

Influences of Cu-doped and Sr vacancy on the room magnetoresistance of $\text{La}_{0.67}\text{Sr}_{0.33-x-y}\text{Cu}_x\text{MnO}_3$ [☆]

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Abstract

Single-phase perovskite-type manganese oxides $\text{La}_{0.67}\text{Sr}_{0.33-x-y}\text{Cu}_x\text{MnO}_3$ ($x = 0.10, 0.15, y = 0.00, 0.03$) polycrystalline samples were synthesized by sol–gel method, where x is the fraction of Cu doped at Sr site, y is the fraction of Sr vacancy. The X-ray diffraction analyses of the samples revealed that all the samples are single-phase with perovskite structure. It is found that the room temperature magnetoresistance (MR) of Cu-doped sample with Sr vacancy is obviously larger than the un-doped $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ sample. Under an applied field of 1.8 T, there is an MR maximum 23% of $\text{La}_{0.67}\text{Sr}_{0.15}\text{Cu}_{0.15}\text{MnO}_3$ at 300 K, whose field susceptibility is about 17%/T below 1.2 T. This field susceptibility around room temperature is highly improved as compared to one of the reported single-phase perovskite structure materials. Therefore, it is important for the potential application of this MR material.

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1. Introduction

Magnetoresistive properties of perovskite manganese have been widely investigated in the past few years owing to their importance for fundamental research and potential use in magnetic device [1–4]. In general, the magnetoresistance

(MR) magnitude of single crystals and epitaxial thin films reaches a maximum only near their Curie temperature (T_C), which is not at room temperature, therefore severely limit their practical utilities [5–8]. The colossal magnetoresistance (CMR) for the general formula $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ ($A = \text{Sr}, \text{Ca}, \text{Ba}, \text{etc.}$), is generally understood in terms of double-exchange (DE) interaction between Mn^{3+} and Mn^{4+} . However, Mills et al. [9–11] argued that the DE mechanism alone could not quantitatively account for some features of the CMR effect in $\text{La}_{1-x}\text{A}_x\text{MnO}_3$, such as the magnitude of the resistivity and the magnitude of

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CMR. A strong Jahn-Teller electron–phonon coupling, arising from the deformation of the Mn^{3+}O_6 octahedra due to Jahn-Teller effect, should play an important role. CMR in LaMnO_3 has been reported without any divalent ion substitution [12,13], from which Mn^{4+} ions can be present by controlling La or oxygen deficiency in stoichiometry. In this paper, we have studied the Sr^{2+} vacancy and Cu-doped dependence of the magnetic properties and MR of $\text{La}_{0.67}\text{Sr}_{0.33-x-y}\text{Cu}_x\text{MnO}_3$ by X-ray diffraction, magnetization, and the resistivity measurements.

2. Experiment

Polycrystalline samples $\text{La}_{0.67}\text{Sr}_{0.33-x-y}\text{Cu}_x\text{MnO}_3$ ($x = 0.10, 0.15, y = 0.00, 0.03$) were prepared by the sol–gel method [14] as follows: stoichiometric amounts of La_2O_3 , $\text{Sr}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$ and $\text{Mn}(\text{NO}_3)_2$ were dissolved in dilute HNO_3 solution. Suitable amounts of citric acid and ethylene glycol as coordinate agent were added and a completely homogeneous transparent solution was achieved. This solution was subjected to slow evaporation at 360 K until a highly viscous residual was formed, and a gel was developed during heating at 473 K for 24 h. Then the gel was thermally treated at 873 K for 5 h for the purpose of organic precursor decomposition. After grinding, all the samples were calcined in air at 1073 K for 10 h and furnace cooled. These powders were pressed into pellets and then sintered in air at 1673 K for 12 h. This method has the advantage of using low-temperature synthesis, which not only results in smaller grains but also produces a high-purity and homogeneous sample.

The phase identification of samples at room temperature has been carried out by the X-ray diffraction (XRD) with an 18 kW Rigaku max-RB diffractometer with CuK_α radiation in the 2θ range of $10\text{--}90^\circ$. The magnetization measurements were carried out with a Lake Shore vibrating sample magnetometer (VSM) in the temperature region of $300\text{--}400$ K. We plotted a tangent line at the maximum of $|\text{d}M/\text{d}T|$ along the curve of magnetization versus temperature, then extrapolated the tangent line to the temperature axis and

obtained a crossing point which is taken as the Curie's temperature (T_C). All the Curie's temperature measurements were performed at applied field 0.05 T. The morphology was obtained by S-570 scanning electron microscopy (SEM). The temperature and magnetic field dependences of the resistivity were measured (using Oxford Maglab Exa Measurement System) with the standard DC four-probe method and the applied field was parallel to the direction of current.

