Influence of Nonstoichiometry on Magnetocaloric Effect in $(La_{0.7}Ca_{0.3})_{1-x}Mn_{1+x}O_3$

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Magnetocaloric effect in $(La_{0.7}Ca_{0.3})_{1-x}Mn_{1+x}O_3$ manganites with x = 0, 0.1, 0.2 has been investigated. It is found a strong influence of nonstoichiometry caused by excessive manganese on the magnetic entropy change. The magnetocaloric effect was evaluated from the isothermal curves of spontaneous magnetization versus the applied magnetic field by using the well-known thermodynamical Maxwell relation. The maximum entropy value, $|\Delta S_{\text{max}}^{\text{max}}|$, near the ferromagnetic-paramagnetic phase transition is shown to increase with the manganese content. The La_{0.56}Ca_{0.24}Mn_{1.2}O₃ manganite exhibits the largest $|\Delta S_{\text{max}}^{\text{max}}|$ value equal to 3.09 J kg⁻¹ K⁻¹ at 15 kOe near $T_{\text{C}} = 267$ K. The magnetocaloric effect values obtained allow to propose that the studied manganites are promising materials for future cooling application.

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1. Introduction

In recent years, the manganites belong to the intensively studied functional materials not only as materials with the colossal magnetoresistance [1, 2], but also as materials with perspective magnetocaloric properties [3–11]. Among these are the hole-doped manganites $(Ln_{1-x}A_x)_{1-y}Mn_{1+y}O_3$, where Ln is the lanthanide (La, Pr, Nd) and A is the alkaline-earth ion (A = Ca, Sr, Ba). In the $(La_{0.7}Ca_{0.3})_{1-x}Mn_{1+x}O_3$ compounds studied, the multivalent states of Mn ions arise not only due to substitution of Ca for La, but also owing to an excess of manganese. The excessive manganese, Mn_{1+x} , means that its content is increased with respect to both lanthanum and calcium ones in contrast to stoichiometric composition. The magnetic properties of these manganite oxides are defined first of all by the variation of the double exchange interaction between the Mn^{3+} and Mn^{4+} ions arising from change in the Mn^{3+}/Mn^{4+} ratio as a result of Mn content change. The compounds with an excess of manganese are of interest as materials, having the second-order paramagnetic-ferromagnetic phase transition close to a first-order one and the Curie temperature $(T_{\rm C})$ close to room temperature [12, 13], whose magnetic entropy can be controlled by varying Mn content. These properties make the manganites studied excellent candidates as working materials in magnetic refrigerators.

This work is a result of studies of magnetic and magnetocaloric properties of $(La_{0.7}Ca_{0.3})_{1-x}Mn_{1+x}O_3$ manganites with an excess of manganese (x = 0, 0.1, 0.2), where strong influence of nonstoichiometry on magnetic entropy value was established.

Our compounds establish larger values of magnetic entropy change than the most of other nonstoichiometric manganites reported [8].

2. Experimental details

The magnetocaloric properties measurements were performed at the samples with a general composition formula $(La_{0.7}Ca_{0.3})_{1-x}Mn_{1+x}O_3$ whose magnetic properties have been studied in Refs. [12, 13]. Detailed synthesis procedure as well as the crystal-structure characterization of the samples are also described in Refs. [14, 15]. In brief, the compounds with an excess of manganese (x = 0, 0.1, 0.2) were prepared by a ceramic technology using the double synthesizing annealing (at 900–950 °C) and sintering in air at 1150°C with the subsequent slow cooling. All the specimens examined by X-ray diffraction (XRD) method with Cu K_{α} radiation at room temperature were found to be single-phase and have the slightly distorted cubic structure (Fig. 1). The structural symmetry does not change with Mn doping. The *a* parameter of unit cell decreases with increasing x as a result of the rise of concentrations of dissolving in perovskite structure B-ions (Mn³⁺ with r = 0.785 Å and Mn⁴⁺ with r = 0.67 Å) having the smallest ion radius in comparison with A-ions (La³⁺ with r = 1.50 Å and Ca²⁺ with r = 1.48 Å). It testifies on dissolubility of excessive manganese in matrix structure of perovskites studied.

