Angular dependence of the magnetoelectric coefficient on multiferroic BiFeO$_3$ thin film


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We report synthesis of multiferroic BiFeO$_3$ thin films as a magnetoelectric material. Films were prepared by using RF magnetron sputtering technique in pure oxygen atmosphere at 0.4 mbar grown on Pt/TiO$_2$/SiO$_2$/Si substrates at 600$^\circ$C. Films were characterized by x-ray diffraction (XRD), Atomic force microscopy (AFM) and angular-dependent magnetoelectric coefficient ($\alpha_{ME}$). XRD pattern shows a predominant perovskite structure. The ME coefficient was measured via a lock-in technique in Sn/BiFeO$_3$/Pt capacitor structure varying the angle $\varphi$ (0 $< \varphi < \pi/2$) between the applied DC magnetic field and the vector tangential to the surface of the sample.

Keywords: Multiferroic; magnetoelectric materials; grain size.

Se presenta la síntesis de películas delgadas del multiferroico BiFeO$_3$ como material con respuesta magnetoelectrónica. Las películas fueron preparadas mediante la técnica de RF magnetrón sputtering en atmósfera de oxígeno puro a 0.4 mbar sobre sustratos Pt/TiO$_2$/SiO$_2$/Si a 600$^\circ$C. Las películas fueron caracterizadas por difracción de rayos X (XRD), microscopía de fuerza atómica (AFM) y la dependencia angular del coeficiente magnetoelectrónico ($\alpha_{ME}$). El patrón de difracción de rayos X muestra una estructura tipo perovskita predominante. El coeficiente $\alpha_{ME}$ se midió a través de la técnica lock-in en la estructura tipo condensador Sn/BiFeO$_3$/Pt, variando el ángulo $\varphi$ (0 $< \varphi < \pi/2$) entre el campo magnético DC aplicado y el vector tangente a la superficie de la muestra.

Descriptores: Multiferroicos; materiales magnetoelectrónicos; tamaño de grano.

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1. Introduction

Multiferroic materials simultaneously exhibit ferroelasticity, ferromagnetism, ferroelectric polarization and coupling between them. Due to the nontrivial coupling in the lattice between magnetic and electric domains, the magnetization can be controlled applying an electric field, and likewise the polarization can be controlled through a field magnetic, known as Magnetoelectric effect [1-3]. It allows that the magnetic polarization can be switched by applying an electric field; likewise the ferroelectric polarization can be switched by applying a magnetic field.

Bismuth ferrite BiFeO$_3$ is a rhombohedral distorted perovskite belonging to space group R3c. This material has a Curie temperature of 1083 K [4] and a Neel temperature of 640 K [5]. The ferroelectric polarization lies along the pseudocubic [111] leading to the formation of eight possible polarization variants The magnetic moments of Fe are ferromagnetic coupling within the pseudocubic planes (111) and antiferromagnetic between adjacent planes; the antiferromagnetic moments are oriented perpendicular to the direction [111]. This symmetry allows an inclination of the antiferromagnetic sublattice, resulting in a macroscopic magnetization: known as weak magnetization [6].

Superimposed on the antiferromagnetic ordering there is a spin spiral structure in which the antiferromagnetic axis rotates through the crystal with a wavelength of 620 Å [5]. The spiral spin structure leads to the cancellation of any macroscopic magnetization that may occur, dificulting the observation of the linear magnetoelectric effect [7], but not the quadratic term [8]. However, the spiral structure can be suppressed in thin films; perhaps due to anisotropy induced by the stress during the growth of the samples, and the linear magnetoelectric effect can be observed [6-9].

2. Experimental details

BiFeO$_3$ thin films were grown on a substrate Pt/TiO$_2$/SiO$_2$/Si, with a substrate temperature during growth of 600$^\circ$C, using RF magnetron sputtering technique under optimal deposition parameters summarized in Table I [10-12].

