Polar properties of Eu$_{0.6}$Y$_{0.4}$MnO$_3$ ceramics and their magnetic field dependence

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Abstract

Eu$_{1-x}$Y$_x$MnO$_3$, compared against other magnetoelectric systems, exhibits very distinctive features. Its magnetoelectric properties are driven by the magnetic spin of the Mn$^{3+}$ ion, but they can be drastically changed by varying the content of Y$^{3+}$, which does not carry any magnetic moment. Although the $x = 0.40$ composition has been studied extensively, some basic areas still remain to be thoroughly understood. Thus, this work is aimed at studying some of its polar properties and their magnetic field dependence as well. The experimental results reported here show that this material is very easily polarizable under external electric fields, and so, whenever the polarization is obtained from time integration of the displacement currents, an induced polarization is superposed on the spontaneous one, eventually masking the occurrence of ferroelectricity.

We have found clear evidence for the influence of a magnetic field in the polar properties of Eu$_{0.6}$Y$_{0.4}$MnO$_3$. The study of electric polarization of Eu$_{0.6}$Y$_{0.4}$MnO$_3$ under an external magnetic field yields a value with the same order of magnitude of the remanent polarization as was determined from polarization reversal experiments. The comparison of the magnetically induced changes in the polarization obtained for polycrystalline samples and single crystals confirms the threshold magnetic field value for the polarization rotation from the $a$-direction to the $c$-direction, and provides evidence of the importance of the granular nature of the samples in the polar response to the magnetic field.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The magnetoelectric effect has attracted a lot of attention, motivated by the very interesting fundamental issues that are put forward, as well as by the need for novel memory and sensor devices, where the polarization is controlled by a magnetic field or vice versa [1, 2]. Among the materials presenting a magnetoelectric effect, orthorhombic ReMnO$_3$ (with Re a rare earth ion) has drawn particular attention in the last few years, but some aspects concerning the coupling between electric polarization and magnetic properties are not completely clarified. In particular, the family of orthorhombic compounds Eu$_{1-x}$Y$_x$MnO$_3$, with $x < 0.55$, is very interesting, because these materials exhibit a rich variety of phase transitions from incommensurate to commensurate antiferromagnetic phases, some of them with a ferroelectric
character, depending on the $x$ value [3]. The fine-tuning of the physical properties through controlled doping with the non-magnetic $Y^{3+}$ ion, without increasing either the magnetic or the structural complexity, enables a more direct approach to the understanding of those microscopic mechanisms which lead to the magnetoelectric effect.

Hemberger et al [3], Ivanov et al [4] and Yamasaki et al [5] have proposed $(x, T)$ phase diagrams, for Eu$_{1-x}$Y$_x$MnO$_3$ single crystals, with $0 \leq x < 0.55$, obtained by using both identical and complementary experimental techniques. Although the phase diagrams proposed by these authors present discrepancies as regards the magnetic phase sequence and the ferroelectric properties for $0.15 < x < 0.25$, there is a quite good agreement concerning the phase sequence for $0.25 < x < 0.55$. For this range of compositions several main issues have been reported. Ferroelectricity has an improper character, and it probably stems from the inverse effect of the Dzyaloshinskii–Moriya interactions [5–7]. A strong magnetoelectric coupling has been evidenced from the effect of applied magnetic fields on their ferroelectric and optical properties [5, 8, 9]. A synchrotron radiation study has shown that the antiferromagnetic phases have modulated structures [5], which apparently stem from the competition from ferromagnetic and antiferromagnetic interactions. Moreover, their electric polarization occurs in a direction perpendicular to the magnetic modulation wavevector [5, 8, 9].

In particular, the Eu$_{0.6}$Y$_{0.4}$MnO$_3$ composition has been intensively studied, as it exhibits very interesting and rather unique properties. The phase sequence of Eu$_{0.6}$Y$_{0.4}$MnO$_3$, depicted in figure 1, will be reviewed in the following.

