Heat Stagnation of Dy-Doped La$_{2/3}$Ca$_{1/3}$MnO$_3$ Manganese Oxides in the Measurement Process of Warming and Cooling

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ABSTRACT: (La$_{1-x}$Dy$_x$)$_{2/3}$Ca$_{1/3}$MnO$_3$ samples with the perovskite structure were prepared by the sol–gel method, and the R–T curves of the samples in 0–3000 Gs magnetic field during warming and cooling processes were compared. It is found that the transition temperature ($T_c$) of the samples decreases and peak resistance ($R_p$) of the samples increases with the increase of Dy concentration in the same magnetic field. In addition, for the samples with the same Dy concentration, $T_c$ of the samples increases and magnetoresistance (MR) of the samples decreases with the increase of the magnetic field, and the increase of $T_c$ as well as the decrease of resistance is more obvious during the cooling process than those during the warming one. Besides, the variation of MR during the cooling process is also larger than that during the warming one.

1. INTRODUCTION

The doped manganese perovskites with the general formula A$_{1-x}$B$_x$MnO$_3$ (A = La, Nd, Dy, etc., and B = Ca, Sr, etc.) are of great significance in basic research and practical application.$^{1-3}$ Currently, a lot of research work in substitution focuses on the optimally doped compound La$_{2/3}$Ca$_{1/3}$MnO$_3$. Despite many reports and studies concerning this, further research is still necessary to make full use of these samples. Most experimental and theoretical results showed that the key factors influencing the transport properties of manganese oxide A$_{1-x}$B$_x$MnO$_3$ compounds are the radius, magnetic moment, and doping concentration of rare earth ions at the A-site.$^{2-6}$ There were many reports on the A$_{1-x}$B$_x$MnO$_3$ samples prepared by the solid-state reaction method, which focused on the effects of magnetic moment of rare earth ions doped at the A-site on the transport properties of the samples.$^7$ Because the samples prepared using the sol–gel method are evenly mixed at the molecular level, the synthesis temperature is relatively low and the diffusion of different compositions is in the nanometer range, the samples would have quite different electromagnetic transport performance compared to those prepared using the solid-state reaction method. A large number of experiments showed that the preparation methods of the materials are closely related to particle size and physical properties of manganese oxides.$^{8,9}$ However, there are few systematic studies about the heat stagnation of Dy-doped manganese oxides prepared by the wet-chemical method, which is a relatively large atomic magnetic moment element in lanthanide metals.

Herein, the electrical transport properties of (La$_{1-x}$Dy$_x$)$_{2/3}$Ca$_{1/3}$MnO$_3$ were investigated through the temperature dependence of resistance in 0–3000 Gs magnetic field, and the relationships between the warming and cooling processes were also discussed.

2. RESULTS AND DISCUSSION

2.1. Crystal Structure of (La$_{1-x}$Dy$_x$)$_{2/3}$Ca$_{1/3}$MnO$_3$. X-ray diffraction (XRD) patterns of (La$_{1-x}$Dy$_x$)$_{2/3}$Ca$_{1/3}$MnO$_3$ samples are shown in Figure 1. As shown, all the samples expressed the diffraction peaks of the manganese oxide perovskite structure, and there were no impurity peaks in the XRD patterns even if the Dy-doped concentration is up to 0.4. The results indicated that Dy atoms took the place of the La-site in (La$_{1-x}$Dy$_x$)$_{2/3}$Ca$_{1/3}$MnO$_3$ samples, and all the samples had good crystallographic properties.

2.2. R–T Relationships of (La$_{1-x}$Dy$_x$)$_{2/3}$Ca$_{1/3}$MnO$_3$ during the Warming and Cooling Processes. Figures 2 and 3 show the temperature dependence of resistance of (La$_{1-x}$Dy$_x$)$_{2/3}$Ca$_{1/3}$MnO$_3$ samples ($x = 0.05, 0.1, 0.2, 0.3,$ and $0.4$, respectively) during the warming process in the magnetic fields of 750 and 3000 Gs, respectively. Compared with the internal resistance of the measuring system, the resistance of the high Dy-doped sample ($x = 0.4$) in 10–68 K is out of range; so

