Correlation between structure, dielectric, and ferroelectric properties in BiFeO$_3$–LaMnO$_3$ solid solution thin films

Abdelilah Lahmar,$^{1}$ Salah Habouti,$^{1}$ Claus-Henning Solterbeck,$^1$ Mohammed Es-Souni,$^{1,}\text{a}$ and Brahim Elouadi$^2$

$^1$Institute for Materials and Surface Technology, University of Applied Sciences Kiel, 24149 Kiel, Germany
$^2$Laboratoire d’Elaboration, Analyse Chimique et Ingénierie des Matériaux, Université de La Rochelle, 17042 La Rochelle Cedex 01, France

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Chemical solution processed BiFeO$_3$ thin films usually show high leakage currents and poor ferroelectric properties. The optimizations of processing conditions and doping with appropriate elements have been among the most promising strategies to enhance the overall properties of BiFeO$_3$ thin films. However, detailed studies on the effects of doping elements on the structure and through it on the properties are still lacking. In this work we investigate the interplay between structure and dielectric-electric-ferroelectric properties of BiFeO$_3$–LaMnO$_3$ [Bi$_{1-x}$La$_x$Fe$_{1-x}$Mn$_x$O$_3$ (0≤x≤0.1)] solid solution thin films grown on Pt-terminated silicon substrates. The BiFeO$_3$–LaMnO$_3$ system is shown to undergo a structural transition from monoclinic to orthorhombic-tetragonal with various degrees of orthorhombic distortion. All LMO-containing films show a Debye-like dielectric relaxation with the activation energy of 0.90 eV. Both dielectric relaxation and leakage current mechanisms were interpreted in terms of ionized oxygen vacancy hopping. On the basis of comparative studies on individual doping with La and Mn it is shown that Mn is responsible for the dielectric anomaly and structural transition whereas La alone seems to stabilize the perovskite structure. A correlation between the degree of orthorhombic distortion, leakage current, and polarization properties was also found, with a minimum of leakage current and fairly high polarization at the highest distortion. © 2009 American Institute of Physics. [DOI: 10.1063/1.3063813]

I. INTRODUCTION

The first report$^1$ on BiFeO$_3$ (BFO) dates from 1957, and a ferroelectric hysteresis was reported in 1970.$^2$ However, it is only since huge polarization properties and (controversial) moderate magnetization have been shown for pulsed laser deposited heteroepitaxial$^{1-5}$ films that this material has seen an astonishing revival with publications number soaring in the past years. This revival of interest may be understood if we take into consideration that BFO is the only known monolithic material that could exhibit multiferroism (simultaneous existence of ferroelectricity and magnetism) at room temperature. These properties are directly related to the structure and electronic configurations of the elements in the lattice. BFO has a distorted rhombohedral structure that belongs to the polar (R3c) space group. The high relative ionic displacements along the [111] polar direction and the high Curie transition temperature of 810 °C would impart to this material high polarization properties. Moreover BFO is antiferromagnetic with a Neel temperature of 380 °C. It shows weak ferromagnetism due to its distorted (R3c) structure and spin canting which would imply multiferroism at room temperature.$^6-9$ However, as it seems several structural variants of this material could exist,$^{3,9,10}$ which would explain the large scatter in the polarization properties reported mainly for thin films. An additional reason for the scatter in the properties of BFO may also be found in its limited thermodynamic stability. Indeed the phase diagram of the system Bi$_2$O$_3$–Fe$_2$O$_3$, although still under discussion, shows in all suggested versions that BFO is a line compound. Such a situation usually results in the appearance of secondary phases in case of slight deviation from the ideal stoichiometry and might explain the reported instability of BFO.$^{16}$ Additionally, the defect chemistry of BFO is complex due to the existence of volatile Bi and the different oxidation states that can be taken by Fe and Bi ions. This may translate in specific behaviors as to the structural, electrical, and magnetic properties. For instance BFO films are prone to high leakage currents which seem to be governed by deep ionized traps, purportedly due to the existence of Fe$^{2+}$ species.$^{17,18}$ Fe$^{2+}$ ions have also been shown to contribute a large part to magnetization.$^{5,15}$ In a previous work$^{19}$ we have shown that doping with LaMnO$_3$ (LM) could substantially improve the polarization as well as the magnetic properties of BFO. Because of the similarities of the ionic radii and valences of the elements involved, and the similar perovskite structures of LM and BFO, the property improvement was quite intriguing. Its understanding has to take into consideration possible changes in structure and defect chemistry.

