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The low frequency internal friction and electric magnetic properties in $La_{0.7}Pb_{0.3}MnO_3$ bulk materials

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Abstract

The polycrystalline samples of $La_{0.7}Pb_{0.3}MnO_3$ synthesized by the sol–gel method were studied by the low frequency internal friction measurements and the resistance and ac susceptibility measurements. There are two internal friction peaks at 258 and 198 K, respectively, the peak positions of which do not shift with frequency but the peak heights of which decrease with increasing frequencies. The modulus softening is evident at the corresponding temperatures. Corresponding to the two internal friction peaks, there are two resistance peaks, and a sharp rise and a following continuous decrease of ac susceptibility. It is suggested that the high temperature peaks correspond to the paramagnetic (PM) to ferromagnetic (FM) transition, while the low temperature peaks originate from the process of an anti-ferromagnetic phase (AFM) separating from the ferromagnetic matrix (phase separation) in polycrystalline materials. The peak positions of internal friction and resistance will move towards higher temperature when the sample was annealed in flowing oxygen, and the low temperature peaks become smaller.

Keywords: Internal friction; Phase separation; CMR effect; $La_{0.7}Pb_{0.3}MnO_3$

1. Introduction

After being discovered in the early 1950s [1], doped perovskite manganese oxides of the general formula, $R_{1-x}A_xMnO_3$ (where R is a trivalent rare earth element such as La, Nd, and Pr, while A is an alkaline earth element such as Ca, Ba, Sr, and Pb), have attracted renewed interest in the recent past on account of the colossal magnetoresistance (CMR) and related phenomena [2–5]. The $La_{1-x}Pb_xMnO_{3-\delta}$ (LPMO) material attracts yet much attention, because its transition temperature from metal to insulator (M–I) is close to or beyond room temperature. The ferromagnetic phase transition is simultaneous with a transition from metal to insulator in these kinds of materials, which is explained by Zener [6] with double-exchange (DE) mechanism. However, there are some arguements about the mechanism, Millis et al. [7] suggest that electron–phonon coupling arising from the distortion of the MnO_6 octahedron due to the Jahn–Teller (J–T) effect should play an important role in CMR compounds. Therefore, the mechanism of the CMR effect remains unclear and triggers a lot of researches. The internal friction technique is a non-destructive but sensitive tool, not only for studying defects and microscopic processes but also for studying the phase transitions in the ferroelectric and CMR materials [8–10]. In this paper, we have studied the relationships between internal frictions of low frequency and transport properties in manganese oxide LPMO.

2. Experimental

The powders of LPMO with nominal composition of $La_{0.7}Pb_{0.3}MnO_3$ were prepared with sol–gel method from stoichiometric mixtures of La_2O_3, $Pb(NO_3)_2$, $Mn(NO_3)_2$, dilute HNO_3, and CH_4N_2O. Then, the extra-fine LPMO powders were reground and pressed into bars (70 mm × 4 mm × 1.8 mm) and sintered at 1250 °C for 20 h. The XRD diffraction pattern of bulk, which was measured by powder X-ray diffractometer (Japanese Rigaku D/Max-γA) using Cu Kα radiation at room temperature, reveals that

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the sample is a single phase of pseudo-tetragonal structure, with $a \approx b = 5.60$ Å and $c = 7.78$ Å. The low frequency internal frictions were measured from 100 to 300 K in a torsion pendulum in the forced vibration mode at a strain amplitude of about 3×10^{-5}. Three vibration frequencies (0.1, 0.3, and 1.0 Hz) were used in one measurement run of ascending temperature with a heating rate of about 2 K/min. The dc resistances of the bulk were measured by the four-probe method from 50 to 300 K. A magnetic field of 0.5 T was applied parallel to the surface of the sample to check the CMR effect. The ac susceptibility of LPMO bulk was measured by mutual inductance method from 100 to 300 K under an ac magnetic field of 0.15 G varying with a frequency of 1000 Hz.

