STRUCTURAL AND MAGNETIC PROPERTIES OF PARTIALLY ORDERED Pr$_{0.5}$Ba$_{0.5}$Mn$_{1.9}$Ti$_{0.1}$O$_{3-\delta}$ MANGANITE

S.Kh. Estemirova$^{a,b}$, V. Ya. Mitrofanov$^{a,b}$, S. A. Uporov$^{a,b}$, G.A. Kozhina$^{a,b}$, K.Yu. Shunyaev$^{a,b}$

$^a$Institute of Metallurgy, Ural Branch of the Russian Academy of Sciences, 101 Amundsen St., Ekaterinburg 620016, Russia
$^b$Ural Federal University, 19 Mira St., 620002, Ekaterinburg, Russia

ABSTRACT

Structural and magnetic properties of partially ordered Ba- and Ti-substituted PrBaMn$_{1.9}$Ti$_{0.1}$O$_{6-\delta}$ manganites with oxygen content $\delta = 0, 0.02, 0.09$ were investigated in a wide temperature range. The tetragonal crystal structure of all samples is stable in the temperature range of 100-1073 K. In the range of $T = 170-190$ K, a structural anomaly was detected (the appearance of a superstructural peak at $2\theta \sim 24.5^\circ$). The nature of the anomaly has not been established and requires additional research. The magnetic entropy change in samples with $\delta = 0, 0.02, 0.09$ were calculated from magnetic field dependences of magnetization obtained at different temperatures from 5 to 300 K. A relatively large value of the magnetocaloric effect (MCE) over a wide temperature range was established. The MCE characteristics are significantly reduced for the sample with $\delta = 0.09$ in comparison with the stoichiometric one. It has been shown that the maximum change in magnetic entropy and relative cooling power (RCP) increase monotonically with increasing magnetic field and reach values $\sim 1.4$ J/kg K and 240 J/kg, respectively, at $\mu_0 \Delta H = 5$ T for samples with $\delta = 0, 0.02$.

Keywords: rare-earth manganites, structural and magnetic properties, magnetocaloric effect.

INTRODUCTION

One of the main tasks of ensuring environmental safety is to limit emission of wastes from various industries and technologies to the atmosphere and hydrosphere. These include cooling technologies that use traditional refrigerants which destroy the ozone layer of the earth. A radically new approach is the magnetic cooling technology employing solid-state materials (alloys, intermetallics, oxides) which exhibit magnetocaloric effect (MCE). These materials are not only environmentally friendly, but also economically and technologically more profitable.

Substituted rare-earth manganites are materials with magnetocaloric effect. By varying the chemical composition, it is possible to obtain manganites with different MCE characteristics over a wide temperature range. Along with varying chemical composition, one more parameter can control properties of half-doped R-Ba-manganites: the ordering of the R$^{3+}$ and Ba$^{2+}$ cations to create a sandwich structure where the MnO$_2$ layer is between the RO and BaO layers. The result of the ordering is a distortion of the MnO$_6$ octahedron, which leads to a change in the structural and physical properties [1-5]. At present, the ordered basic compound of RBaMn$_2$O$_6$ has been studied in detail. It was of interest to study the structural and magnetic properties of RBaMn$_2$O$_{6-\delta}$ double manganite with a partial (fixed) replacement of manganese.
and varying oxygen content ($\delta$). In the present work, Ti-substituted double praseodymium-barium manganite was chosen.

1 EXPERIMENT

The polycrystalline $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{Mn}_{0.95}\text{Ti}_{0.05}\text{O}_{3+\delta}$ compound was synthesized by ceramic technology from praseodymium, manganese, titanium and barium oxides with purity not lower than 99.95% at $T = 1550^\circ$C. The ordered double manganite $\text{PrBaMn}_{1.9}\text{Ti}_{0.1}\text{O}_6$ was obtained by the method of topotactic reactions [4], which included the reduction of $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{Mn}_{0.95}\text{Ti}_{0.05}\text{O}_{3+\delta}$ to $\text{PrBaMn}_{1.9}\text{Ti}_{0.1}\text{O}_5$ ($\text{Ar/O}_2$ mixture, $\text{P}_{\text{O}_2} = 10^{-18}$ atm., $T = 950 ^\circ$C) and its subsequent oxidation in an oxygen atmosphere at $T = 800 ^\circ$C.

To obtain solid solutions with different oxygen content, the samples were annealed at $T = 950 ^\circ$C, $\text{P}_{\text{O}_2} = 1$ (hereafter S1 sample), $\text{P}_{\text{O}_2} = 10^{-5}$ atm. (hereafter S2 sample) and $10^{-10}$ atm. (hereafter S3 sample).