On the basis of the thermal equilibrium theory of crystal defects [16], we have considered the following assumptions regarding the excessive manganeses and vacancies problem in the nonstoichiometric $(La_{0.7}Ca_{0.3})_{1-x}Mn_{1+x}O_3$ samples. The compounds with an excess of manganese were prepared by solid reaction method with the high calcination temperature. Therefore we have assumed that in our samples, as a result of a charge disproportionation reaction $Mn^{3+} + Mn^{3+} \rightarrow$

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Fig. 1. X-ray diffraction patterns of the $(La_{0.7}Ca_{0.3})_{1-x}Mn_{1+x}O_3$ samples $(x = 0 \ 0.1 \ 0.2)$.

 $\mathrm{Mn}^{2+} + \mathrm{Mn}^{4+}$ [17], there are three kinds of manganese ions: Mn^{3+} and Mn^{4+} ions, which, as usually, occupy the B sites and Mn^{2+} ions occupying the A sites together with La^{3+} and Ca^{2+} ions as well as there are cationic vacancies at the A sites. The most preferable ions among the Mn ions are the Mn^{2+} ions having the largest ionic radius (r = 0.83 Å), which can occupy the A-position and, as it was synthesized in Ref. [18], can substitute a part of La ions. Since the vacancy space of the B site is smaller than that of the A site, we have assumed that the anion vacancies should also be at the B sites. Our assumptions are confirmed by the results of studies of self-doped perovskite manganites [19–21].

The contents of multivalent manganese ions (Mn^{2+} , Mn^{3+} and Mn^{4+}) as well as vacancies at A and B sites in the real structure of studied solid solutions were estimated using the ionic structure analysis [14, 22] taking into account both the degree of occupation of the A and B sites and fulfillment of an electroneutrality condition at oxidation-reduction processes. It is demonstrated in Table I, where the molar contents of La^{3+} , Ca^{2-} , Mn^{2+} , and $V_A^{(c)}$ at the A sites, Mn^{3+} , Mn^{4+} , and $V_B^{(a)}$ at the B sites and O^{2-} ions in the defect perovskite structure of $(La_{0.7}Ca_{0.3})_{1-x}Mn_{1+x}O_3$ samples vs. manganese content are presented, when the contents of the O^{2-} ions are normalized to 3.

The field and temperature dependences of magnetization were measured on pressed samples (d = 3 mm, l = 6 mm) over the temperature range 238–290 K and in magnetic field up to 15 kOe using a vibrating sample magnetometer. The field change was slow enough to consider all magnetization processes as isothermal. The isothermal magnetization was measured with field steps TABLE I

Molar contents of La³⁺, Ca²⁻, Mn²⁺, and V_A^(c) at the A sites, Mn³⁺, Mn⁴⁺, and V_B^(a) at the B sites and O²⁻ ions in the defect perovskite structure of $(La_{0.7}Ca_{0.3})_{1-x}Mn_{1+x}O_3$ samples vs. manganese content.

x		The A	sites		The B sites			
	La ³⁺	Ca^{2-}	Mn^{2+}	$V_{A}^{(c)}$	Mn^{3+}	Mn^{4+}	$V_{\rm B}^{\rm (a)}$	O^{2-}
0	0.70	0.30	0	0	0.70	0.30	0.21	3
0.1	0.58	0.25	0.02	0.15	0.71	0.29	0.22	3
0.2	0.51	0.22	0.10	0.17	0.68	0.32	0.24	3

of 1 kOe in a range of 0-15 kOe and with temperature steps of 2-3 K over a temperature range around the magnetic phase transition.

3. Results and discussion

In Fig. 2, the isothermal magnetization curves for La_{0.56}Ca_{0.24}Mn_{1.2}O₃ manganite at different temperatures near $T_{\rm C}$ over a magnetic field range of 0–15 kOe are presented. The experimental M(H) dependences were transformed into H/M versus M^2 plots in a temperature range of 238–273 K which were used to determine spontaneous magnetization and the Curie temperature. The temperature dependence of spontaneous magnetization (Fig. 3) was determined by fitting to the experimental Arrot plots for $T < T_{\rm C}$ [23] and by their extrapolation to H = 0.



Fig. 2. Magnetic field dependence of magnetization of $La_{0.56}Ca_{0.24}Mn_{1.2}O_3.$

It is seen that at the phase transition temperature, $T_{\rm C}=267$ K, the ferromagnetism abruptly and rapidly develops. The relatively narrow temperature interval of the PM–FM phase transition is observed, while there is no temperature hysteresis. Therefore the transition observed can be identified as a second-order transition close to a first-order one. The Curie temperature is found to increase insignificantly with increasing Mn content (Table II).