3. Results and discussion

Fig. 1 shows the temperature dependencies of the resistance under 0 and 0.5 T magnetic field and the ac susceptibility of a LPMO sintering sample. There are two resistance peaks in the sample, indicating two metal–insulator (M–I) transitions. For simplicity, the peak at high temperature is denoted as P1 with the peak temperature of $T_{\mathrm{P1}} = 253$ K, and the peak at low temperature is denoted as P2 with $T_{\mathrm{P2}} = 205$ K. When a magnetic field of 0.5 T is applied, the resistances in the whole temperature range become smaller, and both P1 and P2 peaks shift to higher temperature. According to the definition of MR ratio, $\mathrm{MR} = (R_0 - R_{\mathrm{H}})/R_0$, where R_0 and R_{H} are the resistances in a zero field and an applied magnetic field, respectively, a maximum MR ratio of about 22% occurs at 248 K and the MR ratio keeps at 10% at lower temperatures.

As shown in Fig. 1, with decreasing temperature, the ac susceptibility (χ) keeps at a small value at high temperatures, but rises sharply around Curie temperature ($T\mathrm{c} = 255$ K), indicating a paramagnetic (PM) to ferromagnetic (FM) phase transition, and then decreases slowly below 230 K. The coincidence of Tc with T_{P1} indicates that the P1 peak corresponds to a transition from PM to FM phase. At temperatures below 230 K, the continuous decrease of χ with decreasing temperature implies that there may be some anti-ferromagnetic (AFM) phase in the sample. In other words, after passing through the first transition from PM to FM, an AFM phase has been separated from FM matrix (phase separation). Because there is no apparent variation in χ–T curve around T_{P2}, the assignment of P2 peak to the process of phase separation needs more experimental evidences.

Similar phenomena associated with the double resistance peaks were reported in the literatures and many different mechanisms were suggested. Some authors assigned the low temperature peak (P2 peak) to tunneling effects through grain boundaries and interfaces [11]. The double resistance peaks in lithium-doped $\mathrm{LaMnO_3}$ were reported and a mechanism of magnetic inhomogeneity was proposed for the P2 peak [12]. In self-doped and potassium-doped $\mathrm{LaMnO_3}$ [13–15], the double resistance peaks were also reported and the mechanism of AFM phase separating from the FM matrix was assigned to the P2 peak. In strontium-doped $\mathrm{LaMnO_3}$ [16], a relatively high P2 peak was observed, and was explained to be associated with a process of structural phase transition. In our case, the P2 peak is higher than P1 peak, as in the strontium-doped $\mathrm{LaMnO_3}$ [16], but there is no structural phase transition at temperatures around P2 peak in LPMO sample.

To understand the mechanism of P2 peak, we measured the internal friction and the relative shear modulus of LPMO samples. The shear modulus is relative because it is proportional to the real value of shear modulus of the sample and the proportionality factor is dependent only upon the torsion pendulum and the size of sample. The temperature dependence of internal friction and elastic modulus at three different frequencies for a LPMO sample is shown in Fig. 2. The elastic moduli increases with temperature decrease and after

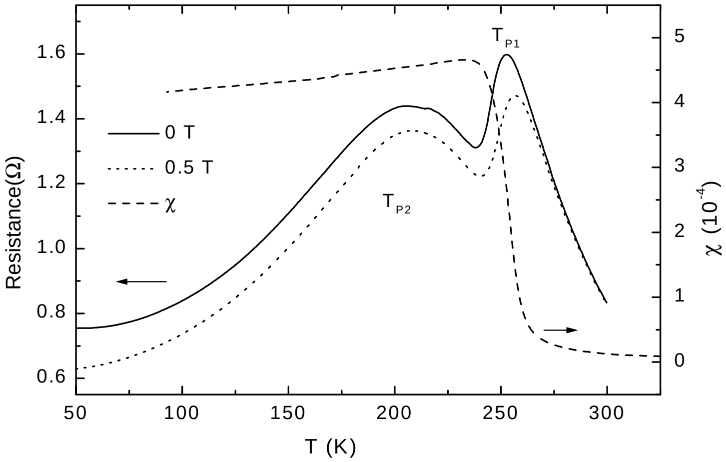

Fig. 1. Temperature dependencies of resistance and ac susceptibility for a $\mathrm{La_{0.7}Pb_{0.3}MnO_3}$ sample. The real line and the dot line are the resistance at zero and 0.5 T magnetic field, respectively, while the dash line represents the ac susceptibility.

