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MAGNETIC AND MAGNETOTRANSPORT PROPERTIES OF $La_{0.7}Ca_{0.3}Mn_{1-x}(Zn,Cu)_xO_3$

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ABSTRACT

Magnetic and magnetotransport properties of two perovskite manganite samples of $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ and $La_{0.7}Ca_{0.3}Mn_{0.95}Cu_{0.05}O_3$ prepared by conventional solid-state reaction have been studied in detail. Experimental results revealed that the temperature dependences of magnetization and resistance varied strongly around the phase-transition temperature. Maximum magnetoresistance (MR) values of $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ and $La_{0.7}Ca_{0.3}Mn_{0.95}Cu_{0.05}O_3$ under an applied field of 400 Oe were about 21.4 % and 11.0 %, respectively. The maximum magnetic-entropy change (ΔS_M) was 2.73 J/kg.K for $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$, and 3.34 J/kg.K for $La_{0.7}Ca_{0.3}Mn_{0.95}Cu_{0.05}O_3$ when the applied field was 45 kOe. Both the MR and ΔS_M values obtained from two samples were smaller than those of the parent compound $La_{0.7}Ca_{0.3}MnO_3$. This was due to the change in the Mn^{3+}/Mn^{4+} ratio caused by Zn and Cu dopants, which led to a change in the type of the ferromagnetic-paramagnetic phase transition.

Keywords: Perovskite manganites, magnetic entropy, magnetotransport property.

ABSTRAK

Sifat-sifat magnetik dan magnetotransport dari dua sampel manganite perovskit yakni $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ dan $La_{0.7}Ca_{0.3}Mn_{0.95}Cu_{0.05}O_3$ yang disiapkan dengan reaksi solid-state konvensional telah dipelajari secara mendetail. Hasil penelitian menunjukkan bahwa pengaruh suhu terhadap variasi magnetisasi dan resistensi sangat kuat di sekitar suhu fase-transisi. Nilai magnetoresistance (MR) maksimum $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ dan $La_{0.7}Ca_{0.3}Mn_{0.95}Cu_{0.05}O_3$ dalam medan magnet sebesar 400 Oe masing-masing sekitar 21,4% dan 11,0%. Perubahan entropi magnetik maksimum (ΔS_M) ketika menggunakan medan sebesar 45 kOe masing-masing sebesar 2,73 J/kg.K untuk $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$, dan 3,34 J / kg.K untuk $La_{0.7}Ca_{0.3}Mn_{0.95}Cu_{0.05}O_3$. Nilai MR dan ΔS_M yang diperoleh dari ke dua sampel itu lebih kecil dari pada senyawa induk $La_{0.7}Ca_{0.3}MnO_3$. Hal ini karena perubahan harga rasio Mn^{3+} / Mn^{4+} sebagai akibat dopan Zn dan Cu, yang menyebabkan perubahan fase transisi feromagnetik ke paramagnetik.

Kata kunci: *Perovskite manganites, magnetic entropy, magnetotransport property.*

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INTRODUCTION

Recently, many works have been made to study magnetic and magnetotransport properties of perovskite-type manganites $La_{1-y}Ca_yMnO_3$ [1-7]. This material system is applicable in recording/reading heads, magnetic sensitive sensors, and magnetic refrigerators working around room temperature. By the Ca-concentration change, leading to a change in the Mn^{3+}/Mn^{4+} ratio and lattice parameters, one can control easily their magnetic and electrical properties. Together with these studies, the replacement of metals (such as Ni, Al, Co and so forth) for Mn in $La_{1-y}Ca_yMnO_3$ has been also carried out [3, 8]. This would lead to a remarkable change in the bond length ⟨Mn-O⟩ and the bond angle ⟨Mn-O-Mn⟩, which influence directly on the magnetic interactions in the system.

