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Short communication

Magnetic phase transition in $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ ceramic composites

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Abstract

Magnetic phase transition characteristic in $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ composites with different grain size was investigated in this work. There were double maxima in $|dM/dT|–T$ curves for the composites with grain size in the range of 100–200 nm sintered at relative low temperature for short time, which indicated that two paramagnetic–ferromagnetic (PM–FM) transitions happened. The PM–FM transition temperatures of T_{c1} and T_{c2} were the contribution of grain boundary and grain, respectively. T_{c1} varied with Ta_2O_5 content and sintering condition, whereas T_{c2} remained almost the same value. For the composites with grain size larger than 500 nm sintered at high temperature for long time, single magnetic phase transition behavior was observed.

Keywords: Magnetic properties; Perovskites; Composites

1. Introduction

As a strongly correlated electron system, the rare earth doped perovskite manganese which has colossal magnetoresistance (CMR) effect has been extensively studied, due to exhibiting intriguing physical properties such as insulator–metal transition, charge ordering, orbital ordering and phase separation [1–3]. Recently, in the research of CMR materials perovskite manganese-based composites have drawn much attention, as the observed enhanced low-field magnetoresistance (LFMR) in this kind of composite [4,5]. When an insulating second phase material (Ta_2O_5) was introduced to the parent phase of perovskite manganese, for example, LFMR enhancement was observed over a wide range of temperature from 50 to 350 K, which had been reported in our previous work [6]. The magnetic property was complicated, especially for the paramagnetic–ferromagnetic transition. However, it has not been discussed in detail. In this work the magnetic phase transition characteristic in $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ composites was studied.

2. Experimental

The $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) powders were prepared by sol–gel method as described by Siwach et al. [7], in which the precursor powders were calcined at 1000 °C for 2 h in air atmosphere. The precursor LSMO powders were then mixed with commercial Ta_2O_5 powders with Ta_2O_5 weight fraction of $x = 0\%$, 4%, 10%, 15% and 25%. The mixed powders were ground and pressed into pellets. The wafers were sintered at 1000–1200 °C for 10 min–20 h in air. Superconducting quantum interference device magnetometer (SQUID, Quantum Design) was used to measure magnetization versus temperature. The microstructural characteristics were performed using a scanning electron microscope (SEM, Quanta 200).

3. Results and discussion

The microstructure, phase characteristics, magnetic and transport properties for $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ composites have been discussed in the previous paper [6]. It was found that a small amount of Ta ions entered into LSMO grains near the grain surface region and LFMR enhancement was observed

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Table 1
Magnetic phase transition temperature (T_c) and average grain size for different samples.

	Sample	T_{c1} (K)	T_{c2} (K)	T_c (K)	Grain size
Group I	Ta_2O_5 0%, 1000 °C 10 min	283.0	345.2		100 nm
	Ta_2O_5 4%, 1000 °C 10 min	304.0	345.1		100 nm
	Ta_2O_5 10%, 1000 °C 10 min	305.0	344.5		100 nm
	Ta_2O_5 15%, 1000 °C 10 min	295.0	345.3		100 nm
	Ta_2O_5 4%, 1000 °C 2 h	309.0	345.5		200 nm
Group II	Ta_2O_5 4%, 1000 °C 20 h			352.0	500 nm
	Ta_2O_5 4%, 1100 °C 2 h			344.0	700 nm
	Ta_2O_5 4%, 1200 °C 2 h			311.0	1 μm

over a wide range of temperature from 50 to 350 K. No significant change in the grain size was observed with the addition of Ta_2O_5. The average grain size for different samples is shown in Table 1.

Fig. 1 shows the temperature dependence of magnetization, $M(T)$, under an applied field of 5 kOe for $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ composites sintered at 1000 °C for 10 min. All samples exhibit a transition from high temperature paramagnetic behavior to low temperature ferromagnetic behavior. The magnetic transition happens over a wide range of temperature, about 200 K, which is a typical characteristic for perovskite manganese composites. Different from that for traditional ferromagnets, the paramagnetic–ferromagnetic (PM–FM) transition for perovskite manganese oxide is characterized by phase separation. The PM–FM transition commonly happens over a wide range of temperature [2,8,9]. In this kind of material, the PM–FM transition temperature, T_c, could be determined as the temperature of the maximum value for $|dM/dT|$ [3,10–13].

