Dimensional and Chemical Control of Colossal Magnetoresistance in New Manganites

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The effects of structural, electrical and magnetic properties with the isovalent chemical substitution of Ca^{2+} into the Sr^{2+} sites in new series of two-dimensional $\text{La}_{1.2}(\text{Sr}_{1.8-x}\text{Ca}_x)\text{Mn}_2\text{O}_7$ compounds ($x = 0 \sim 0.8$) and three-dimensional $\text{La}_{0.6}(\text{Sr}_{0.4-x}\text{Ca}_x)\text{MnO}_3$ compounds ($x = 0 \sim 0.4$) are investigated. The Curie temperatures (T_C) decreased from 135 K to 102 K and 370 K to 270 K for $x = 0$ to 0.4 in $\text{La}_{1.2}(\text{Sr}_{1.8-x}\text{Ca}_x)\text{Mn}_2\text{O}_7$ and $\text{La}_{0.6}(\text{Sr}_{0.4-x}\text{Ca}_x)\text{MnO}_3$, respectively. The antiferromagnetic behavior with Néel temperature around 30 K was found in the $x = 0.8$ sample in $\text{La}_{1.2}(\text{Sr}_{1.8-x}\text{Ca}_x)\text{Mn}_2\text{O}_7$. The composition induced structural variation has been found in $\text{La}_{0.6}(\text{Sr}_{0.4-x}\text{Ca}_x)\text{MnO}_3$. All the results demonstrate that the dimensionality and chemical size play an important role in controlling the colossal magnetoresistance in manganites.

KEYWORDS: Colossal Magnetoresistance; $\text{La}_{1.2}(\text{Sr}_{1.8-x}\text{Ca}_x)\text{Mn}_2\text{O}_7$; $\text{La}_{0.6}(\text{Sr}_{0.4-x}\text{Ca}_x)\text{MnO}_3$

1. Introduction

Recently, there has been revived interest in mixed valence manganese perovskites. The Ruddlesden-Popper $R_{n+1}\text{Mn}_n\text{O}_{3n+1}$ system (R = rare earth) exhibits a colossal magnetoresistance (CMR) in a relatively small temperature range around the Curie temperature (T_C)¹⁾. A suitable substitution of A^{2+} ions for R^{3+} ions results in $\text{Mn}^{3+}/\text{Mn}^{4+}$ mixed valency, and hence the strong coupling between the magnetic ordering and the electrical conductivity demonstrates a strong relationship between the electrical resistivity and the spin alignment which has been explained by the double-exchange mechanism^{2,3)}.

In the $n = \infty$ compounds, the gradual replacement of Ca^{2+} by Sr^{2+} in $\text{La}_{0.75}(\text{Ca}_{0.25-x}\text{Sr}_x)\text{MnO}_3$ results in an increase in T_C from ~ 225 K of $x = 0$ to ~ 340 K of $x = 0.25$ ⁴⁾. The phase transformation from orthorhombic to rhombohedral by increasing the Sr content has been observed in the $\text{La}_{0.75}(\text{Ca}_{0.25-x}\text{Sr}_x)\text{MnO}_3$ system. However, a detailed study on the phase transformation is needed.

The compounds with the $n = 2$ member exhibited a conducting ferromagnet with a MR [$\rho(0)/\rho(H)$] ratio higher than those of the $n = 3$ and $n = \infty$ members. This implies that a lower dimensionality is more favorable for CMR. Many interesting studies have been carried out on the manganites with $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ compound, which is a conducting ferromagnet with a T_C of 130 K and with a high MR value⁵⁾. On the other hand, the manganites $\text{La}_{n-nx}\text{Ca}_{1+nx}\text{Mn}_n\text{O}_{3n+1}$ have been performed by Asano *et al.*⁶⁾. In the $\text{La}_{1.2}\text{Ca}_{1.8}\text{Mn}_2\text{O}_7$ layered compound, they have observed a ferromagnetic transition at $T_C = 240$ K and a higher MR ratio than those of $n = 3$ and $n = \infty$ materials. Therefore, the solid solution properties between Sr^{2+} and Ca^{2+} resulting in $\text{La}_{1.2}(\text{Sr}_{1.8-x}\text{Ca}_x)\text{Mn}_2\text{O}_7$ should be of interest.

