Effect of the calcination process on the magnetotransport properties in co-precipitation derived La$_{0.67}$Ca$_{0.33}$MnO$_3$ ceramics

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Abstract:

La$_{0.67}$Ca$_{0.33}$MnO$_3$ (LCMO) attracts considerable attention as a quintessential example for colossal magnetoresistance (CMR), metal-insulator transition and related temperature coefficient of resistance (TCR) studies. Here, co-precipitation method was utilized to prepare the LCMO ceramics, whose magnetotransport properties as a function of calcination temperature ($T_{cal}$) and calcination time ($t_{cal}$) were investigated. The magnetotransport properties of these LCMO ceramics were significantly enhanced compared with LCMO derived by sol-gel methods. The TCR of LCMO increased firstly and then decreased as the $T_{cal}$ increased, whereas the metal-insulator transition temperature ($T_{MIT}$) shifted towards to the lower temperature. Magnetoresistance (MR) increased as $T_{cal}$ rose and reached 82.4 % at $T_{cal}$ = 800 °C. The mechanism of such magnetotransport properties with different temperature ranges was discussed. The optimal TCR of 32.3% K$^{-1}$ in LCMO was prepared with $T_{cal}$ = 500 °C and $t_{cal}$ = 8 h, showing that co-precipitation method would facilitate the potential application of LCMO in infrared detecting and magnetoresistive switching.

Keywords: La$_{0.67}$Ca$_{0.33}$MnO$_3$; TCR; MR; calcination process; co-precipitation method.

1. Introduction

The past decades have witnessed the intensive study of manganite $R_{1-x}B_x$MnO$_3$ ($R$
is La, Sr, Nd etc., and B is divalent alkaline earth element) due to their rich electronic properties, which arise from interplay among lattice, spin, charge, and orbital [1]. Among them, La$_{1-x}$Ca$_x$MnO$_3$ is a typical mixed-valence compound obtained by substituting La for Ca from the parent compound, antiferromagnetic (AFM) insulator LaMnO$_3$. LCMO has been paid extensive attention, owing to the colossal magneto-resistive (CMR) effect and the potential applications for magnetic sensors, memory devices, etc. [2-5]. Furthermore, there exists a paramagnetism-ferromagnetism transition generally accompanied by a metal-insulator transition (MIT) in LCMO [6], which is well accepted as a result of competition between double exchange of Mn$^{3+}$/Mn$^{4+}$ and Jahn-Teller effect [7,8]. A sharp MIT with a low resistivity can generate a large TCR, which makes the CMR manganites of great application potential in infrared detecting and bolometer, etc. [9,10], which motivated this study.

TCR is usually related to the grain size, crystallinity and homogeneity of the ceramic powders. These electrical and magnetotransport properties rely drastically on the preparation methods as well as preparation conditions. Many techniques can be used to prepare LCMO powders, such as the solid phase reaction [11], spray-drying [12], sol-gel method [13], co-precipitation method [14]. As for conventional solid phase reaction, a relative high calcination temperature, long calcination time and multiple grinding and sintering processes are necessary to obtain high-quality LCMO ceramics. A solution of particular concentration and a co-current flow atomization system are required of spray-drying, which increased the preparation complexity and cost. Sol-gel method also has several disadvantages, the raw materials for the sol-gel method are expensive, the operation is complicated, the process time is long and the prepared samples are prone to crack. Notice that, the chemical co-precipitation method is simple in operation and mild in condition, which is utilized in this study to prepare LCMO ceramics.

The composition and morphology of the sample can be precisely controlled by changing the calcination temperature ($T_{\text{cal}}$) and calcination time ($t_{\text{cal}}$) [15-20]. Previous studies reported the electrical properties and TCR of La$_{0.67}$Ca$_{0.33}$MnO$_3$, with
maximum $TCR$ of $9.7\% \cdot K^{-1}$ and corresponding metal-insulator transition temperature ($T_{MIT}$) of $267.59$ K [21,22]. Therefore, it is of importance to further explore different calcination process to enhance $MR$ and $TCR$ in co-precipitation derived LCMO ceramics.