The absolute values of differential of magnetization, $|dM/dT|$, for $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ composites sintered at 1000 °C for 10 min are given in Fig. 2. Obvious double maxima are observed in $|dM/dT|$–T curves. The low and high temperatures of the maximum value for $|dM/dT|$ are defined as T_{c1} and T_{c2}, respectively. The values of T_{c1} and T_{c2} for different samples are listed in Table 1.

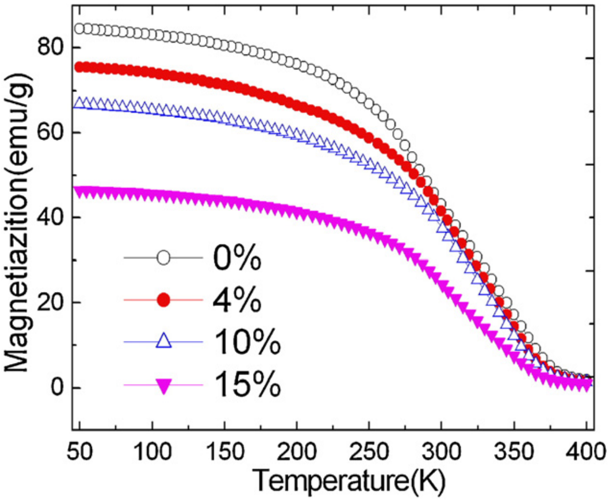

Fig. 1. Temperature dependence of magnetization at 5 kOe for $(1-x)La_{0.7}Sr_{0.3}MnO_3/xTa_2O_5$ composites sintered at 1000 °C for 10 min.

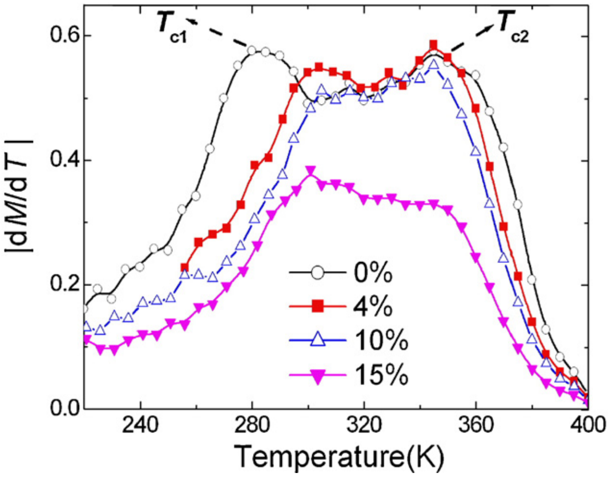

Fig. 2. Temperature dependence of $|dM/dT|$ for $(1-x)La_{0.7}Sr_{0.3}MnO_3/xTa_2O_5$ composites sintered at 1000 °C for 10 min.

The double maxima in $|dM/dT|$–T curves fade away with increasing sintering temperature and time and clearly single PM–FM transition peak can be seen. Fig. 3 shows temperature dependence of $|dM/dT|$ for composites containing 4% Ta_2O_5 sintered from 1000 °C for 10 min to 1200 °C for 2 h. Two magnetic phase transition peaks could also be seen for the sample sintered at 1000 °C for 2 h. When sintering condition exceeds 1000 °C for 20 h, single magnetic phase transition peak appears and the transition temperatures are listed in Table 1.

