Effect of the glycerol dispersant on the structure, electrical transport and magnetoresistive properties of La0.67Ca0.33MnO3 ceramics prepared by the sol-gel routine

Yuchen Xie  
Kunming university of Science and Technology

Chunling Liu  
Kunming university of Science and Technology

Yating Shen  
Kunming university of Science and Technology

Shaozheng Wang  
Kunming university of Science and Technology

Ping Yu  
Kunming university of Science and Technology

Yule Li  
Kunming university of Science and Technology

Qingming Chen  
Kunming university of Science and Technology

Hui Zhang
harry_zhang71@163.com

Kunming university of Science and Technology

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Abstract

In this paper, the sol-gel technique is employed to synthesize polycrystalline La$_{0.67}$Ca$_{0.33}$MnO$_3$ (LCMO) ceramics, where methanol is chosen as the solvent. The crystal structure, morphology, as well as electrical and magnetoresistive properties. Moreover, the effect of amount of the dispersant glycerol on the properties of LCMO ceramics is studied. X-ray diffraction (XRD) results showed that all samples crystallized in single phases with orthogonal perovskite structure (pnma space group), without any detectable impurity phases. Results reveal that the grain size of LCMO ceramics exhibits an initial increase followed by a decrease, accompanied by a similar behavior in the temperature coefficient of resistance (TCR) and magnetoresistance (MR). When the volume ratio of glycerol and methanol reached 2%, the grain size is determined to be 7.30 µm, with TCR value of 25.02% K$^{-1}$ at T = 263.2 K, and MR value recorded at 55.40%. The study elucidates the influence of glycerol on LCMO polycrystalline ceramics and optimize the fabrication process, thereby improve the electric transport property and magnetoresistance.

1. Introduction

The perovskite manganese oxides, for instance, La$_{1-x}$Ca$_x$MnO$_3$, have attracted significant attention due to their unique electrical and magnetic properties, such as colossal magnetoresistance (CMR) [1–3], ferromagnetic (FM)-paramagnetic (PM) transitions [4], and metal-insulator transitions (MIT) [3, 5]. These phenomena endow such materials with promising potential applications, including magnetic sensors, magnetic storage, magnetic refrigeration, and bolometer/infrared imaging, etc.[6, 7] The principles underlying these phenomena can be explained using mechanisms such as Jahn-Teller (J-T) distortion [5, 8], double exchange (DE) [9], spin polarization tunneling effect [10] and grain boundary (GB) effects [11]. Zener [9] utilized the double exchange model to explain the electrical property changes during the FM-PM phase transition. Due to the metallic behavior arising from DE mechanism and insulating behavior caused by J-T distortion, that is, the competition of DE between Mn$^{3+}$ and Mn$^{4+}$ ions and J-T distortion of Mn$^{3+}$ ion leads to the metal-insulator transition of La$_{1-x}$Ca$_x$MnO$_3$ [12–14].

In La$_{1-x}$Ca$_x$MnO$_3$ based bolometric devices, the temperature coefficient of resistance (TCR) and the metal-insulator transition temperature ($T_P$) are crucial parameters. In recent years, lots of efforts have been paid on preparing La$_{1-x}$Ca$_x$MnO$_3$ with high TCR and $T_P$ approaching room temperature. Many researchers have reported on the routine of elemental addition/substitution to achieve high TCR while also shift $T_P$ as close to room temperature as possible. For example, H.C. Jiang et al. [15] employed silver added La$_{0.7}$Ca$_{0.3}$MnO$_3$ thin films, leading to a notable enhancement in the metal-insulator transition temperature of the samples along with a reduction in resistivity. Mishra D.K. et al [16]. used cerium doped La$_{0.67}$Ca$_{0.33}$MnO$_3$ thin films with metal-insulator transition temperatures and Curie temperature $T_C$ close to room temperature. Y.L. Li et al. [17] studied cobalt-doped La$_{0.7}$Ca$_{0.3}$MnO$_3$, i.e., La$_{0.67}$Ca$_{0.33}$Mn$_{1-x}$Co$_x$O$_3$ ceramics, achieving a transition temperature of 242.8 K and a TCR value of 44.2%·K$^{-1}$ when $x = 0.02$. 
Nevertheless, those efforts to optimize the fabrication process can also effectively enhance TCR and improve other properties of La$_{1-x}$Ca$_x$MnO$_3$.