In a recent Raman study we found indications for a monoclinic structure of pure BFO and a structural transition to orthorhombic upon doping with LM, together with the appearance of Jahn–Teller (JT) distortion.$^{19}$ Doping with Mn ions seems to be crucial for the octahedral distortions and
structural transition in BFO-LM thin films. This is in agreement with a recent study on the phase diagram of BiFe$_1-x$Mn$_x$O$_3$ polycrystals, which predicts an orthorhombic structure for low $x$ values.  

The present paper aims at investigating the effects of LM additions on the structure, dielectric, and polarization properties of BFO-LM thin films. It is shown that the structure is highly influenced by the addition of LM. A dielectric relaxation is observed and appears to be intimately associated with the incorporation of Mn ions into the lattice. The functional properties correlate well with the degree of structural distortion induced by LM doping, whereby LM concentrations around 5 mol% seem to be critical for low leakage currents and high ferroelectric polarization properties.

II. EXPERIMENTAL

The thin films were fabricated via spin coating on a commercial (111)-Pt/Ti/SiO$_2$/Si substrate heterostructure. Detailed description of precursor solution preparation and thin films fabrication were reported elsewhere. Briefly, the starting reagents are Bi-acetate, La-acetate, Mn- and Fe-acetate lactonate dissolved in a mixture of acetic acid and distilled water. The pyrolysis was conducted on the hot plate at 260 °C, then the final annealing was performed in a preheated tube furnace in a saturated oxygen atmosphere between 600 and 650 °C. The stoichiometries prepared were Bi$_{1-x}$La$_x$Fe$_{1-x}$Mn$_x$O$_3$ system with $x=0\%$, 2\%, 4\%, 5\%, 6\%, 8\%, and 10\%, in the following as (BFO-xLM). For comparison BFO films with either 5% of Mn (BFO-5Mn) or 5% La (BFO-5La) were also processed. The ellipsometric thin film thickness was approximately 235 nm.

A. Devices and measurements

The microstructures were checked using x-ray diffraction (XRD) (Seifert 3000 PTS 4-circle diffractometer, Cu $K\alpha=1.5418$ Å) and atomic force microscopy (AFM) (SIS GmbH, Herzogenrath, Germany). Lattice parameter refinements were performed using both DHKL and AFPAR softwares (complex program of CNRS, France). X-ray photoelectron spectroscopy (XPS) characterization of the films was performed using the Omicron Full Laboratory System with Al $K\alpha$ soft x-ray radiation source. Systematic shifts of the XPS spectra (due to surface charging effect) were corrected using the 1s line of carbon at 285.0 eV. For electrical measurements, round Pt electrodes of 0.6 mm diameter were sputtered to provide the front contact and subsequently annealed for 15 min at 400 °C.

III. RESULTS

A. Structural properties

AFM phase images of the film microstructures obtained are shown in Fig. 1 for three different compositions. The films were crack-free, fine grained, and smooth with an AFM mean root square roughness of 5 nm.

Figure 2 shows XRD spectra of all stoichiometries in-pure phase thin films were obtained. We notice that splitting of the 110 line observed for the pure BFO film disappears gradually for the doped films. This observation was also reported for La-modified heteroepitaxial BFO—a recent study on the phase diagram of

![Image](https://via.placeholder.com/150)

