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Ferroelectric phase transition in strained multiferroic $(Bi_{0.9}La_{0.1})_2NiMnO_6$ thin films

E. Langenberg,[1,a)] I. Fina,[2] P. Gemeiner,[3] B. Dkhil,[3] L. Fàbrega,[2] M. Varela,[1] and J. Fontcuberta[2]
[1]*Departament Física Aplicada i Òptica, Universitat de Barcelona, Martí i Franquès 1, 08028 Barcelona, Spain*
[2]*Institut de Ciència de Materials de Barcelona, CSIC, Campus de la UAB, 08193 Bellaterra, Spain*
[3]*Laboratoire Structures, Propriétés et Modélisation des Solides, UMR CNRS-Ecole Centrale Paris, Grande Voie des Vignes, 92295 Châtenay-Malabry Cedex, France*

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We report here temperature-dependent x-ray structural and Raman spectroscopy data, on the ferromagnetic double-perovskite $(Bi_{0.9}La_{0.1})_2NiMnO_6$ epitaxial thin films. Results indicate a ferroelectric transition occurring at about 450 °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 ($Bi_2BB'O_6$) in a rock-salt configuration, such as Bi_2FeCrO_6 (Ref. 2) or Bi_2NiMnO_6 (BNMO) (Ref. 3), are drawing much of the attention lately. These oxides tend to be ferromagnetic or ferrimagnetic, a property being scarcely present in multiferroics perovskites where antiferromagnetism prevails.[1] In double perovskites, ferromagnetic interactions are designed by choosing appropriately the B-B' cations, i.e., B and B' having empty e_g and half-filled e_g *d*-orbitals, respectively, as in BNMO. Ferroelectricity in these compounds arises from the stereochemical activity of the lone-pair $6s^2$ electrons of Bi^{3+} ions, which drives the non-centrosymmetric distortion of the lattice.

BNMO and La_2NiMnO_6 are ferromagnetic below (T_{FM}) 140 K and 280 K, respectively.[3,4] The solid solution of $(Bi_{1-x}La_x)_2NiMnO_6$ (BLNMO) may be of interest since, as La^{3+} is not a stereochemical active ion, the partial replacement of Bi^{3+} might drop down the ferroelectric transition temperature (T_{FE})—485 K in bulk BNMO (Ref. 3)—towards T_{FM}. Thus, the approaching of the two ferroic transition temperatures may enhance the magnetoelectric coupling,[5] which was predicted to be small in BNMO.[6] We have recently demonstrated that B-site order is maintained despite randomly distributed (Bi, La) cations and the electronic configuration of Ni^{2+} and Mn^{4+} is preserved,[7] guaranteeing long-range ferromagnetic coupling. In bulk, BLNMO remains non-centrosymmetric monoclinic C2 for $x \leq 0.2$,[8] but robust confirmation of ferroelectric character of BLNMO has not been reported yet.[9] On the other hand, it is known that epitaxial strain may also severely modify the polarization and critical temperatures in ferroelectric thin films,[10–14] thus giving an additional opportunity for closing the T_{FM}–T_{FE} gap.

Here, we will provide conclusive experimental evidence that strained $(Bi_{0.9}La_{0.1})_2NiMnO_6$ (BL10NM) thin films are indeed ferroelectric and from structural and Raman data, we infer a phase transition occurring at about $T_{FE} \approx 450$ K.

Single-phase epitaxial $(Bi_{0.9}La_{0.1})_2NiMnO_6$ thin films (100 nm thick) have been grown by pulsed laser deposition on conductive 0.5% Nb-doped $SrTiO_3$ (001) (STO) substrates. Substrate temperature and oxygen pressure during deposition were 620 °C and 0.5 mbar, respectively (see Ref. 15 for further details). Reciprocal space maps[15] have confirmed that BL10NM films are coherently strained on STO, thus adopting a tetragonal-like unit cell: $a_{BL10NM} = b_{BL10NM} = a_{STO} = 3.905$ Å (at room temperature). The misfit strain (–0.70%) was estimated assuming that the lattice parameters of La-doped Bi_2NiMnO_6 bulk is not significantly different from that of undoped Bi_2NiMnO_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_α wavelength. The zero of the goniometer was corrected at room temperature by using {00l} (l = 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, $\alpha_{STO} \sim 4.2 \times 10^{-5}$ Å/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 emphasis the fact that the film parameter, below 450 K, gradually

a)Author to whom correspondence should be addressed. Electronic mail: eric.langenberg@ub.edu.

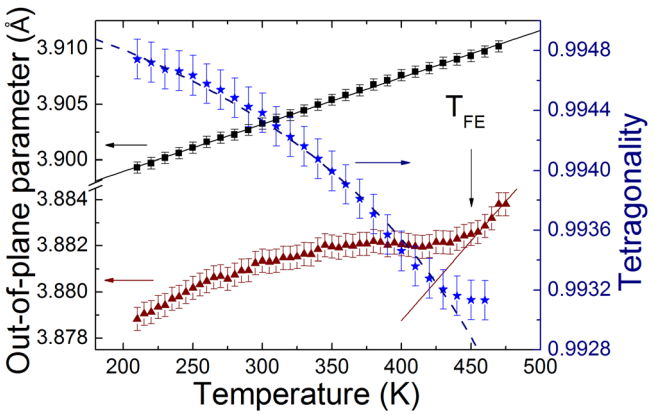

FIG. 1. (Color online) (left axis) Temperature dependence of the out-of-plane lattice parameter of both substrate (solid square symbols) and film (solid triangle symbols); (right axis) Temperature dependence of tetragonality of BL10NM films (star symbols). The dashed line shows the fitting (see text).

