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# Na-doped $La_{0.7}Ca_{0.3}MnO_3$ compounds exhibiting a large magnetocaloric effect near room temperature

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## ABSTRACT

In this work, we have investigated the magnetic properties and the magnetocaloric effect of $La_{0.7-x}Na_xCa_{0.3}MnO_3$ compounds, which were prepared by a conventional solid-state reaction technique. The Rietveld refinement results suggested that the samples are single phase belonging to an orthorhombic structure (space group *Pnma*). Analyzing temperature dependence of magnetization $M(T)$ revealed that the Curie temperature ($T_C$) increases with increasing Na content ($x$). Their $T_C$ value is found to be 260–298 K for $x$=0.0–0.1, respectively. Base on $M(T)$ data measured at different applied magnetic fields ($H$), temperature dependence of magnetic entropy change $\Delta S_m(T)$ data for all the samples was calculated by using a phenomenological model. In the vicinity of $T_{C,}$ $-\Delta S_m(T)$ curve reaches a maximum value (denoted as $|\Delta S_{max}|$), which gradually increases with increasing $H$. Under 12 kOe, the value of $|\Delta S_{max}|$ is in a range of 1.47–5.19 J/kg K corresponding to the relative cooling power RCP=57.12–75.88 J/kg. Applied the universal master curve method for the magnetic entropy change, we concluded that Na-doped in $La_{0.7-x}Na_xCa_{0.3}MnO_3$ compounds leads to modification the nature of the magnetic phase transition from the first- to the second-order.

## 1. Introduction

In the last two decades, since the giant magnetocaloric effect (MCE) near room-temperature (RT) in $Gd_5Ge_2Si_2$ alloy was discovered [1], the RT MCE has become one of the most attractive fields for both basic and applied researches. Among these, the MCE in perovskite manganites (so called manganites) has been also widely investigated that can be referenced in a large number of publications. It is shown that some manganites exhibit the giant MCE comparable with $Gd_5Ge_2Si_2$ alloy. For example, a maximum magnetic entropy change ($|\Delta S_{max}|$) about 7.8 J/kg K corresponding to the relative cooling power (RCP) about 124 J/kg was observed in $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) compound at 20 kOe [2]. Nevertheless, this compound has a Curie temperature ($T_C$) only 260 K, which is too low for RT applications. According to Dagotto et al. [3], $T_C$ value of LCMO compound can be controlled by doping suitable elements into La/Ca-site (so-called A-site in the $ABO_3$ perovskite structure), which is related to a disorder caused by a size mismatch at A-site. It is also shown that $T_C$ of LCMO compound significantly increases by doping the monovalent metals [4–8]. Koubaa et al. [5] reported the effect of some monovalent metals substituted into A-site on the MCE of $La_{0.65}M_{0.05}Ca_{0.3}MnO_3$ compounds with M=Na, Ag, and K. They found the value of $|\Delta S_{max}|$ to be about 3.0–5.16 J/kg K under an applied field change of 50 kOe. Recently, a study on the MCE of $La_{0.8-x}Ag_xCa_{0.3}MnO_3$ compounds with $x$=0–0.1 has been also reported [7]. It suggested that Ag substituted into A-site leads to a slight increase in $T_C$ from 214 to 234 K and modified their nature of the magnetic phase transition form the first- to the second-order. Under 30 kOe, $|\Delta S_{max}|$ value was found in the range of 6.86–4.15 J/kg K corresponding to RCP =188.6–195.5 J/kg for $x$=0–0.1, respectively [7]. Ho et al. [8] also indicated that Na substituted into A-site of $La_{0.7}Ca_{0.3-x}Na_xMnO_3$ compounds ($x$=0–0.09) leads to enhancement $T_C$ from 255 to 271 K. For $x$=0.09 (namely $La_{0.7}Ca_{0.21}Na_{0.09}MnO_3$), the $|\Delta S_{max}|$ value was found to be about 6.9 J/kg K corresponding to RCP=236 J/kg under a field change of 40 kOe [8]. These values are quite high if comparing with those of other manganites. However,

