The properties of magnetic moment and specific heat of La$_{0.7}$Ca$_{0.3}$MnO$_3$ polycrystalline at different resistance state

Wu Z H$^1$, Chen L D$^2$, Wang Q$^3$, Liu X J$^2$, Yu W D$^2$, Li X M$^2$

1 School of Urban Development and Environmental Engineering, Shanghai Second Polytechnic University, Shanghai 201209, P. R. China
2 State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P.R. China

E-mail: cld@mail.sic.ac.cn

Abstract. The electric-pulse-induced resistance switching behavior was studied in bulk La$_{0.7}$Ca$_{0.3}$MnO$_3$ polycrystalline at room temperature. The relationship between the thickness and the threshold value of electric pulse on La$_{0.7}$Ca$_{0.3}$MnO$_3$ bulk was studied. It was found that the threshold value of electric pulse depends on the thickness of samples. The decrease of the magnetic moment and specific heat in the low resistance state on La$_{0.7}$Ca$_{0.3}$MnO$_3$ are opposite to that observed on La$_{0.9}$Ca$_{0.1}$MnO$_3$. These phenomena may be associated with the different ground states of La$_{0.9}$Ca$_{0.1}$MnO$_3$ and La$_{0.7}$Ca$_{0.3}$MnO$_3$. The change of magnetic configuration would change the specific heat arising from ferromagnetic spin-waves component and charge carriers.

1. Introduction

The perovskite Re$_{1-x}$A$_x$MnO$_3$-based (Re=rare earth ions, A=alkaline ions) manganates have attracted extensive interest for their colossal magnetoresistance (CMR) effect in the past decades[1-6]. Recently, an electric-pulse-induced switching of electrical resistance (EPIR) was discovered in Re$_{1-x}$A$_x$MnO$_3$ (Re=rare earth ions, A=alkaline ions). This effect provides a possibility of a new nonvolatile memory, called resistance random access memory (RRAM), which is very promising for its easy fabrication, fast switching speed, high recording density, low power consuming, and nondestructive readout. However, the mechanism of such EPIR phenomenon has still not been completely exposed. It is not clarified whether the resistance change is dominated by the bulk effect or the interface effect between the electrode and the sample [7-11]. To better understand the electric properties of these materials and to make contact with various proposed models, it is important to measure the fundamental properties of manganite perovskites with EPIR effect. Specific heat is regard as a useful method for the study of physical properties. At high temperature, specific heat data probes the nature of the magnetic, structural and electronic phase transition. At low temperature, the data yields information on lattice, electronic and magnetic excitations. We expect the analysis of the low temperature specific heat data ($C$) can provide accurate values of lattice, electronic and magnetic components in the ferromagnetic (FM) state. In this paper, the electric-pulse-induced resistance (EPIR) switching behavior and specific heat of LCMO at different resistance states was studied in bulk La$_{0.7}$Ca$_{0.3}$MnO$_3$ polycrystalline. It was found that the decrease of the magnetic moment and specific heat in the low resistance state on
2. Experimental procedure

Single phase La_{0.7}Ca_{0.3}MnO_3 (LCMO) powder was synthesized by a chemical solution deposition (CSD) method, using La(CH_3COO)_3·2H_2O (99.9%), Ca(CH_3COO)_2·H_2O (99.99%) and Mn(CH_3COO)_2·4H_2O (99.999%) as the raw materials \(^7\). The La_{0.7}Ca_{0.3}MnO_3 polycrystalline ceramics were prepared by Spark Plasma Sintering (SPS), with subsequent heat treatment in air at 900 °C for about 5h. Disc-shaped samples (Φ4mm × 1.6 mm) were cut out of the bulk polycrystalline. Two silver pads as electrodes 3mm in diameter were deposited on the disc-shaped sample surface. Electric pulses were provided by AVIR-3-B-QTKA Pulse Generator. Resistance was measured with a two-probe method in which a constant current (1 μA) was applied (Keithley 2410) to the junction while the voltage in the circuit was measured (Keithley 2000). The magnetization properties measurements were performed in commercial Quantum Design Physics Property Measurement System (PPMS). Specific heat measurements of La_{0.7}Ca_{0.3}MnO_3 polycrystalline at electric-pulse-induced different resistance states were carried out by using the thermal relaxation method from 2K to 20K. The background signal, including the exact amount of Apiezon N used to paste the sample on the platform, was recorded in a first run, and subtracted from the total heat capacity. The different resistance states used in magnetic moment and specific heat measurement were modulated at room temperature. First, a negative/positive electric pulse was applied to the sample (80V, 30ns; the resistance of the system was modulated to a stable resistance state) and then the temperature dependence of magnetic moment/specific heat was measured. After the magnetic moment/specific heat measurement, the temperature was increased to room temperature and another positive/negative electric pulse was applied.