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the data of the sample were only collected from 68 to 290 K. According to the previous study, the resistance of La$_{0.7-x}$Dy$_x$Sr$_{0.3}$MnO$_3$ significantly increased with the increase of Dy concentration, which is consistent with our results. The $R$–$T$ curves of the samples did not show obvious difference in 750 and 3000 Gs magnetic fields. It was only found by carefully comparing Figures 2 with 3 that $T_c$ of samples decreased with the increase of Dy concentration or the decrease of magnetic field. As the magnetic moment of the trivalent Dy ions is almost the same as Ho ions (the variation of ionic radius is only 1.2 pm, about 1% of ion radius of Dy), Dy and Ho-doped have similar influences on the La$_{2/3}$Ca$_{1/3}$MnO$_3$ system. In previous studies, the system of Ho-doped manganese oxide has been analyzed, and it was showed that the lattice structure of La$_{2/3}$Ca$_{1/3}$MnO$_3$ can be divided into two sublattice layers, that is, the La(Ca)–O layer and Mn–O layer, wherein the Mn–O layer being a magnetic layer and La(Ca)–O layer being the non-magnetic layer. The system below $T_c$ dominated by the Mn–O–Mn interactions presents a long-range ferromagnetic ordered structure, and PM-FM phase transformation occurs near the $T_c$. When Dy enters into the La (Ca)–O layer in place of La, the difference of magnetic moment and ionic radius between the trivalent Dy and trivalent La breaks the long-range ferromagnetic order in the Mn–O–Mn layer, which results in the formation of short-range ferromagnetic order in the Mn–O–Mn cluster. As Dy concentration randomly distributed in the La (Ca, Dy)-O layer increases, the La (Ca, Dy)-O layer becomes magnetic gradually because the nature of the magnetic layer is very sensitive to Dy concentration entering the lattice, and the coupling strength of La (Ca, Dy)-O layer and Mn–O magnetic layer is dependent on the Dy-doped concentration. Because of the nature of this coupling, the orderly structure of the system is characterized by the presence of the large amounts of spin clusters. As the doping concentration increases, the number of spin cluster increases, the sizes of spin cluster become smaller, the $T_c$ of the samples obviously shifts to the low temperature direction and the resistance of samples increases significantly with the increase of Dy concentration in the same field. The results are in agreement with the results of Blasco et al., in which the structure and electromagnetic properties of (La$_{1-x}$Tb$_x$)$_{2/3}$Ca$_{1/3}$MnO$_3$ were studied. Figure 4 shows the temperature dependence of resistance of (La$_{1-x}$Dy$_x$)$_{2/3}$Ca$_{1/3}$MnO$_3$ samples ($x = 0.05, 0.1, 0.2, 0.3,$ and 0.4, respectively) during the cooling process in the magnetic field of 2250 Gs. The corresponding $T_c$ and $R_p$ of
processes. The phase transition occurs in a frozen state of the material. The phase transition occurs in a frozen material structure of magnetic ordering, the magnetic moment of lanthanide rare earth ions and the thermal hysteresis of the samples during the warming and cooling processes is in relation to the magnetic ordering phenomenon. Therefore, the “thermal hysteresis” phenomenon is produced only by the measuring direction.

2.3. $R$–$T$ Relationships of the $(\text{La}_{0.7}\text{Dy}_{0.3})_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ Sample in Different Magnetic Fields. It is clear that the thermal hysteresis of the samples during the warming and cooling processes is in relation to the magnetic ordering structure of the material. The phase transition occurs in a frozen magnetic order system in the warming process, more energy is needed than the phase transition occurring during the cooling process, and then $T_c$ during the warming process is higher than that during the cooling one. To explore the connection between the magnetic moment of lanthanide rare earth ions and the material structure of magnetic ordering, the $R$–$T$ relationships of the high Dy-doped $(\text{La}_{0.7}\text{Dy}_{0.3})_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ sample have been investigated. As shown in Figure 5, the temperature dependence of the $(\text{La}_{0.7}\text{Dy}_{0.3})_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ sample around 750, 1500, 2250, and 3000 Gs, respectively, during the warming process.

dependence of resistance of the $(\text{La}_{0.7}\text{Dy}_{0.3})_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ sample during the warming and cooling processes was measured in magnetic field from 0 to 3000 Gs. Magnetic field gradually increased from 0 Gs up to 3000 Gs for both the cooling process (d) and warming process (r). The results showed that there were big differences between the $R$–$T$ curves during the warming and cooling processes in the same field including the $T_c$ and $R_c$. During the warming process, the measured $T_c$ was slightly higher than that during the cooling one. The thermal hysteresis phenomenon has been previously investigated for the low Dy-doped $(\text{La}_{0.7}\text{Dy}_{0.3})_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ samples prepared using the solid-state reaction method.\textsuperscript{13,14} As the samples prepared using the sol–gel method are evenly mixed at the molecular level, the synthesis temperature is lower and the composition of diffusion is in the nanometer range. These differences will make the samples quite different in the electromagnetic transport properties from those prepared using the solid-state reaction method.

