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Ferroelectric phase transition in strained multiferroic (Bi$_{0.9}$La$_{0.1}$)$_2$NiMnO$_6$ thin films

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We report here temperature-dependent x-ray structural and Raman spectroscopy data, on the ferromagnetic double-perovskite (Bi$_{0.9}$La$_{0.1}$)$_2$NiMnO$_6$ epitaxial thin films. Results indicate a ferroelectric transition occurring at about 450$^\circ$C. Low-temperature polarization loops allow to clearly observing polarization switching, thus confirming the multiferroic character of this oxide, and indicate a lower bound of about 6 $\mu$C/cm$^2$. © 2012 American Institute of Physics.

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The possibility of controlling the magnetization (polarization) by an electric (magnetic) field in materials possessing ferroelectric and magnetic order in the same phase has triggered great amount of research in the so-called multiferroic materials due to the expectations in the applications that may arise in magnetoelectronics.$^1$

In the search for multiferroic materials, Bi-based double-perovskite structures (Bi$_3$BB$'$_3O$_9$) in a rock-salt configuration, such as Bi$_2$FeCrO$_6$ (Ref. 2) or Bi$_2$NiMnO$_6$ (BNMO) (Ref. 3), are drawing much of the attention lately. These oxides tend to be ferromagnetic or ferrimagnetic, a property of Bi$_2$FeCrO$_6$ (Ref. 2) or Bi$_2$NiMnO$_6$ (BNMO) (Ref. 3), are drawing much of the attention lately. These oxides tend to be ferromagnetic or ferrimagnetic, and are of interest since, as La-doped Bi$_2$NiMnO$_6$ bulk is not significantly different from that of undoped Bi$_2$NiMnO$_6$ (Ref. 3 was used for bulk data, which yields a pseudo-cubic lattice parameter of 3.877 Å), Temperature dependent x-ray diffraction patterns have been collected using a high resolution, two-axis diffractometer in Bragg-Brentano geometry using Cu-K$_\alpha$ wavelength. The zero of the goniometer was corrected at room temperature by using [001] (1 = 1, 2, 3, and 4) reflections of STO. The (003) Bragg reflections for both substrate and film were then recorded between 200 K and 470 K. The observed reciprocal space maps$^{15,16}$ have confirmed that BL10NM films are coherently strained on STO, thus adopting a tetragonal-like unit cell: $a_{BL10NM} = a_{STO} = 3.905$ Å (at room temperature). The misfit strain ($-0.70\%$) was estimated assuming that the lattice parameters of La-doped Bi$_2$NiMnO$_6$ bulk is not significantly different from that of undoped Bi$_2$NiMnO$_6$ (Ref. 3 was used for bulk data, which yields a pseudo-cubic lattice parameter of 3.877 Å), Temperature dependent x-ray diffraction patterns have been collected using a high resolution, two-axis diffractometer in Bragg-Brentano geometry using Cu-K$_\alpha$ wavelength. The zero of the goniometer was corrected at room temperature by using [001] (1 = 1, 2, 3, and 4) reflections of STO. The (003) Bragg reflections for both substrate and film were then recorded between 200 K and 470 K. The observed linear temperature expansion of STO ensures experimental procedures.

In Fig. 1 (left axis), we show the temperature evolution of the out-of-plane lattice parameter of both BL10NM film and STO substrate (c$_{BL10NM}$ and c$_{STO}$, respectively), determined from the corresponding angular position of the (003) Bragg reflections. Due to thermal expansion, c$_{STO}$(T) linearly increases over the full temperature range with a thermal expansion coefficient, $\alpha_{STO} \approx 4.2 \times 10^{-5}$ A/K. In contrast, c$_{BL10NM}$(T) is non monotonic and clearly displays a kink (arrow) at about 450 K pointing to a phase transition occurring at this temperature. A straight line is plotted to emphasize the fact that the film parameter, below 450 K, gradually