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$La_{0.7}Ca_{0.21}Na_{0.09}MnO_3$ compound has a $T_C$=271 K somewhat far below RT and it reaches high magnetic entropy change ($\Delta S_m$) only under the large magnetic field changes. In an attempt to further understand the influence of Na substituted into A-site of LCMO system, we prepared three ceramic samples of $La_{0.7-x}Na_xCa_{0.3}MnO_3$ with $x$=0, 0.05, and 0.1 and investigated their magnetic property and the MCE. Using the theoretical approaching method [9] performed on temperature dependences of magnetization data measured at different applied fields, we could predict the MCE of $La_{0.7-x}Na_xCa_{0.3}MnO_3$ compounds via their characteristic parameters, such as $\Delta S_m$, RCP, the change of the specific heat change $\Delta C_P(T,H)$, and the adiabatic temperature change $\Delta T$. Our results pointed out that a partial replacement of $La^{3+}$ by $Na^+$ in LCMO compound modifies the nature of the phase transition from the first- to the second-order. Together with increasing $T_C$ value towards RT, the magnetic phase transition region has been also significantly extended. Therefore, their RCP value increases from 57.12 to 75.88 J/kg, making $La_{0.7-x}Na_xCa_{0.3}MnO_3$ compounds to become more useful for RT magnetic cooling applications.

## 2. Experimental

Three bulk samples with compositional formula $La_{0.7-x}Na_xCa_{0.3}MnO_3$ ($x$=0, 0.05, and 0.1) were prepared by a solid-state reaction method. $La_2O_3$, CaO, $Na_2O_3$, and Mn (99.9%) were chosen as starting materials. Stoichiometric ratios of these powders were thoroughly milled and mixed for 2 h, and then annealed in air at 700 °C for 12 h. After several times of the pre-annealing and grinding, the obtained mixtures were pressed into pellets under a pressure 5000 psi by using a hydraulic press, and sintered at 1400 °C in air for 24 h. After fabrication, the purity and the RT crystal structure of the samples were checked by an X-ray diffractometer (Bruker AXS, D8 Discover) using Cu-$K_\alpha$ radiation. Data was recorded by step-scan mode in a range of 2θ=10–90° with a step size of 0.009°. Oxygen non-stoichiometric in the samples was checked by the iodometric titrations indicating that the oxygen excesses or deficiencies are insignificant ($\delta \approx \pm 0.005$). Temperature dependences of magnetization at different applied magnetic fields were performed on a vibrating sample magnetometer (VSM) in a temperature range from 100 K to 350 K and magnetic field up to 12 kOe. The statistical errors of the equipment are about ± 1 K, ± 10 Oe, and $10^{-4}$ emu for temperature, magnetic field, and magnetization, respectively.

## 3. Results and discussion

Fig. 1(a) shows the RT X-ray diffraction (XRD) patterns for all the samples. It indicates that the samples are single phase, without any trace of secondary phase. Some XRD peaks exhibit a gradual change in the shape of the double-peak when Na concentration increasing, inset of Fig. 1(a). This suggests a gradual modification in the lattice parameters. However, all the XRD peaks are very suitable for a PDF card No. 49-0416 [10] in the standard database, where the Miller-indexes of the XRD peaks belong to an orthorhombic structure (space group *Pnma*). It means that the orthorhombic structure is not be changed by the substitution of Na, however, the lattice parameters should be modified. Based on XRD data, lattice parameters were calculated by using the Rietveld refinement technique and listed in Table 1. Fig. 1(b) shows a representative of XRD pattern for the sample $x$=0.1 with its Rietveld refined one. These results pointed out that the structure refinement of the samples with $x$=0–0.1 is completely performed in an orthorhombic system with the space group *Pnma*. It means that Na is doped into A-site in the host lattice. The lattice parameters in Table 1 indicate that the volume of the unit cell ($V$) slightly increases with increasing Na concentration. This could be associated the substitution of $Na^+$ ion with a slight larger ionic radius for $La^{3+}/Ca^{2+}$ ion with a slight smaller radius in A-site. Besides, we can see that the Mn-O bond length decreases, while the Mn-O-Mn bond angle increases with increasing Na concentration, which weakly distorts $MnO_6$ octahedron in their structure.