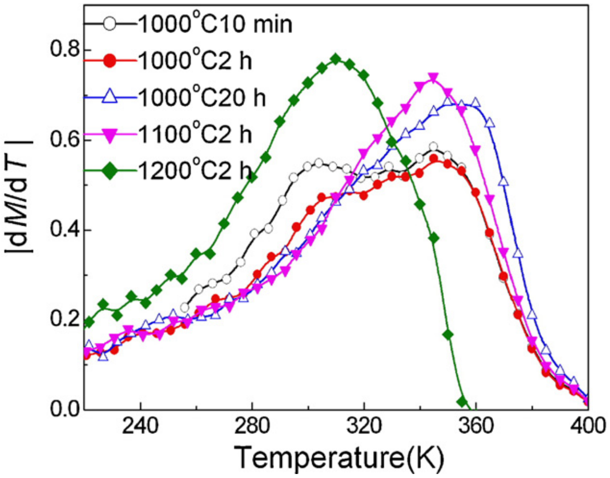

Fig. 3. Temperature dependence of $|dM/dT|$ for $(1-x)La_{0.7}Sr_{0.3}MnO_3/xTa_2O_5$ composites ($x = 4\%$) prepared at different sintering condition.

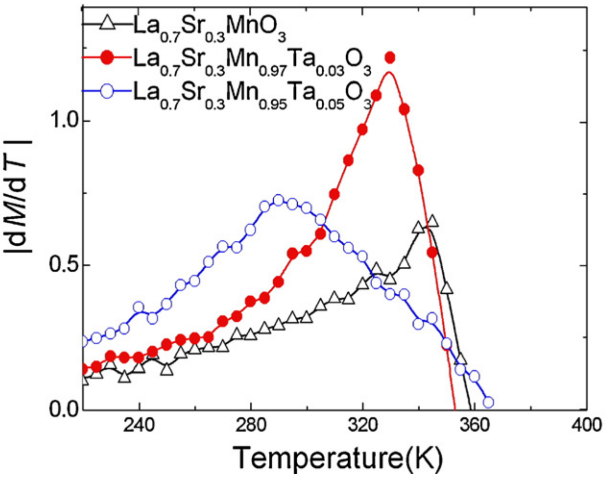

Fig. 4. Temperature dependence of $|dM/dT|$ for Ta substituted $La_{0.7}Sr_{0.3}MnO_3$ ($La_{0.7}Sr_{0.3}Mn_{1-x}Ta_xO_3$) prepared by solid-state reaction sintering at 1200 °C for 2 h.

All samples in this work could be classified into two groups, shown in Table 1. Group I corresponds to the samples with grain size $d \leq 200$ nm sintered at relatively low temperature for shorter time and Group II corresponds to the samples with grain size $d \geq 500$ nm sintered at higher temperature for longer time. In Group I, T_{c2} remains almost the same value and T_{c1} varies significantly with Ta_2O_5 content. In Group II, T_c obviously decreases with increasing sintering temperature. The decrease of T_c is the substitution effect of Mn site by Ta in LSMO grains.

To verify the substitution effect of Ta, a series of $La_{0.7}Sr_{0.3}Mn_{1-x}Ta_xO_3$ ($x = 0$, 0.03 and 0.05) were prepared by the standard solid-state doping reaction, taking stoichiometric amounts of La_2O_3, $SrCO_3$, $Mn(CH_3COO)_2 \cdot 4H_2O$ and Ta_2O_5 powders as the starting materials. The mixed powders were ground and pressed into pellets and then sintered at 1200 °C for 2 h. Clearly single PM–FM transition can be observed from $|dM/dT|$–T curves, shown in Fig. 4. T_c decreases with the increase of Ta substitution due to enhanced local structural distortions [14,15]. For the samples in this group, the increase of sintering temperature will make Ta_2O_5 further react with LSMO grains. In this process, Ta ion will substitute Mn site to decrease of T_c, which is a doping effect.

Then, the behavior of two magnetic phase transitions in $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ composites is discussed. In the $La_{0.67}Ca_{0.33}Mn_{1-x}V_xO_3$ compound studied by Atalay et al. [16,17], two Curie temperatures were also observed, which was explained by the existence of two different ferromagnetic phases: one is rich in La and Mn, and the other is rich in Ca and V. Similar phenomenon has been reported in $La_{2/3}Ca_{1/3}MnO_3/CuMn_2O_4$ [18] and $La_{2/3}Ca_{1/3}MnO_3/MgO$ composites [19]. However, the compound they studied had large grain size (>10 μm), which was far bigger than the $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ composites in this study.

