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Effect of Zn substitution on para- to ferromagnetic transition temperature in La_{0.67}Ca_{0.33}Mn_{1-x}Zn_xO_3 colossal magnetoresistance materials

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I. INTRODUCTION

The invention of high temperature superconductivity (HTSc) in perovskite oxide cuprates\(^1,2\) initiated a hectic research of material scientists towards similar perovskite oxides, which might not be cuprates or even not superconductors. A novel material, with the nominal formula RE\(_{1-x}\)E\(_a\)MnO\(_3\)\(_{2+\delta}\) (where RE = La, Pr, Nd, Sm, etc, \(E_a\) = Ca, Sr, Ba, Pb, etc.), belonging to perovskite oxide magnets, was reinvented in 1993.\(^3,4\) These compounds show a very large colossal magnetoresistance (CMR) that makes them interesting for practical applications. Besides their potential practical applicability, the fundamental research on knowing the actual mechanism of the CMR phenomenon has also attracted great interest.\(^5,12\) What is known by now is that \(T_p\), the paramagnetic-to-ferromagnetic (pf) transition temperature, where the CMR occurs, is highly sensitive to \(x\), the doping concentration and \(\delta\), the oxygen deficiency in RE\(_{1-x}\)E\(_a\)MnO\(_3\)\(_{2+\delta}\) samples.\(^8,12\) By changing \(x\) with fixed \(\delta\) or vice versa, one essentially changes the Mn\(^{3+}/\)Mn\(^{4+}\) ratio in these compounds.\(^7,13\) There exists a clear relation between \(T_p\) and the amount of Mn\(^{4+}\) ions. In addition, most of these compounds go through a structural phase transition (trigonal to orthorhombic) often coupled with the pf transition and accompanied with a change in sign of charge carriers at \(T_p\).\(^14,15\)

The doping mechanism for changing Mn\(^{3+}/\)Mn\(^{4+}\) ratio in the CMR materials is quite similar to that as followed for the HTSc compounds to control effective Cu valency. In both cases variation of the Mn/Cu valency is achieved by either alliointal substitution and/or by changing overall oxygen content which determines the value of \(T_p\) or \(T_c\)(superconducting transition temperature). Similar to HTSc compounds, both Cu and Mn can be substituted partially by other 3d metals like Co, Ni, Fe, and Zn. In case of CMR compounds, Mn-site (3d) metal substitutions were also carried out\(^16–22\) and the results were explained in terms of changed Mn\(^{3+}/\)Mn\(^{4+}\) ratio.\(^6\) \(T_p\) decreased monotonically with increasing Fe concentration and disappeared for 18 at. % Mn/Fe substitution.\(^16–18\) Keeping in mind that Cu/Zn substitution in HTSc cuprates resulted in interesting physics, it seemed useful to study the same in CMR materials also. This is the aim of present study. \(T_p\) decreases with an increase of \(x\) as it is seen from resistivity, magnetization, and heat capacity versus temperature measurements. The relative decrease of \(T_p\) with Mn/Zn substitution is similar to that observed for other 3d metal substitutions on Mn-site,\(^19–21\) but different to Fe.\(^16–18\) We could find only few reports\(^21,22\) on Mn-site Zn substitution in CMR materials and that also for fixed Zn concentration of 5 at. %\(^21\) and 15 at. %.\(^22\)

II. EXPERIMENT

Samples of the series La\(_{0.67}\)Ca\(_{0.33}\)Mn\(_{1-x}\)Zn\(_x\)O\(_3\) with \(x\) = 0.0–0.50 were synthesized through a solid-state reaction route. Magnetization measurements were performed on a physical property measurement system from Quantum Design, in an applied dc field of 0.5 T. Heat capacity measurements were carried out in temperature range from 100 to 300 K.
K using a commercial scanning calorimeter (DSC-2, from Perkin Elmer). Neutron diffraction patterns at room temperature were obtained using the research reactor facility at the University of Missouri.

III. RESULTS AND DISCUSSION

Figure 1 shows the neutron diffraction patterns for La$_{0.67}$Ca$_{0.33}$Mn$_1$O$_3$ system with $x = 0.0$ and 0.15, taken at room temperature. The vertical bars marked at the bottom set of fitted and observed spectrum are for the LaCaMnO$_3$ (CMR compounds) with space group Pnma.

