Synthesis and Properties of Pr$_{1-x}$Rb$_x$MnO$_3$ (0.05 ≤ x ≤ 0.08) with Perovskite-Type Structure

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Abstract: Rb-substituted Pr$_{1-x}$Rb$_x$MnO$_3$ (0.05 ≤ x ≤ 0.08) was successfully synthesized by solid state reaction. Powder X-ray diffraction showed that all the compounds were orthorhombic with the space group of Prma. Spin glass behaviors were observed for all the compounds at low temperature, suggesting the competition between ferromagnetic and antiferromagnetic. The temperature dependence of the resistivity for the compound Pr$_{0.95}$Rb$_{0.05}$MnO$_3$ at 0 and 2 T magnetic field was also investigated. The compound shows semiconducting behavior, and the band gap is 0.3 eV. The maximum magnetoresistance is about 30% at 2 T magnetic field near 116 K.

Key words: Perovskite, Spin glass behavior, Semiconductor, Magnetoresistance

I. INTRODUCTION

In the last several decades, there has been a great interest in the development of new materials with the Mn containing perovskite structure because of their uniquely magnetic and electrical properties. Stoichiometric LaMnO$_3$ shows antiferromagnetic and semiconducting behavior, while La$_{1-x}$A$_x$MnO$_3$ (A=Ca, Sr, Ba and Pb) shows a paramagnetic to ferromagnetic transition coupled with an insulator to metal transition. This transition was first reported by Jonker and Vansanten [1, 2] and was also found for their rare-earth homologues. Zener proposed the mechanism of this transition on double exchange interaction [3]. The origin of the ferromagnetism is due to the order of spin moment S=3/2 in the 3d$_{5/2}$ orbital of Mn via transfer of the 3d$_{3/2}$ electrons through the 2p$_{σ}$ orbital of the oxygen ion located at the center of two Mn ions in the perovskite type structure.

Another remarkable property of these compounds is the so-called colossal magnetoresistance (CMR) [4-13]. CMR is a property of some materials, mostly manganese-based perovskite oxides, that enables them to dramatically change their electrical resistance in the presence of a magnetic field. The magnetoresistance of conventional materials enables changes in resistance of up to 5%, but materials featuring CMR may demonstrate resistance changes by orders of magnitude. For example, in bulk La$_{1-x}$Sr$_x$MnO$_3$, a reduction of resistance with more than three orders in magnitude is reported [4].

Recently alkali metal substituted LnMnO$_3$ have also been studied. Because of its +1 valence state, alkali metal can induce the increase in valence state of Mn more efficiently. La$_{1-x}$A$_x$MnO$_3$ (A=Na, K, or Rb) systems reported by Shimura et al. [14] showed similar properties to divalent ion substituted lanthanum manganites. Na- and K-substituted PrMnO$_3$ have also been studied by Jirak et al. and Shivakumara et al. [15, 16]. In this work, Rb-doped PrMnO$_3$ was prepared, and its electrical and magnetic properties were investigated.

II. EXPERIMENTS

Pr$_{1-x}$Rb$_x$MnO$_3$ compounds were prepared by a conventional solid state reaction method. Pr$_6$O$_{11}$ (99.9%, Sinopharm Chemical Reagent Co., Ltd.), Rb$_2$CO$_3$ (99.5%, Sichuan State Lithium Materials Co., Ltd.) and MnCO$_3$ (99%, Sinopharm Chemical Reagent Co., Ltd.) were weighted in the nominal compositions of Pr$_{1-x}$Rb$_x$MnO$_3$ (x=0.05, 0.10, 0.15) with an excess of 100% of Rb$_2$CO$_3$ to compensate the loss due to evaporation. The mixed powders were calcined in air at 850, 1000, and 1100 °C for 24 h with intermediate grinding, and then were pressed into pellets and sintered at 800 °C for 48 h in the oxygen flow. Finally, the products were washed with hot distilled water to eliminate soluble impurities and dried at 120 °C in air.

Phase analysis of the products was examined by X-ray diffraction (XRD) using a Philips X’pert Pro Super X-ray diffractometer with Cu Kα radiation (λ=1.54187 Å) at room temperature (40 kV, 30 mA). The XRD data for indexing and cell-parameter calculation were collected in a continuous scan mode with a

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The compositions of the compounds were determined by energy dispersive X-ray (EDX) spectroscopy on a JEOL-2010 transmission electron microscope at an acceleration voltage of 200 kV. The actual Mn$^{4+}$ and oxygen content was determined by the redox titration based on the reduction of Mn$^{3+}$ and Mn$^{4+}$ by Fe$^{2+}$ with the method of Bloom et al. [18]. The magnetic measurements were measured in commercial physical property measurement system (PPMS, quantum design). The temperature dependence of the resistivity for the compound Pr$_{0.92}$Rb$_{0.08}$MnO$_{3.02}$ was measured by a standard four-probe method.

