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Influence of synthesis methods and calcination temperature on electrical properties of $La_{1-x}Ca_xMnO_3$ ($x=0.33$ and 0.28) ceramics

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Abstract: $La_{1-x}Ca_xMnO_3$ ($x=0.33$ and 0.28) powders were prepared by both coprecipitation and sol–gel methods. Circular pellets with different radial shrinking ratios (RSR) were obtained by changing the calcination temperature of the powders. The influence of the powder synthesis process and the shrinking ratio of the sample on the structural, morphological and electrical properties of the ceramics were investigated. It has been found that sol–gel method is more efficient and stable to obtain ceramic samples with good electrical properties. The radial shrinking ratio of the ceramic increases with the decreasing calcination temperature. The experimental results show that RSR significantly affects the electrical properties of the ceramics prepared by coprecipitation method and has negligible influence on the samples made by sol–gel method. The coprecipitation samples with larger RSR have higher insulator to metal transition temperature T_p which is comparable to that of the sol–gel samples.

Keywords: A. Sol–gel; Coprecipitation; Calcination temperature; $La_{1-x}Ca_xMnO_3$; Radial shrinking ratio

1. Introduction

$La_{1-x}Ca_xMnO_3$ (LCMO) system with the colossal magnetoresistance (CMR) effect has attracted extensive attention in the last decades due to its special physical properties and potential applications in magnetic recording, magnetic refrigeration, bolometer, *etc*. [1–3]. The competition between paramagnetic (owing to Jahn–Teller effect) or antiferromagnetic insulating state and ferromagnetic metallic state is generally believed to be the foundation of the rich physical properties in CMR materials. The CMR effect heavily depends on the ratio and distribution of Mn^{3+} and Mn^{4+} ions, the sample preparation routes and the applied magnetic field [4,5]. The magnetoresistance (MR) as large as 127,000% was first observed in $La_{0.67}Ca_{0.33}MnO_x$ by Jin et al. [6]. From then on, many efforts have been made to enhance this effect by doping or substituting Ca with other elements, such as Ag, Ba and Sr [7–10].

The insulator to metal transition temperature T_p is an important parameter to evaluate the electrical properties of LCMO material. It has been found that T_p value strongly depends on the synthesis methods. Temperature coefficient of resistivity (TCR, defined as $TCR\%=1/R(dR/dT)\times 100\%$) is usually related to the homogeneity, crystallinity and grain size of the ceramic. These electrical properties rely heavily on the synthesis methods as well as preparation conditions. A number of techniques are available to prepare LCMO powders, such as the conventional solid phase reaction, reactive milling, sol–gel, spray-drying, *etc*. [11–14]. Among these methods, chemical processing, especially the sol–gel technique has more advantages than the solid phase method to synthesize the ultrafine powders with precise stoichiometry and uniform size. Moreover, this method has a good repeatability. On the other hand, the sintering schedule can be used to effectively control the grain size, phase homogeneity and thus the electrical and magnetoresistivity behaviors of LCMO ceramics, which have been reported by many authors [15–18]. However, few reports have been found to study the relationship between the calcination temperature and the physical properties of the LCMO materials.

The current work reports the influence of different powder synthesis methods and calcination temperatures on the radial shrinking ratio, structural and electrical properties of $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.72}Ca_{0.28}MnO_3$ ceramics. The

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relationship between electrical properties and RSR of different ceramics is also discussed.

2. Experimental

Two different methods, coprecipitation and sol–gel were employed to synthesize $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.72}Ca_{0.28}MnO_3$ precursor powders. The details of the preparation process were referred in our previous works [19,20]. $La_{0.72}Ca_{0.28}MnO_3$ ceramics were prepared to verify the conclusions obtained from $La_{0.67}Ca_{0.33}MnO_3$ compound. All the precursor powders prepared by coprecipitation and sol–gel methods were calcined from 500 °C to 900 °C for 16 h in air. Then the powders were pressed (under 12 MPa) into circular pellets with a diameter of 20 mm. All the pellets were sintered at 1150 °C for 16 h and subsequently slowly cooled to room temperature. Finally the $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.72}Ca_{0.28}MnO_3$ ceramics with different diameters were obtained. Based on the synthesis method and calcination temperature of the ceramics, we label the bulk samples prepared by sol–gel method as S1–S7, and coprecipitation method as C1–C4.