3. Results and discussion

The structural characterization of the powder sample was determined by means of X-ray diffraction (XRD). The XRD patterns obtained for typical powder samples with $x = 0.00, y = 0.00$; $x = 0.15, y = 0.00$ and $x = 0.15, y = 0.03$ are shown in Fig. 1. The results indicate that the materials are a single phase with perovskite structure without any other secondary or impurity phase, and the characteristic peaks are the same as those of the perovskite previously reported [15].

Fig. 2 shows the SEM morphology for $\text{La}_{0.67}\text{Sr}_{0.18}\text{Cu}_{0.15}\text{MnO}_3$ with heat processing first at 873 K for 5 h then 1073 K for 10 h in atmosphere. From Fig. 2 we know that the prepared

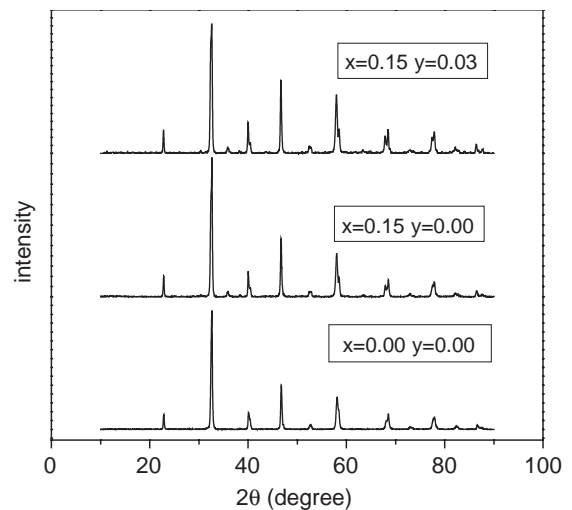


Fig. 1. X-ray diffraction patterns for $\text{La}_{0.67}\text{Sr}_{0.33-x-y}\text{Cu}_x\text{MnO}_3$ polycrystal powders.

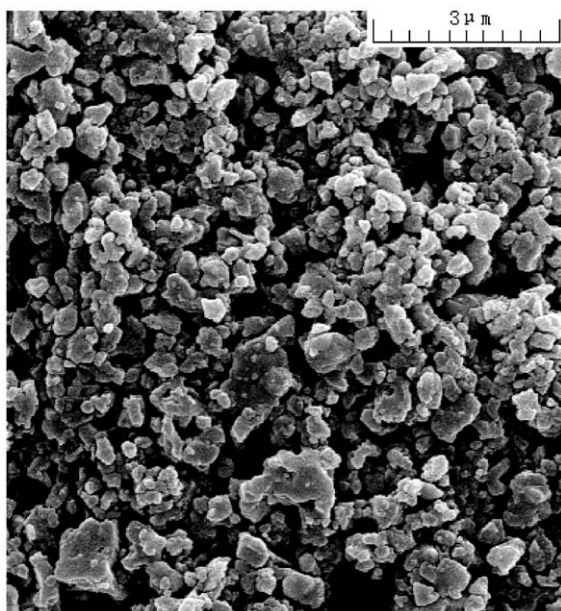


Fig. 2. SEM micrograph of $\text{La}_{0.67}\text{Sr}_{0.18}\text{Cu}_{0.15}\text{MnO}_3$ powder.

sample by the sol–gel method possesses homogeneously globular-shaped grains; the grain size is about 150 nm, but the larger grains of reunited bodies of the smaller grains.

Fig. 3 shows curves of the magnetization versus temperature for the compounds at applied field 0.05 T. The compounds have a Curie's temperature of 375, 333, 321, 335 and 305 K for $x = 0.00$, $y = 0.00$; $x = 0.10$, $y = 0.00$; $x = 0.15$, $y = 0.00$; $x = 0.10$, $y = 0.03$ and $x = 0.15$, $y = 0.03$, respectively, as shown in Table 1, which is determined by the method as in Section 2 and Fig. 3. From Fig. 3 we know that the Curie's temperature (T_C) decreased obviously by Cu doped and Sr^{2+} vacancy, and that their magnetization changes with x and y . A few Cu-doped at Sr site can increase magnetization, and Sr vacancy will decrease magnetization.