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deviates from the normal linear behavior. This transition can be even better appreciated in the tetragonality ratio \( \frac{c_{\text{BL10NM}(T)}}{a_{\text{BL10NM}(T)}} \); in computing this ratio, it is assumed that BL10NM remains coherent on the STO substrate and thus \( a_{\text{BL10NM}(T)} = a_{\text{STO}(T)} \); from the cubic structure of STO, it follows that: \( c_{\text{BL10NM}(T)} = c_{\text{STO}(T)} \). These tetragonality values are depicted in Fig. 1 (right axis). The enhancement of the \((c/a)_{\text{BL10NM}(T)}\) is very apparent at low temperatures and gradually reduced when approaching 450 K. This behavior is obviously consistent with having a ferroelectric phase below this temperature, in which the spontaneous polarization induces an enlargement of the out-of-plane lattice parameter. The tetragonality ratio \( c_{\text{BL10NM}(T)}/a_{\text{BL10NM}(T)} \) data can be well fitted (dashed line through the data) by using \( c_{\text{BL10NM}(T)} = a_{\text{BL10NM}(T)} \times T + B \times \sqrt{T^* - T} \) and \( a_{\text{BL10NM}(T)} = a_{\text{STO}(T)} = a_{\text{STO}} \times T^* + a_{\text{STO}} \times T \).\(^{16}\) We recall that this \( B \times \sqrt{T^* - T} \) expansion of the out-of-plane cell parameter is typical of ferroelectric with out-of-plane polarization developing at \( T < T^* \).\(^{13}\) The excellent fitting of our data to this function gives an additional hint on the nature of the transition observed at \( T^* \) which we thus identify with \( T_{\text{FE}} \) and allows to suggest \( T_{\text{FE}} \approx 450 \) K for the ferroelectric transition temperature of BL10NM films.

To bring additional evidence for this transition, we have also recorded Raman spectra between 80 K and 620 K—temperature step of 20 K—using a T64000 triple Raman spectrometer (Jobin-Yvon-Horiba). This technique is well adapted to investigate phase transitions not only in pure BNMO systems but other lanthanide double-perovskites.\(^{17,18}\) Characteristic to the double-perovskite structure is the presence of a pronounced phonon mode around 600 cm\(^{-1}\) and broad phonon mode around 500 cm\(^{-1}\), associated with stretching and anti-stretching/bending vibrations of B(B')O\(_6\) octahedras, respectively.\(^{18}\) The high frequency mode was demonstrated to be very sensitive to phase transitions.\(^{18}\) In our Raman spectra (Fig. 2(a)), this high frequency phonon \( \omega(T) \) strongly shifts to low wavenumbers as temperature increases. The temperature dependence of \( \omega(T) \) is shown in Fig. 2(b) (solid symbols). It is clear that \( \omega(T) \) displays a well pronounced change of slope at about 400 K. This signature is also clear in the temperature dependence of the corresponding linewidth \( \Delta \omega(T) \) [Fig. 2(b) right axis]. These characteristic changes in \( \omega(T) \) and \( \Delta \omega(T) \) occur at temperatures remarkably close to \( T_{\text{FE}} \) as inferred from x-ray data presented above. We thus conclude that they signal the occurrence of a ferroelectric phase transition at \( T_{\text{FE}} \approx 430 \) K (±20 K). We note that similar features were also observed in Raman spectra of Bi\(_2\)NiMnO\(_6\) thin films grown on NdGaO\(_3\).\(^{18}\)

Therefore, both x-ray diffraction and Raman spectroscopy data indicate that the ferroelectric phase transition in BL10NM occurs around \( T_{\text{FE}} \approx 450 \) K. It is clear that the ferroelectric transition temperature of BL10NM films is somewhat reduced compared to bulk BNMO one (≈485 K).\(^{3}\) This reduction could just be due to the partial replacement of Bi by La; however, as a matter of fact, in Bi\(_2\)NiMnO\(_6\) films on NdGaO\(_3\), a similar \( T_{\text{FE}} \) had been reported thus suggesting that strain rather than Bi-La substitution is the dominant effect on the \( T_{\text{FE}} \) reduction. It is remarkable that the sensitivity of these double perovskites on strain is much more modest than typically found in other ferroelectric, such as...
BaTiO$_3$, whose Curie temperature is strongly dependent on strain; indeed, in a 0.70% of tensile strain, as found here, produces a change of $T_{FE}$ by about 150 K. It may be enlightening to notice that in BiFeO$_3$ $T_{FE}$ remains also roughly unchanged for 0.70% of tensile strain.\cite{13}