The crystal structural and phase purity of ceramics were examined by X-ray diffraction (XRD) with Cu K_α radiation (1.54056 Å) at room temperature. The surface morphologies and particle sizes of the samples were characterized by scanning electron microscope (SEM). The resistance of the ceramics was measured by using conventional four-probe method in the temperature range from 100 K to 300 K.

A parameter $\delta\% = (d_0 - d_1)/d_0 \times 100\%$ was defined to characterize the RSR of ceramic (d_1 and d_0=20 mm represent the ceramic diameter after and before sintering, respectively). The relationships between δ and the T_p and TCR values were also investigated.

3. Results and discussion

3.1. Structural and morphological characterization

Calcination temperature is usually thought to have a significant effect on the grain size and other properties of the bulk samples. Few works have been reported to research this relationship at present. In our experiments, the calcination temperature was changed from 500 °C to 900 °C, meanwhile the sintering temperature was fixed at 1150 °C. As expected, the pellets with different RSR were obtained. Some selected experimental parameters and results are listed in Table 1, in which relative density is defined as the ratio of the experimental density to the theoretic density. The results demonstrate that reducing calcination temperature is beneficial to decrease the size of the ceramics and improve the density of the bulk. In most cases, the density of the ceramic prepared by sol–gel method is higher than that of coprecipitation samples.

Fig. 1(a) and (b) shows the XRD patterns of $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.72}Ca_{0.28}MnO_3$ ceramics prepared by different methods. All the samples have the single LCMO phase with perovskite-type crystal structure, regardless of the prepared method or ceramic size. These results indicate that the prepared method of the powders or the RSR of the ceramics have negligible influence on the formation of single LCMO phase.

Table 1
The experimental data of $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.72}Ca_{0.28}MnO_3$ ceramics.

Sample	Ca content	Calcination temperature (°C)	Diameter (d_1) (mm)	$\delta = (d_0 - d_1)/d_0 \times 100$ (%)	Relative density (%)	T_p (K)	TCR (%)
C1	0.33	550	16.1	19.5	59.82	273.23	5.1
C2	0.33	900	18.7	6.5	43.44	250.68	1.5
C3	0.28	550	16.7	16.5	55.04	266.61	1.4
C4	0.28	900	18.8	6	63.85	209.29	2.1
S1	0.33	500	14.9	25.5	78.48	267.59	9.7
S2	0.33	550	16.0	20	63.99	270.08	4.5
S3	0.33	600	17.1	14.5	68.52	271.94	4.3
S4	0.33	800	18.3	8.5	70.18	272.08	7.4
S5	0.33	900	19.2	4	66.06	271.83	8.4
S6	0.28	550	16.6	17	63.61	260.85	7.1
S7	0.28	900	18.4	8	61.90	254.75	2.0

The morphologies and particle sizes of $La_{0.67}Ca_{0.33}MnO_3$ powders calcined at 900 °C are shown in Fig. 2. It can be seen that the coprecipitation powders have the particle sizes bigger than 400 nm, and the particles tend to aggregate to a sheet-like material. The particle sizes of the sol–gel powders distribute in the range between 100 nm and 200 nm, and the sizes and shapes of the particles are more uniform. We may expect that ceramics prepared by sol–gel powders have more homogeneity phase as well as physical properties.

Fig. 3(a) and (b) shows the morphologies of the sol–gel ceramic samples S1 and S5 which were calcined at 500 °C and 900 °C, respectively. It can be seen that grain size of sample S1 distributes between 2 μm and 4 μm and sample S5 distributes mainly from 1 μm to 2 μm. Obviously, sample S1 has a more uniform particle size and less pores, while sample S5 has more pores. Sample C2, which was prepared by coprecipitation method, has smaller grain size as well as more pores than the sol–gel samples. Thus this coprecipitation ceramic sample has more grain boundaries and other defects which will give worse electrical transport properties.