As shown in Figure 5, in the low magnetic field in situ, and all of the experimental parameters were the same except for the variable temperature direction. Therefore, the “thermal hysteresis” phenomenon is produced only by the measuring direction.

| Dy-doped concentration $x$ | 0.05 | 0.1 | 0.2 | 0.3 |
|-----------------------------|------|-----|-----|-----|
| $T_c$ (r) 750 Gs (K)        | 180.1| 132.0| 121.0| 85.0|
| $T_c$ (d) 2250 Gs (K)       | 176.1| 129.8| 119.8| 80.0|
| $T_c$ (r) 3000 Gs (K)       | 180.9| 134.0| 124.0| 88.9|
| $R_c$ (r) 750 Gs (kΩ)       | 0.387| 3.183| 4.844| 1027|
| $R_c$ (d) 2250 Gs (kΩ)      | 0.405| 2.994| 3.993| 1439|
| $R_c$ (r) 3000 Gs (kΩ)      | 0.330| 2.730| 3.608| 849.2|

Table 1. $T_c$ and $R_c$ of $(\text{La}_{0.7}\text{Dy}_{0.3})_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ during the Warming (r) and Cooling (d) Processes in the Magnetic Field of 750, 2250, and 3000 Gs, Respectively

Figure 6 shows the temperature dependence of resistance of the $(\text{La}_{0.7}\text{Dy}_{0.3})_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ sample during the warming process in 0–3000 Gs magnetic fields. It could be found that in the temperature region of 50–100 K, the resistance around $T_c$ significantly reduced with the increase of the magnetic field. As a result, the sample in this temperature region had better magnetoresistance (MR) in 0–3000 Gs magnetic fields.

Figure 7 shows the temperature dependence of resistance of the $(\text{La}_{0.7}\text{Dy}_{0.3})_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ sample during the warming process in 0–3000 Gs magnetic fields. Comparing Figures 6 with 7, it could be seen that in the temperature region of 70–100 K, the increase of $T_c$ as well as decrease of resistance was more obvious during the cooling process than that during the warming one.

Figure 8 shows the variation of MR of the $(\text{La}_{0.7}\text{Dy}_{0.3})_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ sample around $T_c$ during the warming and cooling processes in different magnetic fields. The results indicated that the MR increased with the increase of magnetic field and was remarkably larger during the cooling process than that during warming one. Besides, the variation of MR during the cooling process was also larger than that during the warming one.

As shown in Figure 5, in the low magnetic field in situ, and all of the experimental parameters were the same except for the variable temperature direction. Therefore, the “thermal hysteresis” phenomenon is produced only by the measuring direction.
Hysteresis was found for the large atomic magnetic moment, a relatively large thermal hysteresis was found during the warming process. 2250, and 3000 Gs, respectively, during the warming process.

2250, and 3000 Gs, respectively.

Figure 8. Variation of MR of (La$_{1-x}$Dy$_x$)$_{2/3}$Ca$_{1/3}$MnO$_3$ in 750, 1500, 2250, and 3000 Gs, respectively.

3. CONCLUSIONS

In the study on the influence of Dy-doped (La$_{1-x}$Dy$_x$)$_{2/3}$Ca$_{1/3}$MnO$_3$ perovskite structure with a relatively large atomic magnetic moment, a relatively large thermal hysteresis was found for the first time and its mechanism was analyzed in detail.

(1) The electrical transport properties of (La$_{1-x}$Dy$_x$)$_{2/3}$Ca$_{1/3}$MnO$_3$ samples were not only affected by different Dy-doped concentration and magnetic field but also closely related with the measuring process. It was found that $T_c$ of the samples decreased and MR of the samples increased with the increase of Dy concentration in the same field, and $T_c$ of the samples increased with the increase of the magnetic field with the same Dy concentration.

(2) For (La$_{0.7}$Dy$_{0.3}$)$_{2/3}$Ca$_{1/3}$MnO$_3$ sample in 0–3000 Gs magnetic fields, the increase of $T_c$ as well as decrease of resistance was more obvious during the cooling process than that during the warming one. Besides, the variation of MR during the cooling process was also larger than that during the warming one.

4. EXPERIMENTAL SECTION

The polycrystalline ceramic (La$_{1-x}$Dy$_x$)$_{2/3}$Ca$_{1/3}$MnO$_3$ was prepared by the sol–gel method using a stoichiometric mixture of La(NO$_3$)$_3$, Dy$_2$O$_3$, CaCO$_3$, and MnCO$_3$ in the aqueous solution of nitric acid. The solution was mixed till all the reactants completely dissolved and then C$_2$H$_5$OH and HOCH$_2$CH$_2$OH was added with continually mixing to form completely transparent solution. Next, the solution was slowly heated from 348 to 371 K to evaporate part of the solvent. The gel formed during cooling from 371 K to room temperature and then decomposed by heating to autoignition to form the precursor powders which were used to prepare the final samples. After annealing the precursors at 973 K for 12 h, the powders were pressed into pellets with a diameter of 10 mm and thickness of 1 mm. Finally, the sintering process was carried out at 1273 K for 24 h. The crystal structure of the prepared samples was characterized by XRD. The temperature dependence of resistance during the warming and cooling processes was measured by the standard four-probe method from $T = 10–300$ K in 0–3000 Gs magnetic field.

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Notes
The authors declare no competing financial interest.

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