

Effect of Eu-doping on the magnetic and magnetoresistive properties of $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$

Hai-bo Li · Ming Feng · Na Li · Mei Liu · Xi-cheng Gou

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Abstract The effects of Eu-doping in the A-site on the magnetic and magnetoresistive properties of $\text{La}_{0.65-x}\text{Eu}_x\text{Ca}_{0.35}\text{MnO}_3$ ($x=0, 0.05, 0.10, 0.15$) bulk samples have been investigated. All samples have a single perovskite structure. The Curie temperature T_C decreases with increasing Eu content from 268 K for $x=0$ to 141 K for $x=0.15$. The magnetoresistivity increases with increasing Eu content. Upon an application of a magnetic field of 2.0 T the maximum magnetoresistivity of 97.3% for the $\text{La}_{0.50}\text{Eu}_{0.15}\text{Sr}_{0.35}\text{MnO}_3$ was obtained. It provides an effective way to obtain the high magnetoresistance in the polycrystalline manganites.

Keywords Sol–gel · Manganites · Curie temperature · Magnetoresistance

1 Introduction

For more than 10 years, perovskite manganites $\text{Re}_{1-x}\text{A}_x\text{MnO}_3$ (Re=trivalent rare earth; A=divalent alkaline earth metal or monovalent alkali metal) have received special attention due to the colossal magnetoresistance (CMR) and other intricate physical phenomena in them [1–6]. The

double exchange (DE) interaction [7] between Mn^{3+} and Mn^{4+} ions, along with the Jahn-Teller distortion, leads to the appearance of the so-called CMR in such systems. Millis et al. argued that the physics of manganites is dominated by the interplay between a strong electron–phonon coupling and the large Hund coupling effects that optimizes the electronic kinetic energy by the formation of ferromagnetic phase [8, 9]. In addition, a phase segregation dependent mechanism about the coexistence of ferromagnetic metal clusters and paramagnetic regions is developed in order to explain the unusual transport properties near T_C [10–12]. However, other factors, namely, average A-site cationic radius, mismatch effects, competition between the ferromagnetic and the charge-ordered phases, vacancies in La and Mn sites and the oxygen stoichiometry, also play an important role.

In this paper, we investigate the effects of Eu concentration on the Curie temperature and magnetoresistive properties of the bulk polycrystalline $\text{La}_{0.65-x}\text{Eu}_x\text{Ca}_{0.35}\text{MnO}_3$ manganites. The T_C and CMR effect of perovskite manganites can be adjusted by A-site doping, which is beneficial for manipulating magnetoresistivity that occurs in various temperature ranges.