![Figure 1](image1)

**FIG. 1.** Fitted and observed Neutron diffraction patterns for La$_{0.67}$Ca$_{0.33}$Mn$_1$O$_3$ system with $x = 0.0$ and 0.15, taken at room temperature.

The Mn–O bond distances also are significant digit 0.15! on the composition, are La$_{0.67}$Ca$_{0.33}$Mn$_1$O$_3$. The Mn–O bond lengths for these samples deduced from Rietveld analysis of the neutron diffraction data are listed in Table I. The lattice parameters and oxygen content are nearly the same for all $x$ up to 0.15 due to nearly similar ionic size of Mn$^{3+}$ and Zn$^{2+}$. The Mn–O(1) and Mn–O(2) bond distances also are nearly unchanged. Some oxygen occupancies refine to more than one which may be renormalized to conclude some deficiency in metal ions.

Figure 2 depicts the magnetization ($M$) versus temperature. Obviously the $T_p$-transition temperature ($T_p$) decreases with increasing $x$. This is corroborated by the insulator-to-metal transition temperature seen as a large anomaly in the electrical resistivity measurements (plots are not shown). As expected, for most of the polycrystalline bulk materials $T_p$ is not sharp, but the $T_p$ transition takes place over a broad temperature range of nearly 5–50 K, depending on $x$. The transition temperature ($T_p$) derived from $M(T)$ curves are tabulated in Table II. They were determined as the crossing point between the $M(T)$ curve, extrapolated from high temperatures, and the tangent on the inflection point on the high-

![Figure 2](image2)

**FIG. 2.** Magnetization vs temperature plots for La$_{0.67}$Ca$_{0.33}$Mn$_1$Zn$_x$O$_3$ system.

x-ray diffraction patterns of all the La$_{0.67}$Ca$_{0.33}$Mn$_1$Zn$_x$O$_3$ samples show that Zn substitutes isostructurally up to $x = 0.30$ beyond which the $x$-patterns contain some extra lines. Lattice parameters, oxygen content, and selected bond lengths for these samples deduced from Rietveld analysis of the neutron diffraction data are listed in Table I. The lattice parameters and oxygen content are nearly the same for all $x$ up to 0.15 due to nearly similar ionic size of Mn$^{3+}$, and Zn$^{2+}$. The Mn–O(1) and Mn–O(2) bond distances also are nearly unchanged. Some oxygen occupancies refine to more than one which may be renormalized to conclude some deficiency in metal ions.

![Table I](image3)

**TABLE I.** Lattice parameters, oxygen content, fractional occupancies, and selected bond lengths for La$_{0.67}$Ca$_{0.33}$Mn$_1$Zn$_x$O$_3$ ($x = 0.0, 0.05, 0.10,$ and 0.15). The numbers in parentheses give the estimated deviation in the last significant digit(s). Typical atomic positions, which vary slightly depending on the composition, are La(0, 0, 1/2, 0), Ca(0, 0, 1/2, 0), Mn(0, 0, 1/2, 0), O(1) (1/2, 1/4, 0), and O(2) (1/4, 0, 3/4).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_p$ (K)</th>
<th>$T_p$ ($C_p$) (K)</th>
<th>($\Delta S_{trs}$)(J/mol K)</th>
<th>$\Delta S_{trs}$ (J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0.0$</td>
<td>277</td>
<td>274</td>
<td>6.4</td>
<td>12.8</td>
</tr>
<tr>
<td>$x = 0.03$</td>
<td>270</td>
<td>271</td>
<td>6.5</td>
<td>12.8</td>
</tr>
<tr>
<td>$x = 0.05$</td>
<td>255</td>
<td>253</td>
<td>5.1</td>
<td>10.7</td>
</tr>
<tr>
<td>$x = 0.1$</td>
<td>238</td>
<td>240</td>
<td>3.75</td>
<td>8.9</td>
</tr>
<tr>
<td>$x = 0.15$</td>
<td>220</td>
<td>225</td>
<td>2.9</td>
<td>7.7</td>
</tr>
<tr>
<td>$x = 0.2$</td>
<td>185</td>
<td>...</td>
<td>2.3</td>
<td>7.3</td>
</tr>
<tr>
<td>$x = 0.3$</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

![Table II](image4)

