compositions are $\text{La}_{0.833}\text{Na}_{0.138}\text{O}_3$, $\text{La}_{0.833}\text{K}_{0.097}\text{MnO}_3$, $\text{La}_{0.833}\text{Rb}_{0.042}\text{MnO}_3$ and $\text{La}_{0.833}\text{Cs}_{0.063}\text{MnO}_3$, respectively. Many alkaline metal loss during sintering process is obvious for these samples. Especially rubidium and cesium losses are clear.

Magnetic properties of the prepared samples without containing divalent cations were examined. Magnetization at $T=77$ K and $\mu_0H=1.5$ T, Curie temperature for $\text{La}_{5/6}\text{AM}_{1/6}\text{MnO}_3$ (AM=Na, K, Rb, Cs) ceramics sintered at 1473 K for 7.2 ks in air are summarized in Table 1. Each sample shows magnetization of about $100\text{--}110 \mu\text{Wb}\cdot\text{m}\cdot\text{kg}^{-1}$ which is comparable to the magnetization obtained in $\text{La}_x\text{Me}_x\text{MnO}_3$ (Me: divalent cations)⁽¹¹⁾. These large magnetization indicate that the ratio of created Mn^{4+} to total Mn by substituting La^{3+} for monovalent cations such as Na^+ , K^+ , Rb^+ and Cs^+ is about 20-30 %. Curie temperature

Fig. 1 X-ray diffraction patterns for $\text{La}_{5/6}\text{AM}_{1/6}\text{MnO}_3$ ceramics sintered at 1473K for 7.2ks in air (AM=Na, K, Rb, Cs).

Table 1 Magnetic properties for $\text{La}_{5/6}\text{AM}_{1/6}\text{MnO}_3$ sinterd at 1473K for 7.2ks in air (AM: alkaline metal).

Alkaline metal	Magnetization / $\mu\text{Wb}\cdot\text{m}\cdot\text{kg}^{-1}$	Curie temperature / K
Na	111	340
K	97	338
Rb	103	268
Cs	108	254

Fig. 2 Temperature dependence of resistivities and magnetoresistance effects for $\text{La}_{5/6}\text{AM}_{1/6}\text{MnO}_3$ (AM=Na, K) ceramics sintered at 1473K for 7.6ks in air.

Fig. 3 Temperature dependence of resistivities and magnetoresistance effects for $\text{La}_{5/6}\text{AM}_{1/6}\text{MnO}_3$ (AM=Rb, Cs) ceramics sintered at 1473K for 7.6ks in air.

is above room temperature for sodium and potassium containing samples, or is below room temperature for rubidium and cesium containing samples. Curie temperature tends to lower as unit cell parameter $\alpha(\alpha)$ increases.

Figure 2 shows temperature dependence of zero-field resistivities and magnetoresistance effects for polycrystalline isotropic $\text{La}_{5/6}\text{Na}_{1/6}\text{MnO}_3$ and $\text{La}_{5/6}\text{K}_{1/6}\text{MnO}_3$ ceramics. Studied samples show metallic conductivity, that is, the temperature coefficient of resistivity is positive below 300 K, which is near their Curie temperature. Resistivities and MR ratio versus temperature curves exhibit anomaly around 300 K. As measuring temperature rises, the resistivities of samples increase rapidly, then decrease like electron hopping conductivity around 300 K. Whereas the MR ratio decreases gradually, then exhibits a sharp peak as measuring temperature rises. Epitaxial or well-textured manganite films grown on a single crystal substrate tend to show very small magnetoresistance effects well below or above Curie temperature⁽³⁴⁾.

Figure 3 shows temperature dependence of resistivities and magnetoresistance effects for $\text{La}_{5/6}\text{Rb}_{1/6}\text{MnO}_3$ and $\text{La}_{5/6}\text{Cs}_{1/6}\text{MnO}_3$ ceramics sintered at 1473 K for 7.2 ks in air. These samples also show anomalous resistivity and magnetoresistance effect versus temperature curves. Two resistivity peaks are observed clearly for the samples with rubidium and cesium. Same situation is reported for $\text{La}_{0.9}\text{Na}_{0.1}\text{Mn}_{0.9}\text{Cu}_{0.1}\text{O}_3$ ceramics, and it is proposed that different scattering mechanisms are occurred at lower or higher temperature resistivity peaks⁽³⁰⁾. Magnetoresistance effects tend to exhibit maxima around resistivity peaks at higher temperatures for $\text{La}_{5/6}\text{AM}_{1/6}\text{MnO}_3$ (AM=Rb, Cs)

Fig. 4 Relationships between magnetoresistance effects and applied magnetic field for $\text{La}_{5/6}\text{K}_{1/6}\text{MnO}_3$ ceramic measured at 77K and 77K.

ceramics. $\text{La}_{5/6}\text{Cs}_{1/6}\text{MnO}_3$ sample shows large magnetoresistance effect $\Delta\rho/\rho_0 \approx -40\%$ at 240 K, but $\Delta\rho/\rho_0 \approx -20\%$ at 240 ± 10 K.

