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Room temperature multiferroicity in $\text{Ga}_{0.6}\text{Fe}_{1.4}\text{O}_3\text{:Mg}$ thin films

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We report on the multiferroic behavior of 2%-magnesium-doped $\text{Ga}_{0.6}\text{Fe}_{1.4}\text{O}_3$ thin film at room temperature. The sample was grown by pulsed laser deposition on a Pt-coated Yttrium-Stabilized Zirconia substrate. Magnetic measurements indicate a net magnetization of 105 emu/cm^3 at 295 K, and the persistence of magnetic ordering above room temperature. Ferroelectric measurements show clear polarization switching with negligible contribution from leakage currents, with a polarization of $0.2 \mu\text{C/cm}^2$ and a coercive field of 133 kV/cm . Scanning probe microscopy confirms the low leakage current and detects a stable piezoelectric signal. This could open original perspectives for the application of single-phased multiferroic systems. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4808349>]

Multiferroics which simultaneously present both electric and magnetic orders at room temperature are expected to give rise to unexplored yet exciting electronic devices. It is, for example, possible to conceive enhanced data storage media such as four states memories¹ when the two orders are not coupled. A coupling of the orders through a magnetoelectric coupling allows the conception of the low power consuming magnetoelectric random access memories (ME-RAMs), thanks to the electric control of magnetization.² Due to thermodynamic considerations, the magnetoelectric effect is enhanced for multiferroic materials,³ i.e., materials within which lie simultaneously two primary ferroic properties. For all these reasons, multiferroic materials receive nowadays a considerable interest.^{4–7} $\text{Ga}_{2-x}\text{Fe}_x\text{O}_3$ ($0.8 \leq x \leq 1.4$) (GFO) oxides, which crystallize in an orthorhombic structure (S.G: $Pc2_1n$) with $a \sim 8.7 \text{ \AA}$, $b \sim 9.4 \text{ \AA}$, and $c \sim 5.1 \text{ \AA}$, are promising candidates for such applications, because of their ferromagnetic behavior⁸ and important magnetoelectric effect.⁹ Their Néel temperature increases with the Fe/Ga ratio and reaches 370 K for $x = 1.4$.

The electrical polarization of GaFeO_3 has been estimated by first principles calculations to the considerable values of 25 (Ref. 10) or 59 (Ref. 11) $\mu\text{C/cm}^2$, along the b -axis. These values are about ten times higher than the value roughly estimated from the positions of the atoms in the cell by Arima *et al.*⁸ To date, there has been only one experimental study concerning the possible ferroelectricity (reversible polarization) of GFO.¹² This study shows indications of ferroelectricity for a polycrystalline $x = 1.0$ powder sample at temperatures below 100 K. The measured polarization (ca. $0.3 \mu\text{C/cm}^2$) is mainly reversible, but also shows a small irreversible contribution ($0.075 \mu\text{C/cm}^2$). The authors attribute the reversible part to a polarization contribution within the ac plane. Such a contribution is only possible when inversion symmetry is broken due to cationic site disorder.

The irreversible contribution would be along the b -axis and has, therefore, to be compared to the one calculated in the theoretical works. Yet, the polycrystalline nature of the sample does not allow verifying the symmetry arguments presented in Ref. 6. For this reason, ferroelectric measurements should be performed on crystallographically oriented materials which are also required for potential applications.

We have recently produced high quality thin films of this material.¹³ However, the important leakage currents observed in these films have precluded any ferroelectric characterization. The leakage currents are attributed to an oxygen sub-stoichiometry of the films. The involved reduction of Fe^{3+} to Fe^{2+} that follows the charge deficiency might affect the electrical resistivity of GFO thin films through a hopping mechanism.^{14,15} These leakage currents are very likely to overshadow the polarization (P–E signal) and often lead to misinterpretations of the ferroelectric loops.¹⁶ Such problems have been observed in other oxide systems like BiFeO_3 , YMnO_3 , or $\text{Ni}_3\text{V}_2\text{O}_8$ [Ref. 17 and references therein]. Leakage mechanisms in ferroelectric thin films have been the topic of several recent studies.^{17–20} Various groups have explored the effects of doping in thin films in order to reduce the leakage current, as evidenced in Ti-doped BiFeO_3 ,²¹ Mg-doped $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ ²² or Dy-doped SrTiO_3 ,²³ and more particularly Mg doping of bivalent iron oxides.²⁴ We have demonstrated in a previous work²⁵ that the leakage current varied in Mg-doped GFO thin films with the dopant concentration. A minimum was observed for a 2% Mg doping (% of substituted Fe), for which, the Fe^{2+} being totally replaced with Mg^{2+} , the leakage current was four orders of magnitude lower than for undoped films. In the present paper, we focus on this particular composition, 2% Mg-doped $\text{Ga}_{0.6}\text{Fe}_{1.4}\text{O}_3$, since we expect that it presents the most favorable properties concerning both the magnetic (high Néel temperature owing to the high Fe content, $x = 1.4$) and electric (lowest leakage currents owing to the 2% Mg doping) aspects. The minimization of the leakage

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FIG. 1. θ - 2θ XRD patterns of the (a) undoped and (b) 2% Mg-doped $\text{Ga}_{0.6}\text{Fe}_{1.4}\text{O}_3$ thin films.

currents should enable the ferroelectric characterization of the films.