Structural studies were performed by XRD in the range of 80–1073 K using a Shimadzu XRD-7000 diffractometer equipped with low and high temperature chambers in Cu$K_\alpha$ radiation. The study of magnetic properties was performed using a vibrating sample magnetometer (VSM). The temperature dependences of the magnetization $M(T)$ were obtained in the ZFC and FC modes in an external magnetic field of 0.01 T in the temperature range from 4 K to 300 K. The isothermal magnetization curves were measured in fields up to 5 T at various temperatures.

2 RESULTS AND DISCUSSION

2.1 Structural properties of $\text{PrBaMn}_{1.9}\text{Ti}_{0.1}\text{O}_{6-\delta}$ ($\delta = 0.00, 0.02, 0.09$)

All synthesized compounds had a tetragonal crystal structure, space group P4/mmm. The content of the impurity phase of barium manganate was less than 0.5%. Diffraction patterns of all samples are presented in Fig. 1.

A decrease in the oxygen content occurs without a change in the crystal structure, but is accompanied by an increase in the half-width of the diffraction lines due to an increase in the concentration of oxygen vacancies.

The unit-cell parameters were calculated from the Bragg line positions using the least squares method. The results of the analysis, as well as the parameter of oxygen nonstoichiometry are presented in table 1.
It is known that the disordered composition \((\text{Pr}_{0.5}\text{Ba}_{0.5})\text{MnO}_3\) crystallizes in a cubic system, space group \(\text{Pm\text{-}3m}\). Ordering leads to a phase transition from a cubic to a tetragonal structure (space group \(\text{P4/mmm}\)) with the doubled (compared to the initial cubic) parameter \(c\). In this case, the peak \((0\ 0\ 1/2)\) appears at small angles \((2\Theta\sim12.5^\circ)\), the intensity of which is the higher, the higher the degree of ordering of \(\text{Pr}\) and \(\text{Ba}\) [5].

Tab. 1. Unit cell Parameters of the \((\text{space group P4/mmm})\) and oxygen content (parameter \(\delta\)) of solid solution \(\text{PrBaMn}_{1.9}\text{Ti}_{0.1}\text{O}_{6-\delta}\).

<table>
<thead>
<tr>
<th>Sample</th>
<th>(a), Å</th>
<th>(c), Å</th>
<th>(V), Å(^3)</th>
<th>(\delta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>3.900 (2)</td>
<td>7.794 (9)</td>
<td>118.5 (2)</td>
<td>0.00</td>
</tr>
<tr>
<td>S2</td>
<td>3.903 (8)</td>
<td>7.804 (8)</td>
<td>118.8 (2)</td>
<td>0.02</td>
</tr>
<tr>
<td>S3</td>
<td>3.907 (1)</td>
<td>7.807 (6)</td>
<td>119.0 (2)</td>
<td>0.09</td>
</tr>
</tbody>
</table>

X-ray diffraction analysis of all samples shows that the intensity of this peak is low, and high-intensity Bragg peaks do not have well-defined splitting. This may indicate a low degree of ordering of the praseodymium and barium ions in a single-phase tetragonal material. It is also possible that the material contains both cubic and tetragonal phases, or tetra-phases with different degrees of tetragonal distortion.

Structural studies performed in the range of 80–1073 K in the heating mode (Fig. 2) show an increase in the unit cell parameters with increasing temperature.
Fig. 2. Temperature dependence of the unit cell parameters of samples S1 (a, b), S2 (c, d), S3 (e, f). The dashed line is a refinement of the temperature dependence with polynomials of the first and third degree.

The parameters and volume of the unit cell for the S3 sample increase linearly with temperature over the entire temperature range (Fig. 2 e, f). For S1 and S2 samples, a part of the temperature dependence above 450 K can be described by a linear function. Below this temperature, the dependence is described by a polynomial of the third degree.
Fig. 3. Fragments of diffraction patterns of samples PrBaMn$_{1.9}$Ti$_{0.1}$O$_{6-\delta}$ ($\delta=0.00, 0.02, 0.09$) at different temperatures, showing a superstructural peaks.