La$_{1-x}$Ca$_x$MnO$_3$ ceramic can be synthesized using methods including co-precipitation [18, 19], sol-gel [20, 21], and solid-state reaction [21, 22]. When compared to alternative approaches, ceramics produced using the sol-gel method possess the benefits of homogeneous composition and simplified procedures [23]. However, during the utilization of the aforementioned ceramic preparation processes, particle aggregation can occur, resulting in a substantial decrease in the uniformity and fineness of the powder [22]. This leads to a decline in the properties of the ceramic. By incorporating dispersants during the preparation process, the generation of particle aggregation can be effectively suppressed. Y.F. Zhang et al. [24] employed PEG-400 as a dispersant to synthesize Ca$_3$Co$_4$O$_3$ nanoparticles with particle sizes ranging from 30 to 50 nm. F. Golestani-Fard et al. [25] utilized the sol-gel method to prepare SiC-B$_4$C nano-powders, adding APC dispersant to prepare nanoparticles with sizes smaller than 10 nm. Masoud Peymannia et al. [26] synthesized nano CoAl$_2$O$_4$ pigments via the co-precipitation method and analyzed the dispersion effects and mechanisms of different dispersants, such as SDS, CTAB, Triton X-100, and poly (AA-co-IA). When the energy barrier between particles is low, non-ionic dispersants can be chosen, and particle dispersion can be achieved through steric hindrance effects. Glycerol, as a common alcohol dispersant in the sol-gel preparation process, features low addition amounts, higher dispersibility compared to other dispersants, and the capability to reduce environmental pollution caused by dispersants.

In this study, La$_{0.67}$Ca$_{0.33}$MnO$_3$ (LCMO) was prepared using sol-gel routine, with glycerol serving as the dispersant. Different volume ratio of glycerol and methanol ($r_v$, 0%, 2%, 4%, 6%, 8%) of glycerol were incorporated during the sol-gel synthesis of the LCMO component powder. The investigation aimed to examine the impact of glycerol content on the structure, microstructure, elemental distribution, electrical transport properties, and magnetoresistive performance of La$_{0.67}$Ca$_{0.33}$MnO$_3$ polycrystalline ceramics.

2. Experiment Details

The La$_{0.67}$Ca$_{0.33}$MnO$_3$ polycrystalline ceramics were prepared using the sol-gel method. Firstly, appropriate amounts of La(NO$_3$)$_3$·6H$_2$O, Ca(NO$_3$)$_2$·4H$_2$O, Mn(NO$_3$)$_2$, and citric acid (AR, all chemicals purchased from Aladdin Reagent Co., Ltd.) were taken according to their relative contents. The pre-weighed reagents were sequentially added to a beaker and dissolved in methanol. Subsequently, different $r_v$ of 0%, 2%, 4%, 6%, and 8% was added separately, followed by heating and stirring to obtain a hydrogel. The hydrogel was then dried in an oven at 140°C to obtain the dried gel. After grinding, the samples were placed in a tube furnace and subjected to an initial firing at 500°C for 480 minutes, followed by a final firing at 1450°C for 720 minutes. This process led to the preparation of the required series of ceramic samples.

In this experiment, the crystalline structure, crystalline properties, and phase purity of the materials were characterized using an X-ray diffractometer (XRD, Rigaku Ultima IV, JP, Cu Kα radiations). The surface
morphology was observed using a scanning electron microscope (SEM, XL30ESEM-TMP, NED, 1.0×10⁻⁸ A, 20kV). The distribution of various elements on the sample surface was investigated using an energy-dispersive spectrometer (EDS). The resistivity-temperature (ρ-T) curve was obtained through four-point probe measurements to analyze the characteristics of resistance variation with temperature. Based on this, the changes in material structure and phase transition were analyzed. The samples underwent magnetoresistance (MR) testing to examine the changes in resistance with temperature under 0T and 1T magnetic fields, elucidating the electrical transport properties under varying magnetic fields.