2% Mg-doped $\text{Ga}_{0.6}\text{Fe}_{1.4}\text{O}_3$ films (hereafter denoted GFO:Mg) have been grown by Pulsed Laser Deposition (PLD) using a KrF excimer laser ($\lambda = 248$ nm) with a 10 Hz repetition rate. The energy density of the laser on the target was tuned to 1 J/cm^2 and the distance between the target and the substrate was fixed to 5 cm. The $\text{Ga}_{0.60}\text{Fe}_{1.37}\text{Mg}_{0.03}\text{O}_3$ target used for the deposition was synthesized from the solid state reaction of Fe_2O_3 (99.99%, Prolabo), Ga_2O_3 (99.99%, Fluka A.G.), and MgO (99.99%, Prolabo) using an optimized ceramic processing.²⁶ The final powders were uniaxially compacted into 1 in. diameter pellets and sintered in a platinum crucible at 1450°C for 25 h in air. A 20 nm thick Pt conducting layer was deposited under vacuum at 775°C on Yttrium-stabilized zirconia (YSZ) (111) substrates (Crystal GmbH). A GFO:Mg layer of about 150 nm thickness was then deposited under 1 millibar N_2/O_2 (80%/20%) at 830°C . After the deposition, the samples were cooled down to room temperature under the same gaseous atmosphere.

The thin films crystallographic structure was characterized by x-ray diffraction (XRD). θ - 2θ scans, φ -scans and reciprocal lattice mappings were performed using a Rigaku SmartLab diffractometer equipped with a rotating copper anode ($K\alpha_1 = 0.154056$ nm). Energy dispersive spectroscopy (EDX) coupled to a Scanning Electron Microscopy technique (JEOL 6700F) was used to ensure the composition of the samples and study the surface of the films. The analyses were performed at an energy of 5 keV, which ensures that the whole EDX signal can only originate from the GFO film

and not from the Pt base electrode. The surface morphology was characterized by atomic force microscopy (AFM) measurements (n-Tracer, Nanofocus Inc.). The magnetic properties were studied using a superconducting quantum interference device magnetometer (SQUID MPMS XL, Quantum Design). The ferroelectric properties of the films have been analyzed by using a commercial TF analyzer 2000 from aixACCT after depositing $40 \times 40 \mu\text{m}^2$ gold top electrodes by means of e-beam evaporation through a resist mask designed by optical lithography. The electrical characterization using the atomic force microscope has been obtained using a Dimension 3100 Bruker instrument in the so-called “Tunneling AFM” (TUNA) mode. Contact mode platinum coated tips have been used. The lowest measurable current is in the 100 fA range. The voltage is applied to the sample, with the tip being grounded. PFM images have been obtained using a NT-MDT NTEGRA AFM, using stiffer platinum coated tips (stiffness in the $2\text{--}10 \text{ N.m}^{-1}$ range). An external lock in amplifier (Signal Recovery 7280) has been used to measure the piezo force microscope (PFM) phase and amplitude. More details about the PFM operating mode can be found elsewhere.²⁷

The θ - 2θ diffractograms shown in Fig. 1 demonstrate that the GFO:Mg film is epitaxially grown along the b -axis on the Pt/YSZ (111) substrate without any parasitic phase. The epitaxial relationships of the Mg-doped sample are the following: YSZ(111)/Pt(111)/GFO(010), with variants every 60° , YSZ[01-1]/Pt[01-1]/GFO[100], YSZ[1-10]/Pt[01-1]/GFO[100], and YSZ[10-1]/Pt[01-1]/GFO[100]. These epitaxial relationships are the same as for the undoped GFO.¹³ Lattice parameters were determined from x-ray reciprocal space mapping (RSM) (not shown) of the GFO (040), (062), and (570) diffraction peaks. The results are listed in Table I, as well as the chemical compositions of the films, estimated from energy dispersion x-ray spectroscopy coupled with scanning electron microscopy (SEM-EDX). The AFM observation (not shown) of the GFO:Mg film reveals a homogeneous surface morphology with a root mean square roughness equal to 0.9 nm. This value is in the same range as that observed for undoped samples which means that Mg-doping does not deteriorate the film roughness.