2.1. Atomic force microscopy (AFM)

The morphology of the deposited films was analyzed by the AFM technique. The growth of columnar films is a result of the nucleation process where atoms in the initial stage of

<table>
<thead>
<tr>
<th>Target BiFeO$_3$</th>
<th>(1 In. diameter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working pressure</td>
<td>4 $\times$ 10$^{-1}$ mbar</td>
</tr>
<tr>
<td>Target-substrate distance</td>
<td>30 mm</td>
</tr>
<tr>
<td>Deposition time</td>
<td>120 min</td>
</tr>
<tr>
<td>Thickness films</td>
<td>456 nm</td>
</tr>
<tr>
<td>RF Power Density</td>
<td>13.61 W/cm$^2$</td>
</tr>
<tr>
<td>substrate</td>
<td>Pt/TiO$_2$/SiO$_2$/Si</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>600 $^\circ$C</td>
</tr>
</tbody>
</table>
of growth by thermodynamic equilibrium are grouped into zones on the substrate preference, resulting in the deposition process continues around these regions.

2.2. Magnetoelastic coefficient $\alpha_{ME}$ detection

When a ME material is exposed to a magnetic field $H$, a voltage $V$ appears. Additionally if a small AC field $h = h_0 \sin \omega t$ superimposed onto a DC bias field $H$, the total field: $H_{total}=H+h_0 \sin \omega t$. Lock-in technique measures the effective value of a small voltage AC ($V_{out}$) which is induced in the sample when we apply a small AC magnetic field [13] instead of measuring the charge or voltage ME as a static method. This method also allows measuring the phase shift signal. However, this phase change is approximately constant during the DC magnetic field variation. By changing the DC magnetic field can explore the effect of ME in different parts of the sample work. In addition to varying the frequency of AC magnetic field, one can measure the response of the material for different time scales. The signal is filtered by the lock-in and noise is dramatically reduced.

Figure 1 shows the assembly for the $\alpha_{ME}$ measurement. pm 5192 Programmable Synthesizer/ Function Generator feeds the coil that will produce the AC magnetic field; a sample holder placed the film at the desired angle; the DC magnetic field is produced by an electromagnet powered by PM 2811 programmable power supply 60V/5A/60W. The voltage signal induced in the sample is acquired by a Lock-in EG&G model 5210, which is responsible for filtering noise, using as reference the signal feeding the coil, ensuring the fidelity of the measured signal.

![Figure 1](image1.png)

**Figure 1.** Magnetoelastic measurement system using lock-in technique in Sn/BiFeO$_3$/Pt capacitor structure. An oscilloscope allows continue monitoring of the reference signal, the voltage signal induced in the sample for each sample configuration, for an angle $\phi$ (0 < $\phi$ < $\pi$/2) between the applied DC magnetic field and the vector tangential to the surface of the sample.

**Figure 2.** XRD spectrum of the BiFeO$_3$ films grown on 600$^\circ$C substrate Pt/TiO$_2$/SiO$_2$/Si. The peaks marked with an asterisk (*) correspond to the phase Bi$_2$O$_3$.

**Figure 3.** Dependence $\alpha_{ME}$ with frequency at $T = 300$ K, $H = 300$ Oe. Inset shows the microstructure of the film with a grain size of 438 + 11 nm.

3. Results and analysis

Figure 2 shows the diffraction pattern for BiFeO$_3$ films grown on a substrate Pt/TiO$_2$/SiO$_2$/Si, at a substrate temperature during the growth of 600 $^\circ$C; prominent peak corresponds to the Platinum (111).

BiFeO$_3$ peaks, indexed in the graph, can be identified the perovskite structure. Additional peaks (*) can be attributed to the bismuth oxide Bi$_2$O$_3$, may be crystallized due to a Bi excedent and to the existence of this phase in the BiFeO$_3$ target. The indexation of the peaks of the film was made from the work of Moreau et al. [14]. According to this result we can say that our films grew with a perovskite structure as majority phase. The crystalline symmetry of the film may permit
ANGULAR DEPENDENCE OF THE MAGNETOELECTRIC COEFFICIENT ON MULTIFERROIC BiFeO$_3$ THIN FILM

Using the assembly described in Fig. 1, we studied the ME effect in thin films of BiFeO$_3$ depending on the frequency, DC magnetic field configuration and the angle between the film and the DC magnetic field. Figure 3 shows the dependence of $\alpha_{ME}$ with the frequency of AC magnetic field for ($\phi=0$). The applied DC magnetic field was 300 Oe, reaching a saturation value of about 7.1 KHz. The measurements were made at room temperature. Note that the ME coefficient increases linearly with frequency, in the range of 1 to 7.1 KHz. In this frequency range, the discharge process occurs through the sample resistance, then $\alpha_{ME}$ and increases linearly with frequency, but above this value, this process takes place through the capacitance [13].

