THE LARGE MAGNETOCALORIC EFFECT ABOVE ROOM TEMPERATURE IN MANGANITES (La$_{1-x}$Pr$_x$)$_{0.67}$Pb$_{0.33}$MnO$_3$

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1. Introduction

The discovery of Magnetocaloric Effect (MCE) in perovskite Ln$_{1-x}$A$_x$BO$_3$ (Ln = rare earths, A = alkaline elements, B = Mn or Co) associated with the ferromagnetic-to-paramagnetic transition at the Curie temperature ($T_c$) has attracted considerable attention [1, 2]. In recent years, the MCE has not only been studied in cobaltite but also in manganite [3-5]. Hwang et al. have studied the crystal structure and magnetic scaling behavior of La$_{1-x}$Pb$_x$MnO$_3$ perovskites ($x = 0.0 \div 0.5$) and have shown that all the samples crystallize on the rhombohedral structure [6]. In our previous work [7, 8], two systems La$_{1-x}$Pb$_x$MnO$_3$ and Pr$_{1-x}$Pb$_x$MnO$_3$ ($x = 0.0 \div 0.5$) have been investigated. In the case of La$_{1-x}$Pb$_x$MnO$_3$, the samples have symmetry decreased from cubic ($x = 0.5$) to rhombohedral ($x = 0.4$) and triclinic ($x = 0.3, 0.2, 0.1$). The maximum value of magnetic entropy change, $|\Delta S_m|_{\text{max}}$, is found to be 1.53 J/kg.K for the sample $x = 0.3$ ($T_c = 358$ K). Especially in the second system, all the samples have orthorhombic structure and with $x = 0.1$ the sample exhibits the giant magnetocaloric effect (GMCE), $|\Delta S_m|_{\text{max}}$ reached 3.68 J/kg.K. In this work we report our investigation of structure, magnetic property and magnetocaloric effect in manganites (La$_{1-x}$Pr$_x$)$_{0.67}$Pb$_{0.33}$MnO$_3$ ($x = 0.0, 0.5$).

2. Experimental procedure

The manganites La$_{0.67}$Pb$_{0.33}$MnO$_3$ (N°1) and (La$_{0.3}$Pr$_{0.1}$)$_{0.67}$Pb$_{0.33}$MnO$_3$ (N°2) were prepared by using a conventional powder solid-state reaction method. The structure of the samples was examined by Bruker X-ray Diffractometer D5005. The microstructure and chemical composition were studied in a 5410LV Jeol Scanning Electron Microscope (SEM), which includes an energy dispersion spectrometer (EDS). The magnetization measurements were performed with VSM DMS 880 Digital Measurement Systems.

3. Results and discussion

![Fig.1. SEM pictures of the surface of studied sample.](image1)

![Fig.2. X-ray diffraction patterns of studied samples.](image2)
In order to prevent the evaporation of Pb during the synthesis, presintering and sintering processes were performed at not too high temperature. The SEM pictures in Fig. 1 showed that the samples are homogeneous and there is no melting of samples. Without and with an amount of Pr substituted for La, the grain size still remains, about 0.7 μm. The EDS spectrum of the studied samples (not shown here) indicates that there are no strange elements and the sample compositions are similar to the nominal ones.

Fig. 2 presents the X-ray diffraction patterns of the studied samples. We can see that both samples are of single phase and no impurity peak was observed in the power diffraction patterns. The crystallographic structure analysis using X-ray diffraction shows that the sample N°1 has triclinic symmetry. The amount of Pr substituting for La in the sample N°2 results in decreasing of average ionic radius, \(<r_A>\), therefore changes the structure symmetry from triclinic to orthorhombic. The lattice parameters of studied samples are displayed in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(&lt;r_A&gt;) (Å)</th>
<th>(a) (Å)</th>
<th>(b) (Å)</th>
<th>(c) (Å)</th>
<th>(α) (°)</th>
<th>(β) (°)</th>
<th>(γ) (°)</th>
<th>(V) (Å³)</th>
<th>(T_C) (K)</th>
<th>(T_r) (K)</th>
<th>(T_c) (K)</th>
</tr>
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<tbody>
<tr>
<td>N°1</td>
<td>5.586</td>
<td>5.498</td>
<td>5.565</td>
<td>5.713</td>
<td>90.00</td>
<td>90.00</td>
<td>90.56</td>
<td>351.0</td>
<td>345</td>
<td>300</td>
<td>310</td>
</tr>
<tr>
<td>N°2</td>
<td>5.492</td>
<td>5.498</td>
<td>5.565</td>
<td>7.754</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>335.4</td>
<td>310</td>
<td>300</td>
<td>315</td>
</tr>
</tbody>
</table>

The zero-field-cooled (ZFC) and field-cooled (FC) magnetization measurements were carried out in the applied field of 20 Oe. Fig. 3 shows that the ZFC and FC magnetization curves of two samples are separated from each other at low temperatures, i.e. the samples exhibit the spin glass-like state. The doping of Pr for La causes an asynchrony in structure and lead to the decreasing of internal magnetization. Hence, the ZFC and FC curves are separated strongly in the sample N°2 at low temperature range.

The temperature at which the ZFC and FC magnetization curves are splitted is called irreversibility temperature, \(T_r(<T_C)\) [9]. The magnitude of the splitting and the temperature \(T_r\) decrease with increasing external field. In addition, the low field ZFC magnetization curves show a cusp at a so-called spin freezing (or spin-glass transition) temperature \(T_x\). Similar to \(T_r\) temperature, \(T_x\) also shifts to a lower temperature and the cusp in the ZFC curve is smeared out to broad maximum. The nature of these phenomena is the competition between (local) anisotropy (decreasing with increasing temperature, so allowing an increasing of magnetization) which is the reason of decreasing magnetic order, when temperature is approached \(T_C\). The \(T_C\) decreases from 345 K (N°1) to 310 K (N°2) when Pr is half doped for La. Therefore, with smaller \(<r_A>\) in sample N°2, \(T_c\) of the sample is decreased [10].
To evaluate the magnetic entropy change, $\Delta S_m$ vs. $H$ isotherms of two samples have been measured at various temperatures around the $T_c$ in applied field up to 13.5 kOe. The isothermal entropy change can be calculated by the thermodynamic relation [11]:

$$\Delta S(T, H) = S(T, 0) - S(T, H) = \int_{0}^{H_{\text{max}}} \frac{\partial M(T, H)}{\partial T} dH$$

where, $S(T, 0)$ and $S(T, H)$ are the entropy without and with applied magnetic field, respectively.

The magnetic entropy change as a function of temperature for studied samples is presented in Fig. 4. The values of $|\Delta S_m|_{\text{max}}$ for two samples are quite high, reached 1.86 J/kg.K ($N^{01}$) and 1.45 J/kg.K ($N^{02}$). Pr substituted for La leads to slightly decreasing of $|\Delta S_m|_{\text{max}}$. These materials can be considered as good magnetic refrigerant materials operating at temperatures above room temperature. Note that the maximum of the applied magnetic field is just 13.5 kOe.

4. Conclusions

The manganites $(La_{1-x}Pr_x)_{0.67}Pb_{0.33}MnO_3$ ($x = 0.0, 0.5$) were prepared with single-phase triclinic and orthorhombic structure, respectively. There is spin glass-like state occurring in the samples. The $T_c$ for the sample $N^{01}$ is 345 K and the sample $N^{02}$ is 310 K. Two samples are considered as large-magnetocaloric materials working at above room temperatures.

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References