**Table 1**
The structural parameters of $La_{0.7-x}Na_xCa_{0.3}MnO_3$ compounds with $x$=0–0.1.

| $x$ | 0 | 0.05 | 0.1 |
|---|---|---|---|
| $a$ (Å) | 5.4577 | 5.4497 | 5.4496 |
| $b$ (Å) | 7.7066 | 7.7154 | 7.7189 |
| $c$ (Å) | 5.4742 | 5.4776 | 5.4779 |
| $V$ (Å$^3$) | 230.25 | 230.31 | 230.43 |
| Mn-O (Å) | 1.9296 | 1.9289 | 1.9262 |
| Mn-O-Mn (deg.) | 163.36 | 163.79 | 164.93 |
| $\chi^2$ | 3.81 | 4.21 | 3.97 |
| $<r_A>$ (Å) | 1.3540 | 1.3555 | 1.3570 |
| $\sigma^2$ ($10^{-4}$ Å$^2$) | 0.8413 | 1.4485 | 2.0106 |
| $t_G$ | 0.9686 | 0.9747 | 0.9809 |
| $W$ ($10^{-2}$) | 9.915 | 9.932 | 9.995 |

The previous reports have also revealed that the magnetic and electrical properties of manganites strongly depend on concentration of $Mn^{3+}$ and $Mn^{4+}$ ions, which can be modified by changing A-site substitution content. This is closely related to the average radius of the cations located at A-site $<r_A>$, the variance of the A-site radius distribution $\sigma^2 = \sum y_i r_i - <r_A>^2$, and the Goldsmith tolerance factor $\tau_G = (<r_A> + r_O)/\sqrt{2}(r_B + r_O)$, where $r_A$, $r_B$, and $r_O$ are the ionic radii at A, B, and O-sites in $ABO_3$ structure. Among, if the

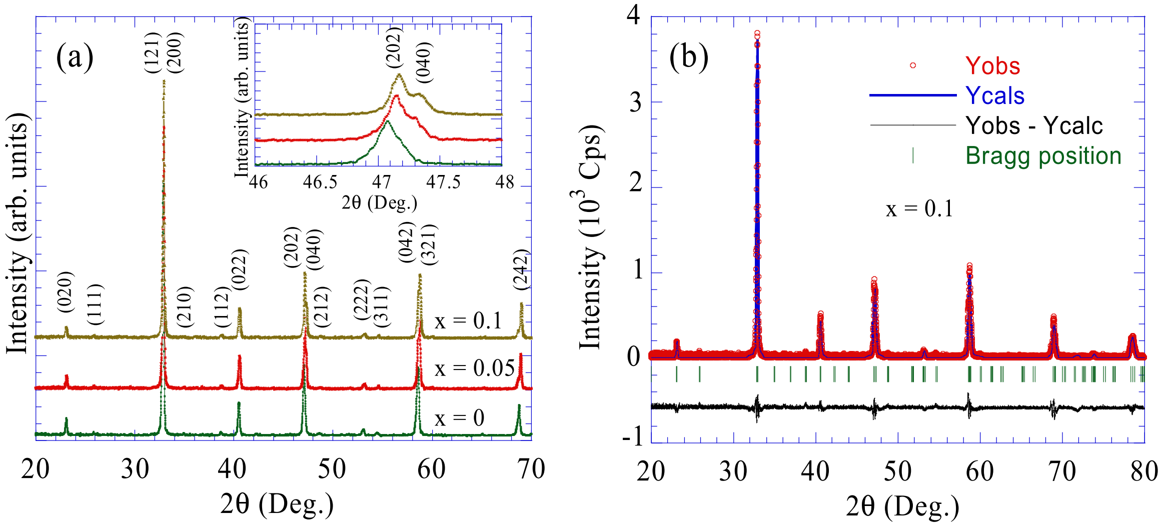

**Fig. 1.** (a) XRD patterns for $La_{0.7-x}Na_xCa_{0.3}MnO_3$ compounds with $x$=0–0.1. (b) Rietveld refined pattern for a representative sample $x$=0.1.