In the previous work [3], we studied influences of Ni- and Co-substitutions on the magnetotransport property of $La_{0.7}Ca_{0.3}Mn_{1-x}(Ni,Co)_xO_3$. It was observed at the Curie temperature (T_C) that the maximum magnetoresistance (MR) value under an applied field of 400 Oe for the Ni- and Co-doped samples was about 17.0% and 8.0%, respectively, which was smaller than those of $La_{0.7}Ca_{0.3}MnO_3$. The coexistence of antiferromagnetic interactions, due to exchange pairs Ni-Mn and Co-Mn, besides the ferromagnetic Mn^{3+}-Mn^{4+} interaction was proposed to explain the MR data obtained. To gain more insight into this material system, we prepared $La_{0.7}Ca_{0.3}Mn_{1-x}(Cu,Zn)_xO_3$ compounds (where Mn ions was substituted partly by Cu and Zn ions) and studied their magnetic and magnetotransport properties.

EXPERIMENT

Two polycrystalline samples of $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ and $La_{0.7}Ca_{0.3}Mn_{0.95}Cu_{0.05}O_3$ were prepared by the solid-state reaction method, used commercial powders $MnCO_3$, $CaCO_3$, La_2O_3 ZnO and CuO (99.9 % purity) as the precursors. These powders combined with appropriate masses were well-mixed, pressed into pellets, and then pre-sintered at 900 ^oC for 2 hrs. After several times of the intermediate grinding and heat treatment, the pellets were annealed at 1050 ^oC for 24 hrs in air. The process is shown in Figure 1.

The crystallographic structure of the final products was examined by an X-ray diffractometer (Brucker D5005). The magnetic field dependence of resistance in the temperature range of 100 - 300 K was investigated by the standard four-probe method. Magnetic measurements with respect to temperature and the magnetic field were performed on a superconducting quantum interference device (SQUID).

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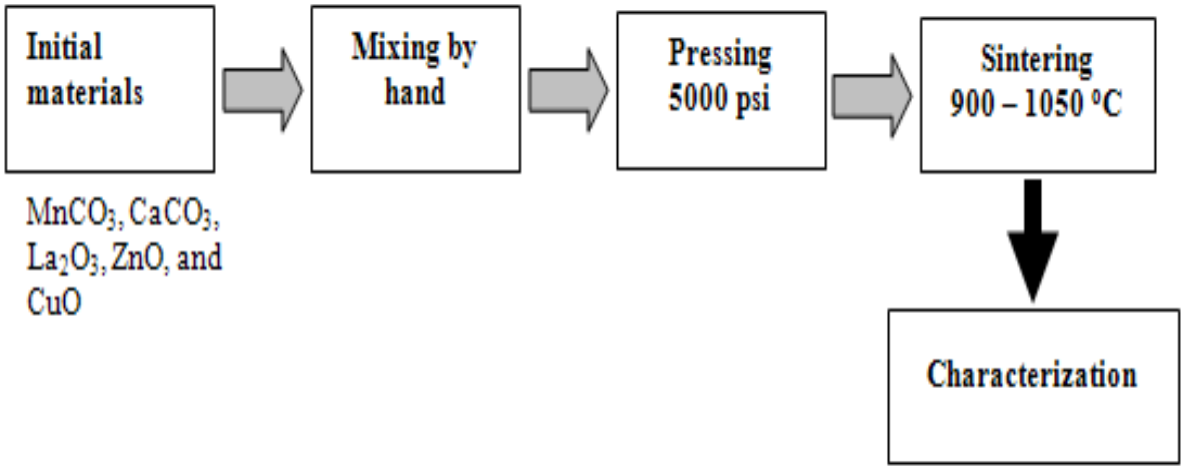

Figure 1. Diagram shows preparation of $La_{0.7}Ca_{0.3}Mn_{1-x}(Zn,Cu)_xO_3$ bulks.