Dielectric measurements at 5 K have been done by using a pair of Pt-sputtered top electrodes. In Fig. 3, we show the positive-up-negative-down (PUND) (Ref. 19) current versus time ($\tau$-voltage) recorded using triangular voltage (rise time of 25 $\mu$s, equivalent to 10 kHz) and using aixACCT TF analyzer 2000 set up, as pulse generator and current detector.

Whereas the current resulting from P and N pulses (labeled with P and N in Fig. 3) contains the overall current, which resulting from U and D pulses (labeled with U and D in Fig. 3) only contains the non-ferroelectric part since the sample is already polarized. Thus, by subtracting the current from the U pulse from that of the P pulse (and similarly D from N), we only obtain the current related to the switch of the ferroelectric domains. The two current peaks that appear in P and N curves, absent in U and D curves, unequivocally reveal the ferroelectric character of BL10NM films. The polarization current versus voltage $I(V)$ data extracted from this measurement (once subtracted the non-ferroelectric contributions) is shown in the inset of Fig. 3, in which the ferroelectric peaks can be observed. The coercive field is about 220 kV/cm.\cite{20}

The observed asymmetry in the $I(V)$ curves could reflect some sort of dielectric inhomogeneity in the film or, more likely, it could be related to differences in the metal-insulator interfaces. Moreover, the current near the maximum applied voltages is not zero, which indicates that not all ferroelectric domains have been switched. The integration of the $I(V)$ curves allow to determine a remanent polarization of about (6 ± 3) $\mu$C/cm$^2$.\cite{20} The relatively large error is due to the leakage existing in the films and the modest measured polarization ($\sim$6 $\mu$C/cm$^2$).\cite{21} This modest value goes in parallel with the rather small expansion ($\approx$0.16%) of the out-of-plane cell parameter (Fig. 1). Finally, assuming that bulk monoclinic structure is weakly deformed because of the small tensile strain (0.7%), it is reasonable to believe that the polarization axis remains far from the [001] growth direction and, therefore, the measured polarization ($\sim$6 $\mu$C/cm$^2$) may be a lower bound for the actual value.

In summary, we have observed ferroelectric domain switching current in (Bi$_{0.9}$La$_{0.1}$)$_2$NiMnO$_6$ films, which conclusively demonstrates their multiferroic character. The low-temperature remanent polarization is estimated to be $\sim$6 $\mu$C/cm$^2$; accuracy limited by the losses. A phase transition has been observed by Raman an x-ray diffraction at about 450 K and attributed to the setting of the ferroelectric order. The ferroelectric Curie temperature is found to be similar to that reported in non-substituted Bi$_2$NiMnO$_6$ films and only slightly smaller than in bulk, and we thus argued that strain, rather than La-substitution, is responsible for the modest decrease of $T_{FE}$. We strengthen that a similar small effect of strain appears to be characteristic of other Bi-based ferroelectric perovskites, such as BiFeO$_3$. This finding might stimulate further research on other double perovskites, particular strain effects, and alternative chemical substitutions aiming to further approach critical temperatures and, eventually, enhance magnetoelectric coupling.


16. Fitting constants, $\Delta S_{STO}$ and $\Delta S_{BLINOM}$ are the thermal linear expansion coefficients and $\Delta C_{STO}$ and $\Delta C_{BLINOM}$ are the extrapolation values of the linear thermal expansion at 0 K for STO and BL10NM, respectively. B is a general fitting constant for the ferroelectric contribution.
20. The error is determined by the experimental error and the standard deviation (5 events). The values of the coercive field correspond to the electric field value of the current peak that corresponds to the ferroelectric switching.