Given that the sintering conditions for all samples are the same, we may conclude that the powder synthesis method and calcination temperature strongly affect the particle size and radial shrinking ratio of ceramic. When increasing the calcination temperature, the RSR of ceramic will decrease. This result may be induced by the particle growth mechanism. First, the nano-scale powders can be easily synthesized by chemical method and the grain size of the powders will be small for a low calcination temperature. It is well known that the smaller grains have higher surface energy. While the small grains grow up, they will exclude the pores among the particles faster and more complete. Finally, the ceramics will contain larger grains and less grain boundaries and thus become more density. According to Table 1, for both the two methods, the smaller ceramic was achieved when the calcination temperature was lower. In addition, the sizes of the samples have certain influence on their T_p and TCR values, which will be discussed in the following sections.

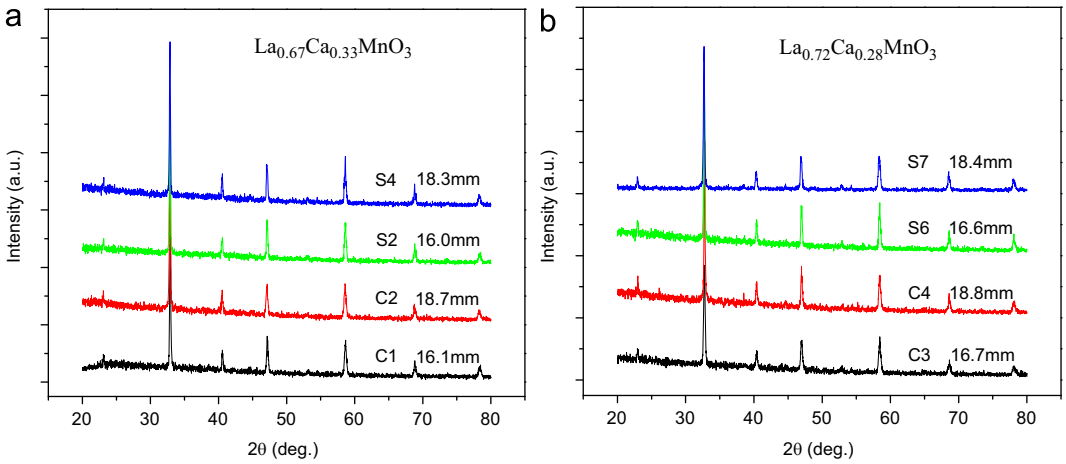

Fig. 1. XRD patterns of (a) $La_{0.67}Ca_{0.33}MnO_3$ and (b) $La_{0.72}Ca_{0.28}MnO_3$ ceramics synthesized by different methods.

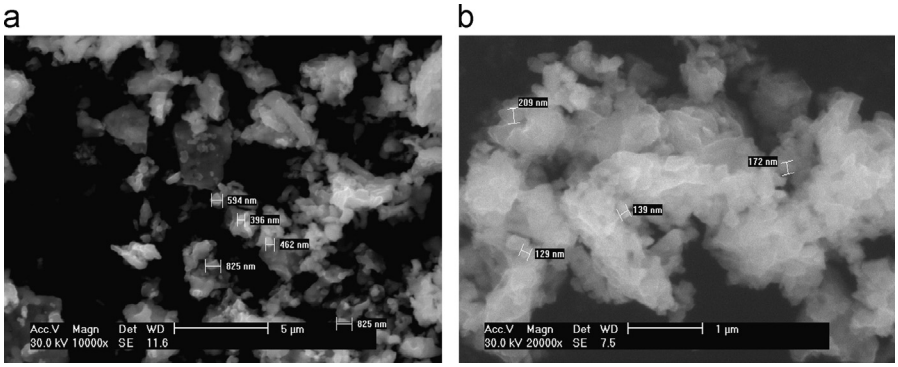

Fig. 2. SEM micrographs of $La_{0.67}Ca_{0.33}MnO_3$ powders calcined at 900 °C and prepared by (a) coprecipitation and (b) sol–gel method.