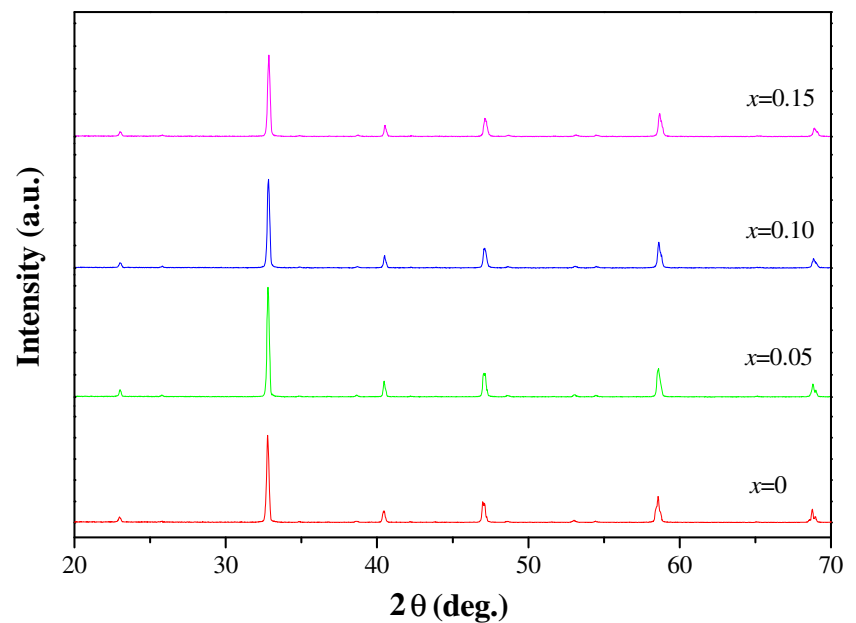
2 Experimental

A series of $\text{La}_{0.65-x}\text{Eu}_x\text{Ca}_{0.35}\text{MnO}_3$ ($x=0, 0.05, 0.10, 0.15$) bulk samples were synthesized by sol–gel technique. The analytical grade chemicals, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Eu_2O_3 , $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2$ were used as starting materials, with desired molar ration $\text{La} : \text{Eu} : \text{Ca} : \text{Mn} = 0.65-x : x : 0.35 : 1$ were dissolved in pure water, then the citric acid and glycol were added to the mixture. The mixture was magnetically stirred for 2 h. Clear and transparent sol was obtained after

H.-b. Li (✉) · M. Feng · N. Li · M. Liu · X.-c. Gou
Key Laboratory of Functional Materials Physics and Chemistry
of the Ministry of Education, Jilin Normal University,
Siping 136000, People's Republic of China
e-mail: lihaibo@jlnu.edu.cn

M. Feng · N. Li
School of Materials Science and Engineering,
Harbin Institute of Technology,
Harbin 150001, People's Republic of China

Fig. 1 XRD patterns at room temperature for $\text{La}_{0.65-x}\text{Eu}_x\text{Ca}_{0.35}\text{MnO}_3$ ($0.0 \leq x \leq 0.15$)



complete dissolution, which was evaporated on a water bath at 363 K to remove the excess water, and then the gel was formed. The gel was dried at 473 K in baking oven until xerogel was formed. The xerogel was slowly heated to 873 K and pre-calcined for 5 h to make the organic matter decompose completely. The obtained powders were ground, pelletized, and calcined at 1,473 K for 10 h.

The structure of polycrystalline $\text{La}_{0.65-x}\text{Eu}_x\text{Ca}_{0.35}\text{MnO}_3$ samples were characterized by X-ray diffraction (XRD) using a D/max-2500/PC system with the $\text{Cu K}\alpha$ radiation and measured at room temperature. The magnetic

measurements were performed by using Lake Shore M-7407 vibrating sample magnetometer (VSM), and resistivity data were obtained by Quantum Design MPMS-XL-5 system with a standard four-probe method.

3 Results and discussion

Figure 1 shows the X-ray diffraction patterns for $\text{La}_{0.65-x}\text{Eu}_x\text{Ca}_{0.35}\text{MnO}_3$ samples with $0.0 \leq x \leq 0.15$ at room temperature.

Fig. 2 Temperature-dependence of magnetization for the $\text{La}_{0.65-x}\text{Eu}_x\text{Ca}_{0.35}\text{MnO}_3$ samples in a magnetic field of 0.05 T