RESULTS AND DISCUSSION

Before investigating the magnetic and magnetotransport properties of the samples, we checked their quality based on an X-ray diffractometer. It was revealed that the samples were the single phase in an orthorhombic structure (belonging to the space group *Pnma*), see Figure 2. There was no trace of secondary phases related to the starting powders. Based on the XRD data, we determined the lattice parameters of $La_{0.67}Ca_{0.33}Mn_{0.9}Zn_{0.1}O_3$ to be a = 5.441 Å, b = 7.697 Å, and c = 5.434 Å, and of $La_{0.67}Ca_{0.33}Mn_{0.95}Cu_{0.05}O_3$ to be a = 5.467 Å, b = 7.707 Å, and c = 5.447 Å. Meanwhile, those for the parent compound $La_{0.7}Ca_{0.3}MnO_3$ were a = 5.453 Å, b = 7.728 Å, and c = 5.471 Å [3].

One can see clearly that the lattice parameters of the samples $La_{0.67}Ca_{0.33}Mn_{0.9}Zn_{0.1}O_3$ and $La_{0.67}Ca_{0.33}Mn_{0.95}Cu_{0.05}O_3$ were slightly decreased as comparing to those of $La_{0.7}Ca_{0.3}MnO_3$. This is due to the substitution of Zn^{2+} and Cu^{2+} ions for the Mn^{3+} and Mn^{4+} ions in the manganite structure; because the ionic radii of Zn^{2+} (0.74 Å) and Cu^{2+} (0.73 Å) are greater than those of Mn^{3+} (0.66 Å) and Mn^{4+} (0.60 Å). Under such the circumstance, the concentration of Mn^{3+} and Mn^{4+} ions was varied, which influenced magnetic and magnetotransport properties of the samples as being presented below.

Following the structural investigations, we studied the magnetic properties and magnetocaloric effect of these samples. Figure 3 shows the temperature dependence of the zero-field cooled magnetization, $M(T)$, under an applied field of 50 Oe.

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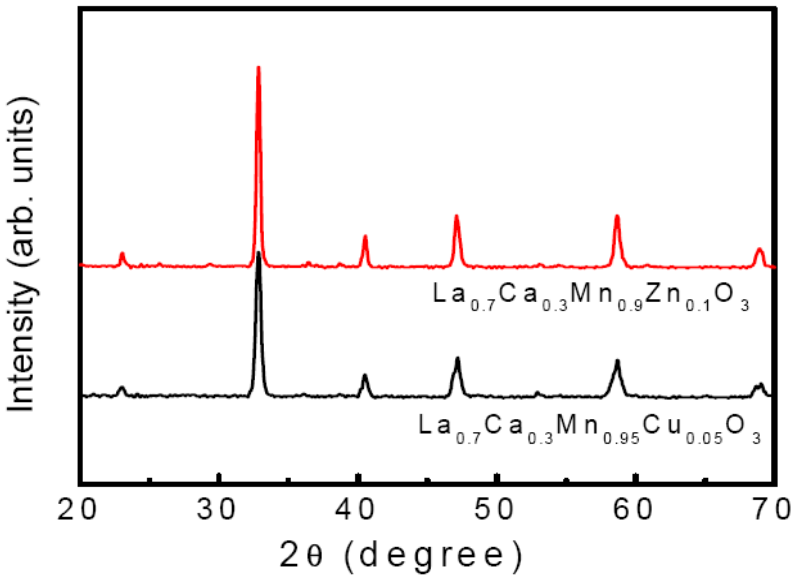

Figure 2. XRD patterns of $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ and $La_{0.7}Ca_{0.3}Mn_{0.95}Cu_{0.05}O_3$. The samples are the single phase in an orthorhombic structure (the space group *Pnma*).

