Chemical pressure control of Curie temperature in La$_{0.6}$(Ba$_{0.4-x}$Ca$_x$)MnO$_3$

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Abstract

The effects on structural and paramagnetic to ferromagnetic transitions by isovalent chemical substitution of smaller Ca$^{2+}$ into the bigger Ba$^{2+}$ sites in La$_{0.6}$(Ba$_{0.4}$Ca$_{1-x}$)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 in the Mn-O(1) bond length along the c-axis which corresponds to the Jahn-Teller distortion of the distorted MnO$_6$ octahedra in the orthorhombic cell. This effect gives rise to a decrease in $T_C$ (the temperature of the paramagnetic to ferromagnetic transition) with increasing Ca content. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Rare-earth manganites have been the subject of considerable investigation since the discovery of their colossal magnetoresistance (CMR) properties [1]. The CMR materials exhibit a metal–insulator transition by isovalent chemical substitution of smaller Ca$^{2+}$ into the bigger Ba$^{2+}$ sites in La$_{0.6}$(Ba$_{0.4}$Ca$_{1-x}$)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 in the Mn-O(1) bond length along the c-axis which corresponds to the Jahn-Teller distortion of the distorted MnO$_6$ octahedra in the orthorhombic cell. This effect gives rise to a decrease in $T_C$ (the temperature of the paramagnetic to ferromagnetic transition) with increasing Ca content. © 2002 Elsevier Science B.V. All rights reserved.

1. Experimental

High purity powders of La$_2$O$_3$, BaCO$_3$, CaCO$_3$ and MnO$_2$ were weighed in appropriate proportions to obtain the nominal compositions of La$_{0.6}$(Ba$_{0.4}$Ca$_{1-x}$)MnO$_3$ with...
The ideal crystal structures of La$_{0}$ (from 0.9613 for $x = 0.0$ to 0.9203 for $x = 0.4$) with the addition of Ca, increasing the strain in La$_{0}$ (Ba$_{0.1-x}$Ca$_x$)MnO$_3$. The chemical compositions of the samples of the series 3. Results and discussion

The powder XRD patterns of the La$_{0}$ (Ba$_{0.1-x}$Ca$_x$)MnO$_3$ (0 ≤ $x$ ≤ 0.4) compositions are shown in Fig. 1. All the compositions of the series are of single phase. For the samples with $x = 0.0$–0.4, all the peaks in the respective pattern can be indexed on the basis of a rhombohedral unit cell (space group R-3c) with $a = 0.2$ and an orthorhombic cell (space group Pbnm) with $a = 0.3$–0.4. The refinement result of the structural parameters in the La$_{0}$ (Ba$_{0.1-x}$Ca$_x$)MnO$_3$ compounds at room temperature for the two space group symmetries are listed in Table 1. The ideal crystal structures of La$_{0}$ (Ba$_{0.1-x}$Ca$_x$)MnO$_3$ with rhombohedral cell ($x < 0.3$) and orthorhombic cell ($x ≳ 0.3$) are shown in Fig. 2. The samples of La$_{0}$ (Ba$_{0.1-x}$Ca$_x$)MnO$_3$ with $x < 0.3$ have the crystallographic space group symmetry of R-3c which possesses undistorted MnO$_6$ octahedra. The cell symmetry perovskite was identified by the observation of the reflection with the limiting conditions on $hkl$: $-h + k + l = 3n$ with $n = 0$ for the XRD as shown in Fig. 1. However, the samples with $x ≥ 0.3$ exhibit the Pbnm space group which indicates a distortion in the MnO$_6$ octahedra. Therefore, an increase in the Ca content in La$_{0}$ (Ba$_{0.1-x}$Ca$_x$)MnO$_3$ will lead to an increase in the distortion of the MnO$_6$ octahedra. The basic perovskite lattice constants ($a_0$ and $c_0$) decrease as the Ca content increases (as shown in Fig. 1). 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 Ba$^{2+}$ ion (1.47 Å for C.N. = 9). The dependence of the cell volume and Mn–O bond distances on the effective ionic radius of the A-site ($r_A$) is shown in Table 1. An increase in the Mn–O (1) bond distance (along the c-direction of MnO$_6$ octahedra) in the $x ≳ 0.3$ 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 $a$ and $b$ directions 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 $x > 0.3$. Moreover, decrease in the tolerance factor ($t_{factor}$) with increasing Ca doping was found (as shown in Table 1). The tolerance factor is defined as $(r_A + r_B)/2(r_A + r_B)$, where $r_A$, $r_B$, and $r_B$ are the ionic radii of the A, B cations and oxygen, respectively, in the perovskite ABO$_3$ structure. The $t_{factor} = 1$ for a compound with an ideal perovskite structure. If $t_{factor} < 1$, the strain within the compound is increased. Therefore, the $t_{factor}$ decreases (from 0.9613 for $x = 0$ to 0.9203 for $x = 0.4$) with the addition of Ca, increasing the strain in La$_{0}$ (Ba$_{0.1-x}$Ca$_x$)MnO$_3$. The chemical compositions of the samples of the series