In present work, calcination process effect on the electrical transport and magnetotransport properties of LCMO ceramics. $T_{cal}$ of $400, 500, 650$ and $800$ °C were used since the synthesis of the LCMO phase started at about $500$ °C and completed at about $800$ °C [21]. The maximum $TCR$ reached to $32.3 \% \cdot K^{-1}$ at $T_{cal} = 500$ °C and maximum $MR$ is $82.8 \%$ at $T_{cal} = 800$ °C, which are largely enhanced compared with the sample derived by sol-gel method [23]. In the region of $T < T_{MIT}$, the $\rho$-$T$ could be demonstrated by the electron-electron scattering. In the region of $T > T_{MIT}$, conductive mechanism was explained through the small polaron hopping ($SPH$) model. In addition, the resistivity ($\rho$) can be fitted by phenomenological percolation model over the entire temperature scope. Our study provides a new synthesis method for the application of LCMO materials in infrared detectors, contactless magnetoresistive switches, and memories to some extent.

2. Experiments

La$_{0.67}$Ca$_{0.33}$MnO$_3$ (LCMO) ceramics were synthesized with the co-precipitation method. High purity powders (La(NO$_3$)$_3$·$n$H$_2$O, Ca(NO$_3$)$_2$·4H$_2$O, Mn(NO$_3$)$_2$·4H$_2$O, and (NH$_4$)$_2$CO$_3$) were weighed according to the stoichiometric ratio, and deionized water (approximately 50 mL) were added to the mixture. (NH$_4$)$_2$CO$_3$ powder was added to the mixed solution as a precipitator. The resulting solutions were magnetically stirred for about 40 min. Then, the samples were filtered, washed with deionized water, and the precipitates were separated from the water after standing for 14 h. The white solid powder was formed by drying in an oven at $140$ °C for 6 h. The dried precipitates were calcined in a muffle furnace at $400$ °C, $500$ °C, $650$ °C, and $800$ °C. The calcined powders were ground again. To break the hard agglomerates and improve the activity of effective densification during sintering processes, the milled powder was pressed
into pellets at 15 MPa. In the ambient atmosphere, pellets were sintered in a muffle furnace at 1450 °C for 12 h. The $t_{\text{cal}}$ was set to 0, 2, 8, and 24 h at $T_{\text{cal}} = 500 ^\circ$C.

The structure and crystallinity of the LCMO samples were studied by powder X-ray diffraction ($XRD$, Rigaku Ultima IV) with Cu Ka radiation. The surface morphologies and microstructures were characterized by scanning electron microscope ($SEM$, Hitachi SU8010). The resistivity was measured with the standard four probe method within a temperature range of 150-300 K. The magnetoresistance ($MR$) was measured with a magnetic measurement system within a temperature range of 150-300 K.

### 3. Results and discussions

#### 3.1. Structure of LCMO samples

$XRD$ patterns of the LCMO ceramic samples calcinated at different temperatures are shown in Fig. 1. All samples possessed the orthorhombic perovskite structure, no impurity phases. Insets showed a magnified view of the strongest diffraction peak (121), which shifted toward lower angles as the $T_{\text{cal}}$ rose, indicating an increased volume of the unit cell. The fitting parameter values are represented in Table 1. The crystal structure of ceramic samples was orthorhombic, which space group was Pnma. The fitting parameters (a, b and c) significantly changed at different $T_{\text{cal}}$. The cell volume (v) increased as the $T_{\text{cal}}$ increased from 400 °C to 500 °C and decreased from 500 °C to 800 °C. The Mn-O-Mn bond distances and Mn-O bond angles of all ceramics changed as the $T_{\text{cal}}$ changed, which would strongly affect the transport properties.