The temperature dependence of the resistivity measured in zero field and in an applied field (1.8 T) for the samples $\text{La}_{0.67}\text{Sr}_{0.23}\text{Cu}_{0.10}\text{MnO}_3$ (a) and $\text{La}_{0.67}\text{Sr}_{0.18}\text{Cu}_{0.15}\text{MnO}_3$ (b) are plotted in Fig. 4. From Fig. 4 we know that resistivity of polycrystalline $\text{La}_{0.67}\text{Sr}_{0.33-x}\text{Cu}_x\text{MnO}_3$ sample is very small and its order is about $10^{-2} \Omega\text{cm}$. Fig. 4

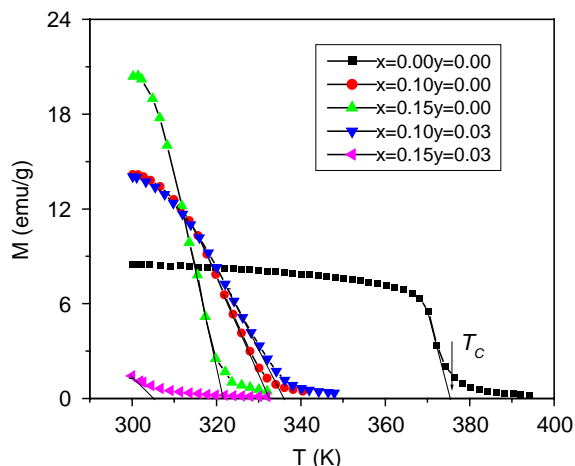


Fig. 3. Curves of magnetization versus temperature for $\text{La}_{0.67}\text{Sr}_{0.33-x-y}\text{Cu}_x\text{MnO}_3$, $x = 0.00$, $y = 0.00$; $x = 0.10$, $y = 0.00$; $x = 0.15$, $y = 0.00$; $x = 0.10$, $y = 0.03$ and $x = 0.15$, $y = 0.03$ at 0.05 T.

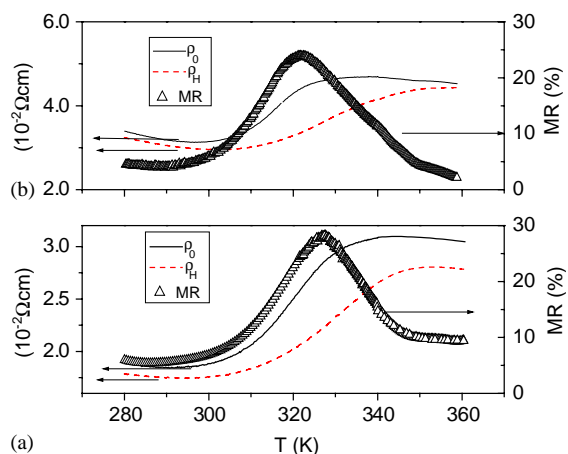


Fig. 4. Temperature dependence of the resistivity measured in zero field and in an applied field (1.8 T) for both manganites: $\text{La}_{0.67}\text{Sr}_{0.23}\text{Cu}_{0.10}\text{MnO}_3$ (a) $\text{La}_{0.67}\text{Sr}_{0.18}\text{Cu}_{0.15}\text{MnO}_3$ (b); The corresponding MR is also indicated.

also shows that the samples possess the metallic conductivity at low temperature and the semiconducting conductivity at high temperatures. The transition is characterized by a resistivity maximum at the temperature T_P about 343 and 335 K for $x = 0.10$ and 0.15, respectively. As it is known, metal–semiconducting transition temperature of

Table 1

Magnetic transition temperature T_C , metal–semiconducting transition temperature T_P , the maximum MR_{MAX} of MR and corresponding to temperature T_{MR} for the $La_{0.67}Sr_{0.33-x-y}Cu_xMnO_3$ compounds with different x and y

x	y	$MR_{MAX}(\%)/T_{MR}$ (K)	T_P (K)	T_C (K)
0.00	0.00	6.8/360	370	375
0.10	0.00	28.5/328	343	333
0.15	0.00	24.5/320	335	321
0.10	0.03	20/328	339	335
0.15	0.03	23/300	307	305

the $La_{0.67}Sr_{0.33}MnO_3$ is about 370 K, so the T_P obviously reduced when Sr is substituted with Cu in $La_{0.67}Sr_{0.33}MnO_3$ partially. The T_P for both samples are given in Table 1.

