Chemical pressure controlled colossal magnetoresistance effects in
\(La_{0.6}(Sr_{0.4-x}Ca_x)MnO_3\)

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Abstract

The effects of structural and paramagnetic to ferromagnetic transition with the isovalent chemical substitution of smaller Ca\(^{2+}\) into the bigger Sr\(^{2+}\) sites in \(La_{0.6}(Sr_{0.4-x}Ca_x)MnO_3\) (0≤x≤0.4) are investigated. With increasing \(x\), a change from the rhombohedral cell (space group: \(R-3c\)) to an orthorhombic cell (space group: \(Pbnm\)) is observed. For \(x\)\(>0.3\), the structural transformation leads to an increase of the Mn–O(1) bond length and the bending of the Mn–O–Mn bond along the \(c\)-axis which corresponds to the Jahn–Teller distortion of the distorted MnO\(_6\) octahedra in the orthorhombic cell. Such effects give rise to a decrease in \(T_C\) (the temperature of the paramagnetic to ferromagnetic transition) with increasing Ca content.

Keywords: A. oxides; B. chemical synthesis; D. crystal structure; D. magnetic properties

1. Introduction

Rare-earth manganites have been the subject of considerable investigation since the discovery of their colossal magnetoresistance (CMR) properties [1–3]. Extremely high magnetoresistance ratios of several orders of magnitude have been found by applying a magnetic field of several Tesla. In all the perovskite-type rare-earth manganites which exhibit CMR effects, manganese is present in both the Mn\(^{3+}\) and Mn\(^{4+}\) valence states. Appearance of the ferromagnetic metallic state in the doped \(La_{1-x}Sr_xMnO_3\) system has been qualitatively explained by the double-exchange interactions resulting from the motion of an electron between Mn\(^{3+}\) (\(t_2g\)\(^e_g\)) and Mn\(^{4+}\) (\(t_2g\)\(^e_g\)) with strong on-site Hund’s coupling [4,5].

An increase in the paramagnetic to ferromagnetic transition temperature (\(T_C\)) with \(x\) and reaching a maximum (~370 K) around \(x=0.4\) was observed in \(La_{1-x}Sr_xMnO_3\) [6]. Moreover, the crystal structure of \(La_{1-x}Sr_xMnO_3\) at room temperature changes from orthorhombic (\(Pbnm\), \(Z=4\); \(x<0.175\)) to rhombohedral (\(R-3c\), \(Z=2\); \(x\geq0.175\)) [6]. With the chemical substitution of Sr\(^{2+}\) for La\(^{3+}\) in \(La_{1-x}Sr_xMnO_3\), the Mn valence is increased with increasing Sr content. The largest influence on the structure is the overall amount of Mn\(^{4+}\) as pointed out by van Roosmalen et al. [7]. With increasing Mn\(^{4+}\) content the unit cell volume decreases and the symmetry changes. With a low Mn\(^{4+}\) content an orthorhombic symmetry with a rather large deviation from the ideal perovskite structure has been observed which is due to ordering the Jahn–Teller distorted MnO\(_6\) octahedra. The ordering is destroyed by an increase in the Mn\(^{4+}\) content, resulting in a rhombohedral symmetry for a high Mn\(^{4+}\) content. Meanwhile, the \(T_C\) is below room temperature in Ca-doped LaMnO\(_3\) (e.g. \(La_{1-x}Ca_xMnO_3\)) but above room temperature in Sr-doped LaMnO\(_3\) [8]. The gradual replacement of Ca by Sr in \(La_{0.75}(Ca_{0.25-x}Sr_x)MnO_3\) results in an increase in \(T_C\) from ~225 K of \(x=0\) to 340 K of \(x=0.25\) [9]. Moreover, the phase transformation from orthorhombic to rhombohedral has been observed in the \(La_{0.75}(Ca_{0.25-x}Sr_x)MnO_3\) system with fixed Mn valence which is difficult to explain as the effect of increasing the Mn valence [9].