#### 3.2. Surface morphologies of LCMO samples

The surface morphologies of the LCMO samples are presented in Fig. 2(a-d). A large number of holes were found at the grains and grain boundaries (GBs) at $T_{\text{cal}} = 400$
This may be because the decomposition temperature of Ca(OH)$_2$ is in the range of 500-650 °C. The excessively low $T_{\text{cal}}$ cannot completely decompose the Ca(OH)$_2$ in the precursor powder, and CO$_2$ will be generated during the calcination process, causing the pores and defects at the grains and GBs. For $T_{\text{cal}}$ above 500 °C, fewer defects were observed, while the densities of all samples increased. To explore the effects of grain size on different $T_{\text{cal}}$, the mean grain sizes of all samples were calculated with Nona Measurer 1.2 Software. The average grain sizes in Fig. 2(a-e) were 13.16, 14.89, 15.05, and 25 μm, respectively. This indicates that increased $T_{\text{cal}}$ would lead to the growth of polycrystalline ceramic grains. This is mainly because with the increase of the $T_{\text{cal}}$, the sample activity will increase, resulting in higher crystallinity. However, when $T_{\text{cal}}$ was 800 °C, the grain size of the powder can reach to 25 μm and the main crystal phase is formed, reducing the sintering activity and affecting the process of secondary recrystallization. In summary, the samples have good sintering activity and few defects at a $T_{\text{cal}}$ of 500 °C.

3.3. Electrical transport properties

The temperature dependence of the resistivity ($\rho$-$T$) of LCMO was measured in the 150-300 K under 0 and 1 T (Fig. 3(a-d)). The $\rho$-$T$ curves indicated that all samples underwent a metal to insulator transition [24,25]. In the low $T_{\text{cal}}$ region of 400-650 °C, the $T_{\text{MIT}}$ and resistivity of LCMO ceramics showed a slight change. When $T_{\text{cal}}$ was lifted from 650 to 800 °C, the ceramics simultaneously showed a sudden drop in $T_{\text{MIT}}$ and a drastic increase in $\rho$. The reduced grain size will enlarge the surface energy. For a $T_{\text{cal}}$ of 400-650 °C, the grain size of the LCMO powder is small (13.16, 14.89, and 15.05 μm, respectively), and the surface energy is larger than the sample of $T_{\text{cal}}$ of 800 °C. As a consequence, the ceramics with-size grains dense and high density was obtained after sintering. The scattering effect of the GBs on the electrons was weakened inducing a low resistivity. Combined with SEM image analysis, the high $T_{\text{cal}}$ of 800 °C is believed to be detrimental to the TCR.
The resistivity for all samples substantially decreased under 1T field, Helman and Abeles's model [26] can be used to explain. This model simulated that the resistivity should flat out gradually with the increase of the magnetic field and eventually vanish at certain critical field. The ρ-T curves showed that the resistivity decreased and the T_{MIT} shifted towards the higher temperature. it will cause delocalization of charge carriers at 1T field, which may lead to the ordering of magnetic spins and decrease the resistivity.

The TCR of the samples prepared at different T_{cal} are shown in Fig. 3(e). The main electrical performance comparison of LCMO samples under different T_{cal} are presented in Table 2. Fig. 3(e) and Table 2 show that the peak TCR increased first and then decreased with the T_{cal} increased. When T_{cal} = 500 °C, the TCR reached 32.3%·K^{-1}, and T_{MIT} shifted toward the low-temperature region, which show the advantages over the previous studies [27,28]. The reason for this phenomenon is that the lower T_{cal} (400 - 500 °C) causes smaller-size precursor particles, produces denser ceramics, which involves fewer GBs and fewer pores, especially the latter; and boosts the transport properties. On the other hand, looser ceramics derived from higher T_{cal} (650-800 °C) can result into poorer conductivity, which is responsible for the low TCR observed in Fig. 3(e). However, for T_{cal} of 400 °C, the organics were not completely evaporated, which suppressed the TCR. In summary, optimal TCR can be found in the LCMO with T_{cal} of 500 °C.

Fig. 3(f) shows the MR versus temperature curves of the LCMO ceramics at 0 T and 1 T magnetic fields. In this case, the MR is defined as $MR = (\rho_0 - \rho_H)/\rho_0 \times 100\%$, where $\rho_0$ and $\rho_H$ are the resistivity values for the 0 and 1T field, respectively. The MR of the LCMO ceramics can be seen as roughly increasing. The MR is as high as 82.4% at T_{cal} = 800 °C, which is higher than the MR of LCMO ceramics prepared by the sol-gel method [29,30].