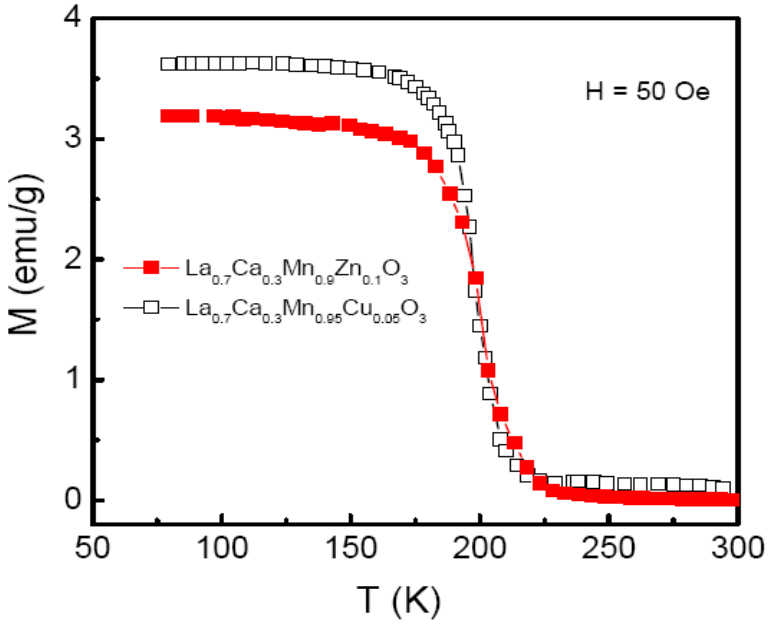

Figure 3. Temperature dependence of the zero-field cooled magnetization for $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ and $La_{0.7}Ca_{0.3}Mn_{0.95}Cu_{0.05}O_3$ under an applied field of 50 Oe.

It appears from Figure 3 that with increasing temperature from 80 to 300 K, there is a rapid decrease of magnetization at a temperature value called Curie temperature, T_C. The T_C values of $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ and $La_{0.7}Ca_{0.3}Mn_{0.95}Cu_{0.05}O_3$ are about 210 and 200 K, respectively. Having compared to $La_{0.7}Ca_{0.3}MnO_3$ with $T_C \approx 220$ K [3, 5, 6] or 260 K [4, 7], it is seen that T_C of our samples

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is slightly decreased. This is due to the fact that the presence of Zn^{2+} and Cu^{2+} ions in the manganite host lattice reduces the coupling possibility between Mn^{3+} and Mn^{4+}, leading to the decrease of T_C compared to the $La_{0.7}Ca_{0.3}MnO_3$ compound. Notably, Zn^{2+} does not contribute the magnetic behavior to $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$, because it is nonmagnetic ion with the full-filled electron configuration of $3d^{10}$. In contrast, the presence of Cu^{2+} (with the unfulfilled electron configuration of $3d^9$) in $La_{0.7}Ca_{0.3}Mn_{0.95}Cu_{0.05}O_3$ could introduce antiferromagnetic interactions between Cu^{2+} and $Mn^{3+,4+}$ ions [9], which compete with the pre-existing ferromagnetic Mn^{3+}-Mn^{4+} interaction. Such situations explain why the T_C and magnetization values of these two samples are different, as can be seen in Figure 3.

Next, we measured isothermal magnetization curves around their phase transition temperature T_C. The applied field was scanned from 0 to 45 kOe, and the temperature increment was 1-2 K. Based on these data, we could assess the magnetocaloric effect through magnetic-entropy change (ΔS_M). Theoretically, the entropy change can be calculated by means of [10]:

$$\Delta S_M(T,H) = \int_{H_1}^{H_2} \left(\frac{\partial M}{\partial T}\right)_H dH \,. \qquad (1)$$

It is integrated numerically in the desired range of temperatures and magnetic fields on the basis of the set of magnetic isotherms $M(H)$ at different temperatures. This equation usually works well for material systems with the second-order magnetic phase transition, because at the first-order magnetic phase transition the derivative $\partial M/\partial T$ becomes infinity. Recently, McMichael *et al*. [11] proposed another simple way to calculate ΔS_M based on the following formula:

$$|\Delta S_M| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H_i \qquad (2)$$

where M_i and M_{i+1} are isothermal magnetization values measured in a magnetic field interval ΔH at temperatures T_i and T_{i+1}, respectively. By using Eq. (2), we calculated ΔS_M for the samples in the magnetic field intervals 15, 30 and 45 kOe. As seen in Fig. 4, ΔS_M increases with increasing the applied field. At a given ΔH, when temperature is lowered, ΔS_M gradually increases and attains a maximum value at temperatures around T_C. If continuously lowering down temperature below T_C, ΔS_M decreases. With ΔH = 45 kOe, the maximum values of ΔS_M for $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ and $La_{0.7}Ca_{0.3}Mn_{0.95}Cu_{0.05}O_3$ are 2.73 and 3.34 J/kg.K, respectively. These values are much smaller than the maximum ΔS value of $La_{0.7}Ca_{0.3}MnO_3$ (about 6.2 J/kg.K for ΔH = 10 kOe) [12].

