# Thermal hysteresis of microwave loss in $(La_{1-x}Pr_x)_{0.7}Ca_{0.3}MnO_3$ film

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We have measured the temperature ($T$) dependencies of the dc resistances ($R_{dc}$) and the microwave loss ($R_{\mu w}$) in a variety of samples of $(La_{1-x}Pr_x)_{0.7}Ca_{0.3}MnO_3$ while varying $x$ from 0 to 0.4. Whereas both the sets of data exhibit maxima, the ac loss peak is much flatte and, during cooling, appears at a much lower temperature than the peak temperature in $R_{dc}$. The discrepancy, which vanishes for $x=0$, increases with lowering tolerance factor ($t$) (or increasing $x$). Also $R_{\mu w}$ vs $T$ exhibits large thermal hysteresis for $x=0.4$ indicating that the transition is firs order. Cooling in a magnetic fiel of 9 kOe causes an upward shift of about 20 K in the $R_{\mu w}$ peak, in some of the $x=0.4$ films yielding a large magnetoimpedance. Further, once these film are exposed to a magnetic fiel at low $T$, they fail to recover their virginal behavior on subsequent cooling from room $T$. These film could be brought to their original state by annealing at high $T$. The discrepancy between $R_{dc}$ and $R_{\mu w}$ implies that the system is inhomogeneous at low $T$, providing, for the firs time, microwave absorption evidence that manganites exhibit multiphase behavior. Presumably, disorder and strain (increasing with $x$) combine to stabilize a mixed phase.
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On account of the subtle competition among interactions involving charge, spin, orbital motion, and lattice, the perovskite manganites $(R^{3+},A^{2+})(Mn^{3+},Mn^{4+})O_3$, exhibit a rather complex phase diagram.[1] That is, by making modest variations in temperature, composition, magnetic field etc., one can access a variety of magnetic (ferromagnetic, antiferromagnetic, spin canting), transport (dirty metal, insulator) charge and/or orbital ordered, as well as multiphase states.[1–3] In addition, strains (local and macroscopic) can be expected to play a significan role and in particular, the size of the $R^{3+}$ ion profoundly influence the structure and concomitantly the cooperative Jahn–Teller effect[1,2] of the $Mn^{3+}$ ions. The last is roughly described in terms of the tolerance factor[2,3]

$$t=\frac{\langle r_{R-O}\rangle}{\sqrt{2}\langle r_{Mn-O}\rangle}.$$

Here, we report studies of the temperature and fiel dependence of the dc resistance ($R_{dc}$), microwave absorption ($R_{\mu w}$) and ferromagnetic resonance (FMR) in bulk-sintered, micron-size powders, and pulsed-laser-deposited (PLD) film of $(La_{1-x}Pr_x)_{0.7}Ca_{0.3}MnO_3$ with $x=0$, 0.2, 0.4 (designated $x$PLCMO below). It is found that with increasing $x$ (reducing $t$), a marked difference develops between the dc and the ac response (Table I). That is, for $x=0$, the peak temperature ($T_p$) in the dc resistance and the temperature ($T_m$) of the maximal rf loss nearly coincide. It should be noted that this has been observed for several samples of $x=0$ in different forms such as powders, polycrystalline sintered pellets, single crystals, and thin films For $x=0.2$, the difference increases to around 20 K.

The largest effect is for $x=0.4$ (lowest $t$) and that is discussed in detail here. The $T_m$ is tens of degrees lower especially during cooling. Also, the microwave loss exhibits a significantl larger thermal hysteresis as well as greater sensitivity to magnetic field ($H$). Finally, in some films we have observed a magnetic "history" effect: if the fil is exposed to a magnetic fiel at low temperatures, it fails to recover its virgin state on subsequent cooling from 300 K, well above the magnetic transition temperature.