Define the magnetoresistance by $MR(\%) = [\rho_0 - \rho_H]/\rho_0 \times 100\%$, where ρ_0 and ρ_H stand for the resistivities at 0 and 1.8 T, respectively. Application of a magnetic field considerably reduces the resistivity over the whole temperature range, so a negative MR effect can be observed for all samples. We obtain the MR as a function of temperature, which is also plotted in Fig. 4. The value of MR increased then decreased with the increase of temperature for both samples. So there is maximum MR at a certain temperature; the peak of MR is 28.5% at 328 K and 24.5% at 320 K for $x = 0.10$ and 0.15, respectively. Although the peak of MR decreased with the increase of Cu, corresponding temperature of peak reduces towards room temperature, which is a good tendency for application of these materials. The maximum MR (MR_{MAX}) and corresponding temperature (T_{MR}) for both samples are also given in Table 1.

Fig. 5 shows the resistivity versus temperature in zero field and in an applied (1.8 T) for both manganites: $La_{0.67}Sr_{0.20}Cu_{0.10}MnO_3$ (a) and $La_{0.67}Sr_{0.15}Cu_{0.15}MnO_3$ (b), in which Sr vacancy fraction are the same $y = 0.03$, but there the Cu fraction is different. From Fig. 5 we know that the resistivity of polycrystalline $La_{0.67}Sr_{0.33-x-y}Cu_xMnO_3$ sample is very small and its order is about $10^{-2}\Omega\text{cm}$. The resistivity of samples possessed metallic conductivity at low temperature

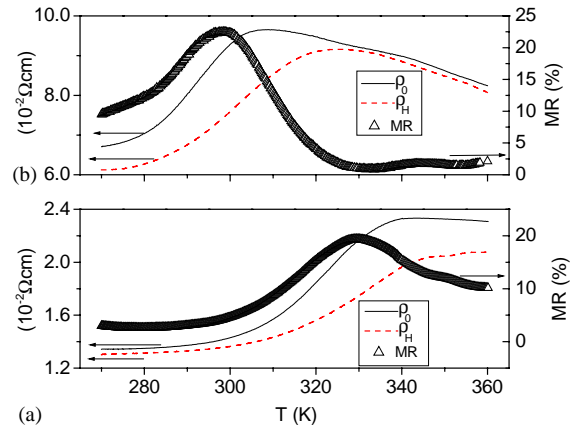


Fig. 5. Temperature dependence of the resistivity measured in zero field and in an applied field (1.8 T) for both manganites: $La_{0.67}Sr_{0.20}Cu_{0.10}MnO_3$ (a); $La_{0.67}Sr_{0.15}Cu_{0.15}MnO_3$ (b). The corresponding MR is also indicated.

and the semiconducting conductivity at high temperatures. The transition temperature T_P is 339 and 307 K for $x = 0.10, y = 0.03$ and $x = 0.15, y = 0.03$, respectively. It is observed that T_P reduces largely comparing to the samples without vacancy ($y = 0.00$). The MR versus temperature also plotted in Fig. 5. We obtain the peak magnitude of MR as 20% at 328 K and 23% at 300 K for $x = 0.10, y = 0.03$ and $x = 0.15, y = 0.03$, respectively. The MR_{MAX} and T_{MR} are also given in Table 1. So we reduced the corresponding temperature of the maximum MR by Sr vacancy and made this temperature close to room temperature, which is important for the potential application of this MR material.

The applied field dependence of MR was measured for fields up to 6 T at 300 K for $La_{0.67}Sr_{0.15}Cu_{0.15}MnO_3$ and shown in Fig. 6. It clearly indicates a larger response in magnetic fields below 1.2 T. Here we define the field susceptibility by $dMR(\%)/dH$, so the field susceptibility is about 17%/T below 1.2 T. Thereby field susceptibility around room temperature is highly improved compared to the reported single-phase perovskite structure materials. We can see that the value of MR at 300 K increases with the increase of field, and reaches 43.3% when the applied field is up to 6 T, at which it is still not saturated.