3. Results and discussion

3.1 Crystal structure analysis

We prepared a series of La₀.₆₇Ca₀.₃₃MnO₃ samples using the sol-gel technique, with glycerol dispersant amount of 0%, 2%, 4%, 6%, and 8%. Their XRD patterns were measured, and Fig. 1 (a) shows the XRD diffraction pattern of the prepared ceramics. Comparison with the standard PDF NO.49–0416 cards reveals that all samples feature sharp diffraction peaks, suggesting the excellent crystallinity of the materials. Furthermore, they all exhibit the standard perovskite structure, without any presence of impurities.

The XRD refined patterns of LCMO ceramics are depicted in Fig. 1 (b-f). In the figure, "x" represents the diffraction data, the red line denotes the fitted data, the blue short vertical lines represent the fitted diffraction peak positions, and the blue line indicates the difference between the measured and fitted values. The figure shows that there is a strong agreement between the experimental results and the fitted results, providing additional confirmation of the samples' single-phase structure. In Table 1, the refined structural parameters are summarized, including space group, lattice constants (Å), unit cell volume (Å³), Mn-O bond length, Mn-O-Mn bond angle, R-factor, and goodness of fit factor. From the table, it can be observed that all samples have orthogonal perovskite structure (Pnma space group), and the lattice constants and unit cell volumes show little variation with increasing glycerol content.

Table.1 Cell information and refinement parameter of La₀.₆₇Ca₀.₃₃MnO₃ ceramics
<table>
<thead>
<tr>
<th>Additive amount</th>
<th>0%</th>
<th>2%</th>
<th>4%</th>
<th>6%</th>
<th>8%</th>
</tr>
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<tbody>
<tr>
<td>Space group</td>
<td>Pnma</td>
<td>Pnma</td>
<td>Pnma</td>
<td>Pnma</td>
<td>Pnma</td>
</tr>
<tr>
<td>Lattice parameter(Å)</td>
<td>a</td>
<td>5.448</td>
<td>5.456</td>
<td>5.460</td>
<td>5.437</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>7.700</td>
<td>7.711</td>
<td>7.715</td>
<td>7.709</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>5.465</td>
<td>5.474</td>
<td>5.476</td>
<td>5.437</td>
</tr>
<tr>
<td>Lattice volume(Å³)</td>
<td>V</td>
<td>229.231</td>
<td>230.307</td>
<td>230.657</td>
<td>227.885</td>
</tr>
<tr>
<td>Bond lengths</td>
<td>Mn-O₁</td>
<td>1.952</td>
<td>1.961</td>
<td>1.943</td>
<td>1.941</td>
</tr>
<tr>
<td></td>
<td>Mn-O₂</td>
<td>1.946</td>
<td>1.922</td>
<td>1.840</td>
<td>1.700</td>
</tr>
<tr>
<td>Bond angles</td>
<td>Mn-O₁-Mn</td>
<td>161.065</td>
<td>158.928</td>
<td>166.030</td>
<td>166.313</td>
</tr>
<tr>
<td></td>
<td>Mn-O₂-Mn</td>
<td>156.704</td>
<td>158.775</td>
<td>158.858</td>
<td>161.052</td>
</tr>
<tr>
<td>Consistency factor</td>
<td>R_p</td>
<td>0.068</td>
<td>0.114</td>
<td>0.158</td>
<td>0.1120</td>
</tr>
<tr>
<td></td>
<td>R_wp</td>
<td>0.046</td>
<td>0.089</td>
<td>0.122</td>
<td>0.091</td>
</tr>
<tr>
<td>Fitting factor</td>
<td>λ</td>
<td>1.563</td>
<td>1.565</td>
<td>1.515</td>
<td>1.510</td>
</tr>
</tbody>
</table>

