Effect of sodium substitution on the structural, magnetic and magnetocaloric properties of $\text{La}_{0.5}\text{Ca}_{0.5}$MnO$_3$ perovskite manganites

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Abstract

The perovskite-type $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Na}_x\text{MnO}_3$ ($0.05 \leq x \leq 0.2$) ceramic samples were prepared using the solid-state reaction at high temperature. The X-ray powder diffraction refinement by means of the Rietveld technique reveals that all our samples are single phase and crystallize in the orthorhombic structure with Pbnm space group. Lattice parameters and unit cell volume are found to increase with increasing the average A-site ionic radius $<r_A>$. The substitution of calcium by monovalent element (Na) in La$_{0.5}$Ca$_{0.5}$MnO$_3$ drives the system from a charge ordering state to a ferromagnetic behaviors observed near room temperature for all our substituted compounds with a Curie temperature $T_C$ slightly decreasing from 297K for $x=0.05$ to 278K for $x=0.2$. Magnetic entropy change $\Delta S_M$, deduced from magnetization measurements versus magnetic applied field at several temperatures, shifts to higher values with increasing Na content and reaches 1.14J/kgK and 3.1J/kgK for La$_{0.5}$Ca$_{0.3}$Na$_{0.2}$MnO$_3$ under magnetic applied field of 2T and 7T respectively.

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1. Introduction

Manganite systems $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{Ln} = \text{La, Pr, Nd and A} = \text{Ca, Sr and Ba}$) exhibit a rich collection of interesting and intriguing properties, which can be tailored for a wide variety of applications such as low loss power delivery, quantum computing, ultrahigh-density magnetic data storage, and more recently spintronic applications [1–4]. The discovery of the colossal magnetoresistance effect (CMR) in these materials in 1994 spurred their study. Soon enough it was realized that CMR exhibiting materials possess many features which make them very fascinating. First of all, these compounds are found to undergo a distinctive double phase transition under cooling from a paramagnetic weakly conductive insulating like state to a ferromagnetic more conductive metallic like state. These

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two transitions occur at what is conveniently described as the Curie temperature \( T_C \) and the so-called charge carrier localization temperature \( T_{MI} \), respectively.

In the mixed-valence manganese oxides, the strong correlations among spin, orbital and lattice degree of freedom play crucial roles [5,6] mainly for the intermediate-hole-doped \( \text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \) compounds, generally characterized by relatively small A-site ionic radius \( <r_A> \). For \( \text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \) specimen, a first transition from paramagnetic (insulator) to ferromagnetic (metallic) phase occurs around \( T_C =234K \) followed by a second transition with further cooling towards an antiferromagnetic insulating state at \( T_N =163K \) [7]. The antiferromagnetic phase is characterized by charge and spin ordering with a real space rearrangement of \( \text{Mn}^{3+} \) and \( \text{Mn}^{4+} \) ions in a checkerboard pattern [8–10]. This charge ordering (CO) phase is amenable to external perturbations such as magnetic field, chemical pressure, etc..., which reflects a strong competition between the CO state and the ferromagnetic phase associated to the double exchange interaction.

Besides these fascinating properties, that the perovskite manganites exhibit, leading to potential applications in magnetic storage, these compounds have also been found to present a giant magnetocaloric effect (MCE) under moderate magnetic applied field [11]. This property reveals that the CMR manganites are good candidates for the magnetic refrigeration technology [12–14]. In fact, the growing demand of environmental friendly and energetically efficient technologies, based on solid state materials replacing greenhouse or ozone depleting refrigerating gases, spurs the scientists to discover new magnetic refrigerant with outstanding figure of merit that will make the technology competitive with respect to the conventional ones. A promising class of materials, in this respect, is that in which a first order structural phase transition is induced by the magnetic field [15–18]. The main requirements in a magnetic materiel to posses large magnetocaloric effect are the large spontaneous magnetization, belonging to a class of heavy rare-earth metals [15], as well as the sharp drop in magnetization associated with the ferromagnetic to paramagnetic transition at the Curie temperature [19,20]. The MCE is then intrinsic to magnetic materials and is induced by the coupling of magnetic sublattices under an external magnetic applied field, which affects the magnetic part of the total entropy owing to a magnetic-field variance. The MCE can be quantified by means of an extensive parameter that is the isothermal magnetic entropy change \( |\Delta S_M| \). The interesting magnetocaloric properties observed in rare-earth manganites were not reported until 1996 [11].