**FIG. 1.** (Color online) (A) AFM topography phase images of BFO-2LM, (B) BFO-5LM, and (C) BFO-8LM.

The dielectric properties and their temperature dependence were obtained using a computer-controlled Agilent 4192 A impedance analyzer equipped with a hot stage ensuring a temperature control of ±0.5 K. The ac driving signal amplitude was 25 mV. Ferroelectric polarization was investigated at room temperature using a ferroelectric test system (TF Analyzer 2000, aixACCT). Voltage- and temperature-dependent leakage currents were measured using a computer-controlled set-up including a high-precision electrometer (Keithley 6517A) and a heating stage which allows the temperature to be controlled with an accuracy of ±0.5 K. Current density–voltage ($J$–$V$) characteristics were acquired in the step mode with a delay time from 30 to 200 s to allow for sample discharging. The signal was applied to the bottom electrode in all cases. The temperature was measured with a thermocouple placed on the sample surface.

| TABLE I. Lattice parameter ratios $a/b$, $c/a$, and $c/b$ and calculated cell volumes of BFO-xLM($0<x<1$) and BFO-5Mn. |
| --- | --- | --- | --- |
| $a/b$ | $c/a$ | $c/b$ | $\nu$ ($\AA^3$) |
| BFO | 1.004 | 1.002 | 1.005 | 61.52 |
| BFO-2LM | 1.002 | 0.997 | 0.999 | 60.976 |
| BFO-4LM | 1.004 | 1.003 | 1.008 | 61.239 |
| BFO-5LM | 1.010 | 1.001 | 1.011 | 61.269 |
| BFO-6LM | 1.001 | 1.007 | 1.008 | 60.97 |
| BFO-8LM | 1.000 | 1.007 | 1.007 | 61.03 |
| BFO-10LM | 1.000 | 1.005 | 1.006 | 61.613 |
| BFO-5Mn | 1.005 | 1.003 | 1.008 | 61.597 |

![Image](https://via.placeholder.com/150)

**FIG. 2.** (Color online) Room-temperature XRD patterns of thin film specimens: (a) BFO-xLM ($x=0\%$, 2\%, 4\%, 5\%, 6\%, 8\%, and 10\%); (b) BFO-5La and BFO-5Mn.
thin films, with La concentrations in the range from 8% to 15%, and was attributed to decreasing of the monoclinic tilting of the pure BFO-lattice.22

Lattice parameter refinement was performed assuming monoclinic structure for pure BFO and orthorhombic structure for BFO-LM using diffraction patterns from thin films. Table I lists the values of the orthorhombic distortions $a/b$, $c/a$, and $c/b$ and Fig. 3 displays $c/b$ and $a/b$ versus film composition. There is a clear evidence of a fairly sharp increase in the orthorhombic, and hence octahedral, distortion at the BFO-5LM composition. We also notice that the $a/b$ ratio drops steeply at 6% LM and attains unity at 8%, suggesting a structure symmetry change from orthorhombic to tetragonal. These results agree well with Raman spectroscopy results reported in previous work.19

B. Defect structure

BFO may show a variety of defects that can be imputed to different mechanisms: due to volatility of Bi, Bi vacancies may form; these can be compensated by the formation of oxygen vacancies, whereby for each Bi vacancy $\frac{V_{\text{Bi}}}{H_2O}$, $V_{\text{O}}\frac{3}{2}$ are created (following Kröger–Vink notation). Bi depletion of the bulk may also take place following segregation effects driven by the high vapor pressure of Bi oxide. Furthermore, Fe ions may take the oxidation state $Fe^{2+}$ thus leading to acceptor states which could also be compensated by the formation of oxygen vacancies or donor states at the Bi sites, i.e., formation of Bi ions with oxidation states $>3+$. Furthermore, the incorporation of Mn ions which are known to take oxidation states from 2+ to $4+$ also complicates the figure, e.g., the formation of $Mn^{4+}$ could be compensated either by the formation of $Fe^{2+}$, Bi vacancies or annihilation of oxygen vacancies. The oxidation states of the different elements were investigated on BFO-10LM using XPS, because the higher concentration of Mn in these films could facilitate the XPS analysis. Figure 4 displays the results obtained for Bi, Fe, and Mn, and Table II lists the binding energies after correction of charging effects using the carbon peak at 285.0 eV. There is no indication of any oxidation states for Fe other than $Fe^{3+}$ as documented by the positions of the main 2p peaks and plasmon peaks, discussed in some detail by Kothari et al.23 These findings were confirmed by Mössbauer investigations on BFO-5LM powder, where only $Fe^{3+}$ could be found.24 The peak position of Bi shown in Table II also corresponds to that of $Bi^{3+}$.25 With respect to Mn, peak fitting is difficult because of the low intensity of the peaks, the low signal to noise ratio and the large full width at half maximum. Nevertheless, the form of the $2p_{3/2}$ peak and the corresponding binding energy26 (see Table II), as well as the observation of the JT effect, which is associated with $Mn^{3+}$,19 ions do not suggest any other oxidation states than $Mn^{3+}$. These results are based on XPS which is not sensitive to small defect concentrations below 0.1 at. %.