In this paper, we analyze the structural and magnetic properties of the series \(La_{0.6}(Sr_{0.4-x}Ca_x)MnO_3\) which leads us to explore the influence of the phase transformation on \(T_C\).
2. Experimental

High purity powders of La$_2$O$_3$, SrCO$_3$, CaCO$_3$ and MnO$_2$ were weighed in appropriate proportions to obtain the nominal compositions of La$_{0.6}$(Sr$_{0.4-x}$Ca$_x$)MnO$_3$ with 0≤x≤0.4. The mixtures were calcined in air at 900°C for 24 h and then sintered in air at 1400°C for 24 h, 1500°C for 24 h and 1500°C for 24 h with an intermediate grinding after each heating step.

Powder X-ray diffraction measurements were carried out with a SCINTAG (X1) diffractometer (Cu Kα radiation, λ=1.5406 Å) at 40 kV and 30 mA. Data for the Rietveld refinement were collected in the 2θ range 20~120° with a step size of 0.02° and a count time of 10 s per step. The program GSAS [10] was used for the Rietveld refinement in order to obtain the information of crystal structures of La$_{0.6}$(Sr$_{0.4-x}$Ca$_x$)MnO$_3$. Electron diffraction (ED) and high resolution transmission electron microscopy (HRTEM) were carried out using a JEOL 4000EX electron microscope operating at 400 kV. The samples for microscopy were dispersed in alcohol before being transferred to the carbon coated copper grids. A Philips XL30 microscope with energy dispersive spectroscopy (EDS) was used to determine the chemical composition. Scanning electron micrographs (SEM), recorded on the same unit, were used to observe the surface morphology of the samples. Magnetization data were collected using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design).

Fig. 1. XRD patterns of the series La$_{0.6}$(Sr$_{0.4-x}$Ca$_x$)MnO$_3$.

Fig. 2. Rietveld refinement plot of La$_{0.6}$(Sr$_{0.4-x}$Ca$_x$)MnO$_3$ with x=0 at 300 K. The experimental data points are shown as plus (+) signs. The solid line is the calculated profile. The tick marks below the profile indicate the position of allowed Bragg reflections. The difference plot (observed minus calculated) is plotted at the bottom.
3. Results and discussion

The powder XRD spectra of the La$_{0.6}$(Sr$_{0.4-x}$Ca$_x$)MnO$_3$ (0$\leq x \leq$0.4) compositions are shown in Fig. 1. All the compositions of the series are of single phase. For the samples with $x=0$ and 0.4, all the peaks in each pattern can be indexed on the basis of a rhombohedral unit cell (space-group: $R-3c$) and an orthorhombic unit cell (space group: $Pbnm$), respectively. As $x$ increases to 0.3, some reflection planes merge together, which indicates that in...
the region $x < 0.3$ the structure is rhombohedral and for $x \geq 0.3$ the structure becomes orthorhombic. Typical examples of the observed and calculated diffraction profiles of the samples with $x = 0.1$ and $x = 0.4$ are shown in Figs. 2 and 3, respectively. The structural parameters of the La$_{0.6}$(Sr$_{0.4-x}$Ca$_{x}$)MnO$_3$ compounds at room temperature for two space-group symmetries are listed in Table 1. The ideal crystal structures of La$_{0.6}$(Sr$_{0.4-x}$Ca$_{x}$)MnO$_3$ with rhombohedral cell ($x < 0.3$) and orthorhombic cell ($x \geq 0.3$) are shown in Figs. 4 and 5. The samples of La$_{0.6}$(Sr$_{0.4-x}$Ca$_{x}$)MnO$_3$ with $x < 0.3$ have the crystallographic space-group symmetry of R-3c which possesses undistorted MnO$_6$ octahedra. However, the samples with $x \geq 0.3$ exhibit the Pbnm space group which indicates a distortion in the MnO$_6$ octahedra. Therefore, an increase in the Ca content in La$_{0.6}$(Sr$_{0.4-x}$Ca$_{x}$)MnO$_3$ will lead to an increase in the distortion of the MnO$_6$ octahedra. The basic perovskite lattice constants ($a$, $b$, and $c$) decrease as the Ca content ($x$) increases (as shown in Fig. 6). This is simply due to a manifestation of the smaller size of the substituting Ca$^{2+}$ ion [1.18 Å for C.N. (coordination number) = 9] as compared to the bigger Sr$^{2+}$ ions (1.31 Å for C.N. = 9) [11]. In Fig. 7, the Mn–O bond distances are shown. An increase in the Mn–O(1) bond distance (along the $c$-direction of MnO$_6$ octahedra) in the $x \geq 0.3$ samples as compared to the Mn–O distance in the $x < 0.3$ samples has been observed. However, the average Mn–O(2) bond distance (along the $a,b$-direction of MnO$_6$ octahedra) is nearly constant as compared to the compositions with $x < 0.3$. The results are consistent with the distorted MnO$_6$ octahedral structure exhibited by the samples with $x \geq 0.3$.