deviates from the normal linear behavior. This transition can be even better appreciated in the tetragonality ratio $c_{BL10NM}(T)/a_{BL10NM}(T)$; in computing this ratio, it is assumed that BL10NM remains coherent on the STO substrate and thus $a_{BL10NM}(T) = a_{STO}$ (T); from the cubic structure of STO, it follows that: $a_{BL10NM}(T) = c_{STO}(T)$. These tetragonality values are depicted in Fig. 1 (right axis). The enhancement of the $(c/a)_{BL10NM}(T)$ 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 $c_{BL10NM}(T)/a_{BL10NM}(T)$ data can be well fitted (dashed line through the data) by using $c_{BL10NM}(T) = c^0_{BL10NM} + \alpha_{BL10NM} \times T + B \times \sqrt{T^* - T}$ and $a_{BL10NM}(T) = a_{STO}(T) = a^0_{STO} + \alpha_{STO} \times T$.[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_{FE} and allows to suggest $T_{FE} \approx 450$ 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 antistretching/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_{FE} as inferred from x-ray data presented above. We thus conclude that they signal the occurrence of a ferroelectric phase transition at $T_{FE} \sim 430$ K (± 20 K). We note that similar features were also observed in Raman spectra of Bi_2NiMnO_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 $T_{FE} \sim 450$ 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_2NiMnO_6 films on NdGaO3,[18] a similar T_{FE} had been reported thus suggesting that strain rather than Bi-La substitution is the dominant effect on the T_{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

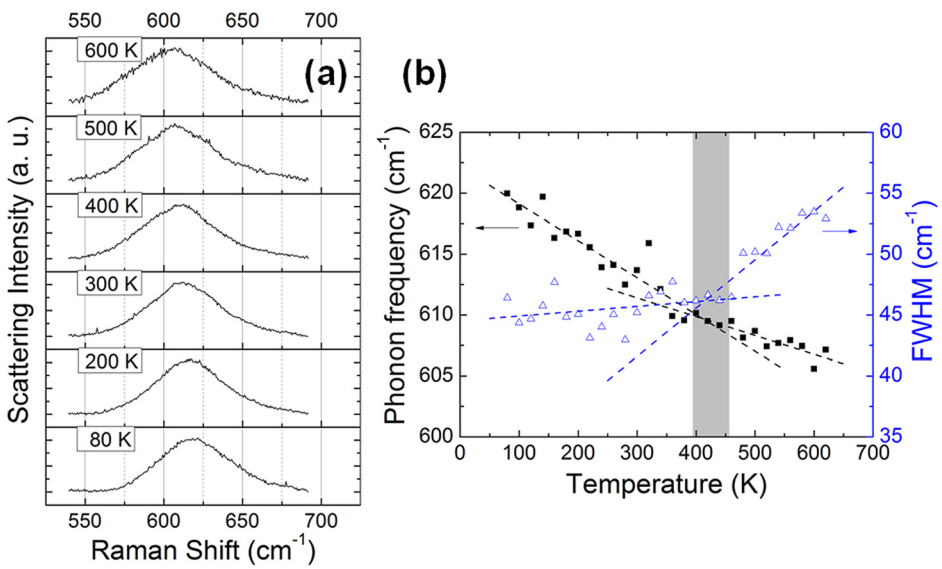

FIG. 2. (a) (Color online) Temperature dependence of Raman spectra of high frequency mode; (b) Temperature dependence of the phonon frequency (solid square symbols, left axis) and linewidth (open triangle symbols, right axis). The dashed lines indicate the slope change of the temperature dependence of phonon frequency and linewidth around T_{FE}.

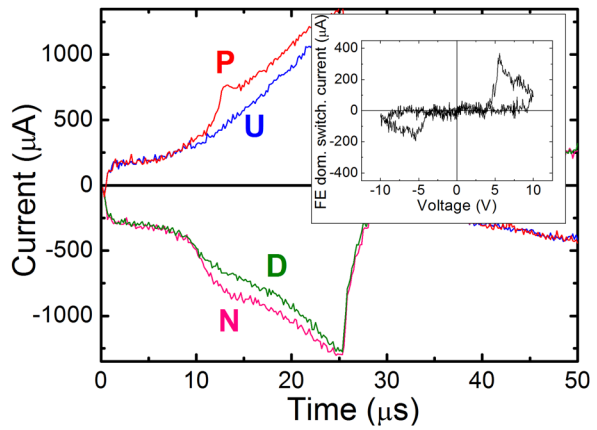

FIG. 3. (Color online) PUND measurement performed on Pt/BL10NM/Nb:STO capacitors at 5 K. Inset: Ferroelectric domain switching current versus applied voltage.

$BaTiO_3$,[12] 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.[12] It may be enlightening to notice that in $BiFeO_3$ T_{FE} remains also roughly unchanged for 0.70% of tensile strain.[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 (~voltage) recorded using triangular voltage (rise time of 25 μs, equivalent to 10 kHz) and using aixACCT TF analyser 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 ± 9 kV/cm.[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) μC/cm^2.[20] The relatively large error is due to the leakage existing in the films and the modest measured polarization (~6 μC/cm^2).[21] This modest value goes in parallel with the rather small expansion (≈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 (~6 μC/cm^2) may be a lower bound for the actual value.

In summary, we have observed ferroelectric domain switching current in $(Bi_{0.9}La_{0.1})_2NiMnO_6$ films, which conclusively demonstrates their multiferroic character. The low-temperature remanent polarization is estimated to be ~6 μC/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_2NiMnO_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.

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