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Dielectric relaxation and magnetodielectric response in epitaxial thin films of La_2NiMnO_6

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Frequency and magnetic field dependent dielectric measurements have been performed on epitaxial thin films of the double perovskite La_2NiMnO_6, revealing a dielectric relaxation and magnetodielectric effect. The films are grown on Nb-doped and $SrRuO_3$-coated $SrTiO_3$ substrates using the pulsed laser deposition technique. While a rapid dielectric relaxation is observed at ~300 K, the relaxation rate increases dramatically at lower temperatures. Below the Curie temperature of La_2NiMnO_6, the dielectric constant increases in a magnetic field for a range of temperature. This temperature range depends on magnetic field and measurement frequency. The results are explained by the influence of a magnetic field on the dipolar relaxation. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2832642]

Single-phase multifunctional materials, in which magnetic and dielectric processes coexist, typically exhibit relaxation of the electric dipole moments[1,2] and magnetic field (H) dependence of the dielectric constant [the "magnetodielectric effect" (MDE)].[2–4] It has been shown that the strong magnetoelectric coupling in perovskite manganites[3,4] is sensitive to the degree of magnetic frustration. However, very recently, Yang *et al.*[2] have observed a dynamically enhanced MDE in La-doped $BiMnO_3$, which they explain in terms of electric relaxation caused by the magnetic field.

The perovskites and double perovskites show a wide variety of electric and magnetic ordering behavior, which can be tuned by compositional changes. The ferromagnetic order in *double* perovskites is a consequence of Goodenough-Kanamori rules,[5] arising from a 180° superexchange interaction between two transition metal cations. The La-based ferromagnetic double perovskite oxides are insulating or semiconducting, and display a MDE.[6–8] Rogado *et al.*[6] have observed ~12% MDE near the Curie temperature (T_C~280 K) in bulk polycrystalline La_2NiMnO_6 (LNMO) samples with applied field in the range of 0.1–1 T. In this letter, we report on the observation of MDE and dipole relaxation in epitaxial thin films of LNMO grown on $SrRuO_3$ (SRO) coated $SrTiO_3$ (STO) substrates and on 0.5 wt % Nb doped $SrTiO_3$ (STNO) substrates. The observation of similar results on the two different bottom conducting contact layers suggests that the behavior is intrinsic to LNMO and not dominated by interface effects. The results indicate the existence of a correlation between the MDE and dipole relaxation, and possibly a coupling of electric and magnetic ordering and fluctuations.

Epitaxial single layer and bilayer thin films of LNMO and LNMO/SRO were grown on (001)-oriented STNO and pure STO substrates, respectively, using the pulsed laser deposition technique. The details regarding the optimized deposition conditions for film growth and the magnetic properties are provided elsewhere.[9] To form the LNMO/SRO bilayer, an 85 Å thick SRO film was first deposited on STO at 700 °C in oxygen ambient of 100 mTorr. The film was then cooled down to room temperature at the same oxygen pressure to mask off part of the film to define the bottom electrode. The partly masked SRO film was heated in oxygen ambient to 750 °C to grow a 3400 Å thick LNMO film in 800 mTorr O_2. LNMO films (850 Å) were also grown directly on the conducting STNO substrates under the same process conditions, without depositing the SRO as a seed layer. Circular Au or Pt contact pads were sputter deposited on top of the LNMO and SRO to perform two probe ac impedance measurements using an HP4294A impedance analyzer as a function of temperature and in-plane magnetic field in a Physical Property Measurement System (Quantum Design).

The impedance (Z) and phase (θ) of a 850 Å thick LNMO film on STNO has been measured at 10 mV rms ac voltage at various temperatures (T) and frequencies (f). To study the nature of the capacitive response, we modeled the film as a parallel network of a resistor (R) and an effective capacitor (C). These two components are related to the measured total impedance and phase of the parallel RC network.[10] The extracted capacitance is proportional to the frequency-dependent complex dielectric function $\varepsilon(\omega)$. The dielectric function can be expressed as the sum of frequency-dependent real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts, $\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega)$. The dissipation factor $\tan\delta$ is then given by $\varepsilon_2(\omega)/\varepsilon_1(\omega)$, where δ is the phase difference between the applied electric field and the induced current. The $\tan\delta$ and $\varepsilon_1(\omega)$ have been calculated from the effective C extracted from the Z and θ measurements as a function of frequency for different temperatures [see Figs. 1(a) and 1(b)].

