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Interfacial contribution to magnetocapacitance in $La_{0.05}Tb_{0.95}MnO_3/La_{0.67}Sr_{0.33}MnO_3/SrTiO_3$ heterojunctions

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Abstract
$La_{0.05}Tb_{0.95}MnO_3/La_{0.67}Sr_{0.33}MnO_3/SrTiO_3$ heterojunctions were fabricated by laser molecular-beam epitaxy. Dielectric properties as functions of temperature (77–320 K) and frequency (10^2–10^6 Hz) of these junctions were investigated in detail. The sample showed a notable magnetoresistive effect due to the contribution of the $La_{0.67}Sr_{0.33}MnO_3$ layer and a diffuse dielectric anomaly which was found to arise from Maxwell–Wagner (MW) relaxation. Both positive and negative magnetocapacitive behaviours were observed. These behaviours were found to be intimately linked to the dielectric anomaly and can be well explained based on the combined role of the MW effect and magnetoresistance.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Materials in which magnetic and electric orders coexist and are coupled—termed 'multiferroics'—have recently become the focus of much research because of their intriguing physics and potential applications [1]. The strong magnetoelectric coupling leads to a characteristic effect of magnetocapacitance (MC), i.e. the change of capacitance by a magnetic field. However, a recent theoretical paper has pointed out that extrinsic MC behaviour unrelated to true magnetoelectric coupling can also be achieved through a combination of magnetoresistance and the Maxwell–Wagner (MW) effect [2]. More generally, an exciting issue in multiferroic systems is the theoretically proposed interfacial magnetoelectric effects [3]. In a ferromagnetic/ferroelectric heterostructure and even in a metal/insulator heterostructure, magnetoelectric effects predicted by first-principles calculations can arise from a purely electronic mechanism not mediated by magnetoelectric coupling. Since few materials in nature exhibit magnetoelectric coupling and the coupling temperatures are usually much lower than room temperature, the extrinsic MC effect might be practically useful. Although the interface-related MC behaviour has been reported in a wide range of materials [4–8], most of them contain a ferroelectric or multiferroic component that might cause confusion with the MC effect related to multiferroic composites, which incorporate both ferroelectric and ferri-/ferromagnetic phases, typically yielding giant magnetoelectric coupling response above room temperature [9]. Thus, to establish clear experimental evidence for interface-related MC behaviour, the investigated system should be free from ferroelectric polarization.

In this paper, we have reported the MC behaviour in $La_{0.05}Tb_{0.95}MnO_3/La_{0.67}Sr_{0.33}MnO_3$ (LTMO/LSMO) heterojunctions. $LaMnO_3$ is chosen because it is a well-known

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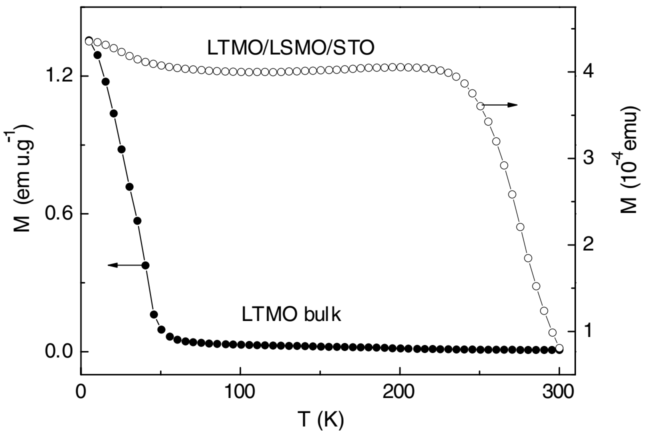

Figure 1. Temperature-dependent magnetization of the LTMO/LSMO/STO heterojunction and LTMO target.

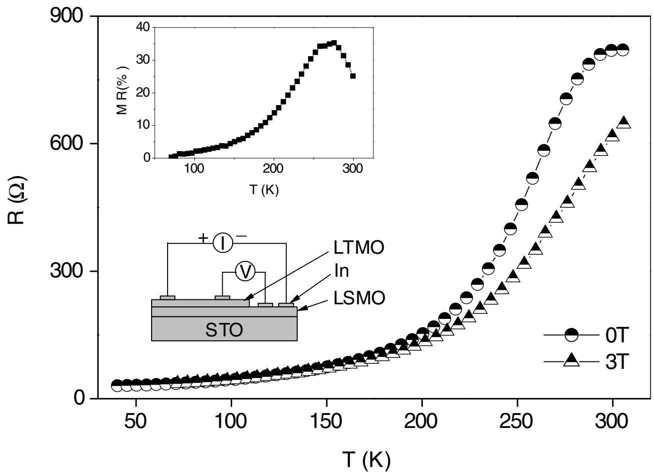

Figure 2. Temperature-dependent resistance of the LTMO/LSMO/STO heterojunction under an external field of zero and 3 T. The lower inset is the scheme of the electric measurements. The upper inset shows the corresponding MR varies with temperature of the junction.