3. Results and discussion

Effects of electric pulses on the two-terminal resistance of the LCMO systems are studied, and the typical results are shown in Fig. 1. Significant variation of the resistance is observed in the Ag/LCMO system. The structure of Ag/LCMO/Ag system is symmetrically. Then the first electric pulse leaded the resistance to increase or decrease randomly. The polarization of the electric pulse which inducing the resistance to HRS is defined as a negative voltage \(^7\). Reversed polarization of the electric pulse which inducing the resistance to LRS is positive voltage (seen bottom of Fig. 1). The ratio of high resistance (R_h) to low resistance (R_l) is as large as ~3. The threshold value of electric pulse (U_{th}) to change the resistance state depends on the thickness of sample. And the polycrystalline bulk sample is much thicker than thin film used in previous study, thereby, the threshold value of electric pulse (80V) employed to change the resistance state of La_{0.7}Ca_{0.3}MnO_3 polycrystalline bulk in our experiment is much larger than the film used (5~15V). The relationship between the thickness and U_{th} on LCMO bulk were studied. It was found that U_{th} depends on the thickness of samples (see Fig. 2). However, U_{th} also depend on original resistance value, top electrodes, number and amplitude of the voltage pulses.

The effect of grain boundary (GB) is a considerable topic. GB plays an important role on the resistance and magnetization properties of polycrystalline LCMO. However, the EPIR phenomenon has been found in SrTiO_3 single-crystalline by Krzysztof Szot (Nature Materials 5, 312) recently. They reported that the switching behaviour is an inherent property of the material. The phenomenon is shown to originate from local modulations of the oxygen content. And in our experiments, the results can be explained by local modulations of the oxygen content. Therefore, we think the EPIR phenomenon of polycrystalline LCMO would be related to the modulating intrinsic properties of pervskite manganites.

The M (H) dependence for HRS and LRS of La_{0.7}Ca_{0.3}MnO_3 polycrystalline at 10K are shown in Fig. 3. The difference of saturated magnetic moment between HRS and LRS is very small. The magnetic moment of HRS is larger than that of LRS. The saturated magnetic moment of HRS and
LRS is counted to be about 2.1μB/Mn in our measurement. The saturated magnetic moment of 2.1 μB / Mn at 10 K is really a small value for the bulk LCMO. Usually, the saturated magnetic moment of bulk La0.7Ca0.3MnO3 is reported about 3.5 μB / Mn [12-15]. In the present experiment, the bulk sample was designed by Spark Plasma Sintering methods. The Spark Plasma Sintering (SPS) progress is a speedy sintering progress in a deoxidized atmosphere. It is often the case that there are lots of oxygen vacancies in sample synthesized by SPS. According to the reports of L. Ghivelder (PRB, 60, 12184) and Ilryong Kim (PRB, 62, 5674), oxygen plays an important role in determining the electromagnetic properties of LCMO, such as the nonuniformly distributed oxygen would induce PS with ferromagnetic-metal and antiferromagnetic-insulator coexistence. The small change of oxygen content would cause phase transition due to the double exchange interaction in manganites. It can be seen from M-H dependence of SPS synthesizing sample, the magnetic moment is not real saturation. This implies the ferromagnetic-metal and antiferromagnetic-insulator coexistence, which could be the cause of low saturated magnetic moment.