All the samples were derived from materials obtained commercially from Microceramics Inc. The sintered pellet is a $mm^3$ block, the micron size powder (fillin factor ∼14%), was held in place with GE7031 glue, and the film were prepared by PLD using an energy density 2 $J/cm^2$, repetition

TABLE I. Four-probe resistance peak temperature ($T_p$) and microwave resistance peak temperatures ($T_{mc}$ and $T_{mw}$) for various samples of $x$PLCMO for $x=0$, 0.2, 0.4.

| Sample | Type | Thickness Å/ substrate | $T_p$ (K) | $T_{mc}$ (K)[a] | $T_{mw}$ (K)[a] |
|---|---|---|---|---|---|
| 0.4PLCMO | Pellet | | 203 | 163 | 199 |
| 0.4PLCMO | Powder | | | 189 | 200 |
| 0.4PLCMO | Film | 600/NGO | 190 | 165 | 194 |
| 0.4PLCMO | Film | 1800/NGO | 190 | 150 | 185 |
| 0.4PLCMO | Film | 3000/NGO | 200 | 165 | 199 |
| 0.4PLCMO | Film | 3000/LAO | 196 | 170 | 197 |
| 0.2PLCMO | Film | 3000/NGO | 238 | 220 | 235 |
| 0PLCMO | Film | 600/NGO | 265 | 260 | 260 |

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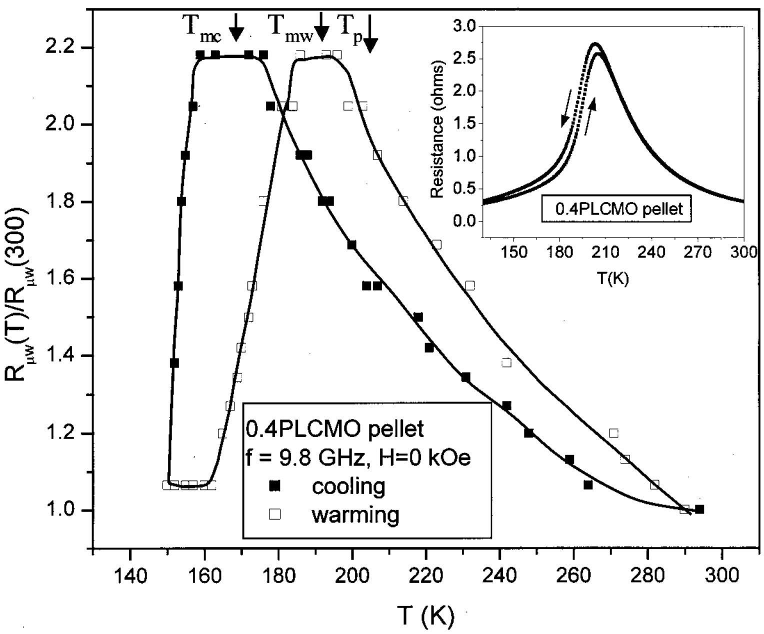


FIG. 1. Temperature dependence of normalized $R_{\mu w}$ for the 0.4PLCMO pellet in zero field The inset shows the corresponding $R_{dc}$ data. As discussed in the text, the thermal hysteresis in microwave loss measurements is much larger than the $R_{dc}$ measurements.

rate 10 Hz and substrate temperature of 820 °C. The oxygen pressure during deposition was 400 mTorr and that during cooling was 400 Torr. We used single crystal substrates of $NdGaO_3$ (NGO) or $LaAlO_3$ (LAO). X-ray diffractometry was used to establish that the samples were *crystallographically single phase.* A four-probe method was used for dc resistance measurements and microwave losses were obtained, using a cavity perturbation technique[4] at 9.8 GHz. Changing to 34 GHz had little effect on the characteristic temperatures. The transport measurements were supplemented by some magnetization and FMR studies. Here we will concentrate on $R_{dc}$ $(T, H)$ and $R_{\mu w}$ $(T, H)$. It should be noted that geometrical effects obviate obtaining absolute values for $R_{\mu w}$. Hence, all the data are normalized to $R_{\mu w}(300,0)$.