**TABLE II.** Para- to ferromagnetic transition temperatures ($T_p$) for La$_{0.67}$Ca$_{0.33}$Mn$_1$Zn$_x$O$_3$ system deduced from magnetization ($M(T)$) and heat capacity ($C_p(T_p)$), change of entropy ($\Delta S_{trs}$) reflected to $T_p$ transition deduced from specific heat curves in the range 100–300 K and taking $x = 0.30$ as reference, and $\Delta S_{trs}$, the transition entropy corrected by contributions estimated from below 100 K and from the magnetic part of $x = 0.30$ sample.
temperature side of the $M(T)$ anomaly. For $x > 0.15$, $T_p$ is no more clearly seen neither in both, $M$ vs $T$ and $R$ vs $T$ measurements, nor in the specific heat $C_p$.

Figure 3 shows the heat capacity ($C_p$) versus temperature plots. The samples ($x = 0$, 0.03, 0.05, 0.075) show well defined peaks, but only a less pronounced hump for $x = 0.1$ and no anomaly for $x = 0.15$ and 0.30 (similar to the $M$ vs $T$ and $R$ vs $T$ experiments). The transitions $T_p(C_p)$ shift to lower temperatures with increased $x$ values and coinide excellently with $T_p(M)$ (see Table II). Thereby, $T_p(C_p)$ have been calculated by application of the same method as used for the determination of $T_p(M)$ (earlier). The change of entropy ($\Delta S_{trs}$) related with $T_p$ can be calculated from $C_p(T)$ by subtracting the lattice contribution. Theoretically, the expected entropy change $\Delta S_{trs}$ for magnetic ordering of a mixture of $Mn^{4+}/Mn^{3+}$ ions is: $\Delta S_{trs}=0.67R \ln 5 + 0.33 R \ln 4 = 12.8 J/mol K$, since for La$_{0.67}$Ca$_{0.33}$MnO$_3$ (similar to other CMR compounds) 1/3 of the Mn ions are Mn$^{4+}$ with spin $S=3/2$ and 2/3 are Mn$^{3+}$ with $S=2$. Obviously the peaks displayed in Fig. 3 show $\Delta S_{trs} \approx 12.8 J/mol K$ as observed by other groups. However, it is noticed that for magnetic transitions near 280 K, a considerable part of entropy is contained in $C_p(T)$ below 100 K. Therefore, in a first step we took the $C_p(T)$ curve (in the range 100–300 K) for $x = 0.3$ (without anomaly) as approximated lattice heat and subtracted this curve from all others. The resulting $\Delta S'_{trs}$ is given in Table II. $\Delta S'_{trs}$ as a function of $x$ decreases as shown in the inset of Fig. 3. The following estimate however shows that for $x = 0$ the expected full entropy is presumably engaged: (i) the entropy below 100 K amounts to $\Delta S_{sat} \approx 12.8 J/mol K$ according to Eq. 22, (ii) assuming a magnetic heat of 2.5 J/mol K for $x = 0.3$ (the present lattice reference) would give an additional $\Delta S_{cor}$, around transition $\cong 3.7 J/mol K$. The full entropy estimated includes these corrections yield: $\Delta S'_{trs} = [(6.4 + 2.5 + 3.7) \pm 1.5] J/mol K$ (for $x = 0$). For the other samples the values, decreasing with $x$ are listed in Table II.

The effect of depression of $T_p$ by $dT_p/dx$ by introduction of Zn is similar to that observed when 3$d$ metals substitute in LaCaMnO$_3$ for $x > 0.10$. But for low $x$ values ($x < 0.10$) it appears that $dT_p/dx$ is much slower in LaCaMnO$_3$ than in La$_{0.67}$Ca$_{0.33}$MnO$_3$. A similar situation is reported in Refs. 21 and 22, where two fixed concentrations of Zn, receptively 5 and 15 at.$\%$ are studied. Relatively higher valence substitution of Fe$^{3+}$/Fe$^{2+}$ at Mn site in La$_{0.67}$Ca$_{0.33}$MnO$_3$ might decrease the Mn$^{4+}$ ratio faster in the system when compared with partial substitution of Mn by fixed valent Zn$^{2+}$. This might be a possible explanation why $dT_p/dx$ decreases less at low $x$ in the present case.

ACKNOWLEDGMENTS

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