C. Dielectric properties

Figure 5(a) exemplary shows the thermal dependence of the dielectric constant ($\varepsilon_r$) at different frequencies for BFO-4LM. Unfortunately, owing to high sample conductivity in the temperature range investigated, these peaks were not well resolved for the loss tangent ($\tan \delta$), dependence on frequency and temperature. We notice that the peak temperature ($T_m$) increases with increasing frequency, particularly at low frequencies, characteristic for relaxation phenomena. Moreover, both $\varepsilon_r$ and $T_m$ decrease with increasing LM amount. These relaxation phenomena were neither observed in pure

| TABLE II. XPS binding energies of BFO-10LM. |
|---------------------|---------------------|---------------------|---------------------|
| $Fe\ 2p_{3/2}$     | $Fe_{3+}$           | $Bi\ 4f_{7/2}$     | $Mn\ 2p_{3/2}$     |
| 711.2 eV            | 719.7 eV            | 158.6 eV            | 641.4 eV            |

FIG. 3. (Color online) Variation of lattice parameters ratio vs composition for BFO-xLM series.

FIG. 4. (Color online) High resolution XPS spectra of Bi, Fe, and Mn in BFO-10LM thin films. Deconvolutions of the peaks are also shown.
BFO nor in La substituted films, but were very well pronounced in the case of Mn doped films. The behaviors of pure BFO, BFO-5Mn and BFO-5La are also shown for comparison in Fig. 5(b).

For dielectric relaxation processes the real and complex part of the complex dielectric function \( \varepsilon^* = \varepsilon' - i\varepsilon'' \) can be expressed using the Debye approximation:\[27\]

\[
\varepsilon'(\omega) = \varepsilon_\infty' + \frac{\varepsilon'_s - \varepsilon_\infty'}{1 + \frac{\omega^2 \tau^2}{\varepsilon_0}}
\]

for the real part. The imaginary part is given by

\[
\varepsilon''(\omega) = \frac{\varepsilon'_s - \varepsilon_\infty'}{1 + \frac{\omega^2 \tau^2}{\varepsilon_0}} + \frac{\omega \tau}{1 + \omega^2 \tau^2},
\]

where \( \varepsilon'_s \) is the static dielectric constant, \( \varepsilon_\infty' \) is the dielectric constant at very high frequencies, where dipolar effects are absent, \( \omega \) is the angular frequency = 2\( \pi f \) and \( \tau \) is the relaxation time.

Since dielectric relaxation processes are thermally activated, the reciprocal of the relaxation time, or more conveniently the relaxation frequency, depends on temperature through the Arrhenius law:

\[
f = f_0 \exp \left( \frac{-E_a}{kT} \right),
\]

where \( f_0 \) is the prefactor, \( E_a \) is the activation energy of the process, \( k \) is the Boltzmann constant, and \( T \) is the absolute temperature. Figure 5(c) exemplary shows a semilogarithmic plot of frequency versus reciprocal of temperature, and the calculated activation energies for the different compositions are listed in Table III together with corresponding values of the prefactor \( f_0 \).