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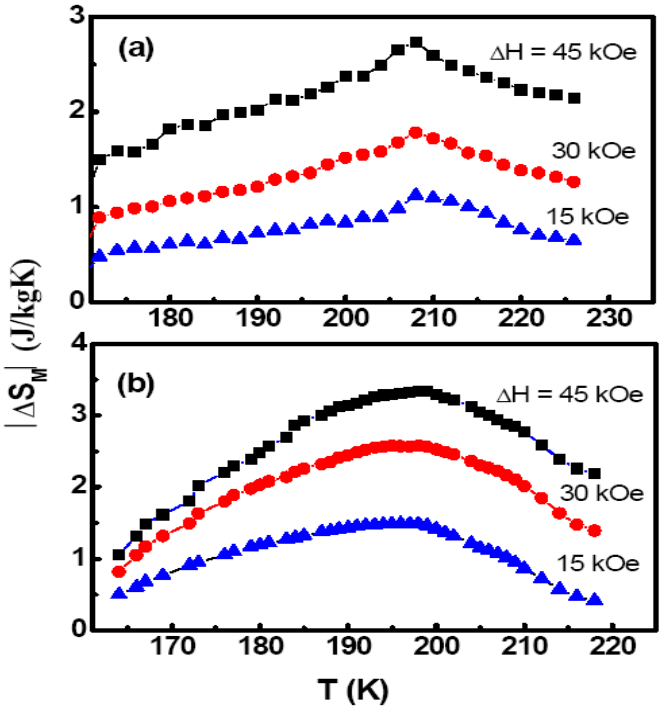

Figure 4. Temperature dependences of the magnetic-entropy change for (a) $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ and (b) $La_{0.7}Ca_{0.3}Mn_{0.95}Cu_{0.05}O_3$ under various applied fields of 15, 30, and 45 kOe.

To understand why there is such a large difference, let pay attention to the ferromagnetic-paramagnetic phase transitions of $La_{0.7}Ca_{0.3}MnO_3$ and a representative sample of $La_{0.7}Ca_{0.3}Mn_{0.95}Cu_{0.05}O_3$. Normally, the $M(T)$ curve of the former shows a sharp phase transition at T_C while that of the latter does not reveal this feature. Alternatively, if performing the plot of H/M versus M^2 for the isotherms $M(H)$, we can see more clearly the difference between the two compounds. Figure 5 shows H/M versus M^2 plots for $La_{0.7}Ca_{0.3}MnO_3$ studied by Mira *et al.* [4] and for our sample $La_{0.7}Ca_{0.3}Mn_{0.95}Cu_{0.05}O_3$. For the case of $La_{0.7}Ca_{0.3}MnO_3$, one can see at some temperatures that H/M versus M^2 curves exhibit the negative slope, Fig. 5(a); a similar result could be met in Ref. [5]. However, only the positive slope is found in the H/M versus M^2 curves for $La_{0.7}Ca_{0.3}Mn_{0.95}Cu_{0.05}O_3$, see Fig. 5(b), and $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ as well (not shown).

According to Banerjee's criterion [13], the negative and positive slopes are indicators of the first- and second-order magnetic phase transitions, respectively. This means that $La_{0.7}Ca_{0.3}MnO_3$ exhibits the first-order magnetic phase transition while our Zn- and Cu-doped samples exhibits second-order transition. In other words, the doping of Zn and Cu into $La_{0.7}Ca_{0.3}MnO_3$ leads to a change in the magnetic phase transition from first order to the second order, and thus results in a remarkable decrease in the maximum ΔS of doped samples, as mentioned.