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, $λ = 1.5406$ A) 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 [9] was used for the Rietveld refinement in order to obtain the information of crystal structures of La$_{0}$ (Ba$_{0.1-x}$Ca$_x$)MnO$_3$. A Philips XL30 microscope with energy dispersive spectroscopy (EDS) was used to determine the chemical composition. The valence of Mn was determined by the X-ray absorption technique: The X-ray absorption experiments were carried out at the Synchrotron Radiation Research Center (SRRC) in Taiwan with electron beam energy of 1.5 GeV and a maximum stored current of 240 mA. The spectra were recorded by measuring the sample current. The incident photon flux ($I_0$) was monitored simultaneously by a Ni mesh located after the exit slit of the monochromator. All the measurements were performed at room temperature. Two cycles of runs were performed for each sample. The reproducibility of the absorption spectra of the same sample in different experimental runs was found to be extremely good. The photon energies were calibrated to an accuracy of 0.1 eV via the known O K-edge absorption peaks of CuO. The valence of Mn was also determined by chemical titration. The samples were dissolved in an excess of 20 ml K$_2$C$_2$O$_4$ (concentration 0.22 N) and 2 ml H$_2$SO$_4$ (concentration 6 N) around 65 °C with a standard solution of KMnO$_4$ [10]. The titration at 65 °C with a standard solution of KMnO$_4$ [10]. The titration at 65 °C with a standard solution of KMnO$_4$ [10].
La$_{0.6}$(Ba$_{0.4}$,Ca$_x$)$_4$Mn$_3$O$_{12}$ were measured by EDS and the fractions of the measured compositions were found to be consistent with the expected nominal compositions.

The O 1s and Mn 2p edge X-ray absorption near edge structure (XANES) spectra of the compositions La$_{0.6}$(Ba$_{0.4}$,Ca$_x$)$_4$Mn$_3$O$_{12}$ (0 ≤ x ≤ 0.4) are shown in Fig. 3(a) and (b). In Fig. 3(a), the spectra correspond to transitions to O 2p character mixed in conduction band. The spectra reflect, through the oxygen–metal hybridization, the same scheme and determine the Mn valence to be around 3.40 ± 0.03 across the series La$_{0.6}$(Ba$_{0.4}$,Ca$_x$)$_4$Mn$_3$O$_{12}$ for 0 ≤ x ≤ 0.4. Moreover, the Mn valence of all the samples as determined by chemical titration is also around 3.43 ± 0.05. Fig. 4 shows 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 $T_C$ from 350 K of $x = 0$ to 275 K of $x = 0.4$ was observed. This suggests that the smaller Ca$^{2+}$ ions substituting in the larger Ba$^{2+}$ 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 3d and O 2p orbitals resulting in a reduced bandwidth ($W$) [14–16]. The average Mn–O(2) bond distance in the orthorhombic cell ($x ≥ 0.3$) and the Mn–O distance in differences in the ionic radius. In Fig. 3(b), the spectra show two broad multiple structures separated by spin–orbit splitting (Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$). The chemical shift is caused by changes in the electrostatic energy at the Mn site driven by changes in the ionic valence in the compounds. It is well established that the effective ionic valence of the compounds can be measured from the chemical shift of the core-level X-ray photoemission [13]. We, therefore, adopt the same scheme and determine the Mn valence to be around 3.40 ± 0.03 across the series La$_{0.6}$(Ba$_{0.4}$,Ca$_x$)$_4$Mn$_3$O$_{12}$ for 0 ≤ x ≤ 0.4. Moreover, the Mn valence of all the samples as determined by chemical titration is also around 3.43 ± 0.05.