The values of \( E_a \) are apart from few exceptions lower than those reported for space charge relaxation in PbTiO\(_3\) base perovskite reported in Ref. 28. The prefactor \( f_0 \) is some-what high for the higher LM concentrations in comparison to the Debye frequency for ion jumps (\( \sim 10^{13} \) s\(^{-1}\)) but the discrepancy is tolerable if the uncertainty for peak temperature determination is taken into account; indeed the relaxation peaks have quite large maxima (see Fig. 5). Similar low temperature relaxation phenomena with fairly similar values of \( E_a \) and \( f_0 \) were also observed for nondoped bismuth titinate ceramics by Schulman et al.\[29\] These authors also had shown that doping with small amounts of Nb\(^{5+}\) suppressed the relaxation peak, and interpreted this in terms of oxygen vacancy annihilation by donor doping (Nb\(^{5+}\)\(1+e'\)). In the present work, the addition of Mn\(^{3+}\), an isovalent ion with Fe\(^{3+}\), leads to the appearance of the relaxation peak far below \( T_N \) while La\(^{3+}\) does not.

A dielectric anomaly has been also reported for BFO near \( T_N \), and was attributed to magnetoelectric coupling in this compound.\[30\] A phenomenon of this type is not likely in our case in the temperature range of the dielectric peaks, since the addition of Mn does not depress \( T_N \) to the extent observed\[23\] (the addition of 10\% Mn has been observed to lead to a \( T_N \) value of the order of 317 °C).

The dielectric anomaly depicted in this work may thus be attributed either to space charge polarization or ion jump mechanisms, both could be mediated by the existence of oxygen vacancies. The latter may form following a variety of mechanisms, e.g., via Bi evaporation during high temperature processing; the formation of Bi vacancies could be compensated by oxygen vacancies, and for each Bi \( \left(V_{Bi}^{\text{m}}\right) \) vacancy \( 3/2\left(V_{O}^{\text{m}}\right) \) are created. The existence of acceptor states, e.g., Fe\(^{3+}\), may also lead to the creation of oxygen vacancies. However, as only Fe\(^{3+}\) species were found by XPS (see Fig. 4), we may conclude that \( V_{Bi}^{\text{m}} \) and \( V_{O}^{\text{m}} \) constitute the main defects in our films. Furthermore, the existence of oxygen vacancies has been shown to lead to an overall augmentation.

### Table III. Activation energy, \( E_a \), and the prefactor \( f_0 \) of the BFO-xLM solid solutions investigated as well as BFO-5Mn.

<table>
<thead>
<tr>
<th>( X ) (%)</th>
<th>BFO-2LM</th>
<th>BFO-4LM</th>
<th>BFO-5LM</th>
<th>BFO-6LM</th>
<th>BFO-8LM</th>
<th>BFO-5Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_a ) (eV)</td>
<td>0.89</td>
<td>0.90</td>
<td>0.90</td>
<td>0.85</td>
<td>0.88</td>
<td>0.91</td>
</tr>
<tr>
<td>( f_0 ) (Hz)</td>
<td>( 4.32 \times 10^{12} )</td>
<td>( 3.05 \times 10^{12} )</td>
<td>( 5 \times 10^{12} )</td>
<td>( 6.7 \times 10^{12} )</td>
<td>( 7.9 \times 10^{12} )</td>
<td>( 7.8 \times 10^{12} )</td>
</tr>
</tbody>
</table>
Fig. 6. (Color online) The leakage current properties at room temperature: (a) J-E curves for the different compositions investigated, except BFO-5La; (b) shows the dependence of leakage current density, J, on LMnO content. Values of J are given at an applied dc electric field of 150 kV/cm for BFO-LM, and at 85 kV/cm for pure BFO. The line is a guide for the eyes; (c) represents the dependence of the effective activation energy for conduction on the reciprocal of temperature and calculation of the trap depth $\phi_B$ assuming the Frenkel–Poole mechanism, Eq. (4). The mean square root regression line is also shown.

of cell volume\textsuperscript{31} in BiMnO$_3$, as also shown Table I. This may constitute further support of the existence of oxygen vacancies in the present films.

Assuming that the main origin of the dielectric peak and its frequency dispersion would lie in space charge polarization and relaxation, the question then arises as to why this phenomenon is not observed for pure BFO and BFO-5La, since the processing conditions were fairly the same. We therefore surmise that the leakage peaks observed in BFO-xLM and BFO-5Mn are related to oxygen-ion-hopping mechanisms, and that the existence of octahedral distortions mediated by the incorporation of Mn ions in the lattice are essential for this process (see below for discussion).