III. RESULTS AND DISCUSSION

A. XRD analysis

The X-ray diffraction patterns of all the compounds reveal that no impurities exist with the initial Pr content from 0.95 to 0.85 (0.05 $\leq x \leq$ 0.15). When $x$ > 0.15, Mn$_3$O$_4$ impurity was observed in the XRD pattern. However, EDX analysis showed that the Rb content of substitution was less than our expectation, and the maximum Rb substitution was 0.08 with the initial Pr to Mn ratio 0.85:1.0 (Table I). The excess Mn seems to be converted into a soluble manganese salt with the excess Rb, since it was found that the distilled water used for washing the products became red-brown quickly in air, moreover, we do not see any detectable impurity phases containing manganese in the XRD patterns. Thus, the range over which single phase compounds could be produced proved to be extremely narrow (0.05 $\leq x \leq$ 0.08) (Table I). This substitution difficulty was also found in other alkali ion substituted lanthanum manganites [15, 16]. It is probably due to the discrepancy of the Pr$^{3+}$ and Rb$^+$, especially the large difference in the ionic radii between Pr$^{3+}$ and Rb$^+$, with Perovskite-Type Structure (Pr$_{1-x}$Rb$_x$MnO$_3$). The temperature dependence of the resistivity for the compound Pr$_{0.92}$Rb$_{0.08}$MnO$_{3.02}$ was measured by a standard four-probe method.

![Graph](image-url)  
FIG. 1 Powder XRD patterns of (a) Pr$_{0.92}$Rb$_{0.08}$MnO$_{3.02}$, (b) Pr$_{0.94}$Rb$_{0.06}$MnO$_{3.02}$, (c) Pr$_{0.95}$Rb$_{0.05}$MnO$_{2.98}$.

![Graph](image-url)  
FIG. 2 Observed (dots), calculated (solid line) and difference (bottom) XRD patterns for Pr$_{0.92}$Rb$_{0.08}$MnO$_{3.02}$.

TABLE I Composition, lattice parameters ($a$, $b$, $c$ and $V$) and content of Mn$^{4+}$ of Pr$_{1-x}$Rb$_x$MnO$_3$.

<table>
<thead>
<tr>
<th>Initial Pr content</th>
<th>Final composition</th>
<th>$a$/Å</th>
<th>$b$/Å</th>
<th>$c$/Å</th>
<th>$V$/Å$^3$</th>
<th>Content of Mn$^{4+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.95 Pr$<em>{0.95}$Rb$</em>{0.05}$MnO$_{2.98}$</td>
<td>5.5299</td>
<td>7.7218</td>
<td>5.4783</td>
<td>233.928</td>
<td>5.2%</td>
<td></td>
</tr>
<tr>
<td>0.90 Pr$<em>{0.94}$Rb$</em>{0.06}$MnO$_{3.02}$</td>
<td>5.4862</td>
<td>7.7298</td>
<td>5.4841</td>
<td>232.565</td>
<td>15.0%</td>
<td></td>
</tr>
<tr>
<td>0.85 Pr$<em>{0.92}$Rb$</em>{0.08}$MnO$_{3.02}$</td>
<td>5.4839</td>
<td>7.7235</td>
<td>5.4720</td>
<td>231.766</td>
<td>20.4%</td>
<td></td>
</tr>
</tbody>
</table>

The lattice parameters of the compounds are summarized in Table I and their XRD patterns are shown in Fig.1. All the compounds can be indexed in the orthorhombic structure with the space group Pnma. The space group of the compounds was confirmed using the FULLPROF program. The observed, calculated and difference of the XRD patterns, for Pr$_{0.92}$Rb$_{0.08}$MnO$_{3.02}$ are given in Fig.2, and the observed pattern is in agreement with the calculated one. The conventional reliability factors, profile factor $R_p$, weighted profile factor $R_{wp}$, expected weighted profile factor $R_{exp}$, Bragg factor $R_B$, and crystallographic factor $R_p$ for the compounds are 12.32%, 11.74%, 6.76%, 3.20%, 3.48% ($x=0.05$); 12.83%, 12.46%, 6.47%, 4.2%, 4.56% ($x=0.06$), and 11.56%, 10.84%, 5.04%, 4.19%, 4.08% ($x=0.08$), respectively. From Table I it can be seen that the unit cell volume decreases with increasing...
B. Magnetic properties

Figure 3 shows the magnetic susceptibilities as a function of temperature for Pr$_{1-x}$Rb$_x$MnO$_3$ at 100 Oe magnetic field. From Fig.3 we can find that the zero-field cooled (ZFC) and field cooled (FC) curves split up at about 130 K. Below 130 K with the decrease of the temperature the magnetic susceptibilities of ZFC curves increase gradually and reach the maximums then decrease. The divergence of the ZFC and FC curves together with the maximums of the ZFC curves suggests that at lower temperatures the compounds show spin glass behavior. At higher temperatures, the compounds are paramagnetic. The temperature at maximum of ZFC curves is called spin-freezing temperature ($T_f$). The $T_f$ of the compounds are 90 K ($x=0.05$), 103 K ($x=0.06$), and 106 K ($x=0.08$) respectively. Spin glass behavior is associated with frustrated systems, resulting from competing interactions. There are Mn$^{3+}$ and Mn$^{4+}$ in Pr$_{1-x}$Rb$_x$MnO$_3$. Superexchange interaction between Mn$^{3+}$/Mn$^{3+}$ and between Mn$^{4+}$/Mn$^{4+}$ would be antiferromagnetic, whereas superexchange or double exchange involving Mn$^{3+}$/Mn$^{4+}$ would be ferromagnetic. These interactions between disordered Mn$^{3+}$ and Mn$^{4+}$ could give rise to frustration and spin glass behavior.