material exhibiting colossal magnetoresistance (CMR) when La^{3+} was partially replaced by other cations. Although $TbMnO_3$ was reported to show magnetoelectric coupling in the temperature range below 50 K [10], the lightly La-doped $TbMnO_3$ has not, to the best of our knowledge, been reported to show multiferroic behaviour. Our results indicate that the MC behaviour reported here can be ascribed to the extrinsic MW origin.

2. Experimental details

Epitaxial thin films of LTMO and LSMO films were deposited on $SrTiO_3$ (0 0 1) (STO) substrates by a computer-controlled laser molecular-beam epitaxy technique [11]. LSMO films were pre-deposited on STO. LTMO was deposited atop the LSMO film through a shadow mask. A XeCl laser ($\lambda = 308$ nm) with a pulse energy density of 2 J cm^{-2} and a repetition rate of 2 Hz was used for the deposition of LTMO and LSMO films. During the deposition, the oxygen partial pressure was kept at 2.3×10^{-1} Pa and the substrate temperature at 630 °C. After the deposition, the samples were annealed *in situ* for 30 min under the deposition conditions and then cooled down to room temperature. The thickness of the LSMO and the LTMO layers were 300 nm and 200 nm, respectively. Magnetic and electrical properties were measured in a superconducting quantum interference device (SQUID). Electrical measurements were carried out using the four-point technique with two indium (In) electrodes pressed on the LTMO film and the other two on the LSMO film (see the lower inset of figure 2). Dielectric properties were measured using an Agilent 4294A precision impedance analyzer. The In slats ($\sim$2 mm^2) well pressed on the LTMO and the LSMO films to confirm Ohmic contact were used as the top and bottom electrodes, respectively. The voltage polarity is defined at the top In electrode. The layout of the device is illustrated in the lower inset of figure 3.

3. Results and discussion

Figure 1 shows the temperature dependence of magnetization (M–T) for the LTMO/LSMO/STO junction and the LTMO target measured with zero-field cooled mode. The ferromagnetic transition (T_C) of the junction, defined as the temperature of the maximum slope in $\mathrm{d}M/\mathrm{d}T$, was found to be 275 K. By comparison with the magnetization of the bulk LTMO, it is clear that the magnetic property of the junction has a contribution mainly from the LSMO layer. The slight upturn at the lowest temperatures in the M–T curve of the junction can be ascribed to the contribution from the LTMO layer.

The temperature-dependent resistance (R–T) of the junction measured with a constant supply of current under an external field of zero and 3 T (tesla) are shown in figure 2. The resistance registers a peak very close to room temperature which cannot be fully detected by SQUID. It is seen that the magnetic field can effectively reduce the resistance, indicating the CMR behaviour. The calculated MR ratio (defined as $[R(0) - R(H)]/R(0)$, where $R(0)$ and $R(H)$ are the resistance at 0 T and 3 T magnetic fields, respectively) shown in the upper inset exhibits a peak near T_C, reflecting the intrinsic CMR effect, i.e. CMR is due to double exchange in the LSMO film [12].

Figure 3 shows the temperature dependence of capacitance (C–T) at different frequencies under an applied magnetic field of zero and 0.2 T. From the figure two interesting features can be extracted: (1) C exhibits a diffuse dielectric anomaly, i.e. there is a broad peak as a function of temperature, with the peak decreasing in magnitude and shifting to higher temperature with increasing measurement frequency. At frequencies higher than 100 kHz the peak disappears completely. (2) The capacitance peak can be notably depressed by the applied magnetic field, indicating the remarkable MC effect in the low-frequency range; whereas at frequencies higher than 100 kHz, the MC effect is unobservable, implying the observed MC effect is intimately linked to the capacitance peak. The upper inset plots the MC ratio obtained at 10 kHz. The ratios at different temperatures have been calculated using the definition $[C(0) - C(H)]/C(0)$, where $C(0)$ is the capacitance in zero