D. Leakage current properties

The leakage current properties at room temperature are displayed in Fig. 6. The data of BFO-5La are not shown since this film was highly conductive. It is interesting to note that the critical composition BFO-5LM is characterized by very low leakage currents. A comparison of the leakage currents of the different compositions investigated is shown in Fig. 6(b). It can be seen that the leakage current density decreases gradually with increasing LM concentration and shows a sharp minimum at 5% LM before it increases again with higher LM contents. This implies that the transport properties in the BFO-LM system are sensitive to the degree of orthorhombic distortion. The higher this distortion is the higher the resistivity of the BFO-LM system.

In previous work\textsuperscript{21} we have shown that conduction in BFO-5LM thin films may be interpreted in terms of the Frenkel–Poole mechanism using\textsuperscript{32}

$$J \propto E \exp \left[ -\frac{q(\phi_B - qE/\pi e)}{k_B T} \right],$$

where $J$ is the current density, $E$ is the electrical field, $q$ is the elemental charge, $T$ is the absolute temperature, $\phi_B$ is the trap height, $e$ is the optical frequency dielectric constant, and $k_B$ is the Boltzmann constant. $\phi_B$ was found to be in the range of 0.94 eV. A similar study conducted on BFO-6LM, which also is characterized by low leakage current, thus making temperature-dependent measurement possible, leads to a similar $\phi_B$ of 0.81 eV as shown in Fig. 6(c). These values are similar to those calculated from the dielectric relaxation above, and to what is generally found for conduction by ionized oxygen vacancy traps, e.g., in lead-zirconate-titanate (PZT) thin films.\textsuperscript{33}

E. Ferroelectric properties

For pure BFO, grown under the conditions reported here no ferroelectric polarization could be measured. Similar properties were found for BFO-5La. Explanation might rely on the high leakage currents characteristic for these films which could hinder polarization switching. However, we have also shown in previous work\textsuperscript{17} that BFO still shows no ferroelectric polarization, although the microstructure was optimized for low leakage current properties.

The figure changes for the BFO-xLM solid solutions. Polarization switching is already shown by BFO-2LM and increases with increasing LM concentration. Figure 7 shows the polarization hysteresis (P-E) curves at 10 kHz for selected compositions. Contributions from space charge polarization can be discerned since (i) polarization does not change with testing frequency, and (ii) the measuring frequency is too high for space charges to follow the field. Figure 8 tentatively shows how polarization depends on LM content and orthorhombic distortion. We do not claim that orthorhombic distortion is the only factor determining the magnitude of polarization, but it seems necessary for inducing ferroelectric polarization. Furthermore, we can see that although dc-leakage currents are high for certain films [see Fig. 6(a)], polarization switching is not hindered. The use of higher testing frequencies is probably suitable in this case,\textsuperscript{34} since space charges or injected charges cannot follow the field at these frequencies.

It is largely agreed upon that Bi is crucial for ferroelectricity via its stereochemically active lone pair electrons, as discussed amply by Ravindran et al.\textsuperscript{35} However, our own and others observations suggest that nonpolar BFO films may be obtained depending on processing conditions and underlying substrate. In our case, the structural modification induced by codoping with La and Mn appears to have a large effect on ferroelectric polarization, although some of the Bi ions are
substituted by La, a nonstereochemically active element. The polarization correlates nicely with the calculated orthorhombic distortion, as shown in Fig. 8. The role of each doping element may be understood if we consider its effect on orthorhombic distortion. While La only moderately affects $c/b$, probably not at all changing the nonpolar character and hence the ferroelectric properties of the BFO lattice, Mn in contrast, leads to a higher orthorhombic distortion which then leads to measurable ferroelectric polarization, as shown in Fig. 9.