In the present work, we seek to explore the effect of disorder on a 50-50 composition on the borderline of ferromagnetic metallic (FMM) and charge ordering insulator (COI). We elaborated using the solid state reaction at high temperature the \( \text{La}_{0.5}\text{Ca}_{0.5-x}\text{Na}_x\text{MnO}_3 \) \( (0.05 \leq x \leq 0.2) \) polycrystalline samples and studied the effect of the Na doping on the structural, magnetic and magnetocaloric properties of the charge ordering \( \text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \) compound.

2. Experimental techniques

Powder samples have been elaborated using the conventional solid-state reaction at high temperature by mixing \( \text{La}_2\text{O}_3, \text{MnO}_2, \text{CaCO}_3 \) and \( \text{Na}_2\text{CO}_3 \) up to 99.9% high purity in the desired proportion according to the reaction:

\[
0.5\text{La}_2\text{O}_3 + 2(0.5-x)\text{CaCO}_3 + x\text{Na}_2\text{CO}_3 + 2\text{MnO}_2 \rightarrow 2\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Na}_x\text{MnO}_3 + \delta\text{CO}_2 + \delta\text{O}_2
\]

The starting materials were intimately mixed, ground, and fired in air at 1000°C for 4 days with intermediate regrinding and repelling. The obtained powders were then pressed under 4 tones into pellets of about 1mm thickness and 13mm diameter and sintered at 1100°C for 4 days in air with several intermediate regrinding and repressing into pellets. Finally, the pellets were rapidly quenched to room temperature. This step was done in order to keep the obtained structure at high temperature. The physical properties depend strongly on the synthesis route and also on the cooling method. Phase purity, homogeneity, and cell dimensions were determined by X-ray diffraction (XRD) at room temperature. Structural analysis was carried out using the standard Rietveld Technique [21, 22].

Magnetization measurements versus temperature and versus magnetic applied field were carried out using a vibrating sample magnetometer in the temperature range 10-300K with an applied field up to 7T. MCE were deduced from the magnetization measurements versus magnetic applied field up to 7T at several temperatures.

3. Results and discussion
The X-ray diffraction spectra of our synthesized samples La\(_{0.5}\)Ca\(_{0.5-x}\)Na\(_x\)MnO\(_3\) with \(x = 0.05, 0.1, 0.15,\) and 0.2 are characterized by the lines of perovskite structure, which confirm the single orthorhombic phase with Pbnm space group as has been observed by Zhu et Coll. \[23\]. The structural parameters were refined using the standard Rietveld technique based on the FULLPROF code. In the profile refinement, we began with scale and background parameters followed by the unit cell parameters. We introduced then the peak asymmetry and the preferred orientation. Finally, we treated the positional parameters and the individual isotropic parameters. The quality of refinement was evaluated through the goodness of the fit indicator \(\chi^2\). A typical X-Ray diffraction pattern at 300K, including the observed and calculated profiles as well as the difference profile of La\(_{0.5}\)Ca\(_{0.3}\)Na\(_{0.2}\)MnO\(_3\) compound is shown in Fig. 1. Detailed results of structural refinement as well as the average size of A-site cations (<r\(_A\)>) and the mismatch effect (\(\sigma^2\)) are listed in Table 1. With increasing the sodium substitution rate, the <r\(_A\)> and consequently the unit cell volume shifts to higher values (Fig. 2), the latter increases from 224.2 Å\(^3\) for \(x = 0.05\) to 227.3 Å\(^3\) for \(x = 0.2\).