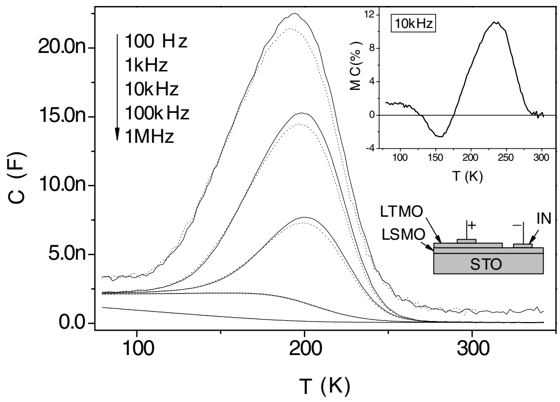

Figure 3. Temperature-dependent capacitance of the LTMO/LSMO/STO heterojunction under an external field of zero (solid lines) and 0.2 T (dotted lines). The lower inset is the scheme of dielectric measurements. The upper inset shows the MC as a function of temperature at 10 kHz of the junction.

field and $C(H)$ is the capacitance in a field. It is seen that the MC ratio evolves as an S-shaped curve with decreasing temperatures. The positive MC ratio peak with a maximum of 11.17% locates between 175 and 300 K, the negative MC ratio peak with a minimum of −2.47% appears in the temperature range 129 K $< T <$ 175 K, while below 129 K, the MC ratios return to positive values again.

Since the observed MC effects are linked with the dielectric anomaly, a better understanding of the anomaly is required before discussing the MC effects. Diffuse dielectric anomalies were reported in various systems in recent years [13], and their physical nature is not clearly understood yet. Many authors tend to believe a MW relaxation origin [14, 15]. In our case, $La_{0.05}Tb_{0.95}MnO_3$ thin film was chosen because the dielectric properties of the parent material $TbMnO_3$ were fully investigated. In $TbMnO_3$ ceramic sample [16] no dielectric anomaly was found but in a thin film [17] the diffuse dielectric anomaly can be easily obtained, which strongly indicates the MW origin of the anomaly. To further identify the interfacial polarization nature of the anomaly, we conducted the impedance analysis, which is a powerful technique in studying the interfacial effect. Shown in the main panel of figure 4 is the complex impedance plot (Z'' versus Z') for the LTMO/LSMO/STO junction at room temperature. It can be clarified that the complex impedance curve consists of two semicircular arcs located in the low- and high-frequency ranges, which were theoretically considered to represent the dielectric contributions from the grain boundaries (interfaces) and grains (bulk), respectively. We therefore try to fit the data using two serially connected R–CPE units, one for the bulk and the other for interfaces, each containing a resistor (R) and a constant phase element (CPE) in parallel as depicted by the upper inset in figure 4. The impedance of a CEP is defined by $1/Z_{\mathrm{CPE}} = Q(j\omega)^n$, where $\omega(= 2\pi f)$ is the angular frequency, j is the square root of −1 and Q and $n(0 \leqslant n \leqslant 1)$ are adjustable parameters independent of the frequency [18]. The fitted impedance curve, shown as a solid line in figure 4, agrees perfectly with the experimental data. The fitting determines the values of parameters R, Q and n

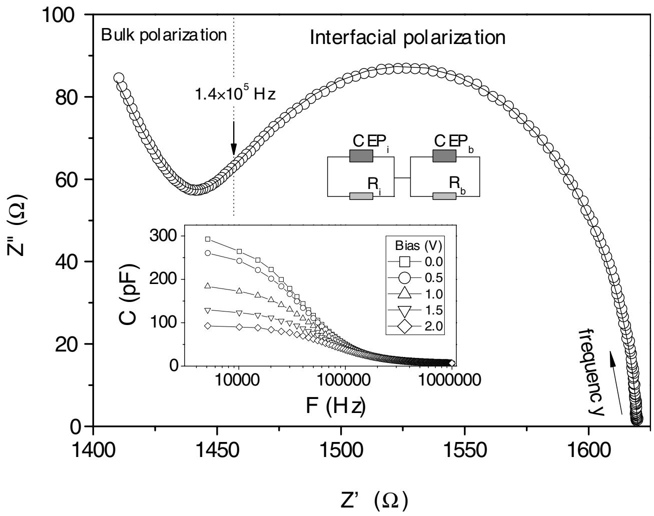

Figure 4. The complex impedance plot of the LTMO/LSMO/STO heterojunction. The solid line is the least-squares fitting based on the equivalent circuit displayed in the upper inset; the vertical dotted line indicates the demarking frequency where the polarization changes from the interfacial type to the bulk type. The lower inset displays the frequency dependence of the capacitance for the junction under different biases.