3.2. Electrical properties

The temperature dependence of resistivity curves of different samples are shown in Fig. 4. It can be seen from the figures and table that the RSR of ceramic markedly affects the insulator to metal transition temperature T_p for the ceramics prepared by coprecipitation method. The resistivity becomes larger and T_p shifts to a lower temperature when the RSR of ceramic is smaller. Only when the RSR is relatively large, the coprecipitaiton sample can achieve a similar T_p compared to sol–gel sample, which is satisfied to the phase diagram as well as previous reports [21–24]. The critical point of the RSR is not clear currently. There are some different interpretations for the decrease of T_p, for instance, the reduction of grain size, the effects of the oxygen vacancies and the grain boundaries *etc.* [25–27]. Since the shift of T_p relates to the different RSR which induced by the different calcination temperatures, we infer that there exists more grain boundaries and pores in ceramics with smaller RSR that will increase the resistivity and decrease T_p.

For ceramic prepared by sol–gel method, the RSR has no obvious influence on T_p and resistivity. All the samples have the similar resistivity and the normal T_p [22–24]. The reason may be that the sol–gel method produces high quality ultrafine precursor powders, in which the components are mixed homogeneously on the atomic scale [13,28]. As for coprecipitation process, different components are mixed on the molecular level. The size of powder particles is larger and the shape is irregular after calcining at the same temperature. In addition, the grain size of sol–gel samples is more uniform and the LCMO phase is more homogeneous. These factors will enhance the electronic transport properties of the sol–gel ceramics.

TCR values derived from the ρ–T curves seem not to be strongly influenced by RSR. But for both the $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.72}Ca_{0.28}MnO_3$ ceramics, the highest TCR values are obtained in the sol–gel samples. The experimental results show that the highest TCR value is 9.7% for $La_{0.67}Ca_{0.33}MnO_3$ ceramic with 25.5% of RSR and 7.1% for $La_{0.72}Ca_{0.28}MnO_3$ ceramic with 17% of RSR. They are high enough for the application of bolometer and infrared devices. It is very important to further investigate the calcination and sintering process which will help to improve the electrical properties of the LCMO materials.

4. Conclusions

We have proposed an effective process to enhance the electrical properties of $La_{1-x}Ca_xMnO_3$ ceramic by changing the calcination condition. When the calcination temperature changed from 500 °C to 900 °C, ceramics with different radial shrinking ratio can be obtained. RSR heavily influence the insulator to metal transition temperature T_p for coprecipitation samples, but has no obvious effect on that for sol–gel samples. Coprecipitation samples with