TABLE II

Maximum entropy change $(|\Delta S_{\rm M}^{\rm max}|)$, relative cooling power $({\rm RCP}(S))$ at the Curie temperature $(T_{\rm C})$ in magnetic field (H) for several magnetic materials considered as active refrigerants.

Matarial	Н	$T_{\rm C}$	$ \Delta S_{\mathrm{M}}^{\mathrm{max}} $	$\operatorname{RCP}(S)$	Defenence	
Material	[kOe]	[K]	$[J \ kg^{-1} \ K^{-1}]$	$[\mathrm{J~kg^{-1}}]$	nererence	
$La_{0.70}Ca_{0.30}Mn_{1.0}O_3$	15	263	1.55	39.8	present work	
$La_{0.63}Ca_{0.27}Mn_{1.1}O_{3}$	15	265	1.97	59.2	present work	
$La_{0.56}Ca_{0.24}Mn_{1.2}O_{3}$	15	267	3.09	42.5	present work	
$La_{0.70}Ca_{0.30}MnO_3$	10	256	1.38	41	[8]	
$La_{0.70}Ca_{0.18}Ba_{0.12}MnO_{3}$	10	298	1.85	45	[5]	
$\mathrm{La}_{2/3}(\mathrm{Ca,Pb})_{1/3}\mathrm{MnO}_3$	20	290	3.6	90	[24]	
$La_{0.70}Ca_{0.25}K_{0.05}MnO_{3}$	20	270	3.95	87	[25]	
${\rm La}_{0.62}{\rm Ca}_{0.33}{\rm Bi}_{0.05}{\rm MnO}_3$	10	246	3.5	53	[26]	

The magnetocaloric effect (MCE) was evaluated from the isothermal curves of magnetization versus the applied magnetic field. According to thermodynamic theory (see e.g. [3]), the total magnetic entropy change $\Delta S_{\rm M}(T, H)$ of the magnetic system during the isothermal magnetization processes in magnetic field H is given by relation

$$\Delta S_{\rm M}(T,H) = S_{\rm M}(T,H) - S_{\rm M}(T,0)$$
$$= \int_0^{H_{\rm max}} \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H,\tag{1}$$

where H_{max} is the maximum external field.



Fig. 3. The temperature dependence of the spontaneous magnetization of $La_{0.56}Ca_{0.24}Mn_{1.2}O_3$ sample.

Figure 4 shows the magnetic entropy change, $\Delta S_{\rm M}(T, H = 15 \text{ kOe})$, around the PM–FM transition as a function of temperature for all the compounds studied. The $|\Delta S_{\rm M}^{\rm max}|$ value at the PM–FM phase transition is seen to increase with increasing manganese content.

The MCE peak occurs near $T_{\rm C}$, where $|(\partial M(T, H)/\partial T)_H|$ is the greatest. The La_{0.56}Ca_{0.24}Mn_{1.2}O₃ manganite exhibits the largest $|\Delta S_{\rm M}^{\rm max}|$ value equal to 3.09 J kg⁻¹ K⁻¹ at 15 kOe.

As was mentioned above, the magnetic properties of



Fig. 4. The magnetic entropy change as a function of temperature near $T_{\rm C}$ in magnetic field of 15 kOe for La_{0.70}Ca_{0.30}Mn_{1.0}O₃ (filled triangles), La_{0.63}Ca_{0.27}Mn_{1.1}O₃ (open circles) and La_{0.56}Ca_{0.24}Mn_{1.2}O₃ (stars).

manganite oxides including magnetization and magnetic entropy change are defined first of all by the double exchange interaction between the Mn³⁺ and Mn⁴⁺ ions. In Table I, it is seen that as a result of increase of nonstoichiometry with increasing x, the Mn⁴⁺/Mn³⁺ ratio increases. The increase of Mn⁴⁺/Mn³⁺ ratio as well as change in Mn–O bond length and Mn–O–Mn bond angle in distorted cubic structure of perovskite are the reason of increase of both the double exchange interaction between the Mn⁴⁺ and Mn³⁺ ions and magnetization. Because of this, the magnetic entropy ΔS change is the greatest in compound with Mn_{1.2}, that it is clearly seen in Fig. 4 and Table II. The narrow width of MCE in La_{0.56}Ca_{0.24}Mn_{1.2}O₃ is obviously also related to modification of the Mn–O–Mn bond angle and Mn–O bond length responsible for increasing ferromagnetic coupling.