![Fig 1. Resistance switching of La0.7Ca0.3MnO3 polycrystalline bulk at room temperature as a function of electric pulse (80V and 20ns).](image1)

![Fig 2. The relationship between the thickness and Uth on LCMO bulk under 1 electric pulse with 30ns length.](image2)

Ions motion driven by electric pulse current has been presented for explaining the resistance switching [16-19]. The electric pulse leads electrochemical creation or diffusion of oxygen vacancy along extended defects, such as dislocations, phase contact boundary and planar defects. During a positive pulse, the electric field drives oxygen ions moving along quasi-one-dimensional extended defects under the electrodes. The vacancies defects are healed and the number of free carriers is increased. Therefore, the filamentary conducting route develops and the resistance transits to the LRS. During a negative pulse, oxygen ions escape from the extended defects and the number of carriers is decreased, and the resistance recovers to the HRS [8-11].

The decrease of the magnetic moment in the low resistance state on La0.7Ca0.3MnO3 is opposite to that observed on La0.9Ca0.1MnO3. These phenomena may be associated with the different ground states of La0.6Ca0.4MnO3 and La0.7Ca0.3MnO3. For La0.7Ca0.3MnO3, the ground state is ferromagnetic (FM) metal, the magnetic moment expected from the spin contribution is $gS\mu_B$, where $S$ is the spin of the ion, which is 3/2 for Mn$^{3+}$ and 2 for Mn$^{4+}$, and the gyromagnetic factor is $g=2$ in both cases. Then the increase of Mn$^{4+}$/Mn$^{3+}$ would decrease the total magnetic moment of La0.7Ca0.3MnO3. The electric pulse leads to electrochemical creation or diffusion of the oxygen vacancy. During the positive pulse, the electric field drives oxygen ions moving along quasi-one dimensional extended defects. The vacancies defects are healed and the number of oxygen ions is increased. The resistance transits to LRS. The increase of oxygen ions would increase the ratio of Mn$^{4+}$/Mn$^{3+}$ and the increase of Mn$^{4+}$/Mn$^{3+}$ would decrease the total magnetic moment of La0.7Ca0.3MnO3. During a negative pulse,
oxygen ions escape from the extended defects and the ratio of Mn$^{4+}$/Mn$^{3+}$ would decrease. The resistance recovers to HRS and the total magnetic moment increases. Therefore, the magnetic moment of La$_{0.7}$Ca$_{0.3}$MnO$_3$ decreases in the low resistance state. On the other hand, for La$_{0.9}$Ca$_{0.1}$MnO$_3$, the ground state is magnetic multiphase coexistence insulator and the insulating character is interpreted as a disorder effect. The motion of oxygen would change the hole density of local regions. The change of hole density would still exist at low temperature and the change of hole density would lead to local AF and FM phase transition. These local ferromagnetic regions would connect ferromagnetic clusters of the nonstoichiometric samples, which are suspected to also be generated by inhomogeneous distribution of oxygen. The magnetic clusters grow to form larger clusters. The larger clusters would decrease the resistance and give rise to the value of magnetic moment. Therefore, the magnetic moment in the low resistance state of La$_{0.9}$Ca$_{0.1}$MnO$_3$ increases.

Fig 3. M-H curves for HRS and LRS of La$_{0.7}$Ca$_{0.3}$MnO$_3$ polycrystalline bulk synthesized by SPS.

Fig 4. The low-temperature specific heat for HRS-1200, and LRS-12 from 2K to 20K. The lines are the best fits to the data as listed in Table I.