Below 200 K in a small temperature range, a low-intensity peak is observed near $2\Theta \sim 24.5^\circ$ in the diffractograms of all samples (Fig. 3). It cannot be associated with a change in the symmetry of the crystal structure, since all the main lines of the X-ray profile remain within the tetragonal symmetry (space group P4/mmm). The appearance of this peak may indicate subtle changes in the crystal structure, for example, the displacement of atoms from their positions in the crystal structure and the formation of modulated crystals [6]. The temperature range of the existence of this "special" crystalline state decreases with decreasing oxygen content in the composition (Fig. 3). Determining the nature of this state requires additional research.

2.2. Magnetic properties of PrBaMn$_{1.9}$Ti$_{0.1}$O$_{6-\delta}$ ($\delta=0.00, 0.02, 0.09$)

Significant differences in the magnetic properties correspond to the ordered and disordered states of praseodymium-barium manganite. Unordered Pr$_{0.5}$Ba$_{0.5}$MnO$_3$. $\delta$ at room temperature is a paramagnetic and goes into a ferromagnetic state at $T_C \sim 150$ K. After ordering, the same composition becomes a ferromagnet at room temperature ($T_C = 310$K), however, when cooled, it passes into an antiferromagnetic state at $T_N = 250$ K [3, 4].

The temperature dependences of the magnetization of the Pr-compound doped with titanium ions (sample S2), measured in the ZFC and FC modes at $\mu_0H = 0.01$ T, are shown in Fig. 4. The Curie ordering temperature, $T_C$, was determined as the temperature at which the $d\chi/dT$ vs $T$ in the FCC mode reaches a minimum (not shown). The result obtained for $T_C$ is $T_C(S2)=86\pm41$ K. The wide minimum on the
$d\chi/dT$ curve reflects substantial inhomogeneity of the sample, i.e. different parts of the powder have a different magnetic field response at the same temperature.

Fig. 4. Temperature dependences of sample magnetization S2, measured in ZFC and FCC modes at $\mu_0H = 0.01$ T.

Figure 5 shows magnetic field dependences of magnetization at 5 K for samples S1, S2 and S3. The shape of $M(H)$ plots for samples S1 and S2 is indicative of the presence of FM ordering. From table 2 it follows that with decreasing oxygen content the values of spontaneous magnetization $M_S$ and $M(5T)$ decrease. The most significant changes are observed for sample S3.

Fig. 5. Magnetic field dependences of magnetization for samples S1, S2 and S3 at 5 K.

Tab. 2 Spontaneous magnetization $M_S$ and magnetization at $\mu_0H=5$ T ($M(5T)$) at $T=5$ K for samples S1, S2 and S3.

<table>
<thead>
<tr>
<th></th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M(5T)$, emu/g</td>
<td>55.3</td>
<td>52.6</td>
<td>21.1</td>
</tr>
<tr>
<td>$M_S$, emu/g</td>
<td>50.3</td>
<td>46.1</td>
<td>9.9</td>
</tr>
</tbody>
</table>

Magnetic field dependences of magnetization were measured in the magnetic field range of 0-5 T and the temperature range 4–300 K with a temperature interval $\Delta T=10$ K and steps in a magnetic field of 0.1 T. In particular, the isothermal magnetization plots of sample S2 are shown in Fig. 6a. To ensure the readability of the Fig. 6, the isotherms and Arrott plots (Fig. 6b) are shown only at temperature intervals of $\Delta T=20$ K. No saturation magnetization is achieved for all the $M(H)$ curves at low temperatures in spite of using high magnetic fields up to 5 T. At the temperatures far above $T_C$, a true paramagnetic behavior is observed, but the $M(H)$
curves at temperatures closer to $T_C$ do not show such behavior indicating the coexistence of short-range FM interactions or FM clusters in samples.

Fig. 6. Magnetic field dependences of magnetization of sample S2 (a); Arrott plots obtained from $M$ vs $\mu_0H$ isotherms of sample S2 (b).

In order to analyze the magnetic properties of sample S2 in detail we plot the so-called Arrot curves [7] represented in the form $H/M$ vs $M^2$ in a wide temperature range (Fig. 6b). In disordered systems a magnetic heterogeneity and distribution of $T_C$ can lead to bending plots. According to Bannerjee's criterion [8], a negative or positive sign of the slope of Arrott plots corresponds to a first-order or second-order magnetic phase transition, respectively. The results obtained for sample S2 show clearly the positive slope in the entire $M^2$ range indicating a second-order magnetic phase transition. Similar results were also obtained for samples S1 and S3 (not shown).