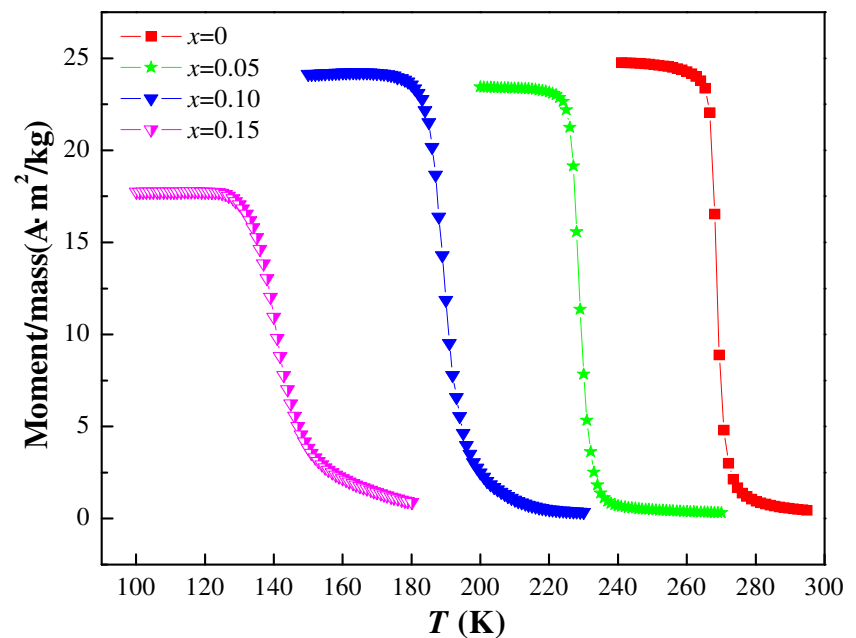
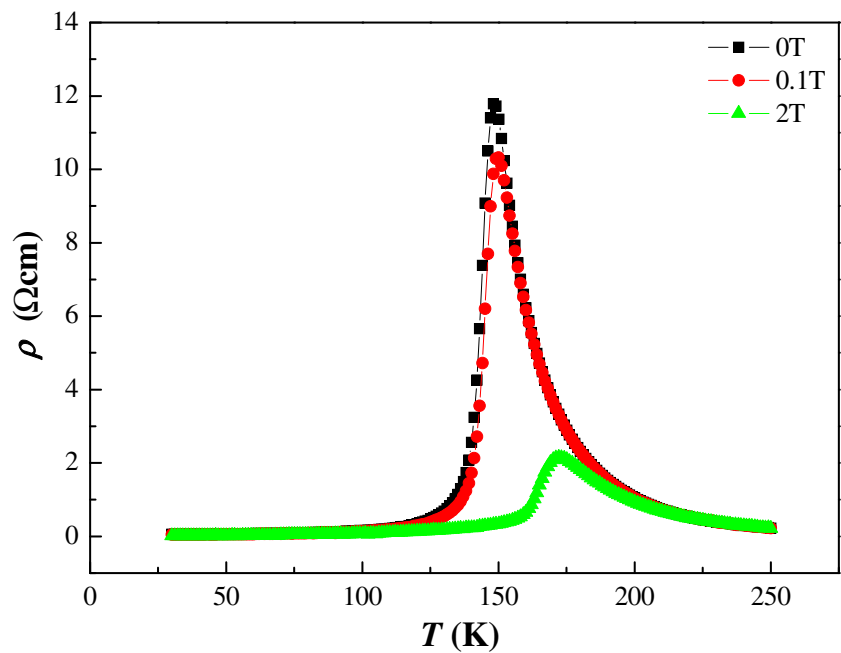


Fig. 3 Temperature-dependency of resistivity for the $\text{La}_{0.5}\text{Eu}_{0.15}\text{Ca}_{0.35}\text{MnO}_3$ sample under an applied magnetic field



All the samples have a single phase perovskite structure without other mixed phases.

Figure 2 shows the temperature-dependent magnetization for $\text{La}_{0.65-x}\text{Eu}_x\text{Ca}_{0.35}\text{MnO}_3$ samples in a magnetic field of 0.05 T, wherein the samples were calcinated at 1,473 K for 10 h. The Curie temperature T_C , defined as a maximum value in $|dM/dT|$, is found to be 267.9, 227.6, 187.9 and 140.8 K (the experimental errors is smaller than one thousandth) for $x=0, 0.05, 0.10, 0.15$, respectively. T_C decreases with increasing Eu content. The decrease of T_C with

increasing Eu content for samples can be attributed to the change in A-site ionic radius $\langle r_A \rangle$ as La atom (ionic radius of 0.102 nm) is replaced by smaller Eu atom (ionic radius of 0.095 nm). As Eu content increases, the average A-site ionic radius $\langle r_A \rangle$ decreases, leading to that both Mn-O bond length and Mn-O-Mn bond angle change. This causes a weakening exchange effect. Consequently, the Curie temperature decreases. The phenomenon has also been revealed in the LaCaMnO_3 based manganite materials doped with R (R=Nd, Gd, Dy, Tb, Ce) [13, 14].

