Sintering temperature impact on carrier concentration of Pr0.1Ca0.9MnO3 samples

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ABSTRACT

Electron-doped perovskite manganese oxide $Pr_{0.1}Ca_{0.9}MnO_3$ samples were synthesized using Sol-gel reaction method at different temperatures. The results of X-ray diffraction suggest that all the samples are single orthorhombic phase with a perovskite structure. Oxygen contents of all samples were determined by iodometric titration. The results show that oxygen loss increases and sample grain size increases with sintering temperature increasing. Therefore, our study results confirm that the oxygen content and electron concentration can be regulated by adopting different sintering temperature, so as to control ultimately the properties of materials.

Key words: Fiber reinforced; Composites; Case Study; Mechanical Properties

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INTRODUCTION

In recent years, for perovskite manganite's system, more attentions have focused on the hole-doped manganite's which display spectacular colossal magneto resistance (CMR) effect [1-6]. In contrast, less work has been done about electron-doped manganite's [7, 8], which also show interesting phenomena of perovskite manganite's. In these phenomena, CMR properties are very important, because of CMR wide application prospects in electronics. But more difference properties exist between hole-doped and electron-doped manganites. First of all, the physical properties of electron-doped manganites are more sensitive to the concentration of charge carrier [9-11]. Second, for electron-doped manganites, CMR exists only in a narrow range of doping. The physical properties of perovskite manganites $R_{1-x}A_xMnO_3$ system are not only associated with the average A-site cationic radius and A-site cationic size mismatch, but also strongly influenced by concentration of charge carriers. Moreover, the phase diagram of $Pr_{1-x}Ca_xMnO_3$ shows the asymmetry hole-doped and electron-doped region [12]. Therefore, further research about the physical properties of electron-doped manganites is still necessary to understand manganites more thoroughly.
In this paper, we study electron-doped manganite $Pr_{0.1}Ca_{0.9}MnO_3$, by changing the sintering temperature to adjust the oxygen content and concentration of charge carriers.Our results give strong evidence for the influence of sintering temperature on the electron concentration of the samples.

EXPERIMENTAL SECTION

The electron-doped perovskite manganese $Pr_{0.1}Ca_{0.9}MnO_3$ samples were prepared using Sol-gel reaction method at different temperatures. First of all, the stoichiometric of Pr_6O_{11}, precalcinated in air at 800℃, were dissolved then mixed with $Mn(NO)_3$ and $Ca(NO3)_2·4H_2O$ in distilled water. The molar ratio of citric acid and metal cations is 1:1 in solution. Second, the solution was heated and stirred in order to form a gel. The gel was evaporated about 7 h at 120℃to get powder. The powder was ground, pressed pieces and sintered about 12 h respectively at800℃, 900℃, 1000℃ and 1300℃.

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RESULTS AND DISCUSSION

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1. Test and analysis of crystal structure

X-ray diffraction (XRD) patterns were collected by the Bede D[1] X-ray diffraction spectrometer with Cu Kα radiation. Figure 1 shows XRD pattern of $Pr_{0.1}Ca_{0.9}MnO_3$ samples at different temperatures. The pattern of $Pr_{0.1}Ca_{0.9}MnO_3$ (PCMO) samplespresents that the PCMO is the single perovskite structure with orthorhombic as determined by XRD patterns. Crystal cell parameters for $a = 0.749198$ nm, $b = 0.531312$ nm, $c = 0.529325$ nm, crystal cell volume $V = 0.21070$ nm^3.
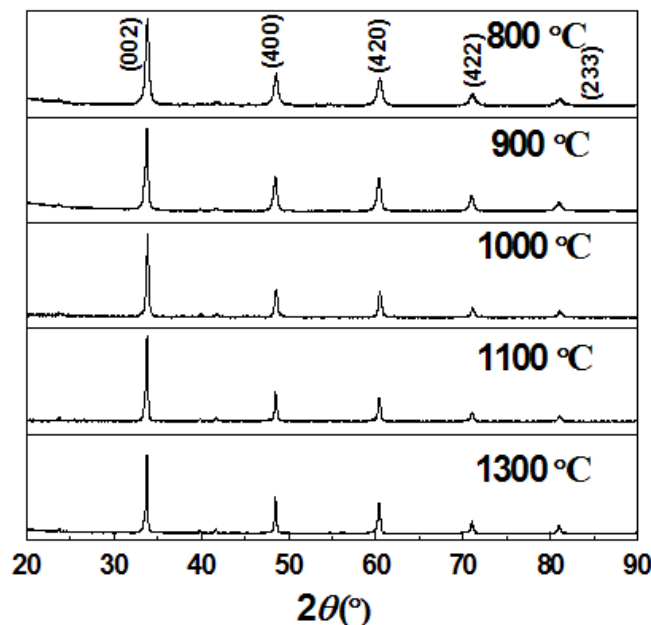