IV. DISCUSSION

Both Raman and XRD investigations show that the structure of BFO is altered by the addition of LM. Pure BFO thin films most probably crystallize in a quasicubic structure with a small monoclinic distortion in agreement with previous work. Codoping with La on the Bi sites and Mn on the Fe sites gradually induce structural changes toward a distorted orthorhombic structure. It is interesting to note that 5% LM is a critical concentration, characterized by highest orthorhombic distortion and constituting a boundary toward a more relaxed structure. Analysis of Mn doped BFO had shown that the structural changes are essentially caused by the incorporation of Mn in the BFO lattice. Further evidence of probably a local JT distortion associated with the substitution of Fe$^{3+}$ ions in the FeO$_6$ octahedra with Mn$^{3+}$ ions could also be obtained from Raman investigations. It is intriguing that this JT distortion appears at such low doping concentrations of LM and Mn which suggests that the ground structure of BFO is not stable, an assumption supported by its many structural variants reported in literature.

In previous work Mn doping of BFO, sometimes combined with La doping, was performed for the sake of improving the functional properties of this compound. However, detailed structural investigations are scarce: we note

![FIG. 7. (Color online) Room-temperature P-E hysteresis loops of (a) BFO-2LM, (b) BFO-5LM, (c) BFO-6LM, and (d) BFO-10LM at 1, 5, and 10 kHz.](image)

![FIG. 8. (Color online) Remnant polarization, $2P_c$, and saturation polarization, $2P_s$, dependence on LMO content. The polarization values are given at 10 kHz testing frequency and room temperature. The orthorhombic distortion, $c/b$, is also shown. The lines are guides for the eye.](image)

![FIG. 9. (Color online) P-E hysteresis loops of BFO-5Mn thin film at different frequencies.](image)
that Sosnowska et al.\textsuperscript{38} did not report any structural transition in BiFeO$_3$–BiMnO$_3$ up to 20\% BiMnO$_3$, but concluded to a change in the antiferromagnetic order and an increase in structural disorder with increasing Mn concentration. In contrast, Azuma et al.\textsuperscript{20} reported a transition from rhombohedral to a metastable orthorhombic structure starting at 20\% BiMnO$_3$. Based on the present results and our previous Raman investigations\textsuperscript{19} it may be concluded that even small concentrations of LM, viz., Mn, down to 2 mol \% lead to destabilizing the structure of BFO.

Doping with La alone, at the moderate level used in this work, is not expected to affect the structure to any substantial extent, in agreement with previous work,\textsuperscript{39} since La$^{3+}$ which substitutes for Bi$^{3+}$ has almost the same ionic radius (1.16 Å in comparison to 1.17 Å for Bi$^{3+}$, assuming octahedral coordination). However, some degradation of the rhombohedral structure may arise because Bi$^{3+}$, a stereochemically active lone pair ion is replaced by La$^{3+}$, a nonstereochemically active ion. Due to its free doublet (6s$^2$), Bi$^{3+}$ hybridizes with oxygen anion O$_2$p causing deformation of oxygen octahedra and stabilization of the rhombohedral structure.\textsuperscript{35} As La$^{3+}$ substitutes Bi$^{3+}$ a decline of the stereochemical activity of Bi–O bonds could be induced. The substitution of Fe$^{3+}$ (d$^5$) on B sites by high spin Mn$^{3+}$ (d$^4$) is expected to cause additional octahedral deformation in a structure which already contain highly deformed FeO$_6$. We might speculate on a cooperative effect of La and Mn for favoring the structural changes at such low concentrations reported here. Further, although we deal with relaxed polycrystalline films, residual stresses which buildup in the film during cooling, could also contribute to driving these changes.