![XRD pattern of La\(_{0.5}\)Ca\(_{0.3}\)Na\(_{0.2}\)MnO\(_3\) sample. Squares indicate the experimental data and the calculated data is the continuous line overlapping them. The lowest curve shows the difference between experimental and calculated patterns. The vertical bars indicate the expected reflection positions.](image)

Table 1. Refined structural parameters of La\(_{0.5}\)Ca\(_{0.5-x}\)Na\(_x\)MnO\(_3\) samples (0 ≤ \(x\) ≤ 0.20) at room temperature.

<table>
<thead>
<tr>
<th>(x)</th>
<th>(a) (Å)</th>
<th>(b) (Å)</th>
<th>(c) (Å)</th>
<th>(V) (Å(^3))</th>
<th>(Rwp) (%)</th>
<th>(\chi^2)</th>
<th>&lt;r(_A)&gt; (Å)</th>
<th>(\sigma^2) (Å(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>5.433(8)</td>
<td>5.409(0)</td>
<td>7.627(2)</td>
<td>224.2</td>
<td>9.97</td>
<td>1.10</td>
<td>1.201</td>
<td>0.000387</td>
</tr>
<tr>
<td>0.10</td>
<td>5.433(5)</td>
<td>5.427(0)</td>
<td>7.636(2)</td>
<td>225.0</td>
<td>13</td>
<td>1.13</td>
<td>1.204</td>
<td>0.000432</td>
</tr>
<tr>
<td>0.15</td>
<td>5.433(2)</td>
<td>5.442(6)</td>
<td>7.651(3)</td>
<td>226.3</td>
<td>14.8</td>
<td>1.11</td>
<td>1.207</td>
<td>0.000459</td>
</tr>
<tr>
<td>0.20</td>
<td>5.432(7)</td>
<td>5.461(8)</td>
<td>7.658(6)</td>
<td>227.3</td>
<td>12.5</td>
<td>1.07</td>
<td>1.21</td>
<td>0.000468</td>
</tr>
</tbody>
</table>
Magnetization measurements recorded as a function of temperature in a magnetic applied field of 50mT show that all compounds undergo a paramagnetic to ferromagnetic transition near room temperature and the antiferromagnetic interaction linked to charge ordering is suppressed. We plot in Fig. 3 the temperature dependence of the magnetization $M(T)$ for $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Na}_x\text{MnO}_3$ ($x=0.2$) sample. Several authors argued that the cation size mismatch influences significantly the charge ordering in $\text{La}_{0.5}\text{A}_{0.5}\text{MnO}_3$ compounds [24–27], this factor is related to the random distribution of cations with different sizes. A theoretical work has been achieved by Motome et al. [28] to explain this empirical evidence for the relation between FMM and COI states and particularly near the phase boundary. The authors show that the disorder tends to weaken both FMM and COI phases, however the last is strongly affected since it requires a long-range phase coherence of the wave function in comparison with the double exchange interaction.

The Curie temperature $T_C$, deduced from extrapolation at $1/\chi=0$ of the Curie-Weiss laws, is found to decrease with Na substitution rate from 297K for $x = 0.05$ to 278K for $x = 0.2$ as can be shown in Fig.4. This behavior is consistent with the increase of both the A-site ionic radius and the mismatch effect.
In order to confirm the ferromagnetic behavior at low temperatures of our samples, we have performed magnetization measurements as a function of the magnetic applied field $\mu_0H$ up to 7T at several temperatures. The magnetization evolution versus magnetic applied field for samples corresponding to $x=0.05$ and 0.2 are plotted in Fig. 5. We can observe, that below $T_C$, the magnetization increases sharply with applied field for $H<0.5T$ and then saturates above 1T.

Fig. 5. Magnetization evolution versus magnetic applied field up to 7T at several temperatures for (a) $x=0.05$ and (b) $x=0.2$.