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Fig.1 The X-ray diffraction pattern of $Pr_{0.1}Ca_{0.9}MnO_3$ samples

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From Fig.1, we can observe clearly that the diffraction peak become gradually sharpening and peak width become narrowing with increasing sintering temperature. Main reason for change of diffraction peak width is that the change of grain size of the samples. The grain size (D) of sample was found to obey Scherer'sEquation

$$D = K\lambda/(B - B_0)\cos\theta \quad (1)$$

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Table .1 The grain size of $Pr_{0.1}Ca_{0.9}MnO_3$ samples

sample	λ(nm)	B(°)	θ(°)	D(nm)
800°C	0.154184	0.35468	33.799	28.4
900°C	0.154184	0.26529	33.733	47.7
1000°C	0.154184	0.22706	33.825	77.3
1100°C	0.154184	0.20133	33.749	>100
1300°C	0.154184	0.17932	33.746	>100

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Where B is the actual measured half peak width, B_0 is the diffraction peak broadening caused by the instrument, K is constant, λ is X-ray wavelength, θ is Bragg diffraction angle. In Table 1 the grain sizes of all samples are shown. Moreover, Table 1 show the B value of 800 ° C sample is the biggest of all, so according to Equation (1) the grain size D of 800 ° C sample is smallest. It is clearly seen that the B value decreases with increasing sintering temperature, but the grain size D begins to grow up with increasing sintering temperature.

2. Test and analysis of the iodometric titration

In order to determine the average state of manganese ion and oxygen content in the samples, the iodometric titration of the $Pr_{0.1}Ca_{0.9}MnO_3$ samples were measured.

A certain amounts of $Pr_{0.1}Ca_{0.9}MnO_3$ samples were dissolved inHCl,at the same time mixed with required amounts of KI. In the process, B site ion of the sample to the original state reacts with KI ion, so I_2 precipitate out. Then I_2 was deoxidized using the known concentration of $Na_2S_2O_3$ solution. After that, the volume of $Na_2S_2O_3$ solution was recorded. According to the volume, the amount of $Na_2S_2O_3$ can be calculated. Then based on the reaction equation, the sample average valence state of ions and the oxygen content of the sample can beachieved.

Table.2 The result of iodometric titration of $Pr_{0.1}Ca_{0.9}MnO_{3-y}$

sample	oxygen loss	average state of manganese ion	$Mn^{3+}: Mn^{4+}$
800°C	0.072	3.758	0.32:1
900°C	0.075	3.752	0.33:1
1000°C	0.081	3.740	0.35:1
1100°C	0.084	3.732	0.37:1
1300°C	0.093	3.716	0.40:1

Table 2 shows the results of iodometric titration. It is clearly seen that oxygen nonstoichiometric occurs in the process of sample preparation. As shown in Table 2, oxygen content decreases and oxygen loss increases with the increase of sintering temperatures.

Sintering temperature increasing from 800 °C to 1000 °C, oxygen loss increases in $Pr_{0.1}Ca_{0.9}MnO_3$ sample, which introduces more e_g electrons into the material. However, when the sintering temperature rise to 1100 °C, further e_g electrons are introduced, which causes the localization of electrons, so that ferromagnetism is suppressed. Consequently, obvious antiferromagnetic property appears forthe sample sintered at 1300 °C.Therefore, through different sintering temperature to adjust carrier concentration and oxygen content of $Pr_{0.1}Ca_{0.9}MnO_3$ samples, we achieve the purpose of control the material physical properties, namely change the magnetic and electrical transport properties of the sample.

CONCLUSION

In summary, the concentration of charge carrier in electron-doped $Pr_{0.1}Ca_{0.9}MnO_3$has been adjusted successfully by adoptingdifferent sintering temperature. We have presented and analyzed the iodometric titration data of $Pr_{0.1}Ca_{0.9}MnO_3$ samples in detail. Measurement based on the iodometric titration has found more oxygen loss in sintering temperature increased from 800 ° C to 1000 ° C. Due to Mn^{4+} ions change into Mn^{3+} ions, $e_g$electronic increase in materials. However, when sintering temperature continues to raise to 1100 ° C, more e_g electron is introduced, and when the concentration is high enough, localization of electrons emerges. Therefore, our study confirms that the oxygen content and concentration of charge carrier can be regulated by adopting different sintering temperature.

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