In this paper, we demonstrate the structural, electrical and magnetic properties with the isovalent chemical substitution of Ca^{2+} into the Sr^{2+} sites in a series of three-dimensional $\text{La}_{0.6}(\text{Sr}_{0.4-x}\text{Ca}_x)\text{MnO}_3$ compounds ($x = 0 \sim 0.4$) and two-dimensional $\text{La}_{1.2}(\text{Sr}_{1.8-x}\text{Ca}_x)\text{Mn}_2\text{O}_7$ compounds ($x = 0 \sim 0.8$).

2. Experimental

High purity powders of La_2O_3 , SrCO_3 , CaCO_3 and MnO_2 were

weighted in appropriate proportions to obtain the nominal compositions of $\text{La}_{0.6}(\text{Sr}_{0.4-x}\text{Ca}_x)\text{MnO}_3$ ($x = 0 \sim 0.4$) and $\text{La}_{1.2}(\text{Sr}_{1.8-x}\text{Ca}_x)\text{Mn}_2\text{O}_7$ ($0 \leq x \leq 0.8$) were prepared by solid state reaction. The mixtures were calcined in air for 24 h at 900 °C and 1200 °C, respectively. Then, the samples were sintered in air at 1400 $\sim$ 1500 °C for 24 h with intermediate grinding after each heating step^{7,8)}. X-ray powder diffraction (XRD) of samples was carried out with a SCINTAG (X1) diffractometer (Cu K α radiation, $\lambda = 1.5406$ Å). Magnetization data were taken from a superconducting quantum interference device (SQUID) magnetometer (Quantum Design).

3. Results and discussion

The powder XRD patterns of $\text{La}_{0.6}(\text{Sr}_{0.4-x}\text{Ca}_x)\text{MnO}_3$ ($x = 0 \sim 0.4$) are shown in Fig. 1. The series samples are single phase. For the samples with $x = 0$ and 0.4, all the peaks in each pattern can be indexed with a rhombohedral unit cell (space group: $R\bar{3}c$) and orthorhombic (space group: $Pbnm$), respectively. As x increases to $x = 0.3$, some reflection planes merge together, which indicates that in the $x < 0.3$ region the structure is orthorhombic and in the $x \geq 0.3$ region the structure becomes orthorhombic. An increase in the Ca content leads to an increase in the distortion of the MnO_6 octahedra.

In Fig. 2 we show the XRD patterns of $\text{La}_{1.2}(\text{Sr}_{1.8-x}\text{Ca}_x)\text{Mn}_2\text{O}_7$ ($x = 0 \sim 0.8$), which are all single phase. The samples can be indexed with tetragonal unit cell (space group: $I4/mmm$). In the inset of Fig. 2, we show the ideal crystal structure of $(\text{La}, \text{Sr}, \text{Ca})_3\text{Mn}_2\text{O}_7$ which consists of double perovskite layers, and each layer is made up of a two dimensional network of MnO_6 octahedra. Along the c -axis, the bilayers are separated from one another by $(\text{La}, \text{Sr}, \text{Ca})\text{-O}$ layers. There are two $(\text{La}, \text{Sr}, \text{Ca})$ sites in this crystal structure: a twelve-coordinate site between the perovskite slabs and a nine-coordinate site between rock-salt slabs.