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Fig. 2. Basic perovskite cell parameters ($a_p$ and $b_p$) as a function of $x$ in La$_{0.6}$Ba$_{0.4-x}$Ca$_x$MnO$_3$. The ideal crystal structure of La$_{0.6}$Ba$_{0.4-x}$Ca$_x$MnO$_3$ ($x < 0.3$) with rhombohedral cell (space group: R-3c) and $x \geq 0.3$ with orthorhombic cell (space group: Pbnm) are shown in the bottom left and top right of the figure, respectively.

Fig. 3. (a) O 1s; (b) Mn 2p edge XANES spectra of samples with nominal composition of La$_{0.6}$Sr$_{0.4-x}$Ba$_x$MnO$_3$ and those of two standards, MnO$_2$ (Mn$^{4+}$) and Mn$_2$O$_3$ (Mn$^{3+}$).
Fig. 4. Temperature dependence of magnetization in a magnetic field of 0.1 T of La$_{0.6}$(Ba$_{0.4-x}$Ca$_x$)MnO$_3$ ($0 \leq x \leq 0.4$).

the rhombohedral cell ($x < 0.3$) is found to be nearly the same, as can be seen from Table 1. This implies the same size of overlap between Mn 3d and O 2p within the $\alpha$- and $\beta$-planes. 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 the overlap between Mn 3d$_{z^2}$ and O 2p$_{z}$, which results in a decrease in $T_C$'s with increasing Ca content. Therefore, the results are consistent with the compositions with $x \geq 0.3$ exhibiting a distorted MnO$_6$ octahedral structure which indicates that the Jahn–Teller distortion along the $c$-axis occurs in the compounds. Such an effect will lead to a decrease in the spatial overlap of the Mn 3d$_{z^2}$ and O 2p$_{z}$ 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). In the inset of Fig. 4, we show the $T_C$'s of La$_{0.6}$(Ba$_{0.4-x}$Ca$_x$)MnO$_3$ as a function of the average radius (assuming ninefold coordination) of the La, Ba or Ca cations, \(\langle r_A \rangle = \left[0.6r_{La}(0.4 - x)r_{Ba} + xr_{Ca}\right]\). The following empirical formula has been used to describe the variation of bandwidth ($W$) in the double exchange mechanism of manganites [17]

\[
W \propto \frac{\cos \omega}{d_{Mn-O}^{3.5}}
\]

where $\omega$ is the tilt angle in the plane of the bond ($\omega = 180^\circ - \alpha$; $\alpha$ is the angle of Mn–O–Mn) and $d_{Mn-O}$ the Mn–O bond length. Increasing $x$ in La$_{0.6}$(Ba$_{0.4-x}$Ca$_x$)MnO$_3$ leads to the increase of Mn–O(1) bond length along the $c$-axis (as shown in Table 1), while keeping the Mn–O–Mn angle constant. The increase of Mn–O(1) may control the decrease of $W$ which results in the decrease in $T_C$. 

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4. Conclusions

We have studied the isovalent substitution of the smaller Ca$^{2+}$ ion for the larger Ba$^{2+}$ ion in the system La$_{0.6}$(Ba$_{0.4-x}$Ca$_{x}$)MnO$_3$. For $x \geq 0.3$, a structural transition occurs from orthorhombic to rhombohedral. This causes a distortion in the MnO$_6$ octahedra, reducing the $T_C$. This study has thus demonstrated that the size of the interpolated cation plays an important role in controlling the crystal structure and $T_C$ in the title series.

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References