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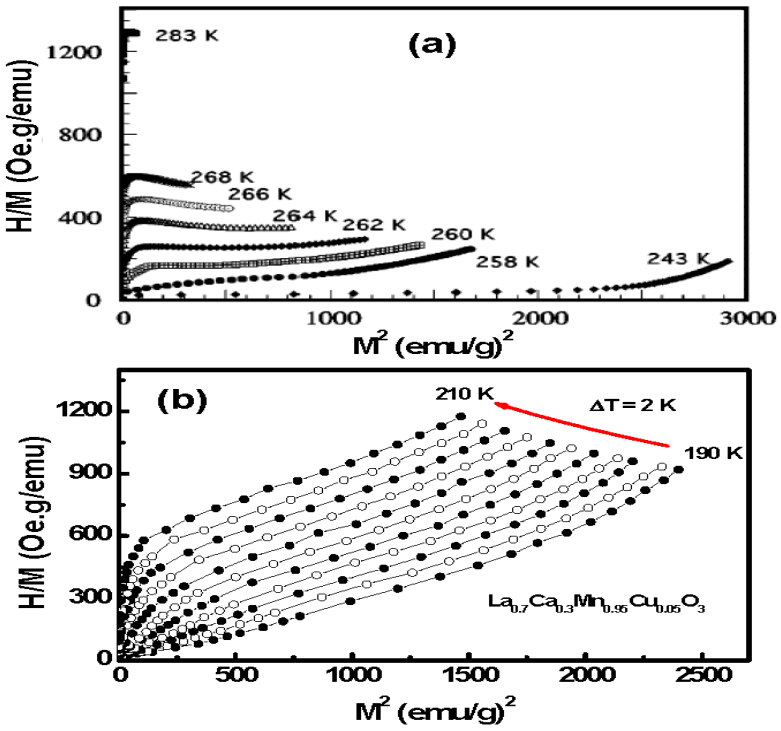

Figure 5. ***H/M*** **versus** M^2 **plots of the isotherms for (a)** $La_{0.7}Ca_{0.3}MnO_3$ **(after Mira *et al.* [4]), and (b)** $La_{0.7}Ca_{0.3}Mn_{0.95}Cu_{0.05}O_3$**. While the negative slope can be found in (a)** $La_{0.7}Ca_{0.3}MnO_3$ **at some temperatures, only the positive slope is found in (b)** $La_{0.7}Ca_{0.3}Mn_{0.95}Cu_{0.05}O_3$**.**

Together with the study of the magnetic properties of the samples, we investigated their magnetotransport properties. Figure 6 shows the temperature dependences of resistance R under applied fields of 0 and 400 Oe. Higher peak resistance generated by the applied field of 0 Oe. It appears from Fig. 6 that with increasing temperature the samples exhibit a metallic-semiconducting phase transition at a temperature named T_p of 190 K for $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ and of 150 K for $La_{0.7}Ca_{0.3}Mn_{0.95}Cu_{0.05}O_3$. With the presence of an applied field of 400 Oe, this T_p temperature is shifted about 5 K towards higher temperatures. Concurrently, the resistance R at temperatures around T_p is decreased rapidly.

Such the tendency seems popular in perovskite manganites [14, 15]. To further assess the variation of R versus the magnetic field, we based on the magnetoresistance (MR) ratio defined by :