Fig. 4 The resistivity as a function of temperature for $\text{La}_{0.65-x}\text{Eu}_x\text{Ca}_{0.35}\text{MnO}_3$ in the zero magnetic field

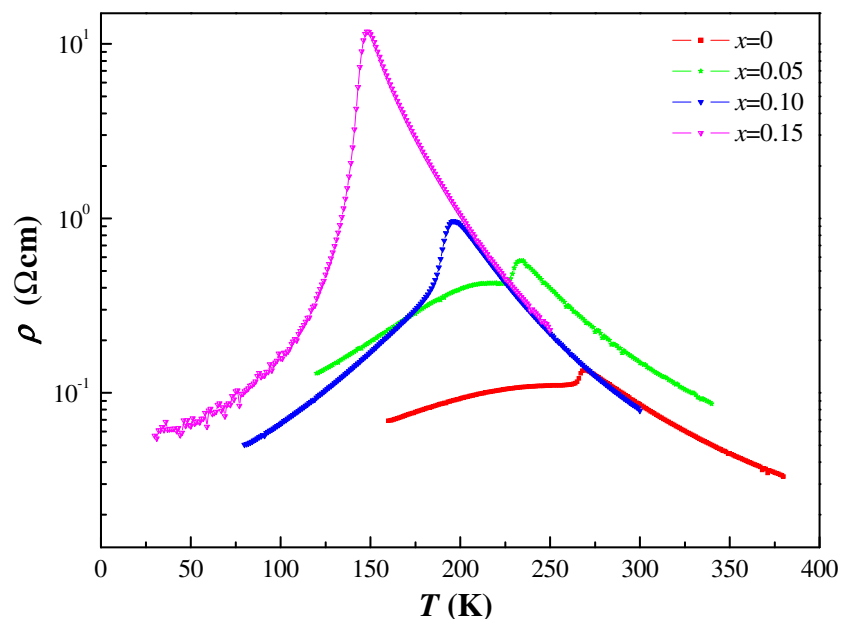
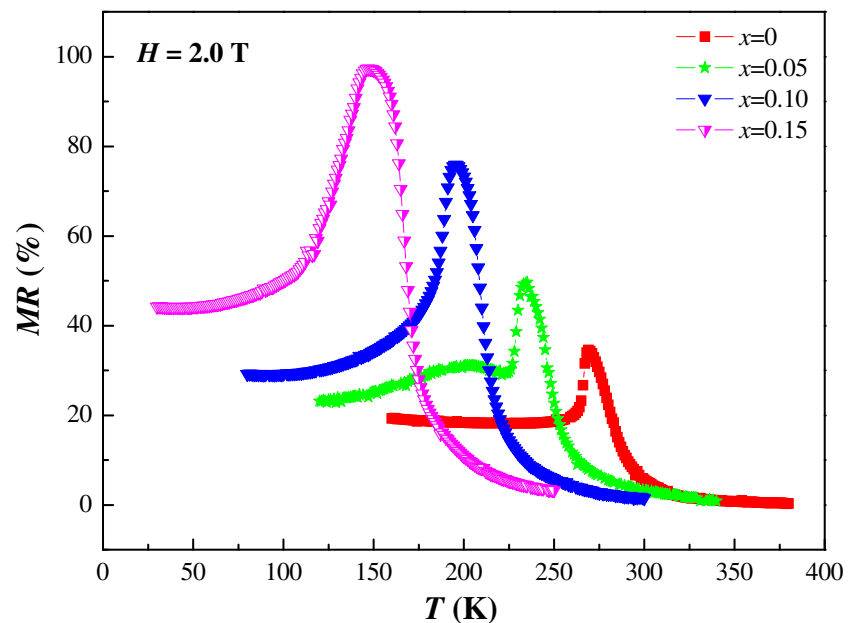