Figure 1 shows the temperature dependence of $R_{\mu w}$ for the 0.4PLCMO pellet in zero field The inset shows the $R_{dc}$ vs $T$ graph. The resistance peak temperature ($T_p$) is 203 K, in agreement with earlier reports.[5] However, the "peak" in $R_{\mu w}$ during cooling occurs at a temperature $T_{mc}$ which is nearly 40 K lower than $T_p$, $R_{\mu w}$ being nearly constant over $\sim$10 K, $T_{mc}$ is taken as the rough midpoint. Indeed, it is the peak temperature during warming ($T_{mw}$) which is close to $T_p$. Accordingly, the thermal hysteresis in the microwave loss measurements is much larger than that in the $R_{dc}$ mea-

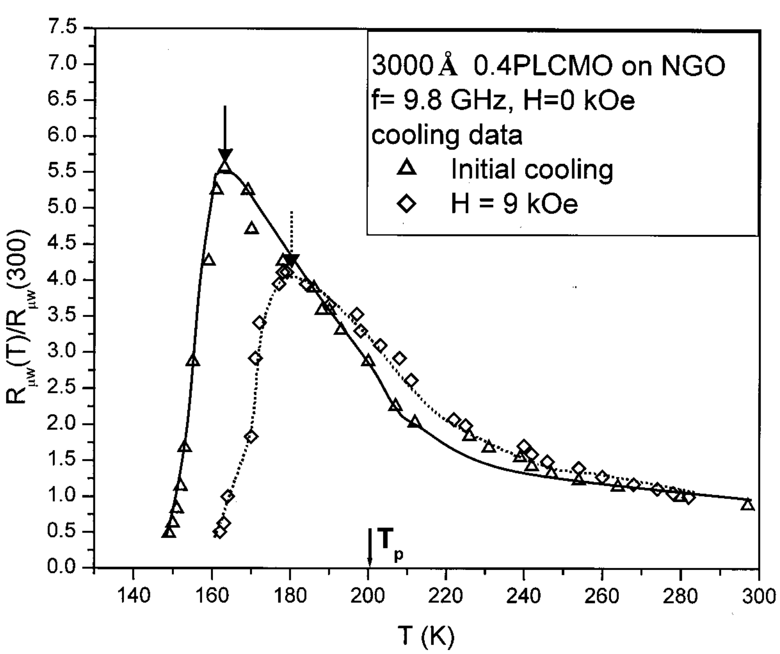


FIG. 2. Temperature dependence of $R_{\mu w}$ for a 3000 Å fil of 0.4PLCMO on NGO in zero and 9 kOe magnetic field $T_{mc}$ is seen to be shifted by $\sim$20 K in magnetic fiel of 9 kOe.

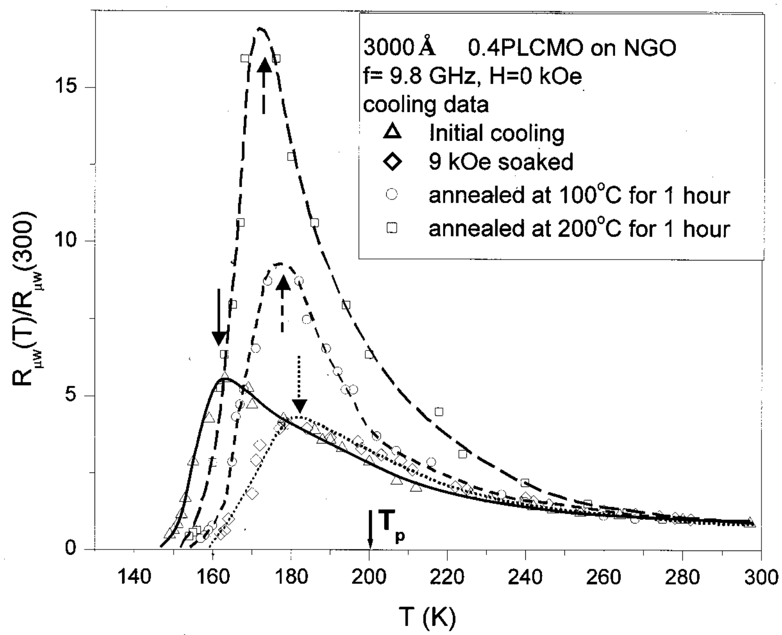


FIG. 3. Magnetic fiel and annealing effects on the temperature dependence of $R_{\mu w}$ for the 0.4PLCMO during cooling. As discussed in the text, the fil exhibits magnetic memory once exposed to fiel at low $T$. Annealing at high $T$ recovers the fil to its original state.