According to the results reported in [3, 5], Eu$_{0.6}$Y$_{0.4}$MnO$_3$ undergoes a paramagnetic–paraelectric to collinear sinusoidal modulated antiferromagnetic phase transition at $T_N = 46$ K, hereafter designated as AFM1. The wavevector $q_{1}$ of the lattice modulation, which is the wavevector of the magnetic modulation through $q_1 = 2\pi q_{mod}$, is approximately 0.58 down to 10 K, presenting a very faint anomaly around 24 K [5]. At $T_1 = 24$ K, this compound undergoes another phase transition, becoming antiferromagnetic (AFM4), with a presumably cycloidal spin arrangement in the $bc$-plane, with the modulation vector along the $b$-axis [5]. This compound exhibits between $T_1 = 24$ K and $T_2 = 22$ K a small spontaneous polarization with components along both $a$- and $c$-axes, with values of the order of 100 $\mu$C m$^{-2}$ [5, 8]. At $T_2 = 22$ K, the orientation of the cycloidal plane changes from the $bc$-to the $ac$-plane, defining another antiferromagnetic spin arrangement phase (AFM2) [9]. In this phase, the component $P_c(T)$ of the polarization increases considerably, attaining a saturation value of about 1200 $\mu$C m$^{-2}$, while the $P_a(T)$ component decreases drastically below $T_2$ [5]. Noda et al [8] found similar results for Eu$_{0.595}$Y$_{0.405}$MnO$_3$, but $P_c(T)$ is only different from zero in the interval 21–25 K. These results have been understood as a spontaneous rotation of the electric polarization from the $c$-direction to the $a$-direction, on decreasing the temperature, even at zero magnetic field. This behaviour contrasts with the one obtained for TbMnO$_3$, in which an external magnetic field is needed in order to induce a polarization rotation [10]. Noda et al [8] and Murakawa et al [9] have shown that a magnetic field applied along the $a$-axis of Eu$_{0.55}$Y$_{0.45}$MnO$_3$ induces a direction switching of the electric polarization, from the $a$-component to the $c$-component, accompanied by an impressive decrease of the electric polarization. This direction switching has been attributed to the magnetic transition of the Mn 3d basal spins alone.

Actually, although a large effort has been made to understand its physical properties, there are still intriguing fundamental questions regarding the nature and origin of ferroelectricity occurring in both AFM4 and AFM2 phases of Eu$_{0.6}$Y$_{0.4}$MnO$_3$. First, it is not clear why in the works referred to above, unusually high electric fields were used to obtain electric polarization, although it is well known that for measuring a spontaneous polarization much lower electric fields are actually required [11]. Moreover, in Y-doped EuMnO$_3$, an $Y^{3+}$ ion distribution can lead to an easily induced electric polarization, even for low polarizing electric fields, which can mask the actual spontaneous polarization, thus making the search for ferroelectricity a much more demanding task [12].

This work was first aimed at studying both the nature and the origin of the electric polarization occurring in the low temperature antiferromagnetic phase transitions of Eu$_{0.6}$Y$_{0.4}$MnO$_3$. Afterwards, a detailed characterization of its physical properties was made, by performing both dielectric and magnetic measurements: the remanent polarization at low temperatures was determined by polarization reversal measurements. The results were subsequently compared with those ones as regards the electric polarization calculated by integrating the displacement currents obtained in heating runs, after cooling the samples under different fixed dc electric fields. This comparison provided evidence of an impressive contribution of the induced polarization to the overall polar response. Our study is still focused on the effect of magnetic fields over the dielectric constant and electric polarization of Eu$_{0.6}$Y$_{0.4}$MnO$_3$, addressed in particular...
to understanding both the magnetodielectric coupling, and the
spin-reorientation transition as regards the occurrence
of induced electric polarization, inside the antiferromagnetic
phases.

Unlike in previous works, the results reported here were
obtained for high quality Eu$_{0.6}$Y$_{0.4}$MnO$_3$ ceramics instead of
single crystals. Despite the granular nature of our samples,
the most relevant features observed for Eu$_{0.6}$Y$_{0.4}$MnO$_3$ single
crystals were very well corroborated, except for both the shape
and the relative magnitude of the response to external fields.
This was especially noticeable when magnetically induced
polarization changes were considered.

2. Experimental details

High quality Eu$_{0.6}$Y$_{0.4}$MnO$_3$ ceramics were prepared by
the sol–gel combustion method. Details of the sample
processing are available in [13, 14]. The phase purity
and the crystallographic and microstructural characterization
of the ceramic samples were checked using x-ray powder
diffraction and scanning electron microscopy with energy
dispersive spectroscopy. The Rietveld analysis of the x-
ray diffraction data shows the absence of secondary phases,
with occupancy factors converging to the nominal composition
of the samples. This result was also confirmed by energy
dispersion spectroscopy. Scanning electron microscopy
analysis reveals a typical ceramic microstructure with regularly
shaped crystal grains ranging from 3 up to 10 μm in diameter.
A detailed study of EuMnO$_3$ and GdMnO$_3$ ceramics prepared
in this way led to results very similar to the ones obtained for
the corresponding single crystals [15].

Low field dc magnetization measurements were carried out using a commercial superconducting quantum interference
SQUID magnetometer, in the temperature range 4–300 K, with
a resolution better than 5 × 10$^{-7}$ emu.