Fig. 5 The magnetoresistance as a function of temperature for $\text{La}_{0.65-x}\text{Eu}_x\text{Ca}_{0.35}\text{MnO}_3$



For Fig. 2, it also can be seen that the ferromagnetic ordering transition occurs in a narrow temperature range, which means a good homogeneity of the samples. The shape of the M - T curve remains almost unchanged although there is a big difference among the Eu content for the samples, and all curves exhibit an abrupt magnetization change near the transition temperature. T_C shifts towards lower temperature with increasing the Eu content, which can be attributed to the increase in the bending of Mn-O-Mn bond angle that causes an enhancement of carrier effective mass or a narrowing of the band width [15, 16]. The working temperature of the potential colossal magnetoresistance material can be changed easily by La-site doping, which is beneficial for the future application in various temperature ranges.

Figure 3 shows the temperature-dependency of resistivity for the $\text{La}_{0.5}\text{Eu}_{0.15}\text{Ca}_{0.35}\text{MnO}_3$ sample under an applied magnetic field. It can be seen from Fig. 3 that application of magnetic field $H=2$ T results in a large decrease of resistivity. The resistivity as a function of temperature for $\text{La}_{0.65-x}\text{Eu}_x\text{Ca}_{0.35}\text{MnO}_3$ in the zero magnetic field are shown in Fig. 4. The obtained values of T_p (metallic-semiconductor transition) are 269 K, 233 K, 196 K, and 148 K, corresponding to the sample with $x=0, 0.05, 0.10,$ and $0.15,$ respectively. As expected $\rho(T)$ reveal an overall increase of the maximum resistivity ρ_{\max} (peak value) and T_p decreases to lower temperature with increasing the Eu content. The sample shows the semiconducting-like and metallic behavior above and below T_p , respectively, similar to that of many other known CMR materials [17, 18].

Figure 5 exhibits the magnetoresistance [$MR = (\rho_0 - \rho_H)/\rho_0 \times 100$] for $\text{La}_{0.65-x}\text{Eu}_x\text{Ca}_{0.35}\text{MnO}_3$ as a function of temperature under an applied magnetic field of zero and

2.0 T. The magnetoresistivity increases with increasing Eu content in an applied magnetic field. The maximum magnetoresistivity for polycrystalline $\text{La}_{0.65-x}\text{Eu}_x\text{Ca}_{0.35}\text{MnO}_3$ ($x=0, 0.05, 0.10, 0.15$) samples have been found to be 34.6%, 49.7, 75.9% and 97.3%, respectively. The strength of the cation disorder increases with increasing x and causes a large increase of the magnetoresistance, similar reports have been seen in [19] and [20]. The changes in magneto-transport properties of $\text{La}_{0.65-x}\text{Eu}_x\text{Ca}_{0.35}\text{MnO}_3$ are attributed to the effective band width reduction with an increasing cation disorder. We observe that the amplitude of MR becomes larger and the peak in MR is somewhat broader with the increasing Eu content. The larger magnitude of MR is due to the fact that a strongly insulating phase is likely to be present, nonmagnetic disorder because of A-site doping should be considered aside from double exchange interaction and Jahn-Teller distortion [21]. It provides an effective way to obtain the high magnetoresistance in the polycrystalline manganites. The maximum magnetoresistivity of 97.3% is observed at 147 K for $\text{La}_{0.5}\text{Eu}_{0.15}\text{Ca}_{0.35}\text{MnO}_3$. The result is of practical importance, because it shows that the $\text{La}_{0.5}\text{Eu}_{0.15}\text{Ca}_{0.35}\text{MnO}_3$ sample is a promising candidate for applications such as magnetic sensors, magnetoresistive read heads, and magnetic recording materials.