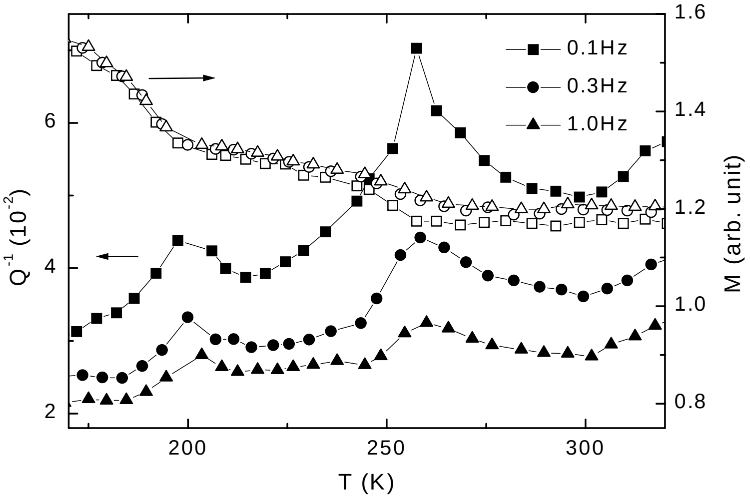

Fig. 2. Temperature dependencies of internal friction and relative elastic modulus measured at three different frequencies for a $La_{0.7}Pb_{0.3}MnO_3$ sample.

passing through a minimum at 258 K, the moduli increases continuously. At 200 K, a kink is observed on the curve of elastic moduli versus temperature. The internal frictions begin to increase with decreasing temperature, and develop a clear peak at 258 K where the moduli have a local minimum. Another lower internal friction peak appears around 200 K, corresponding to the modulus kink.

With decreasing frequency from 1.0 to 0.1 Hz, these two internal friction peaks increase in height but hardly change their positions as shown in Fig. 2. Both the inverse proportionality of the peak height with measuring frequencies and the invariance of the peak position by changing frequencies are typical features of phase transition. These facts indicate that the two internal friction peaks are related to processes of phase transition.

Similar with our previous results [14–16], the peak temperature of the two internal friction peaks coincide very well with T_{P1} and T_{P2}, suggesting the same origins for the internal friction peaks and the resistance peaks. As discussed above, the internal friction peak at high temperature, corresponding to the P1 resistance peak, originates from a transition from PM phase to FM phase. The internal friction peak at low temperature, which corresponds to the P2 resistance peak, is associated with the process of magnetic phase separation in the sample, that is, the AFM phase with less Mn^{4+} ions was separated from the FM matrix. Because the grain boundaries or interfaces cannot cause any internal friction peaks at such low temperature that exhibits characteristics of phase transition, the mechanism of interface tunneling can be excluded for the appearance of P2 peak. The occurrence of magnetic phase separation can be partly illustrated by the decrease of ac susceptibility with temperature in the same temperature range.

The as-prepared sample may contain oxygen deficiency, which will decrease the number of Mn^{4+} ions introduced by Pb^{2+} doping and increase the probability of AFM phase separating from the FM matrix. Therefore, annealing in oxygen atmosphere would affect the P2 peak and the internal