$$MR = \frac{R(H=0) - R(H \neq 0)}{R(H=0)}. \qquad \textbf{(3)}$$

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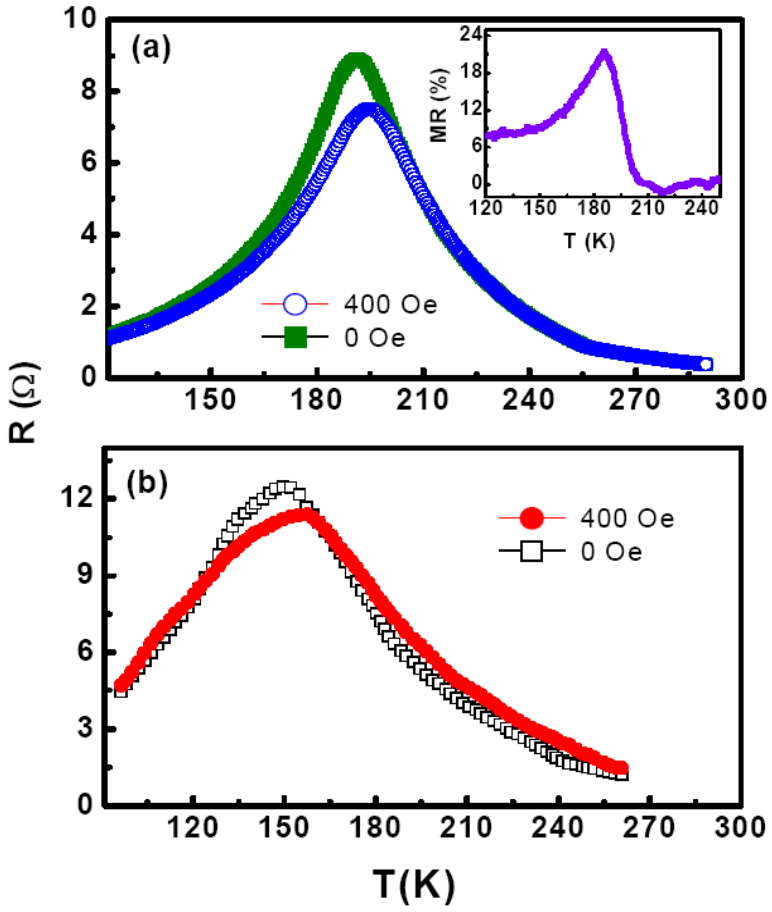

Figure 6. Temperature dependences of resistance of (a) $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ and (b) $La_{0.7}Ca_{0.3}Mn_{0.95}Cu_{0.05}O_3$ under applied fields of 0 Oe and 400 Oe. The inset in (a) shows MR of $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$.

With H = 400 Oe, it was found that MR reached maximum values of 21.4 % at 186 K for $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$, see the inset of Fig. 6(a), and about 11.0 % at 150 K for $La_{0.7}Ca_{0.3}Mn_{0.95}Cu_{0.05}O_3$. The decrease in the MR ratio of the Cu-doped sample compared to that of the Zn-doped one could be due to the presence of anti-ferromagnetic interaction pairs Cu^{2+}- $Mn^{3+,4+}$, which influenced the hopping process of electrons between Mn^{3+} and Mn^{4+} ions.

For a $La_{0.7}Ca_{0.3}MnO_3$ single crystal sample, it was found the MR ratio of about 70 % under an applied field of 500 Oe [14], much higher than those determined from our Zn- and Cu-doped samples. This is probably associated with the grain boundary effects [16] and/or the difference in the magnetic phase transition type between undoped and Zn- and Cu-doped $La_{0.7}Ca_{0.3}MnO_3$ compounds as discussed above.

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CONCLUSION

We prepared polycrystalline perovskite manganites of $La_{0.7}Ca_{0.3}Mn_{0.9}Zn_{0.1}O_3$ and $La_{0.7}Ca_{0.3}Mn_{0.95}Cu_{0.05}O_3$, and studied their magnetic and magnetotransport properties. It was revealed that the presence of Zn and Cu dopants reduced the Curie temperature. While the parent compound $La_{0.7}Ca_{0.3}MnO_3$ exhibited the first-order magnetic phase transition, our samples exhibited the second-order transition. Such the circumstances led to a remarkable decrease in the maximum magnetic-entropy change (ΔS_M) and MR values compared to those of $La_{0.7}Ca_{0.3}MnO_3$. The role of Zn and Cu dopants in the manganite host lattice was also discussed.

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