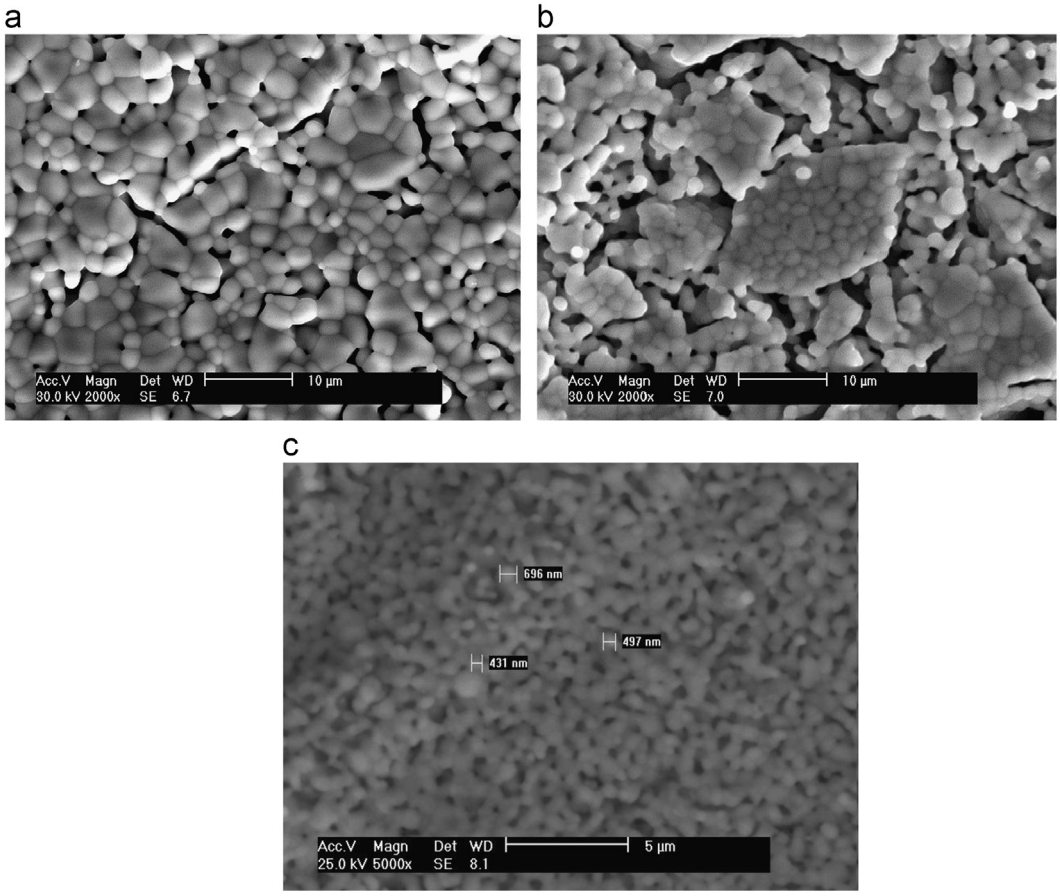

Fig. 3. SEM micrographs of $La_{0.67}Ca_{0.33}MnO_3$ ceramics of (a) S1 (500 °C, δ=25.5%), (b) S5 (900 °C, δ=4%) and (c) C2 (900 °C, δ=6.5%).

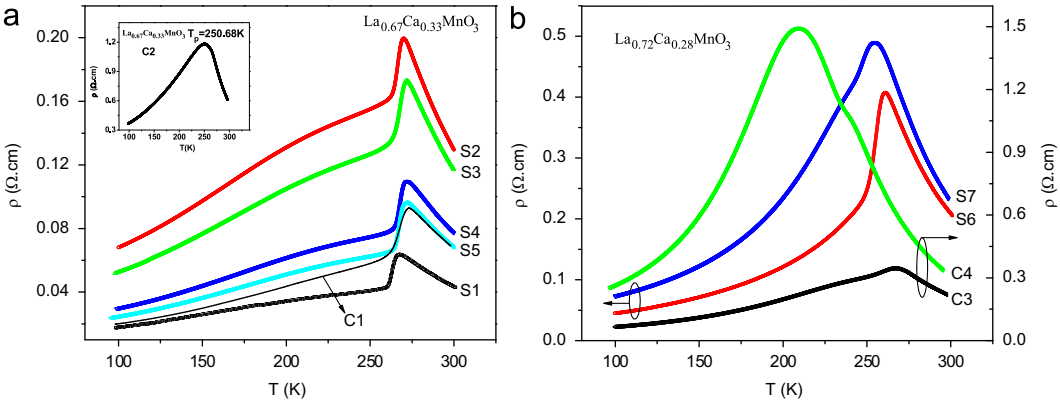

Fig. 4. $\rho-T$ curves of (a) $La_{0.67}Ca_{0.33}MnO_3$ and (b) $La_{0.72}Ca_{0.28}MnO_3$ ceramics synthesized by different methods. The inset shows the $\rho-T$ curve of sample C2.

large RSR have similar electrical properties to sol–gel counterparts. TCR seems to have no direct relationship with the RSR and high TCR are always obtained in smaller ceramics.

Acknowledgments

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