Magnetic measurements show that the GFO:Mg films possess a net magnetization at room temperature of 105 emu/cm^3 . Their Néel temperature is only insignificantly decreased compared to the undoped GFO sample: 364 K (Fig. 2) versus 370 K.¹³ This small decrease is certainly not an obstacle for possible applications.

Dynamic polarization hysteresis (P(E) measurements) and switching current measurements (I(V)) have been acquired at room temperature and at a frequency of 2.5 kHz. A clear polarization switching is observed in the 2%

TABLE I. EDX analysis, cell parameters and roughness of the undoped and 2% Mg-doped GFO films.

Sample	a (Å)	b (Å)	c (Å)	Composition (EDX)	Roughness (nm)
GFO	8.770(5)	9.421(2)	5.076(7)	$\text{Ga}_{0.55}\text{Fe}_{1.45}\text{O}_3$	1.0
GFO:Mg 2%	8.777(3)	9.425(9)	5.083(4)	$\text{Ga}_{0.55}\text{Fe}_{1.43}\text{Mg}_{0.02}\text{O}_3$	0.9

FIG. 2. (a) Field cooled magnetization measurement (in-plane) of the 2% Mg-doped $\text{Ga}_{0.6}\text{Fe}_{1.4}\text{O}_3$ thin film, (b) Magnetization hysteresis loop (in-plane) of undoped and 2% Mg-doped $\text{Ga}_{0.6}\text{Fe}_{1.4}\text{O}_3$ at 295 K.

Mg-doped sample, independently of the prepolarization history of the sample. We measure a polarization $P_S = 0.2 \mu\text{C}/\text{cm}^2$ and a coercive voltage of 2 V ($E_c \approx 133 \text{ kV}/\text{cm}$). Figure 3 shows a square hysteresis loop and pronounced current kinks at the coercive voltage (switching current). The presented data are as-measured, and no dielectric contribution has been subtracted. We attribute the observed pronounced squareness to the rapid field sweep. Decreasing the frequency by 500 Hz indeed reduces the remanent polarization by about 35% with respect to the saturation value (not shown). The dielectric relaxation is certainly an important issue in this system and it will be the subject of future investigations. The switching current could also be clearly

FIG. 3. Dielectric hysteresis loop $P(E)$ and switching current $I(V)$ of the 2% Mg-doped $\text{Ga}_{0.6}\text{Fe}_{1.4}\text{O}_3$ sample acquired at room temperature and a frequency of 2.5 kHz.

evidenced in C-V measurements (not shown). The measured polarization is lower than the value expected from theoretical calculations¹⁰ but it is of the same order of magnitude as the value reported by Saha *et al.*¹² The work of these authors was performed at low temperature (ca. 100 K) on polycrystalline GFO samples, whereas our measurements were performed at room temperature along the *b*-axis, which is expected to be the polar axis in GFO.²⁸ PFM measurements (Fig. 4) were performed on this sample, showing a weak, yet time-persistent contrast within several hours between the +10 V/−10 V applied fields. The very low value of the d_{22} piezoelectric coefficient,²⁹ which is at the origin of the PFM signal, may be responsible for such a weak contrast. TUNA measurements confirm the considerable decrease of leakage current of 2% Mg-doped samples compared to the undoped ones. The microscopic leakage current in the doped sample remains below the 100 fA range when the applied positive or negative voltage is below 10 V. This is in perfect agreement with the leakage current measurements observed in the systematic study previously reported. We, therefore, believe that the polarization switching could only be observed, thanks to the strong reduction of the leakage currents. However, to verify this hypothesis and identify the effects that may be connected with Mg dopant, we need to find other ways to eliminate the Fe^{2+} cations. Thus we are currently

FIG. 4. (a) PFM image ($15 \times 15 \mu\text{m}$) of the 2% Mg-doped $\text{Ga}_{0.6}\text{Fe}_{1.4}\text{O}_3$ thin film. The zone in the outer white dotted rectangle has been poled to +10 V, the zone in the inner white dotted rectangle has been poled to +10 V first, then to −10 V, (b) horizontal section averages over the unpoled red dashed line rectangle and poled red continuous line rectangle regions of Fig. 1(a).

working on an alternative reduction of the leakage currents through oxygen annealing.

In conclusion, a ferroelectric behavior has been evidenced in 2% Mg-doped $\text{Ga}_{0.6}\text{Fe}_{1.4}\text{O}_3$ thin films grown by pulsed laser deposition. The Mg-doping does not lead to any deterioration of the crystalline quality of the films which are still epitaxially grown on the conducting Pt (111) electrode. It also hardly impacts the magnetic properties. The Néel temperature is only decreased by 6 K, as our composition still shows an application compatible Néel temperature of 364 K. Also, the room temperature saturation magnetization is largely preserved (10% decrease). These results evidence the room temperature multi-ferroic behavior of GFO compounds in thin films.

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