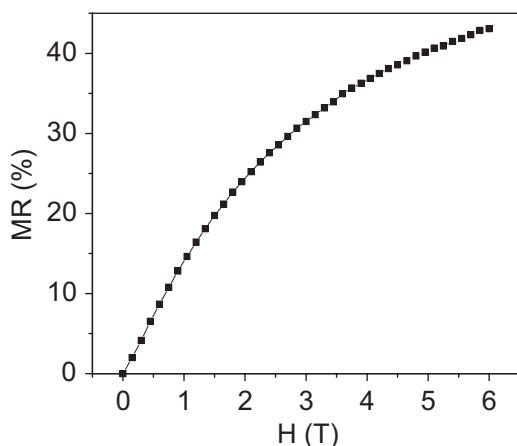


Fig. 6. Field dependence of the MR at 300 K for $\text{La}_{0.67}\text{Sr}_{0.15}\text{Cu}_{0.15}\text{MnO}_3$.

4. Conclusions

In summary, $\text{La}_{0.67}\text{Sr}_{0.33-x-y}\text{Cu}_x\text{MnO}_3$ polycrystalline samples have been successfully synthesized by the sol-gel method. The X-ray diffraction analysis of the samples revealed that they are single phase with perovskite structure. The Curie's temperature (T_C) and transition temperature (T_P) reduce greatly with increase of Cu-doped, so does the temperature corresponding to the maximum MR. Under applied field 1.8 T, we find that the peak of MR is 28.5% at 328 K for $\text{La}_{0.67}\text{Sr}_{0.23}\text{Cu}_{0.10}\text{MnO}_3$ and one is 23% at 300 K for $\text{La}_{0.67}\text{Sr}_{0.15}\text{Cu}_{0.15}\text{MnO}_3$. As is known, the maximum MR of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ is less than 7% at 360 K and less than 3% at room temperature, so we raised the room temperature MR and

maximum MR by Sr substitution with Cu and Sr vacancy obviously. It is important for the potential application of perovskite manganites.

References

- [1] A.P. Ramirez, J. Phys.: Condens. Matter 9 (1997) 8171; Y. Tokura, T. Tomioka, J. Magn. Magn. Mater. 200 (1999) 1.
- [2] J. Fontcuberta, L. Balcells, M. Bibes, J. Navarro, C. Frontera, J. Santiso, J. Fraxedas, B. Martinez, S. Nadolski, M. Wojcik, E. Jedryka, M.J. Casanove, J. Magn. Magn. Mater. 242–245 (2002) 98.
- [3] Chun-Hua Yan, Zhi-Gang Xu, Tao Zhu, Zhe-Ming, Fu-Xiang Cheng, Yun-Hui Huang, Chun-Sheng Liao, J. Appl. Phys. 87 (2000) 5588.
- [4] P. Chen, D.Y. Xing, Y.W. Du, J.M. Zhu, D. Feng, Phys. Rev. Lett. 87 (2001) 1.
- [5] L. Balcells, B. Martinez, F. Sandiumenge, J. Fontcuberta, J. Magn. Magn. Mater. 211 (2000) 193.
- [6] R. Mahesh, M.R. ahendiran, A.K. Raychaudhuri, C.N.R. Rao, Appl. Phys. Lett. 68 (1996) 2291.
- [7] A. Gupta, et al., Phys. Rev. B R15 (1996) 629.
- [8] R. Shreekala, et al., Appl. Phys. Lett. 71 (1997) 282.
- [9] A.J. Mills, P.B. Littlewood, B.I. Shraiman, Phys. Rev. Lett. 74 (1995) 5144.
- [10] A.J. Millis, B.I. Shraiman, R. Mueller, Phys. Rev. Lett. 77 (1996) 175.
- [11] A.J. Millis, Phys. Rev. B 53 (1996) 8434.
- [12] C. Haubeck, F. Helmer, N. Sakai, J. Solid State Chem. 124 (1996) 43.
- [13] A. Gupta, T.R. Mcgruire, P.R. Duncombe, M. Rupp, J.Z. Sun, W.J. Gallgher, G. Xiao, Appl. Phys. Lett. 67 (1995) 3494.
- [14] W. Chen, W. Zhong, D.L. Hou, R.W. Gao, W.C. Feng, M.G. Zhu, Y.W. Du, J. Phys.: Condens. Matter. 14 (2002) 11889.
- [15] R.D. Sanchez, et al., Appl. Phys. Lett. 68 (1996) 134.