The incorporation of Mn$^{3+}$ is responsible for a dielectric relaxation with high activation energy of roughly 0.9 eV. In manganites and manganese based oxides with strong JT distortion dielectric relaxation was also observed and was generally interpreted in terms of small polaron hopping.\textsuperscript{40-43} i.e., thermally activated electron hopping from one localized state to another on equivalent lattice sites. The activation energy reported was in the range from 0.4 eV for LiMn$_2$O$_4$ (Ref. 40) to 0.65 eV for Li-doped $\alpha$-Mn$_3$O$_4$.\textsuperscript{41} The higher activation energies were explained in terms of polaron stabilization by electron-phonon interactions that arise from Mn$^{3+}$ induced JT lattice deformation.\textsuperscript{40} Dielectric relaxation was also observed in Bi-base compounds with a range of activation energies\textsuperscript{20,42,43} from 0.33 to 0.74 eV. Relaxation in these materials has been discussed in terms of hole hopping between Bi 6s and Fermi level in BaBiO$_3$,\textsuperscript{43} hopping of Ti$^{4+}$ ions between equivalent position minima in the case of Bi$_2$Ti$_3$O$_{11}$ (Ref. 42) or hopping of oxygen ions between equivalent positions.\textsuperscript{29} In all these hopping phenomena the existence of oxygen vacancies and their effects on accentuating deformation of MO$_6$ octahedra were outlined. In our case the relatively high activation energy obtained suggests that the relaxation mechanisms are not governed by small polaron hopping, since even in $\alpha$-Mn$_3$O$_4$ the activation energy for this process is smaller.\textsuperscript{41} The BFO-structure depicted in Fig. 10 is drawn according to the optimized structure with Pnma space group calculated by Ravindran et al.\textsuperscript{35} The two highly distorted FeO$_6$ octahedra are rotated by approximately 15° with respect to each other, and there are three Fe–O bond lengths outlined in Fig. 10. This implies different effective valence charges on the O sites. Oxygen ions hopping between sites of equivalent charges could therefore take place leading to relaxation of dipolar defects that could be created as a result of oxygen vacancies. However, as outlined above, the dielectric anomaly was observed solely for the LM and Mn doped BFO thin films. In the absence of a structure resolution of these materials we can only speculate that the JT distortion might accentuate the polar character of the MO$_6$-octahedra, and could drive relaxation phenomena by oxygen ions hopping between sites of equivalent charges.\textsuperscript{29} The activation energy of roughly 0.9 eV derived from the dielectric anomaly supports this assumption.

We have also shown that dc conduction in BFO-LM thin films is probably dominated by ionized deep traps with mean trap depths in the range from 0.8 to 0.9 eV, characteristic for ionized oxygen vacancy traps.\textsuperscript{21} The activation energy obtained is very similar to that obtained from relaxation, and suggests that conduction and relaxation in these films are intimately related. The leakage current density versus LM content shows a peculiar behavior with a sharp minimum at 5\%, corresponding to the highest octahedral distortion. This reminds of the well known effects of lattice distortion on conduction of hole-doped LaMnO$_3$.\textsuperscript{44} At present, in the absence of more advanced structural studies, we can only invoke some similarity to what is known for Ca-doped LaMnO$_3$-epitaxial films, where lattice and JT distortions have been shown to be crucial for the high resistivity of these films.\textsuperscript{44}

Finally the ferroelectric properties also correlate well with the degree of orthorhombic distortion. While in pure BFO films no ferroelectric polarization could be measured even when the microstructure was optimized for high resistivity, the addition of LM leads to high ferroelectric polarization even when the microstructure was optimized for high resistivity.
V. CONCLUDING REMARKS

The results presented in this work show that the addition of LaMnO$_3$ to BiFeO$_3$ induces structural changes to orthorhombic and probably to tetragonal structures. The incorporation of both (La$^{3+}$, Mn$^{3+}$) cations was found to reduce the leakage current and improve the ferroelectric properties of BiFeO$_3$ with an optimum at the critical concentration of 5 mol%. A Debye-like dielectric relaxation with high activation energy of 0.90 eV has been found, similar to that obtained from dc conduction. Both dielectric relaxation and leakage current mechanisms were interpreted in terms of ionized oxygen vacancy hopping. BFO-5%La and BFO-5%Mn thin films were also investigated in order to understand the role of each doping element on the structure, dielectric, and ferroelectric properties of the BFO thin films. It has been demonstrated that the Mn ions are responsible for these structural changes and for the apparition of the dielectric anomaly. A correlation between the degree of orthorhombic distortion, leakage current and polarization properties was also found, with a minimum of leakage current and fairly high polarization at the highest distortion.

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