surements. Marked differences between $T_p$ and $T_{\mathrm{mc}}$ are seen in all the samples (Table I), except for LCMO ($x=0$). Also, invariably, $T_{\mathrm{mw}} \approx T_p$. To summarize, whereas $R_{\mathrm{dc}}$ and $R_{\mu w}$ both exhibit maxima, as a function of $T$, the microwave and dc resistances are way out of step, especially for $x \approx 0.4$, a clear indication that one is not dealing with transport in a homogeneous system.

On cooling in a magnetic fiel of 9 kOe, $T_{\mathrm{mc}}$ shifts to a higher temperature by about 20 K, while $T_p$ is barely affected. Figure 2 shows this on a 3000 Å fil of 0.4PLCMO on NGO. This gives rise to a large magnetoimpedance in the neighborhood of the peak although the magnetoresistance is small. While the results of the previous paragraph were somewhat unanticipated, the biggest surprise is represented by the data shown in Fig. 3. The initial cooling in zero fiel (Fig. 2) gave $T_{\mathrm{mc}} \approx 165$ K. Cooling in 9 kOe yielded $T_{\mathrm{cm}}(H) \approx 182$ K (Fig. 2). However, when this fil was warmed to 300 K and subsequently cooled in zero field the peak temperature remained at 182 K (curve designated "9 kOe soaked" in Fig. 3). That is, the material has developed a magnetic memory once it is exposed to a fiel at low $T$. Long term (days) maintenance at 300 K failed to change this state. In order to recover the virginal $T_{\mathrm{mc}}$ it was necessary to anneal at high $T$. As seen in Fig. 3, annealing at 100 °C (200 °C), gives $T_{\mathrm{mc}} \approx 175$ K (170 K). The fil recovers completely only after annealing at 400 °C. The phenomenon is highly reminiscent of magnetic annealing. However, a detailed explanation eludes us.

Although not presented in detail here, FMR data also exhibit effects of magnetic history in the sense that the low $T$ resonance fiel is altered significantl by previous exposure to fields

It is generally agreed that, depending upon preparation conditions, manganites can exhibit coexistent phases.[1] This would be especially true if the transition leading to the specifi state is firs order. Further, strains and disorder promote such inhomogeneous mixtures. All these ingredients come into play as $x$ is increased in the materials under study. The large thermal hysteresis observed in the microwave loss for $x=0.4$, points to a firs order transition. Reduction of tolerance factor with increasing $x$ causes the Mn–O octahedra not only to distort further, but also to rotate in order to accommodate the steric changes and hence giving rise to increased strains. Disorder is built in as the Pr ions distribute themselves statistically in the $R^{3+}$ sites.

Sensitivity of $T_{\mathrm{mc}}$ to applied field strongly suggests that the large drop in loss for $T<T_{\mathrm{mc}}$ is due to the fir establishment of a low $R_{\mu w}$, ferromagnetic, phase. The persistence of large losses for $T_{\mathrm{mc}}<T<T_p$ is most likely due to high resistance (charge ordered?) regions in the sample. Thus, the most likely scenario is that on lowering $T$ there is a firs order transition at $T_p$ to coexistent ferromagnetic (low $R_{\mu w}$) and presumably charge ordered (high $R_{\mu w}$) phases and the former wins out only when $T<T_{\mathrm{mc}}$. To our knowledge, no previous microwave measurements on manganites have exhibited the phenomena reported here. Measurements involving samples for many different values of $x$ are underway to put these finding on firme footing.

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