### 3.2 Elemental distribution analysis

In order to investigate the elemental distribution of the material, EDS characterization was conducted on the LCMO ceramics with glycerol. The test image is shown in Fig. 2. Apart from La, Ca, Mn, and O, no other impurity elements are detected in the sintered product, indicating high sample purity. Also, all elements are evenly spread across the surface of the sample, corroborating the XRD detection results mentioned earlier. The atomic ratios of La, Ca, Mn, and O are 15.5: 7.9: 22.7: 53.9, which is in basic accordance with the theoretical atomic ratios of the raw materials, which are 0.67: 0.33: 1:3. This indicates that the raw materials for preparing the LCMO sample using the sol-gel technique have reacted almost completely, resulting in good yield and negligible material loss.

### 3.3 Surface morphology analysis

The SEM detection results are shown in Fig. 3 (a-e). It can be observed from the images that with the increase in glycerol content, the crystal morphology of the material undergoes changes, with the overall trend of grain size showing an initial increase followed by a decrease. In comparison to samples without glycerol, those with its addition exhibit a notable increase in grain size after sintering. This phenomenon arises from the effective prevention of aggregation by glycerol acting as a dispersant. Glycerol removes coordinated water molecules from the particle surface and substitutes hydroxyl groups on the particle surface with alkoxyl groups. By displacing water molecules adsorbed on the particle surface, glycerol reduces the action of hydrogen bonds between particles and the capillary forces of aggregation, thereby
maintaining dispersion between particles. Due to its high viscosity, glycerol reduces the crystal growth rate, hindering rapid crystal growth and resulting in a decrease in precursor particle size, thereby enhancing sintering activity. Moreover, glycerol also exhibits mutual solubility with methanol, allowing it to penetrate the interstices between particles during the reaction process, thereby preventing the accumulation and aggregation of LCMO sample particles during the drying stage.

When the $r_v$ reached 2%, the free energy of the grain boundaries promotes grain growth. This results in a decrease in the number of grain boundaries and a reduction in grain surface area, leading to densification of the bulk material. At this point, the grain size is 7.30 $\mu$m. Upon further addition of glycerol, an increase in the number of grain boundary pores occurs, leading to uneven grain sizes and a reduction in density. With a further increase of $r_v$ to 8%, the grain size rapidly decreases, and the number of pores between grain boundaries increases, resulting in uneven grain sizes. The decrease in particle size leads to a significant increase in resistivity, a shift of $T_P$ towards lower temperatures, and a substantial degradation of long-range ferromagnetic order in LCMO ceramics [27]. To summarize, the inclusion of a suitable quantity of glycerol can mitigate particle aggregation between particles, thereby ameliorating the electrical transport characteristics of the material.

### 3.4 Electrical transport property analysis

Figure 4(a) depicts the resistivity-temperature ($\rho$-$T$) curve of the ceramic under a 0 Tesla magnetic field, while Fig. 4(b) illustrates the $\rho$-$T$ curve of the ceramic under a 1 Tesla magnetic field. Across the 150 $\sim$ 300K temperature span, there is a discernible pattern in the electrical resistivity of the specimens, characterized by an initial decline followed by a subsequent rise as the glycerol content increases. The factors influencing the magnitude of electrical resistivity include A-site ion radius, grain size, and sintering quality, with grain size and sintering quality identified earlier in this chapter as the primary factors affecting resistivity in this system.

Analysis of the SEM images reveals pronounced aggregation in samples lacking glycerol, resulting in inferior sintering quality. This is evidenced by smaller grain sizes, increased internal grain boundary density, and elevated porosity at grain boundaries. Consequently, the heightened disorderliness at grain boundaries contributes to an increase in the sample's electrical resistivity [11]. When the $r_v$ reached 2%, the electrical resistivity reached its minimum value of 0.023 $\Omega$·cm, corresponding to a temperature of 268.8 K. At this concentration, the sample exhibits larger grain sizes, improved sintering quality, and higher density, resulting in reduced defect concentration. Furthermore, there is an enhancement in double exchange interactions, coupled with a weakening of electron scattering at grain boundaries. Consequently, the sample's conductivity is augmented, leading to a decrease in electrical resistivity.