For frequencies above 7.1 kHz, the response of $\alpha_{ME}$ reaches a saturation value would correspond to a situation in which all induced electric dipoles are aligned more easily in the direction of the applied field, and its effect on the dielectric surface is to increase the induced charge and in turn more dipoles orient. This increase is enhanced in some way by the microstructure of the films.

The saturation value $\alpha_{ME}$ in thin films is 38.78 V/cmOe. This substantial increase in $\alpha_{ME}$ shows that the effect is more efficient for the material in thin film form compared with bulk [12], most likely due to the thin film microstructure is columnar growth, favors the induction and orientation of induced electric dipoles. Hence, the response of the material to present a electric polarization in the presence of a magnetic field and consequently, a greater accumulation of charge induced on the surface of the dielectric and the appearance of a voltage at the electrodes. The values found in the samples are well above those reported in the literature 3.0 mV/cmOe for the material in thin film form and in the same manner for compounds produced by other techniques, 3.4 mV/cmOe for compound CoFe$_2$O$_4$–BaTiO$_3$ [13] and even for materials produced in bilayers 0.46 V/cmOe of nickel ferrite and PZT composite [13].

Maintaining in 7.1 KHz the frequency, the magnetic field DC was varied. Fig.4 shows the dependence $\alpha_{ME}$ with the magnetic field DC. DC field increases to a maximum value 7.5 Koe, and then back, finding a hysteresis. The hysteretic response of the coefficient with field DC indicates the formation of polarization domains and insofar as decrease the field

Figure 4. Dependence $\alpha_{ME}$ with a DC magnetic field at a frequency of 7.1 KHz to: a-. Longitudinal mode ($\alpha$=0), b-. $\alpha=\pi/6$, c-. $\alpha=\pi/4$ and d-. Transverse Mode ($\alpha = \pi/2$).
is a process of irreversible. To \( \varphi = 0 \), with increasing DC magnetic field, \( \alpha_{ME} \) decreases in the direction of the field; on the other hand, when decrease the magnetic field DC, \( \alpha_{ME} \) begins to increase, but returns so that a minimum hysteresis, to a value of \( \alpha_{ME} \), very close to the initial (See Fig. 4a). To \( \varphi = \pi/6 \), shows a maximum around 1.2 KOe –can be caused by the influence of AC magnetic field, since it is assumed that \( (h_o/H) \ll 1 \), which may not necessarily be met and the DC magnetic field must overcome this condition - and again hysteretic behavior, this may be because for the dipoles is more difficult to reorient in the direction of the applied field (Fig. 4b). To \( \varphi = \pi/4 \), There is a shift to the maximum, which is now around 1.8 KOe. And additionally the hysteresis curve is more noticeable, therefore, there is an increased energy loss, since the dipoles must perform work to reorient in the direction of the field and now the maximum is now located around 1.5 KOe and reaches a lower value than the initial maximum (Fig. 4c). For the latter case \( \varphi = \pi/2 \), dipoles must do much more work to align, the maximum has a larger shift, around 2.1 KOe, so for this shift there is a higher energy loss, because electric domains they need a higher magnetic field to align in the same direction, around 7.5 KOe (Fig. 4d), while for other configurations is approximately 6.0 KOe, note that for this case the DC magnetic field should reach a higher value to meet the condition \( (h_o/H) \ll 1 \).

For each of the cases we studied above, \( \alpha_{ME} \) decreases as the angle increases configuration (Fig. 5), this is probably because when we increase the angle only a DC magnetic field component, this prevents the orientation of dipoles in the direction of the field. Because the excitation of magnetostrictive longitudinal modes and piezomagnetic, is greater than the angular modes, because the geometry of the sample [13], and additionally the DC magnetic field must overcome a barrier associated with the condition \( (h_o/H) \ll 1 \).

4. Conclusions

The dependence \( \alpha_{ME} \) with frequency reaches a saturation value 38.78 V/cmOe to frequency 7.1 KHz. For this frequency was observed a decrease in \( \alpha_{ME} \) by increment the DC magnetic field in the range 0-7.5 KOe. Additionally, a variation in the angle \( \varphi \) causes energy loss and a diminution in \( \alpha_{ME} \) manifested in hysteretic behavior, due to a change in the orientation of the easy magnetization axis, that affect the polarization of material.

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