4 Conclusions

Eu-doped perovskites $\text{La}_{0.65-x}\text{Eu}_x\text{Ca}_{0.35}\text{MnO}_3$ have been synthesized by sol-gel method using citric acid, which structures have been revealed to have a single perovskite structure. The Curie temperature T_C decreases with

increasing Eu content, while the maximum magnetoresistivity increases. As x increased from 0 to 0.15, the Curie temperature T_C for the samples decreased from 268 K to 141 K. We observe that the value of MR reaches its maximum about 97.3% for the $\text{La}_{0.65-x}\text{Eu}_x\text{Sr}_{0.35}\text{MnO}_3$ with $x=0.15$. Very large cation disorder leads to a large increase of the magnetoresistance, which are attributed to the effective band width reduction with x increasing.

References

1. S. Jin, T.H. Tiefel, M. McCormack, R.A. Fastnacht, R. Ramesh, L. H. Chen, *Science* **264**, 413 (1994)
2. M.S. Reis, V.S. Amaral, J.P. Araujo, P.B. Tavares, A.M. Gomes, I. S. Oliveira, *Phys. Rev. B* **71**, 144413 (2005)
3. H. Li, M. Feng, N. Li, X. Zhang, W. Zheng, *Mater. Chem. Phys.* **107**, 377 (2008)
4. M. Feng, H.B. Li, M. Liu, N. Li, W.T. Zheng, *Ceram. Int.* **35**, 345 (2009)
5. P. Dey, T.K. Nath, A. Taraphder, *Appl. Phys. Lett.* **91**, 012511 (2007)
6. K.F. Wang, Y. Wang, L.F. Wang, S. Dong, D. Li, Z.D. Zhang, H. Yu, Q.C. Li, J.M. Liu, *Phys. Rev. B* **73**, 134411 (2006)
7. C. Zener, *Phys. Rev. B* **82**, 403 (1951)
8. A.J. Millis, P.B. Littlewood, B.I. Shraiman, *Phys. Rev. Lett.* **74**, 5144 (1995)
9. A.J. Millis, B.I. Shraiman, R. Mueller, *Phys. Rev. Lett.* **77**, 175 (1996)
10. E. Dagotto, T. Hotta, A. Moreo, *Phys. Rep.* **344**, 1 (2001)
11. A.K. Kundu, M.M. Seikh, K. Ramesha, C.N.R. Rao, *J. Phys. Condens. Matter* **17**, 4171 (2005)
12. V.B. Shenoy, C.N.R. Rao, *Philos. Trans. R. Soc. Lond. A* **366**, 63 (2008)
13. Z.M. Wang, G. Ni, Q.Y. Xu, H. Sang, Y.W. Du, *J. Appl. Phys.* **90**, 5689 (2001)
14. H.Y. Chen, C. Lin, D.S. Dai, *J. Magn. Magn. Mater.* **257**, 254 (2003)
15. J. Fontcuberta, B. Martinez, A. Seffar, S. Pinol, J.L. Garcia-Munoz, X. Obradors, *Phys. Rev. Lett.* **76**, 1122 (1996)
16. S.L. Huang, X.G. Cui, D.H. Wang, Z.D. Han, Y.W. Du, *J. Alloys Compd.* **398**, 184 (2005)
17. E. Tka, K. Cherif, J. Dhahri, E. Dhahri, *J. Alloys Compd.* **509**, 8047 (2011)
18. M.S. Kim, J.B. Yang, Q. Cai, X.D. Zhou, W.J. James, W.B. Yelon, P.E. Parris, D. Buddhikot, S.K. Malik, *Phys. Rev. B* **71**, 014433 (2005)
19. M. Egilmez, I. Isaac, D.D. Lawrie, K.H. Chow, J. Jung, *J. Mater. Chem.* **18**, 5796 (2008)
20. L.M. Rodriguez-Martinez, J. Paul Attfield, *Phys. Rev. B* **63**, 024424 (2000)
21. Q.Y. Xie, B. Lv, P.F. Wang, P. Song, X.S. Wu, *Mater. Chem. Phys.* **114**, 636 (2009)