The temperature dependence of magnetization in a magnetic field of 0.1 T of $\text{La}_{0.6}(\text{Sr}_{0.4-x}\text{Ca}_x)\text{MnO}_3$ ($x = 0 \sim 0.4$) and $\text{La}_{1.2}(\text{Sr}_{1.8-x}\text{Ca}_x)\text{Mn}_2\text{O}_7$ ($x = 0 \sim 0.8$) were shown in Figs. 3(a) and 3(b), respectively. A systematic analysis of the paramagnetic to ferromagnetic transition temperature T_C versus the concentration of Ca^{2+} for $\text{La}_{0.6}(\text{Sr}_{0.4-x}\text{Ca}_x)\text{MnO}_3$ indicates that the T_C 's decreases as the Ca content increases [see Fig. 3(a)]^{7,8)}. In Fig. 3(b), it indicates a sharp paramagnetic to ferromagnetic transition in $\text{La}_{1.2}(\text{Sr}_{1.8-x}\text{Ca}_x)\text{Mn}_2\text{O}_7$ ($x = 0 \sim 0.8$) within the T_C

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Fig. 1. XRD patterns of $\text{La}_{0.6}(\text{Sr}_{0.4-x}\text{Ca}_x)\text{MnO}_3$. The corresponding rhombohedral and orthorhombic structures are shown in the inset of Fig. 1.

Fig. 2. XRD patterns of $\text{La}_{1.2}(\text{Sr}_{1.8-x}\text{Ca}_x)\text{Mn}_2\text{O}_7$. The inset shows the crystal structure of $\text{La}_{1.2}(\text{Sr}_{1.8-x}\text{Ca}_x)\text{Mn}_2\text{O}_7$.

temperature range of 135 ~ 71 K. The antiferromagnetic behavior with Néel temperature around 30 K was found in the $x = 0.8$ sample in $\text{La}_{1.2}(\text{Sr}_{1.8-x}\text{Ca}_x)\text{Mn}_2\text{O}_7$. In Fig. 4, a decrease in T_C from > 350 K for $x = 0$ to 270 K for $x = 0.4$ in $\text{La}_{0.6}(\text{Sr}_{0.4-x}\text{Ca}_x)\text{MnO}_3$ and 135 K for $x = 0$ to 71 K for $x = 0.8$ in $\text{La}_{1.2}(\text{Sr}_{1.8-x}\text{Ca}_x)\text{Mn}_2\text{O}_7$ were observed. It has been shown that T_C is very sensitive to chemical pressure (i.e., structural distortions induced by changing the average radius of the cations).

4. Conclusion

An investigation of the new series of three-dimensional $\text{La}_{0.6}(\text{Sr}_{0.4-x}\text{Ca}_x)\text{MnO}_3$ ($x = 0 \sim 0.4$) and two-dimensional $\text{La}_{1.2}(\text{Sr}_{1.8-x}\text{Ca}_x)\text{Mn}_2\text{O}_7$ ($x = 0 \sim 0.8$) manganites has allowed us to establish a relationship between the ionic size and Curie temperature. This study has demonstrated that the size of the interpolated cation by tuning the concentration between Ca^{2+} and Sr^{2+} plays a role in the controlling the magnetotransport properties of the colossal magnetoresistance $\text{La}_{n-mx}(\text{Sr,Ca})_{1+mx}\text{Mn}_n\text{O}_{3n+1}$ materials.

Fig. 3. Temperature dependence of magnetization at a magnetic field of 0.1 T for (a) $\text{La}_{0.6}(\text{Sr}_{0.4-x}\text{Ca}_x)\text{MnO}_3$ ($x = 0 \sim 0.4$) and (b) $\text{La}_{1.2}(\text{Sr}_{1.8-x}\text{Ca}_x)\text{Mn}_2\text{O}_7$ ($x = 0 \sim 0.8$).

Fig. 4. The transition temperature T_C as a function of x of (a) $\text{La}_{0.6}(\text{Sr}_{0.4-x}\text{Ca}_x)\text{MnO}_3$ and (b) $\text{La}_{1.2}(\text{Sr}_{1.8-x}\text{Ca}_x)\text{Mn}_2\text{O}_7$ compounds.

Acknowledgments

This research is financially supported by National Science Council of the Republic of China under Grant numbers NSC 89-2113-M-002-004 and NSC 89-2113-M-002-030

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