3.4. Mechanism of the transport properties
There are three temperature regimes considered in this study to understand the conduction mechanism of the $\rho$-$T$ of LCMO ceramics prepared by co-precipitation at different temperatures [31,32].

3.4.1 Low-temperature range

Eq. (1) is a famous empirical equation that has provided a fitting method for $\rho$-$T$ in the low-temperature region ($T < T_{MIT}$):

$$\rho_{FM}(T) = \rho_0 + \rho_2 T^2 + \rho_{4.5} T^{4.5},$$  \hspace{1cm} (1)

where $\rho_0$ is the residual resistivity stemming from the GBs, as well as from the scattering mechanisms, which independent of temperature. The $\rho_2 T^2$ is caused by the scattering of electron-electron, which plays a dominant role in the $T < T_{MIT}$ area. The $\rho_{4.5} T^{4.5}$ is produced by the electron-electron, electron-magnon, and electron-phonon scattering in the ferromagnetic (FM) low-temperature region.

The $\rho$-$T$ fitted by Eq. (1) are shown in Fig. 4(a) and Table 3. The squared linear correlation coefficients ($R^2$) are listed. The obtained values of $R^2$ were as high as 99.0% for all samples, which represents the high fitting quality. With application of 1T magnetic field, it can be seen from Table 3 that both the fitting values of $\rho_0$ and $\rho_2$ for all ceramics decreased. Additionally, the GB scattering decreases, which would be resulted in decreases of resistivity. The value of the $\rho_2 T^2$ is greater than that of the $\rho_{4.5} T^{4.5}$ for all ceramics. Consequently, the scattering of electron-electron plays a major role in the conductivity of samples in the $T < T_{MIT}$ regime.

3.4.2 High-temperature range

The $\rho$-$T$ of paramagnetic (PM) high-temperature region is fitted by $SPH$ model. The $SPH$ model could be approximated by an adiabatic Eq. (2).

$$\rho_{PM}(T) = \rho_{OS} T \exp(E_a / K_b T),$$  \hspace{1cm} (2)

where $\rho_{OS}$ is the resistivity coefficient, $E_a$ is the polaron activation energy, and $K_b$ is the Boltzmann constant.
The $\rho$-$T$ fitting results are presented in Fig. 4(b) and Table 4. The results revealed that the SPH model fits the $\rho$-$T$ well. The fitting parameters are shown in Table 4. After 1T magnetic field was applied, the $E_a$ values of all ceramics are decreased, which would due to the addition of an external magnetic field changing the bond angle of Mn-O-Mn. In other words, the effective carrier mass is changed. As a result of this influence, the effective band gap is changed, and the carrier needs higher values of activation energy to cross this gap.

3.4.3 Entire temperature range

The phenomenological percolation model analyzed the $\rho$ over the whole temperature scope, and the combined formula is as follows in Eq. (3).

$$\rho(T) = \rho_{FM}(T)f + \rho_{PM}(T)(1 - f),$$

(3)

where $f$ is the volume fraction of the FM phase and $(1 - f)$ is the volume fraction of the PM phase. LCMO ceramics has been fitted over the whole temperature scope with Eq. (3) and the fitting parameters are demonstrated in Fig. 4(c) and Table 5. $T_{c-mod}$ stands for temperature at maximum resistivity. $U \approx U_0 \left(1 - \frac{T}{T_{c-mod}}\right)$ is the energy difference between the FM and PM states. There are two adjustable fitting parameters, namely, $T_{c-mod}$ and $U_0$. The fitting parameters $T_{c-mod}$ and $U_0/K_B$ are shown in Table 1. Obviously, the value of the $T_{c-mod}$ is very closed to $T_{MIT}$.