At room temperature, ε_1 of LNMO film at various frequencies is ~800–900, which is somewhat higher than the reported bulk value of ~600.[6] As the film is cooled from room temperature in an ac electric field (10 mV_{ac} at 1 kHz), the $\varepsilon_1(\omega)$ decreases slowly, followed by a rapid decrease between 150 and 100 K, after which it remains constant down to the lowest temperatures. A qualitatively similar temperature dependence of ε_1 is observed with increasing frequency, with a shift of the drop-off temperature to higher temperatures. This behavior is also reflected in the shift of

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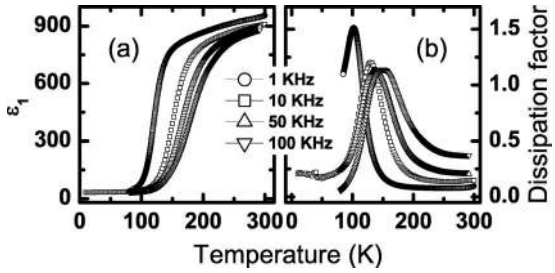

FIG. 1. The temperature dependence of (a) the real part of the dielectric response ε_1 and (b) the dissipation factor measured at different frequencies for a 850 Å thick La_2NiMnO_6 grown on (100)-oriented 0.5 wt % Nb doped $SrTiO_3$ substrate.

the dissipation factor peak shown in Fig. 1(b). Overall, the observed variations in $\varepsilon_1(\omega)$ and the peaks in tan $\delta(\omega)$ are typical signatures of relaxation behavior. These features occur when the frequency of the exciting electric field matches the temperature-dependent relaxation rate of the dipoles and charged particle transitions.[11] As the sample is cooled below room temperature, the decrease in thermal energy results in a lowering of the frequency dispersion, which becomes slower at temperatures below the peak temperature of tan $\delta(T)$. Ultimately, all dipolar motion freezes at a sufficiently low temperature (below 80 K) and the dispersion vanishes, as seen in Fig. 1(a). The negligibly small variation in $\varepsilon_1(\omega)$ below 80 K may be due to a space charge polarization at the LNMO/STNO interface. We have observed a very similar behavior of $\varepsilon_1(\omega)$ and tan $\delta(\omega)$ in measurements of LNMO films with SRO and Au as the bottom and top electrode, respectively.

Using the same parallel network of R and C with a complex dielectric function, we have calculated $\varepsilon_1(\omega)$ for different magnetic fields from Z and θ of the LNMO films measured at various frequencies and temperatures. The qualitative behavior of in-field $\varepsilon_1(\omega)$ is similar to that in zero field. However, the peak shift in tan δ with H demonstrates the influence of the magnetic field on the relaxation of the dipole and the charge particle transitions,[2] and indicates that *electric* dipole fluctuations are influenced by *magnetic* ordering and fluctuations. The change in $\varepsilon_1(\omega)$ with magnetic field [the "magnetodielectric constant" (MDC)] for various temperatures has been calculated using the relation MDC=$[\varepsilon_1(\omega,H)-\varepsilon_1(\omega,0)]/\varepsilon_1(\omega,0)$. The MDC measured at 10 kHz is shown in Fig. 2(a) for 0.5, 1, 3, and 7 T magnetic fields. The MDC is negligibly small (0.17%) in a 0.5 T magnetic field at 10 K. With increasing temperature, MDC increases, exhibiting a peak at $T_P \sim 120$ K, and then again deceases to a negligibly small value. The T_P shifts slightly toward higher temperature when the magnetic field is increased from 0.5 to 7 T, with corresponding increase in the MDC [Fig. 2(a)]. A similar shift of T_P is observed in measurements at increasing frequency, as measured for two different samples in Figs. 2(b) and 2(c), respectively. Although the qualitative behavior of MDC(T) of both the films shown in Figs. 2(b) and 2(c) is similar, the small difference in T_p and significant difference in MDC at 10 kHz are attributed to differences at the bottom and top electrodes in the two samples. While the MDC decreases with increasing excitation frequency, it increases with increasing magnetic field. Although the MDC ($\sim$11%) at 1 T for the 850 Å thick film of LNMO is similar to that in the bulk, the observed T_P is significantly lower than in the bulk.[6] In addition, the LNMO

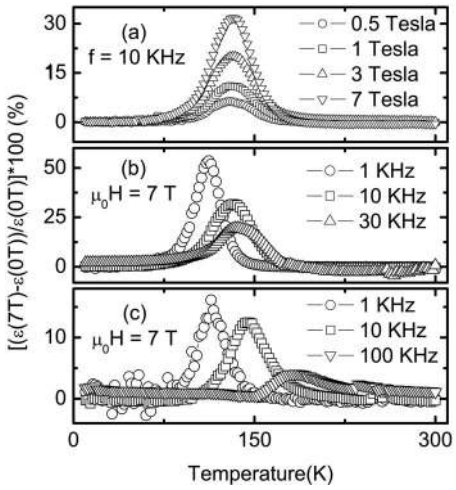

FIG. 2. Temperature-dependent magnetodielectric constant of a 850 Å thick La_2NiMnO_6 grown on 0.5 wt % Nb doped $SrTiO_3$ at several (a) magnetic fields and (b) frequencies. (c) Temperature dependent magnetodielectric constant of a (3400 Å) La_2NiMnO_6/(85 Å) $SrRuO_3$/$SrTiO_3$ sample at different frequencies.

film does not show an anomaly in $\varepsilon_1(H,T)$ in the vicinity of T_C ($\sim$270 K for our films, as compared to the bulk value of $\sim$280 K) as observed in the bulk.[6] This difference in MDC, T_p and $\varepsilon_1(H,T)$ between the thin film and bulk LNMO could be due to a fundamentally different origin of the MDE.