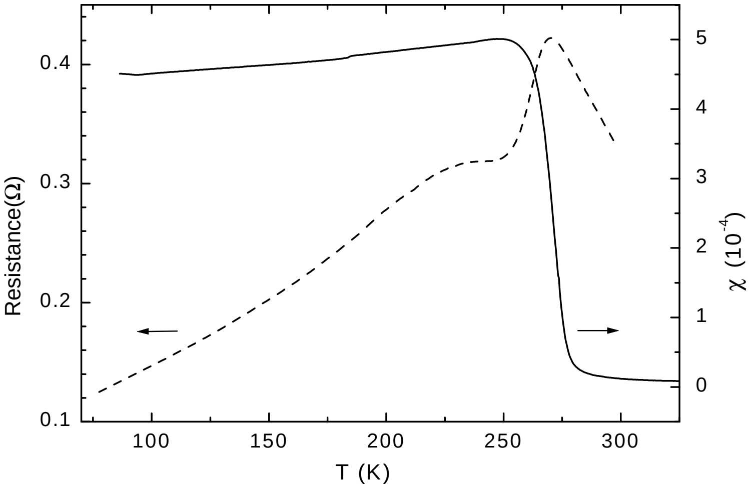

Fig. 3. Temperature dependencies of resistance and ac susceptibility (χ) of a $La_{0.7}Pb_{0.3}MnO_3$ sample annealed in flowing oxygen at 860 °C for 2 h. The dash line is the resistance at zero fields, while the real line represents ac susceptibility.

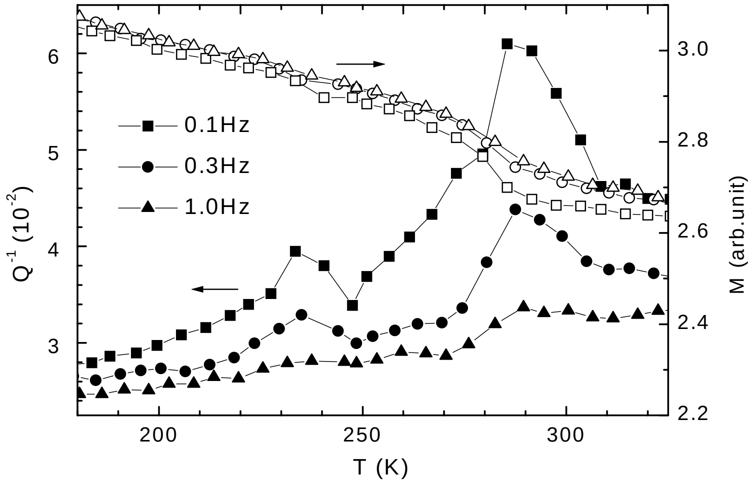

Fig. 4. Temperature dependencies of internal friction and relative elastic moduli for the annealed $La_{0.7}Pb_{0.3}MnO_3$ sample at three different frequencies.

friction peak at low temperature, if they were associated with the phase separation process. It is really the case as shown in Figs. 3 and 4. The temperature dependence of resistance and ac susceptibility of a LPMO sample after annealing in flowing oxygen at 860 °C for 2 h is shown in Fig. 3. Although being shifted toward higher temperature in comparison with the as-prepared sample, two resistance peaks appear still in the annealed sample, and the P2 peak becomes much smaller. The corresponding temperature dependence of internal friction and elastic moduli is shown in Fig. 4. There are still two internal friction peaks corresponding to the resistance peaks. These two peaks have the similar characteristics as in the as-prepared sample, and the low temperature internal friction peak becomes also smaller. The shift of the peaks toward higher temperature after annealing can be understood by the increase in the ratio of Mn^{4+}/Mn^{3+} by changing the oxygen stoichiometry [17].

4. Conclusions

The relationships of electromagnetic properties and internal friction as well as relative dynamic elastic modulus have been measured for sintering and annealed LPMO bulk materials. We have observed two internal friction peaks together with the minima of the elastic modulus, two resistance peaks (P1 and P2 peak), and a sharp rise and then a continuous decrease in ac susceptibility correspondingly. The peaks of internal friction and resistance at higher temperature can be ascribed to a phase transition from PM to FM phase, while the peaks at lower temperature may be interpreted as the phase separation, that is, an AFM phase with less Mn^{4+} ions was separated from the FM matrix. After annealing the sample under flowing oxygen, the peaks of resistance and internal friction shift toward higher temperature and the peaks at lower temperature become smaller.

Acknowledgements

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