as 163 Ω, $2.2 \times 10^{-7}\ \Omega^{-1}\ \mathrm{m}^{-2}\ \mathrm{S}^{-n}$, and 0.97, respectively, for the grain boundary and as 1457 Ω, $4.8 \times 10^{-9}\ \Omega^{-1}\ \mathrm{m}^{-2}\ \mathrm{S}^{-n}$ and 0.66, respectively, for the grain. This reveals that the interfacial polarization separates from its bulk counterpart at the demarking frequency of 1.4×10^5 Hz, as indicated by an arrow in the figure. This fact is further confirmed by the results of the frequency dependence of the capacitance (C–f) under different biases shown in the lower inset of the figure. The fact that capacitance in the frequency range lower than ∼100 kHz decreases rapidly with increasing frequencies and can be greatly depressed by increasing biases confirms the interfacial polarization in the low-frequency range [19]. At frequencies higher than ∼100 kHz, the C–f curves are independent of frequency and bias, indicating the bulk contribution dominates the dielectric behaviour in this frequency range.

Figure 5 presents the C–T curve at 10 kHz under zero and 0.5 V bias for another sample. It is seen that the capacitance peak can be greatly depressed by the bias. We can thus exclude the relaxor origin of the peak, since for a relaxor a small dc bias [20] and even an increasing ac amplitude [21] are favourable for the polarization of ferroelectric clusters and hence enhance the dielectric peak. As already seen, that the bias can greatly depress the low-frequency interfacial polarization and in turn destroy the dielectric anomaly. This result firmly confirm the MW nature of the capacitance peak.

Based on these results, the observed MC behaviours can be explained immediately. The observed MC behaviours are intimately linked with the capacitance peak resulting from MW relaxation. Therefore, it is quite reasonable to attribute the MC behaviours to the MW origin. As a consequence, the MC effects disappear as the interfacial contribution disappears in the frequency range higher than ∼100 kHz, as seen in figure 4. In the framework of MW origin based on the magnetoresistive

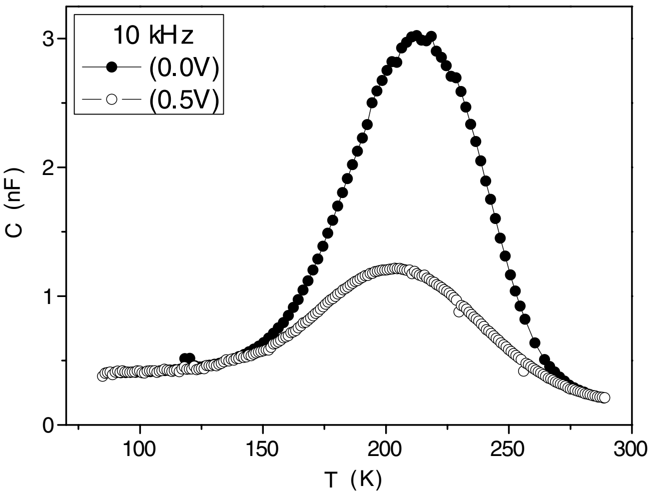

Figure 5. Temperature dependence of capacitance of another LTMO/LSMO/STO heterojunction under a dc bias of zero and 0.5 V.

effect for MC effects [2], the positive and negative MC effects are related to the intrinsic and extrinsic CMR behaviours, respectively. The maximum of the positive MC ratio appears at a temperature very close to the peak temperature of the MR ratio, reflecting the positive MC effect is really related to intrinsic CMR behaviour. Thus, the negative one is contributed from the extrinsic CMR behaviour. Although no evident extrinsic CMR effect characterized by a roughly linear increase with decreasing temperature in the temperature range much lower than T_C, due to spin-polarized tunnelling [22] and/or spin-dependent scattering [23] at grain boundaries, is observed in our sample, we cannot exclude the existence of the extrinsic CMR behaviour in our sample since the columnar structures were demonstrated to be a universal feature of CMR thin films [24]. The large number of grain boundaries between the columnar grains (usual size of ~20 nm) as well as the interface between the LTMO and the LSMO films allow for the coexistence of both intrinsic and extrinsic CMR effects in the sample [25]. Therefore, the coexistence of both positive and negative MC behaviours in our sample is very reasonable. As to the MC ratio returning to positive values in the low temperature range, this is because of the further enhancement of magnetization due to the contribution of the LTMO layer that leads to the suppression of the extrinsic CMR effect.

4. Conclusions

To summarize, dielectric properties of the LTMO/LSMO/STO heterojunctions have been investigated in this work. The dielectric properties were found to be dominated by the interfacial polarization, which showed a relaxor-like capacitance peak in the frequency range lower than 100 kHz. A magnetic field can notably change the capacitance leading to both positive and negative MC effects in our samples. The MC effects were found to have a close link with the capacitance peak and were believed to arise from pure interfacial polarization without any magnetoelectric couplings.

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