In Fig. 3, we show the frequency-dependent ε_1 of LNMO films at various temperatures. At a higher temperature, the dielectric constant at low frequencies remains essentially constant up to a certain cutoff frequency, at which the oscillation period matches the intrinsic time scale of the system—the so-called relaxation time (τ)—and rapidly decreases at higher frequencies. A similar frequency dependence of dielectric constant of LNMO is observed at various magnetic fields. In order to model ε_1 in terms of τ, we have used the Debye model.[12] In the Debye approximation, the frequency response of the dielectric relaxation is given by $\varepsilon(\omega)=\varepsilon_\infty+\{[P_0\tau(1+i\omega\tau)]/[1+(\omega\tau)^2]\}$ and $P_0\tau=\varepsilon_0-\varepsilon_\infty$, where ε_0, ε_∞, and P_0 are the static dielectric constant, the core contribution to the dielectric function, and the dipole moment, respectively. The fit to the dielectric constant of LNMO using the Debye relaxation is indicated by the solid line in Fig. 3. Although there is some ambiguity in τ at temperatures below 80 K, the model fits well with the measured ε_1 of LNMO. The relaxation rate obtained from these fits drops rapidly with increasing temperature. This temperature-dependent relaxation rate indicates an increas-

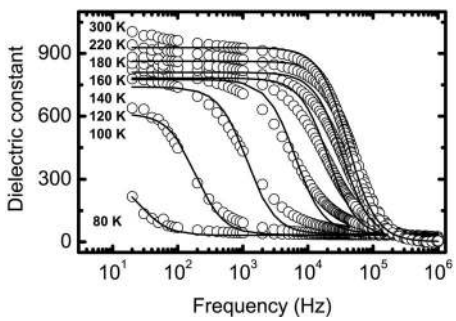

FIG. 3. The frequency dependence of the dielectric constant ε_1 of a 850 Å thick La_2NiMnO_6 grown on 0.5 wt % Nb doped $SrTiO_3$ at several temperatures. The solid lines are the fit to the Debye model.

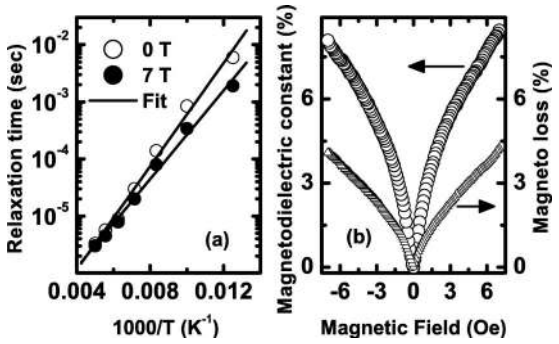

FIG. 4. (a) Temperature dependence of the relaxation time at 0 and 7 T magnetic field. The solid line is the Arrhenius fit to the data. (b) Magnetic field dependent magnetodielectric constant and magnetoloss at 100 kHz measured at a temperature of 150 K.

ing dipole density and a faster polarization process; $\tau = \tau_0 \exp(U/k_BT)$, where τ_0, U, and k_B are the relaxation time at infinitely high temperature, the activation energy, and the Boltzmann constant, respectively. The linear variation of $\log(\tau)$ with inverse temperature, and its Arrhenius fit are shown in Fig. 4(a). The Arrhenius fit yields τ_0 and U values of 66 ns and 31.8 meV (367 K), respectively. The activation energy calculated from the Arrhenius fit is very low compared to the 300 meV band gap of LNMO,[13] suggesting that the dielectric relaxation is not due to the temperature dependence of the conductivity. The relaxation time and, hence, the activation energy is lower at 7 T field, as seen in Fig. 4(a) (τ_0=72 ns and U=30.9 meV) indicating the presence of coupling between the spin and dipolar ordering, which is responsible for the observed MDC(T) in LNMO. However, as the MDC is not proportional to M^2 (M=magnetization) in the entire temperature range below T_C, we rule out phonon-spin coupling[14] as the origin of the magnetoelectric coupling [unlike the case of La_2CoMnO_6 (Ref. 8)].

It has been shown that the ac transport can be influenced by extrinsic parasitic contributions.[15] The possibility of such contributions in our system has been analyzed from the *RC* time at different temperatures. A distinguishing feature is the approximately similar *RC* time with increasing temperature above 120 K, as reflected by the negligible change in the cutoff frequency. We have determined the magnetic field variation of dielectric constant and loss tangent at 100 kHz, significantly faster than the characteristic *RC* time, and a temperature of 150 K, around which the *RC* time (~600 Hz) changes negligibly [see Fig. 4(b)]. The "magnetoloss" is defined in terms of the loss tangent, analogously to the MDC. Both the MDC and magnetoloss increase with increasing magnetic field suggesting that the variation is not due to the magnetoresistance of LNMO or the LNMO-electrode interfaces.[15] Though the influence of extrinsic parasitic contribution cannot be completely ruled out, the presence of MDC at measurement frequencies faster than the *RC* time constant and the presence of positive MDC and magnetoloss suggest that the observed relaxation process and the MDC are intrinsic properties of LNMO.

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