3.5. Effect of $t_{cal}$

Fig. 5(a) is the $\rho$-$T$ curves of LCMO with $t_{cal}$ of 0, 2, 8, and 24 h. For $t_{cal}$ of 0 h (that is, the temperature is lowered just after the sample is heated to 500 ºC), the resistivity is as high as 1.0412 $\Omega \cdot cm$, which is much higher than other study [33]. This may be that Ca(OH)$_2$ etc. are not completely decomposed, resulting in a large number of pores in the target, uneven composition, and low density, which largely improves resistivity. The resistivity of the samples reached a maximum value of 271.3 K at 8 h. From Fig. 5(b), the TCR first increased and then decreased. It reached a maximum value
of 32.3%·K⁻¹ at \( t_{cal} = 8 \) h. In general, the \( T_{cal} \) of 500 °C and the \( t_{cal} \) of 8 h are found to be the optimal sintering parameters for the co-precipitation derived LCMO ceramic.

4. Conclusion

A series of LCMO ceramics were prepared by co-precipitation method. The effect of calcination process on structure and magnetoelectric transport performance of LCMO ceramics was studied, and the conduction mechanism of the \( \rho-T \) was analyzed. Electron-electron scattering played an important role in the region of \( T < T_{MIT} \), SPH dominated in the regions of \( T > T_{MIT} \). Moreover, the \( \rho-T \) curves can also be interpreted by the phenomenological percolation model over the whole temperature range. Compared with sol-gel method, both TCR and MR have been greatly improved. The TCR maximum value is 32.3%·K⁻¹ at \( T_{cal} = 500 \) °C. MR value reached 82.4 % at \( T_{cal} = 800 \) °C. The optimal calcination parameters are \( T_{cal} \) of 500 °C and \( t_{cal} \) of 8 h, which move forward of LCMO for infrared detecting.

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Fig. 1 XRD patterns of the LCMO samples calcinated at 400°C, 500°C, 650°C and 800°C,

Insets are the magnified view of the strongest diffraction peak.
Fig. 2(a–d) SEM micrographs of LCMO samples calcinated at $T_{\text{cal}}$ = 400 °C (a), 500°C (b), 650°C (c), 800°C (d). (e) Grain size with different $T_{\text{cal}}$. 
Fig. 3(a-d) Temperature-dependent resistivity of the LCMO ceramics calcinated at various temperatures. (e) Variation in $TCR$ (% K$^{-1}$) with $T_{cal}$ for LCMO composites. (f) Temperature-dependent magnetoresistance of the LCMO ceramics calcinated at various temperatures.
Fig. 4. Fit curves of electrical resistivity in different temperature range (a) Low temperature range \((T < T_{MIT})\); (b) High temperature range \((T > T_{MIT})\); (c) Entire temperature range.
Fig. 5 (a) Temperature dependence of resistivity when changing the \( t_{cal} \); (b) Variation in TCR (\% K\(^{-1}\)) with \( t_{cal} \) for LCMO composites.
Table 1. Structure and refinement parameters of LCMO samples.

| Calcination temperature (°C) | 400  | 500  | 650  | 800  |
|------------------------------|------|------|------|------|
| Space group                  | Pnma | Pnma | Pnma | Pnma |
| a(Å)                         | 5.4535 | 5.45830 | 5.45560 | 5.45430 |
| b(Å)                         | 7.7076 | 7.71250 | 7.70950 | 7.70970 |
| c(Å)                         | 5.4687 | 5.47280 | 5.47250 | 5.47200 |
| Cell Volume V(Å³)            | 229.8680 | 230.3892 | 230.1730 | 230.1031 |
| d_{Mn-O1} (Å)                | 1.93515 | 1.93638 | 1.93563 | 1.93568 |
| d_{Mn-O2} (Å)                | 1.06601 | 1.06597 | 1.06611 | 1.06616 |
| Mn-O1-Mn (°)                 | 169.4153 | 169.4141 | 169.4106 | 169.4119 |
| Mn-O2-Mn (°)                 | 161.1546 | 161.1550 | 161.1552 | 161.1548 |
| R_e (%)                      | 22.7410 | 22.3173 | 13.8386 | 23.1465 |
| R_p (%)                      | 14.7911 | 15.8047 | 10.1391 | 16.9739 |
| R_b (%)                      | 18.8926 | 19.5795 | 12.3135 | 20.3379 |
Table 2. Main electrical performance comparison of LCMO samples under different calcination temperature