The magnetic entropy change associated with an applied magnetic field variation was calculated from the isotherms of magnetization versus applied field by using the following approximation [9-11]:

$$|\Delta S_M| = \sum (M_n - M_{n+1})_H \Delta H_n,$$

where $M_n$ and $M_{n+1}$ are values of magnetization at temperatures $T_n$ and $T_{n+1}$, respectively, in the applied field $H$. Fig. 7 shows the temperature dependences of magnetic entropy change $|\Delta S_M(T)|$ for samples S1, S2, S3 with changes in the applied magnetic field from 1T to 5 T. It is easy to see that the magnetic entropy change significantly depends on the magnetic field span and exhibits a broad variation with temperature around $T_C$. The largest changes in $|\Delta S_M(T)|$ occurs in the vicinity of the transition temperature $T_C$ and the effect increases with increasing $\mu_0\Delta H$. The maximum entropy changes $|S_M^{\text{max}}|$ are determined from the peaks ($T_{\text{peak}}$) in Fig. 7 and plotted as a function of $\mu_0\Delta H$ in Fig. 8a.
Fig. 7. Temperature dependence of the magnetic entropy change $\Delta S_M(T)$ for samples S1, S2 and S3 for different values of the magnetic field.

It is easy to see that $\max |S_M|$ of all studied samples is directly proportional to magnetic field. For each composition, the peak position shifts to high temperatures with increasing magnetic field (Fig. 8b).

Majority of doped manganites show that the peak position of $|\Delta S_M(T)|$ is nearly unaffected because of the second-order nature of the FM–PM transition. In the case of S1, S2 and S3 samples, we encounter with a slightly different situation – the MCE attained a maximum $\Delta S_M^{\text{max}}$ above the FM–PM transition temperature. The numerical calculations using the Arrott–Noakes equation of state by Franco et al. [12] show that the Curie point ($T_C$) and the temperature where the magnetic entropy change is maximum ($T_{\text{peak}}$) coincide only in the mean field approximation. The Heisenberg model implies that $T_{\text{peak}}>T_C$ even for homogeneous materials.
It is well known that an effective MCE material should have a large $\Delta S_M^{\text{max}}(T)$ value in a wide temperature range. Based on this requirement, the cooling efficiency of a magnetic refrigerant is estimated with the so-called relative cooling power (RCP), defined as the amount of heat transferred between the hot and cold reservoirs. RCP is defined as follows:

$$\text{RCP} = (-S_M^{\text{max}}) \times \Delta T_{\text{FWHM}},$$

where $\Delta T_{\text{FWHM}}$ is the full-width at half-maximum of $(-S_M^{\text{max}})$. The dependences of RCP and $\Delta T_{\text{FWHM}}$ on the magnetic field are shown in Fig. 9a and 9b, respectively.

Figure 9a shows that the RCP values are directly proportional to the magnetic field. Since the transition range broadens in higher applied magnetic fields, $\Delta T_{\text{FWHM}}$ increases with the increase of magnetic field (Fig. 9b). RCP reach the values about $\sim 240 \text{ Jkg}^{-1}$ under an applied field of 5 T for samples S1 and S2. Therefore, one can consider that PrBaMn$_{1.9}$Ti$_{0.1}$O$_{6-\delta}$ exhibits a substantial MCE over a wide temperature range, conferring to this compound an interesting potential for magnetic refrigeration.

It should be noted that additional factors affecting MCE, including chemical homogeneity, minority phases and magnetic anisotropy, distribution of crystal defects, lattice stresses, Curie temperature distribution, the experimental errors can play a significant role.
CONCLUSION

The chemically single-phase, partially ordered Ti-substituted compositions \( \text{PrBaMn}_{1.9}\text{Ti}_{0.1}\text{O}_{6-\delta} \) with oxygen content \( \delta = 0, 0.02, 0.09 \) with a tetragonal structure are obtained, the parameters of which increase with decreasing oxygen content. The crystal structure is tetragonal in the range 80–1073 K. However, a structural anomaly was detected in the range \( T = 170–190 \) K (the appearance of a superstructural peak at \( 2\theta \sim 24.5 \) °), which correlates with the maximum on the \( d\chi/dT \) curve at 180 K for sample S2. The nature of these anomalies requires additional studies. A relatively large value and a wide temperature range of the magnetocaloric effect (MCE) have been established. The MCE characteristics are significantly reduced for the sample with \( \delta = 0.09 \) in comparison with the stoichiometric sample. It is shown that the maximum change in magnetic entropy and relative cooling power (RCP) increase monotonically with increasing magnetic field and reach values of \( \sim 1.4 \) J / kg K and 240 J / kg, respectively, at 5 T for samples \( \delta = 0.00, 0.02 \).

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