Continuing the addition of glycerol leads to an enlargement of grain size and an increase in the number of pores within the sample. Upon reaching 6%, the powder has crystallized and grown, enhancing scattering effects that are detrimental to sintering and consequently resulting in an elevation of electrical resistivity. Upon reaching 8% glycerol content, a drastic reduction in grain size is observed, along with an augmentation in grain boundary density. In proximity to the grain boundaries, a substantial presence of
non-coordinated atoms is noted, intensifying the impact of defect stress fields and giving rise to an insulating layer surrounding the grain boundaries. Meanwhile, the occurrence of magnetic disorder near the grain boundaries becomes a major source of electron scattering, hindering electron transport and consequently raising the material's electrical resistivity.

The TCR curve of LCMO ceramics is illustrated in Fig. 5, where the TCR value characterizes the material's sensitivity to temperature, calculated using the formula depicted in Eq. (1) [28].

$$TCR = \frac{d\rho}{dT} \times \frac{1}{\rho} \times 100\%$$

Where $\rho$ and $T$ represent the electrical resistivity and the corresponding temperature, respectively. As per the definition, it is evident that there is a certain relationship between the TCR of the sample and its electrical resistivity. The primary factor influencing the magnitude of TCR is the size of the temperature range over which the material undergoes the M-I transition, while the uniformity and density of the material affect this transition range. As the ceramic grain size increases, the number of grain boundaries decreases, leading to better chemical homogeneity, which results in a narrower transition temperature range and a higher corresponding TCR value.

According to the TCR graph, the TCR value is 16.89%·K$^{-1}$ in the absence of glycerol, corresponding to a temperature of 261.4 K. As the amount of glycerol added increases, the TCR initially increases and then decreases. When the $r_v$ reached 2%, it achieves the highest value of 25.02%·K$^{-1}$, with a corresponding temperature of 263.2 K. The addition of a small quantity of glycerol can enhance the surface morphology of the sample, leading to larger grain sizes and a reduction in both grain boundaries and pores. This decrease in defects at grain boundaries and pores reduces electron scattering, ultimately resulting in an elevated TCR. When added excessively, there is an increase in particle aggregation between grains, leading to smaller grain sizes and a greater number of grain boundaries per unit volume. Consequently, the scattering caused by impurities and lattice disorder is amplified. Additionally, an excess of grain boundaries leads to the occurrence of spin polarization tunneling phenomena between grains, widening the transition range and consequently resulting in a lower TCR value [10]. However, when the $r_v$ reached 6%, although the grain size is the largest, there is a decrease in TCR. The reason behind this is the enlargement of grain size, combined with the presence of disordered structures at the grain boundaries, which causes an increase in grain resistivity and thus results in a decrease in TCR. Based on the aforementioned analysis, 2% glycerol is deemed the optimal amount for dispersant addition.

### 3.5 Magnetoresistive properties analysis

In Fig. 4(a) and (b), it is noted that with a 1 Tesla magnetic field applied, the resistivity of all samples decreases, while the metal-insulator transition temperature ($T_P$) shifts towards higher temperatures. This is attributed to the alignment of spin directions of adjacent Mn ions under a 1 Tesla magnetic field,
resulting in a decrease in the tilt angle of the magnetic moment of Mn ions within the magnetic domains. As the electron spin scattering decreases, the double exchange interaction strengthens, facilitating electron migration between Mn$^{3+}$ and Mn$^{4+}$ ions, which suppresses the insulating state of the LCMO material. The application of an external magnetic field results in the movement of the material's transition temperature towards higher temperatures, leading to a decrease in resistivity.