Fig. 5 Magnetization curves for $\text{La}_{5/6}\text{K}_{1/6}\text{MnO}_3$ ceramics at 77 K and 300 K. The samples were sintered at 1473 K for 7.2 ks in air.

Relationship between magnetoresistance effect and applied magnetic field was measured at 77 K and 300 K. The results are shown in Fig. 4. At 77 K, MR ratio changes rapidly below a small magnetic field of $\mu_0 H \approx 0.01$ T and gradually above $\mu_0 H \approx 0.01$ T. Whereas MR ratio changes almost linearly at 300 K in the studied magnetic field range. Magnetoresistance effect of polycrystalline isotropic $\text{La}_{5/6}\text{K}_{1/6}\text{MnO}_3$ ceramics is $\Delta\rho/\rho_0 \approx -20\%$ under the conditions that the temperature is 300 K and the external applied magnetic field is 1.5 T. This value is larger than a previously reported MR ratio for polycrystalline ceramics at the same conditions⁽⁹⁾⁽³⁰⁾. Moreover, this MR ratio of studied samples with potassium is larger than that of epitaxially grown $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ thin film⁽¹⁹⁾ and $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ single crystal⁽³⁰⁾, and a little smaller than that of epitaxially grown $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_x$ thin film⁽²⁰⁾ although our sample is polycrystalline and isotropic ceramic. If epitaxially grown or well-textured $\text{La}_{5/6}\text{K}_{1/6}\text{MnO}_3$ thin film without grain boundary is prepared, the largest MR ratio may be obtained at room temperature.

To clarify the different behavior of magnetoresistance effect versus magnetic field below $\mu_0 H = 0.01$ T for $\text{La}_{5/6}\text{K}_{1/6}\text{MnO}_3$ ceramic, the magnetization curves were measured at 77 K and 300 K. The results are presented in Fig. 5. There is a markedly increase of magnetization at $T = 77$ K but is a slowly increase at $T = 300$ K, that is, the ferromagnetically alignment of spins by external magnetic field is easier at 77 K, but difficult at 300 K. If the resistivity is controlled mainly by carrier scattering resulted from thermal spin fluctuation, the ferromagnetical spin alignment brings magnetoresistance effect.

Magnetoresistance effect in double exchange ferromagnetic manganese oxides with perovskite structure is given by the following scaling function in the small magnetization region near Curie temperature,

$$-\frac{\Delta\rho}{\rho_0} = C \left(\frac{M}{M_s} \right)^2 \quad (2)$$

where $\Delta\rho$ is the resistivity difference, ρ_0 is the resistivity in zero magnetic field, M is the magnetization and M_s is the saturation magnetization⁽³⁵⁾. Relationship between $-\Delta\rho/\rho_0$

Fig. 6 Relationship between $-\Delta R/R_0$ and $(M/M_s)^2$ for $\text{La}_{5/6}\text{K}_{1/6}\text{MnO}_3$ ceramic sintered at 1473 K for 7.2 ks in air.

and $(M/M_s)^2$ for $\text{La}_{5/6}\text{K}_{1/6}\text{MnO}_3$ ceramic is shown in Fig. 6. It is known that the coefficient in eq. (2) is $C \approx 1$ for the heavily doped metallic system and the value of C increases as the hole concentration is decreased⁽³⁵⁾. The constant of polycrystalline isotropic $\text{La}_{5/6}\text{K}_{1/6}\text{MnO}_3$ ceramic is $C \approx 2$, which indicates that this sample is not heavily doped metallic system. The value of $C \approx 2$ for studied sample is smaller than that of $C \approx 4$ for $\text{La}_{0.825}\text{Sr}_{0.175}\text{MnO}_3$ single crystal⁽³¹⁾.

IV. Conclusion

Polycrystalline isotropic $\text{La}_{5/6}\text{AM}_{1/6}\text{MnO}_3$ ($\text{AM} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) ceramics with perovskite structure which are partially substituted trivalent La^{3+} for monovalent Na^+ , K^+ , Rb^+ and Cs^+ are prepared by conventional ceramics technique. The result of their magnetic, electrical properties and magnetoresistance effects are summarized as follows:

- (1) All studied samples show ferromagnetic properties. Curie temperature of the samples with sodium and potassium is about 340 K, and is 338 K, respectively. Temperature dependence of resistivities show metallic conductivities below Curie temperature.
- (2) Resistivity and magnetoresistance effect versus temperature curves have the peak near Curie temperature. MR ratio changes dramatically around the resistivity peak for $\text{La}_{5/6}\text{K}_{1/6}\text{MnO}_3$ and $\text{La}_{5/6}\text{Cs}_{1/6}\text{MnO}_3$ ceramics.
- (3) Polycrystalline isotropic $\text{La}_{5/6}\text{K}_{1/6}\text{MnO}_3$ ceramics exhibit large MR ratio of -20% at $T = 300$ K and $\mu_0 H = 1.5$ T. The MR value of this sample is larger than that of $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ single crystal or epitaxially grown $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ thin film.

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