Plots of inverse susceptibility vs. temperature for Pr$_{1-x}$Rb$_x$MnO$_3$ are shown in Fig.4. Plots are linear above 180 K, indicating that the compounds are paramagnetic in this temperature range. The Curie-Weiss constant ($\theta_p$) of the compounds are 121 K ($x=0.05$), 133 K ($x=0.06$), and 142 K ($x=0.08$), respectively. The positive values of the $\theta_p$ suggest that ferromagnetic exchange is dominant in the low temperature range. Figure 5 shows $M$-$H$ loops for Pr$_{1-x}$Rb$_x$MnO$_3$ at different temperatures. The hysteresis loop measured at 5 K displays a typical ferromagnetic behavior and the coercivity force is determined to be 193 Oe (Fig.5(a)). While at 80 K, the coercivity force for the compound is determined to be 11 Oe, which is much smaller than that at 5 K (Fig.5(b)). At higher temperature of 250 K, the linear behavior is observed, because the system has already been in paramagnetic state (Fig.5(c)). Thus, for these compounds, the low temperature state can be described as a ferromagnetic spin glass [20].

C. Electrical properties

The electrical resistivity measured vs. temperature with the four probe method shows that all the compounds were semiconducting. Figure 6 shows the temperature dependence of the resistivity for the Rb ion doping. This phenomenon was also observed in other alkali metal substituted LnMnO$_3$ [15, 16]. The ionic radii of Mn$^{3+}$ ($r_{\text{Mn}^{3+}}=0.53 \text{ Å}, \text{CN}=6$) is smaller than Mn$^{4+}$ ($r_{\text{Mn}^{4+}}=0.58 \text{ Å}, \text{CN}=6$) [19]. In the Pr$_{1-x}$Rb$_x$MnO$_3$, the content of Mn$^{4+}$ increases with increasing Rb content, which result in the volume decrease of the Pr$_{1-x}$Rb$_x$MnO$_3$. DOI:10.1088/1674-0068/23/06/726-730 ©2010 Chinese Physical Society
Pr$_{0.92}$Rb$_{0.08}$MnO$_3$. At low temperature, the compound is insulating. The insulator-metal transition was not found. This may be related to the substitution difficulty which comes from the discrepancy of the Pr$^{3+}$ and Rb$^+$ valencies and the large difference in the ionic radii between Pr$^{3+}$ and Rb$^+$. Further more, Shivakamara et al. found that, at low temperature, the compounds crystallized in orthorhombic structures are insulators and those crystallized in rhombohedral structure will show an insulator-metal transition [16]. This phenomenon was also observed in our compounds. They are all orthorhombic structures and insulators at low temperature. In Fig.6(b), the ln$\rho$ dependence of $T^{-1}$ for Pr$_{0.92}$Rb$_{0.08}$MnO$_3$.02 is given. The band gap calculated from the slope of Fig.6(b) is about 0.30 eV. Figure 7 shows the temperature dependence of the resistivity for the Pr$_{0.92}$Rb$_{0.08}$MnO$_3$.02 at 0 and 2 T magnetic fields. Figure 7(a) is the plot of MR% vs. $T$. The MR% is defined as:

$$\text{MR\%} = \frac{R_0 - R_H}{R_0} \times 100\%$$  \hspace{1cm} (1)$$

where $R_0$ and $R_H$ are the resistance at magnetic fields of 0 and 2 T, respectively. From Fig.7(b), we can find the Pr$_{0.92}$Rb$_{0.08}$MnO$_3$.02 shows a maximum negative MR% of about 30% near 116 K.

IV. CONCLUSION

Pr$_{1-x}$Rb$_x$MnO$_3$ (0.05$\leq$x$\leq$0.08) has been synthesized. Magnetic and electrical properties of these compounds were investigated. The discrepancy of the Pr$^{3+}$ and Rb$^+$, especially the large difference in the ionic radii between Pr$^{3+}$ and Rb$^+$ leads to substitution difficulty of these compounds. All the compounds show spin glass behavior at the low temperature. The compounds are all semiconductors. The band gap of Pr$_{0.92}$Rb$_{0.08}$MnO$_3$.02 is 0.3 eV. The maximum MR% of Pr$_{0.92}$Rb$_{0.08}$MnO$_3$.02 is about 30% at 2 T magnetic field near 116 K.

V. ACKNOWLEDGMENTS

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