The combination of electron diffraction and HRTEM allows us to propose a structural model which is applicable for the formula La$_{0.6}$(Sr$_{0.4-x}$Ca$_{x}$)MnO$_3$. In Fig. 8, we show the HRTEM lattice images recorded along the (a) [001] and (b) [010] zone-axis directions of La$_{0.6}$(Sr$_{0.4-x}$Ca$_{x}$)MnO$_3$ with $x = 0.1$. The corresponding electron diffraction patterns are shown in the insets of Fig.

### Table 1

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<th>Position</th>
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<td>1.13(4)</td>
<td>1.58(3)</td>
<td>1.89(4)</td>
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<td>157.6(5)°</td>
<td>153(2)°</td>
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</table>

Table 1

Refined fractional atomic positions, unit cell and reliability factors (%) at room temperature of (a) La$_{0.6}$(Sr$_{0.4-x}$Ca$_{x}$)MnO$_3$ ($x = 0, 0.1, 0.2$) with the R-3c space-group symmetry and atomic positions RE (La, Sr, and Ca atoms): (0, 0, 0.25), Mn: (0, 0, 0), O: (x, 0, 0.25), (b) La$_{0.6}$(Sr$_{0.4-x}$Ca$_{x}$)MnO$_3$ ($x = 0.3, 0.4$) with the Pbnm space-group symmetry, and atomic positions RE: (x, y, 0.25), Mn: (0.5, 0, 0), O(1): (x, y, 0.25), O(2): (x, y, z).
Fig. 5. The ideal crystal structure of La$_{0.6}$(Sr$_{0.4}$,Ca$_{0.6}$)MnO$_3$ ($x$=0.3) with orthorhombic cell (space-group: Pbnm). The unit cell is shown with a solid line. Part of the MnO$_6$ octahedra is shaded.

Fig. 6. Basic perovskite cell parameters ($a$, and $b$) as a function of $x$ in La$_{0.6}$(Sr$_{0.4}$,Ca$_{0.6}$)MnO$_3$.

Fig. 7. Mn–O Bond distances as a function of $x$ in La$_{0.6}$(Sr$_{0.4}$,Ca$_{0.6}$)MnO$_3$. 
The cell symmetry perovskite was identified by the observation of the reflection with the limiting conditions on $hkl$: $-h + k + l = 3n$ with the $R$ centering of the unit cell, which is consistent with the results of the XRD refinement as shown in Fig. 2. The lattice images along [001] and [010] of the orthorhombic cell are shown in Fig. 8(a) and (b), respectively. In Fig. 9, we show the HRTEM lattice images taken along the (a) [001] and (b) [010] zone-axis directions of the $x=0.3$ member. The corresponding electron diffraction patterns are shown in the insets of Fig. 9(a) and (b). The cell symmetry perovskite was identified by the observation of the reflection with the $P$ centering of the unit cell which is consistent with the results of the XRD refinement as shown in Fig. 3.

The chemical compositions of the samples of the series La$_{0.6-x}$(Sr$_{0.4-x}$Ca$_x$)MnO$_3$ were measured by EDS. The fractions of the measured compositions are consistent with the nominal compositions as shown in Fig. 10(a) and (b). Moreover, a linear relationship between fraction and composition parameter $x$ was found in Ca and Sr [as shown in Fig. 10(b)] which indicates the complete solid solution between Sr and Ca in La$_{0.6-x}$(Sr$_{0.4-x}$Ca$_x$)MnO$_3$.

The morphology and particle size of the samples as observed with a scanning electron microscope (SEM) are
shown in Fig. 11. An increase in the particle size with increasing Ca content (from ~2 μm of x = 0 to ~5 μm of x = 0.4) was observed. This seems to indicate that the incorporation of Ca into the Sr sites can help the grain growth during the sintering process.