| Calcination temperature (℃) | $T_{MIT}$ (K) | $TCR$ (% · K$^{-1}$) | $\rho_{\text{min}}$ (Ω · cm) | $\rho_{296\text{K}}$ (Ω · cm) | Shrinkage ratio (%) |
|-----------------------------|---------------|----------------------|-------------------------------|-------------------------------|-------------------|
| 400                         | 271.1         | 28.8                 | 0.0197                        | 0.0173                        | 0.52              |
| 500                         | 271.3         | 32.3                 | 0.0210                        | 0.0178                        | 0.48              |
| 650                         | 271.6         | 19.4                 | 0.0159                        | 0.0143                        | 0.42              |
| 800                         | 262.4         | 10.8                 | 0.1325                        | 0.0749                        | 0.32              |
Table 3. Low temperature fitting parameters

| Calcination temperature (°C) | Field (T) | \( \rho_0 \) (\( \Omega \cdot \text{cm} \)) | \( \rho_2 \) (\( \Omega \cdot \text{cm} \cdot \text{K}^{-1} \)) | \( \rho_{4.5} \) (\( \Omega \cdot \text{cm} \cdot \text{K}^{-1} \)) | \( R^2 \)  |
|----------------------------|-----------|---------------------------------|----------------|----------------|---------|
| 400                        | 0         | 9.40E-04                        | 4.42E-08        | 3.20E-14       | 0.99948 |
|                            | 1         | 8.46E-04                        | 3.38E-08        | 3.05E-14       | 0.99851 |
| 500                        | 0         | 8.45E-04                        | 5.29E-08        | 3.78E-14       | 0.99932 |
|                            | 1         | 7.71E-04                        | 4.77E-08        | 3.63E-14       | 0.99644 |
| 650                        | 0         | 9.80E-04                        | 1.52E-08        | 5.41E-14       | 0.99846 |
|                            | 1         | 1.03E-03                        | 1.53E-09        | 4.55E-14       | 0.99959 |
| 800                        | 0         | 2.47E-02                        | 7.01E-06        | 2.25E-13       | 0.99932 |
|                            | 1         | 4.77E-03                        | 1.80E-06        | 2.23E-13       | 0.99901 |
Table 4. *SPH* model fitting parameters

| Calcination temperature (°C) | Field (T) | $E_a$ (meV) | $R^2$   |
|------------------------------|-----------|-------------|---------|
| 400                          | 0         | 1.16E-20    | 0.99756 |
|                              | 1         | 9.34E-21    | 0.9982  |
| 500                          | 0         | 1.29E-20    | 0.99656 |
|                              | 1         | 1.11E-20    | 0.99165 |
| 650                          | 0         | 1.33E-20    | 0.99959 |
|                              | 1         | 9.18E-21    | 0.99644 |
| 800                          | 0         | 2.79E-20    | 0.99972 |
|                              | 1         | 2.33E-20    | 0.99854 |
Table 5. Percolation model fitting parameters

| Calcination temperature (°C) | Field (T) | $\frac{u_t}{k_a}$ (K) | $T_{c-mod}$ (K) | R²   |
|-----------------------------|-----------|-----------------------|-----------------|------|
| 400                         | 0         | 4.44E+04              | 2.64E+02        | 0.999|
|                             | 1         | 2.56E+04              | 2.73E+02        | 0.99979|
| 500                         | 0         | 5.44E+04              | 2.65E+02        | 0.99919|
|                             | 1         | 2.75E+04              | 2.73E+02        | 0.99973|
| 650                         | 0         | 3.33E+04              | 2.63E+02        | 0.99846|
|                             | 1         | 2.48E+04              | 2.73E+02        | 0.99986|
| 800                         | 0         | 4.59E+04              | 2.64E+02        | 0.99833|
|                             | 1         | 3.03E+04              | 2.69E+02        | 0.99879|