In order to get a deeper insight in the magnetic transition, we plot in Fig. 6 the so-called Arrott plots ($M^2$ versus $\mu_0H/M$) in the temperature range 20-300K for both La$_{0.5}$Ca$_{0.45}$Na$_{0.05}$MnO$_3$ and La$_{0.5}$Ca$_{0.3}$Na$_{0.2}$MnO$_3$ samples. All the $M^2$ versus $\mu_0H/M$ curves exhibit a positive slope indicating that the ferromagnetic-paramagnetic transition is of second order, according to the Banerjee criterion [29]. The $T_C$ values deduced from the Arrott curves are close to those deduced from M(T) measurements.
Recently, an interesting property has been observed in ferromagnetic manganites known as the magnetocaloric effects (MCE) [30–33]. The origin of this phenomenon is based on the adiabatic demagnetization. In fact, the application of a magnetic field to a ferromagnetic material induces a spin reorientation, decreasing the spin entropy and when we remove this magnetic applied field, the spin system tends to randomize, which increases the spin entropy, and consequently lowers the temperature of the system.

The magnetic entropy changes were determined from magnetization isotherms $M(H)$ at several temperatures, between zero field and a maximum field ($H_0$) using the classical thermodynamic theory based on Maxwell relation:

$$\Delta S_{M} (T) = \frac{1}{\Delta T} \int \left( M(T + \Delta T, H) - M(T, H) \right) dH$$

Where $\Delta T$ is the temperature increment between measured magnetization isotherms ($\Delta H = 10$K for our data).

Fig. 7 displays the temperature dependence of the magnetic entropy change, $\Delta S_M$, for both $x = 0.05$ and 0.2 compounds at several applied field changes. The behavior shows several remarkable features. For each sample, the magnetocaloric effect increases and reaches its maximum near the corresponding Curie temperature where the magnetization drops rapidly. Furthermore, the magnetic entropy $|\Delta S_M|$ shifts to higher values with increasing the monovalent substitution rate and under a magnetic field change of 2T, we obtain $|\Delta S_M|_{max}=0.41$J/KgK and 1.14J/KgK for $x = 0.05$ and 0.2 respectively. This behaviour is consistent with the increase of the mismatch effect induced by substituting calcium by sodium. It should be noted that the maximum of the magnetic entropy change for the studied samples are smaller than that of gadolinium or its compounds [34]; however, the presently studied compounds possesses some characteristics such as easier synthesis route, higher chemical stability, and easier tuning of $T_C$ by element doping.

The evaluation of the refrigeration capacity passes trough the so-called relative cooling power RCP, $RCP=|\Delta S_M|_{max} \times \delta T_{FWHM}$, where $\delta T_{FWHM}$ is the full with of half maximum of the magnetocaloric peak. It is, then, important that the magnetic entropy extend over a large temperature interval. It should be noted that a first order transition is able to concentrate the MCE in a narrow temperature range, whereas a second order transition is usually spread over a broad temperature range, which is the case in our samples and is beneficial for active magnetic refrigeration [35,36]. We have evaluated the RCP values under a magnetic field change of 2T for both samples corresponding to $x = 0.05$ and 0.2. The RCP increases with Na content from 36.31J/kg for $x=0.05$ to 84.75J/kg for $x=0.2$. These values are somewhat smaller than those evidenced in other perovskites but high enough for technical interest.

![Fig. 6. $M^2$ versus $\mu_0H/M$ isotherms for the samples with (a) $x = 0.05$ and (b) $x = 0.2$.](image-url)
4. Conclusion

The single-phase La$_{0.5}$Ca$_{0.5-x}$Na$_x$MnO$_3$ (0.05 ≤ x ≤ 0.2) polycrystalline samples were elaborated using the solid state reaction at high temperature. All our synthesized compounds crystallize in an orthorhombic structure with Pbmn space group. The lattice parameters are found to increase with increasing the monovalent element rate. The substitution of Ca by Na in La$_{0.5}$Ca$_{0.5}$MnO$_3$ sample induces a paramagnetic to ferromagnetic transition near room temperature, with a $T_C$ slightly decreasing from 297K for x = 0.05 to 278K for x = 0.2, and the antiferromagnetic interaction linked to charge ordering is suppressed. The largest magnetic entropy change was observed in La$_{0.5}$Ca$_{0.3}$Na$_{0.2}$MnO$_3$ sample, being 1.14 J/kgK under a magnetic applied field change of 2T. The RCP values are comparable with those obtained in other perovskite-type specimens. The studied compounds may be considered as magnetic materials operated near room temperature.

References