Specific heat results of LCMO at electric-pulse-induced different resistance states from 2K to 20K are shown in Fig. 4. The specific heat shows a distinct increase as the magnitude of resistance states increase. In order to evaluate the various contributions to the specific heat, results for each sample in the ferromagnetic region from 2K to 20K were fitted to the expression

\[ C = \gamma T + \delta T^{3/2} + \beta T^3 \]  

Eq (1)

where \( \gamma \), \( \delta \), and \( \beta \) are constants. These three terms are expected to rise from, respectively, charge carriers, ferromagnetic spin waves, and the lattice. The fitting parameters obtained for all resistance states are given in Table I, and the fitted curves can be seen in Fig 4 as dash dot. It can be seen from the fitting data that the ferromagnetic spin-waves contribution has obvious decrease as the magnitude of resistance states decrease, whereas \( \beta \) almost does not change with the resistance states. And \( \gamma \) increases as the magnitude of resistance states decrease. These results imply that the change of specific heat may come from the change of specific heat of charge carriers and ferromagnetic spin-waves contribution with changing the magnetic configuration. To confirm the change of the specific heat is related to ferromagnetic spin-wave, the difference of specific heat between HRS-1200 and LRS-12 plotted as \( C/T \) versus \( T^{0.5} \) are shown in Fig. 5. The data seem to fall on a single line within a small error for each resistance state, indicating that the above estimate of the spin-wave component is fairly accurate. From \( \beta \) we obtain the Debye temperature by using the standard expression

\[ \theta_D = \left( \frac{12\pi^4 pR}{5\beta} \right)^{1/3} \]  

Eq (2)
where $R$ is the ideal gas constant and $p = 5$ is the number of atoms per formula unit. We get $\theta_D = 326$K for HRS-1200 and LRS-12, are comparable to those previously reported in manganite perovskites. There is no obvious change of $\theta_D$ as the resistance decreases. Then we would like to address the question of the spin-waves contribution to the specific heat. If the spin-wave stiffness constant is $D$, and there is no gap in the excitation spectrum, then we would have

$$\delta = 0.113Ra^3\left(\frac{k_B}{D}\right)^{3/2}$$

Eq (3)

where $a$ is the lattice parameter of the elementary perovskite cell and $k_B$ is the Boltzmann constant. The term 0.113 is a constant related to the cubic lattice. We get $D = 57$meV Å$^2$, and 46meVÅ$^2$ for HRS-1200 and LRS-12, respectively.

![Graph](image)

**Fig 5.** $\Delta C_p$ vs $T^{3/2}$. Here $\Delta C_p$ is specific heat difference as compared with LRS-12. $\Delta C_p = C_{p1200} - C_{p12}$. The lines are the fitting curves.

**Table 1.** Fitting results of the low-temperature specific heat of La$_{0.9}$Ca$_{0.1}$MnO$_3$ at different resistance states

|      | $\gamma$   | $\beta$   | $\delta$  |
|------|-------------|------------|------------|
| HRS-1200 | 3.23781    | 0.28134    | 1.26615    |
| MRS-12    | 4.39612    | 0.27816    | 0.46543    |

The motion of oxygen induced by electric pulses would change the hole density of local regions. The change of hole density would still exist at low temperature and modulate the low temperature magnetic configuration of LCMO. At low resistance state, the regions enriched with oxygen have an enhanced hole density and the holes would establish local ferromagnetic ordering at low temperature. The magnetic clusters grow to form larger clusters where the spins become more ordered. The larger clusters should give rise to the value of $D$, as it is expected to increase the strength of the ferromagnetic coupling. According to Eq(3), the increase of $D$ would decrease the spin-waves contribution to the specific heat. At high resistance state, oxygen ions escape from the extended defects, the spin-waves contribution to the specific heat increases.
4. Conclusion
In conclusion, the EPIR effects are studied in La$_{0.7}$Ca$_{0.3}$MnO$_3$ polycrystalline materials. The magnetic moment and specific heat decreases when the magnitude of resistance states induced by electric-pulse decrease. The decrease of the magnetic moment and specific heat in the low resistance state on La$_{0.7}$Ca$_{0.3}$MnO$_3$ is opposite to that observed on La$_{0.9}$Ca$_{0.1}$MnO$_3$. These phenomena may be associated with the different ground states of La$_{0.9}$Ca$_{0.1}$MnO$_3$ and La$_{0.7}$Ca$_{0.3}$MnO$_3$. These results imply that the change of resistance states would be related to the electric pulse driven oxygen ion motion. The change of specific heat comes from the change of specific heat of charge carriers and ferromagnetic spin-waves contribution with changing the magnetic configuration.

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