The magnetic entropy change for the $La_{0.56}Ca_{0.24}Mn_{1.2}O_3$ sample as a function of temperature near $T_{\rm C}$ for different applied fields: 5, 10 and



Fig. 5. Comparison of the magnetic entropy change for $La_{0.56}Ca_{0.24}Mn_{1.2}O_3$ at different magnetic fields: 5 kOe (filled triangles), 10 kOe (open circles), and 15 kOe (stars).

15 kOe is presented in Fig. 5, which displays a strong influence of a magnetic field on the magnetic entropy change. With increasing magnetic field, the maximum magnetic entropy change slightly shifts towards a higher temperature.

The cooling efficiency of magnetocaloric material can be calculated as [6, 8]:

$$\operatorname{RCP}(S) = -\Delta S_{\mathrm{M}}(T, H) \delta T_{\mathrm{FWHM}}, \qquad (2)$$

where $\Delta S_{\rm M}^{\rm max}$ is the maximum magnetic entropy change and $\delta T_{\rm FWHM}$ the full width at half-maximum of $\Delta S_{\rm M}^{\rm max}$.

Figure 6 presents a comparison of relative cooling power calculated by Eq. (2) for our compounds. The RCP(S) reaches the maximum value of 59.2 J kg⁻¹ in 15 kOe field for the $La_{0.63}Ca_{0.27}Mn_{1.1}O_3$ manganite and has almost the same value for two other compositions.



Fig. 6. Relative cooling power RCP(S) as a function of magnetic field for all compounds.

Comparison of the maximum entropy change $(|\Delta S_{\rm M}^{\rm max}|)$ and relative cooling power $({\rm RCP}(S))$ occurring at the Curie temperature $(T_{\rm C})$ in magnetic field

(H) for several La–Ca based manganites considered as active refrigerants is present in Table II.

4. Conclusions

In present work, the investigations of magnetization and magnetocaloric effect in $(La_{0.7}Ca_{0.3})_{1-x}Mn_{1+x}O_3$ $(x = 0 \ 0.1 \ 0.2)$ compounds have been performed. On the basis of the ionic structure analysis taking into account both the extent of occupation of the A and B sites and fulfillment of an electroneutrality condition at oxidation-reduction processes, the molar contents of La^{3+} , Ca^{2-} , Mn^{2+} ions, and cationic vacancy $V_A^{(c)}$ at the A sites, Mn^{3+} and Mn^{4+} ions, and anion vacancy $V_B^{(a)}$ at the B sites in the defect perovskite structure of $(La_{0.7}Ca_{0.3})_{1-x}Mn_{1+x}O_3$ samples vs. manganese content were determined.

The magnetocaloric effect was evaluated from the isothermal curves of spontaneous magnetization versus the applied magnetic field by using the well-known thermodynamical Maxwell relation. A strong influence of nonstoichiometry caused by an excess of manganese on magnetic entropy value was established. The maximum entropy change, $|\Delta S_{\rm M}^{\rm max}|$, near the ferromagnetic-paramagnetic phase transition increases and temperature width of MCE decreases with increasing manganese content that correlates with the narrow magnetocaloric effect reported for single crystal [8, 27].The La_{0.56}Ca_{0.24}Mn_{1.2}O₃ compound exhibits the largest $|\Delta S_{\rm M}^{\rm max}|$ value equal to 3.09 J kg⁻¹ K⁻¹ at 15 kOe near $T_{\rm C}$ = 267 K. The cooling power $\operatorname{RCP}(S)$ reaches the maximum value of 59.2 J kg⁻¹ in 15 kOe field for $(La_{0.7}Ca_{0.3})_{0.9}Mn_{1.1}O_3$. The MCE and RCP(S) values for manganites studied are comparable with those for another La–Ca-based manganites reported in literature which allows to propose that the $(La_{0.7}Ca_{0.3})_{1-x}Mn_{1+x}O_3$ compounds, especially (La_{0.7}Ca_{0.3})_{0.8}Mn_{1.2}O₃, are promising materials for future cooling application.

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