Rectangularly shaped samples were prepared from ceramic pellets, and gold electrodes were deposited using the
evaporation method. The complex dielectric constant was measured with an HP4284A impedance analyser, in the
10–300 K temperature range, under an ac electric field of
amplitude 100 V m$^{-1}$, in the frequency range 10 kHz–1 MHz.
The displacement currents were measured as a function of
temperature, with a standard short-circuit method, using a
Keithley electrometer, with 0.5 pA resolution, while keeping a
fixed heating temperature rate. The temperature dependence
of the corresponding polarization was obtained by the time
integration of the current density. The temperature dependence
of the electric polarization, the sample was
previously cooled down to 10 K, under an electric field of
78 kV m$^{-1}$. Then, the electric field was removed, and the
temperature dependence of the electric polarization was measured for
1000 s, until polarization stability was obtained. Afterwards,
the sample was heated up to 14 K and the time dependence
of the electric polarization was recorded, with simultaneous
magnetic field oscillation of 90 kOe amplitude.

3. Experimental results and discussion

3.1. Dielectric and magnetic properties

The temperature dependences of the real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of the complex dielectric constant, measured at
several fixed frequencies, are shown in figures 2(a) and (b),
respectively. $\varepsilon'(T)$ presents two anomalies, a shoulder at
$T_1 = 24$ K that marks the AFM1–AFM4 phase transition,
and a peak at $T_2 = 20$ K that marks the AFM4–AFM2 phase transition.$\varepsilon''(T)$ shows two peaks at $T_1$ and at $T_2$, and a broad
anomaly strongly dependent on the frequency, in the 10 kHz–
1 MHz range, suggesting the existence of a relaxation process.
This relaxation process was analysed with a Debye model with
a single relaxation time, assuming an Arrhenius law. Within
the scope of this model, $\varepsilon''(T)$ is given by [16]

$$
\varepsilon''(T, \omega) = \frac{\Delta \varepsilon}{2 \cosh\left(\frac{\hbar \omega}{k_B T} - \frac{1}{\tau}\right)}.
$$

(1)

where $\Delta \varepsilon$ is the dielectric strength, $U$ is the activation
energy associated with the dielectric relaxation process, $k_B$
the Boltzmann constant, and $T_M$ is the temperature of the
maximum value of $\varepsilon''(T)$ for a fixed frequency. In the fitting
procedure, we assume that the main temperature dependence
in equation (1) comes from the argument of the hyperbolic
function. As can be seen in figure 2(a), the value of $\varepsilon''$ is
nearly temperature independent in the temperature range 40–
100 K, so $\Delta \varepsilon$ can be considered as a constant. Figure 3 shows
the natural logarithm of the relaxation time $\tau$ as a function of
the inverse of the temperature. A linear relation between $\ln(\tau)$
and $1/T$ between 41 and 83 K is observed. For $T \approx 40$ K,
a change of slope is observed. The value of the activation
energy, deduced from the best fit of an Arrhenius law to the
experimental data, is displayed in figure 2 for 41 K < $T$ <
83 K, is 0.020 ± 0.003 eV.

Figure 2(c) shows the temperature dependence of the
induced specific magnetic moment, measured under an applied
magnetic field of 50 Oe, in a heating run after cooling the
samples under zero field (curve I), or in a heating run after
cooling the sample with a dc magnetic field of 50 Oe (curve II).
Both curves show a maximum at $T_N = 46$ K, signalling
the transition into the AFM1 phase, in good agreement with
previous published results on single crystals as referred to
above. Below $T_N$, we observed that the induced magnetization
is strongly dependent on how the sample is cooled down. In
fact, upon cooling the sample under an external magnetic field
of 50 Oe, a significant deviation for both curves is revealed, reaching a 20% difference at 5 K. This result evidences some kind of disorder associated with the spin subsystem. This assumption is supported by the incommensurate character of both lattice and magnetic structure in Eu$_{0.6}$Y$_{0.4}$MnO$_3$ for $T < T_N$, whose origin has been attributed to ferromagnetic and antiferromagnetic competitive interactions. Curve II reaches a saturation just below $T_2$, signalling the onset of the AFM2 phase.