Two magnetic phase transition characteristic in $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ composites could be interpreted by considering the different magnetic contribution of grain boundary and grain. The grain size for composites sintered at lower temperature for shorter time (Group I in Table 1) is in the range of 100–200 nm. The proportion of grain boundary phase is so high that it contributes obvious magnetization to the whole sample. The overall magnetic property can be divided into grain and grain boundary with their respective contribution. The phase transition temperature of grain and grain boundary is different, resulting in double maxima in $|dM/dT|$–T curves. The phase transition temperatures of T_{c1} and T_{c2} are the contribution of grain boundary and grain, respectively. The grain boundary is Ta_2O_5 enriched area, so that the corresponding phase transition temperature (T_{c1}) changes obviously with Ta_2O_5 content and sintering condition. By contrast, the phase transition temperature of grain (T_{c2}) remains almost the same value, as Ta_2O_5 has slight reaction with LSMO grains in lower temperature with short time sintering process.

The grain sizes become larger for the samples sintered at higher temperature for longer time (Group II in Table 1), which is confirmed by SEM analysis. Fig. 5 presents typical microstructures for $La_{0.7}Sr_{0.3}MnO_3/Ta_2O_5$ composites sintered at two different temperatures. The grain size of the composite sintered at 1200 °C for 2 h is about 1 μm, 5 times higher than that of the composite sintered at 1000 °C for 2 h. The magnetic contribution of grain boundary for the composite in Grout II becomes negligible to the whole sample. As a result, single PM–FM transition was observed.

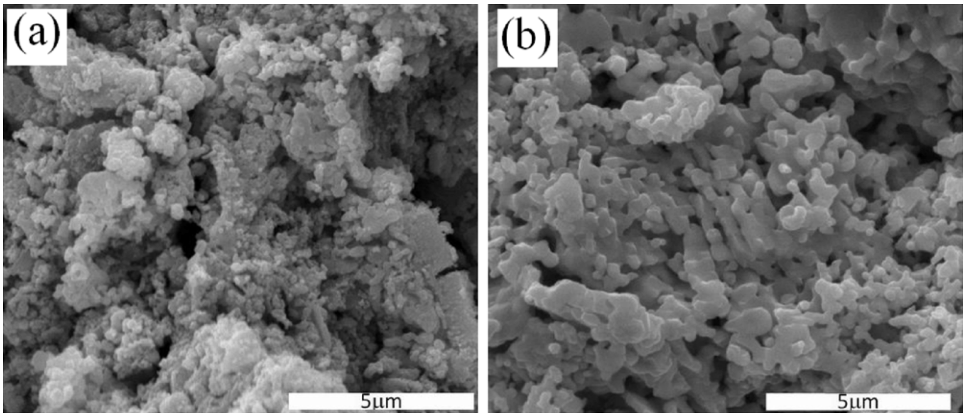

Fig. 5. SEM for $(1-x)La_{0.7}Sr_{0.3}MnO_3/xTa_2O_5$ ($x = 4\%$) composites sintered at 1000 °C for 2 h (a) and sintered at 1200 °C for 2 h (b).

4. Conclusion

Two PM–FM transitions are observed in $La_{0.7}Sr_{0.3}MnO_3$/Ta_2O_5 composites sintered at lower temperature for shorter time. The transition temperatures of T_{c1} and T_{c2} are the contribution of grain boundary and grain, respectively. The value of T_{c1} varies obviously with Ta_2O_5 content and sintering condition, as Ta_2O_5 mainly affects the magnetic properties of grain boundary. Ta_2O_5 has slight reaction with LSMO grains, so that T_{c2} remains almost the same value. Single magnetic phase transition and decreased T_c due to doping effect are observed in the composites sintered at higher temperature for longer time.

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