In Fig. 12, we show the temperature dependence of magnetization in an applied field of 0.1 T. In the temperature range 250–350 K, there is a paramagnetic to ferromagnetic transition in the samples. A decrease in $T_C$'s from $>350$ K of $x = 0$ to 270 K of $x = 0.4$ was observed. This suggests that the smaller Ca$^{2+}$ ions substituting in the larger Sr$^{2+}$ sites leads to a decrease in $T_C$'s. Based on the model of double exchange, a lower $T_C$ corresponds to a poor overlap between Mn 3$d$ and O 2$p$ orbitals resulting in a reduced bandwidth ($W$) [12–14]. The average Mn–O(2) bond distance in the orthorhombic cell ($x = 0.3$) and the Mn–O distance in the rhombohedral cell ($x < 0.3$) is found to be nearly the same, as can be seen from Fig. 7. This implies the same size of overlap between Mn3$d$ and O2$p$ within the $a,b$-plane. An increase in the Mn–O(1) bond lengths in the apical position ($c$-axis) of the orthorhombic cell as compared to that of Mn–O in the rhombohedral may play an important role in decreasing in the overlap between Mn 3$d_{z^2}$ and O 2$p_z$, which results in a decrease in $T_C$'s with increasing Ca content. Therefore, the structural transformation from rhombohedral to orthorhombic by chemical substitution of isovalent Ca$^{2+}$ for Sr$^{2+}$ gives rise to a decrease in $T_C$ due to the poor hybridization between Mn 3$d_{z^2}$ and O 2$p_z$ in the orthorhombic cell. The results are consistent with the compositions with $x \geq 0.3$ exhibiting a distorted MnO$_6$ octahedral structure which indicates the Jahn–Teller distortion along the $c$-axis occurring in the compounds. Such an effect will lead to a decrease in the spatial overlap of the Mn 3$d_{z^2}$ and O 2$p_z$ orbitals.

It has been shown that the $T_C$ is very sensitive to chemical pressure (i.e. structural distortions induced by changing the average radius of the cations) [15–18]. In Fig. 13, we show the $T_C$'s of (Ln,A)MnO$_3$ as a function of the average radius (assuming nine-fold coordination) of the Ln/A (Ln = La or Y; A = Ca, Sr or Ba) cations, $(r_x) = [(1 – x) r_{Ln}$ + $x r_A$, which includes our series La$_{0.4}$(Sr$_{0.4}$,Ca$_{0.6}$)MnO$_3$ and earlier results [15–18]. The following empirical formula has been used to describe the variation of bandwidth ($W$) in the double exchange mechanism of manganites: [12]

$$W \propto \cos \omega / d_{Mn-O}^{3.5}$$

where $\omega$ is the tilt angle in the plane of the bond [$\omega = 180° – \alpha$; $\alpha$ is the angle of Mn–O–Mn] and $d_{Mn-O}$ is the Mn–O bond length. Increasing $x$ in La$_{0.4}$(Sr$_{0.4}$,Ca$_{0.6}$)MnO$_3$ leads to the decrease of the Mn–O–Mn bond angle and the increase of Mn–O(1) bond length along the $c$-axis (as shown in Table 1), both contributing to the decrease of $W$ which results in the decrease in $T_C$.

In conclusion, this study has demonstrated that the size of the interpolated cation, which can be varied by tuning the concentration between Ca$^{2+}$ and Sr$^{2+}$ plays an important role in controlling the crystal structure and $T_C$'s in the series La$_{0.4}$(Sr$_{0.4}$,Ca$_{0.6}$)MnO$_3$.  

Acknowledgements

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Fig. 11. SEM photographs of La$_{0.6}$(Sr$_{0.4-x}$Ca$_x$)MnO$_3$ ($0 \leq x \leq 0.4$).
Fig. 12. Temperature dependence of magnetization at a magnetic field of 0.1 T of La$_{0.6}$(Sr$_{0.4}$Ca$_{0.4}$)$_{0.6}$MnO$_3$ ($0 \leq x \leq 0.4$).

Fig. 13. $T_c$'s of (Ln, Al)MnO as a function of the average radius $<r_e>$ (assuming nine-fold coordination) of the Ln/A (Ln=La or Y; A=Ca, Sr or Ba) cations.

References