The magneto resistence phenomenon in the LCMO series ceramics is statistically analyzed in Fig. 6, with MR defined by Eq. (2) [17].

$$MR = \frac{\rho_0 - \rho_H}{\rho_0} \times 100\%$$

Where $\rho_0$ and $\rho_H$ represent the magnetoresistivity at 0 Tesla and 1 Tesla magnetic fields, respectively. The magnitude of MR reflects the sensitivity of the sample to the magnetic field. Evidently, a high MR is beneficial for the application of magnetic sensor devices. From the graph, it can be observed that as the glycerol content increases, the transition temperature ($T_M$) remains relatively stable, while the sample's MR first increases and then decreases. When $r_v$ reached 2%, the MR reached its maximum value of 55.40%. This is consistent with the trend observed in the SEM images, where the grain size first increases and then decreases with the increasing addition of glycerol [5].

For the LCMO ceramic system used in this experiment, the MR effect can be primarily divided into intrinsic magnetoresistance (MR$_{in}$) [29] and extrinsic magnetoresistance (MR$_{ex}$) [30, 31]. MR$_{in}$ is typically determined by the double exchange interaction between Mn-ions and the interaction between phonons and electrons, and is not significantly influenced by the grain size involved in this experiment [29]. Conversely, MR$_{ex}$ originates from spin-correlated scattering and spin polarization tunneling at phase boundaries and grain boundaries, and its magnitude usually shows a negative correlation with grain size [31]. Under a 1 Tesla magnetic field, the low-field magnetoresistance (LFMR) effect exhibited by the sample near the Curie temperature ($T_C$) is mainly attributed to MR$_{ex}$. Glycerol addition enhances the defects at the grain boundaries of the sample, thereby improving both atomic and magnetic disorder structures, and increasing the interconnectivity between particles. Hence, the attenuation of magnetic disorder in surface atoms of the grains reduces electron scattering, amplifies the chance of tunneling, effectively enhancing LFMR, which in turn reduces resistivity and increases MR.

### 4. Conclusion

In this study, glycerol was selected as the dispersant, and a series of LCMO samples were prepared using the sol-gel routine. The $r_v$ was set at 0%, 2%, 4%, 6%, and 8%. All samples exhibit a perovskite structure, with a space group of $Pnma$. Adding glycerol decreases the aggregation of powder particles, thereby increasing sample density and enlarging grain sizes. Simultaneously, it weakens the electron scattering
ability at grain boundaries and pores, introducing more spin disorder, thereby enhancing the electrical transport properties. Moreover, the reduction in electronic scattering augments the probability of electron tunneling, thereby intensifying the LFMR and resulting in an enhancement of the MR value. When the $r_v$ up to 2%, the sample achieves its peak performance, with a TCR of 25.02%·K$^{-1}$ and MR of 55.40%. This promotes the applications of LCMO ceramics such as infrared detectors and magnetic storage heads.

Declarations

Conflict of interest

The authors declare no competing interests.

Author Contribution

All authors contributed to the study conception and design. Yuchen Xie performed the data curation, formal analysis, and wrote the original draft. Chunling Liu performed validation. Yating Shen performed data curation. Shaozheng Wang performed writing - review & editing. Ping Yu performed conceptualization. Yule Li performed funding acquisition and writing - review & editing. Qingming Chen performed project administration and funding acquisition. Hui Zhang performed conceptualization, supervision, and writing - review & editing. All authors read and approved the final manuscript.

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References


2. P. Lisboa-Filho, A. Mombru, H. Pardo, W. Ortiz, E. Leite, Influence of processing conditions on the crystal structure and magnetic behavior of La_{0.7}Ca_{0.3}MnO_{3+δ} samples, Journal of Physics and Chemistry of Solids 64(4) (2003) 583-591. https://doi.org/10.1016/S0022-3697(02)00353-0


4. E. Pollert, S. Krupička, E. Kuzmičová, Structural study of Pr_{1-x}Ca_{x}MnO_{3} and Y_{1-x}Ca_{x}MnO_{3} perovskites, Journal of Physics and Chemistry of Solids 43(12) (1982) 1137-1145. https://doi.org/10.1016/0022-3697(82)90142-1


**Figures**
Figure 1

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Figure 2

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Figure 3

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Figure 4

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Figure 5

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Figure 6

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