3.2. Polarization reversal

Figure 4 shows some $P(E)$ relations for Eu$_{0.6}$Y$_{0.4}$MnO$_3$, obtained at 330 mHz frequency by applying ac electric fields up to $\pm$1000 kV m$^{-1}$, at different fixed temperatures. For temperatures higher than 30 K, a linear relation between $P$ and $E$ confirms the paraelectric character of the AFM1 phase. For temperatures below 25 K, we observed hysteresis loops with a very elongated shape. These results, together with the ones obtained for $\varepsilon'(T)$, clearly reveal, in good agreement with the results obtained on single crystals, that Eu$_{0.6}$Y$_{0.4}$MnO$_3$ is ferroelectric between 23 K and, at least, 7 K [4, 5]. The remanent polarization $P_r(T)$ presents two maxima, at 20 and 15 K, as can be seen in figure 5. Eu$_{0.6}$Y$_{0.4}$MnO$_3$ is still ferroelectric below 15 K, though its polarization starts to decrease with temperature decreasing until 7 K is reached. It is important to stress that the remanent polarization is much smaller than for common ferroelectrics, reaching a maximum value of just 55 $\mu$C m$^{-2}$. From the $P(E)$ relations, it is clearly shown that the electric polarization never reaches saturation, even for electric fields up to 10 kV m$^{-1}$, which evidences that Eu$_{0.6}$Y$_{0.4}$MnO$_3$ is a very easily polarizable material.

3.3. Displacement currents

Figure 6 shows the temperature dependence of the current density, $J(T)$, obtained from sequential thermal cycles, for different values of the polarizing electric field as follows: the current was measured in heating runs with a temperature rate of 2 K min$^{-1}$, after cooling the sample under several fixed dc electric fields. In figure 6 we can observe two groups of anomalies. A double-peak anomaly below 30 K is clearly associated with the ferroelectric character of the AFM4 and AFM2 magnetic phases, and it will be analysed later on. The anomalies above 30 K do not have a ferroelectric character and are associated with a field induced polarization whose nature can be identified by an appropriate analysis as referred to just below. Above 50 K, we can see three maxima rather close to each other. Just the larger one will be analysed in the following. The nature of the microscopic mechanism underlying the referred to anomaly observed in $J(T)$ can be studied by choosing different cooling/heating conditions, such as the temperature rate and electric field intensity. The amplitude of this peak ($J_{M}$) is strongly dependent on the magnitude of the applied electric field, and the temperature ($T_{M}$) where its maximum occurs remains independent of the magnitude of the electric field, as we can see in figure 6. Figure 7 shows the temperature dependence of the current density, measured in heating runs for different heating rates, after cooling the sample under a dc electric field of 408 kV m$^{-1}$. Unlike the
behaviour of the low temperature anomalies, the temperatures of the maxima, corresponding to the high temperature peaks, increases on increasing the heating rate. The overall behaviour of the anomalies observed above 50 K provides evidence for their dipolar relaxation origin, as follows from the predictions of the Bucci–Fieschi model [17]. In the current literature, these currents are designated as thermally stimulated depolarization currents, and can be expressed as [17]

\[ J(T) = \frac{P_e(T_p)}{\tau_0} \exp \left( -\frac{U}{k_B T} \right) \exp \left[ -\frac{1}{q \tau_0} \int_{T_p}^T \exp \left( -\frac{U}{k_B T} \right) dT \right], \]

(2)

where \( P_e \) is the equilibrium polarization reached at the polarizing temperature \( T_p \), and it depends on the polarizing electric field, \( \tau_0 \) the relaxation time at infinite temperatures, \( U \) the activation energy, \( q \) the temperature rate, and \( k_B \) the Boltzmann constant. The temperature dependence of the relaxation parameters was found by fitting the straightforward expression for \( J(T) \), presented in [17], to the experimental data.

Figure 8 shows the equilibrium polarization \( P_e \) obtained from the best fit of the equation (2) to the experimental results, as regards the peak under study. As we can see, \( P_e \) is proportional to the electric field magnitude. The average value of the activation energy \( (U) \) associated with the relaxation process is \( 0.07 \pm 0.01 \) eV (see figure 8). The relaxation time at infinite temperatures \( (\tau_0) \) is approximately \( 0.015 \pm 0.002 \) s.

It is worth stressing that in the temperature range 40–150 K we found relaxation processes detected through the study of both \( \varepsilon''(T, \omega) \) and displacement currents. Although, as their activation energies are quite different, it is apparent that they should correspond to independent relaxations mechanisms.

The current density displayed in figure 9 was obtained by cooling the sample from room temperature to 50 K, under zero electric field, and then the sample was cooled again from 50 to 7 K, under an applied electric field. At 7 K, and after removing the electric field, the electrodes were short-circuited for 30 min, and the sample heated from 7 to 50 K at a rate of 5 K min\(^{-1}\). For electric fields lower than 408 kV m\(^{-1}\), we observe one
sharp anomaly and also a broad anomaly. For electric fields higher than that value, one shoulder at the lowest temperatures comes up, whose origin is not known yet. As in ceramics there is a random orientation of their different grains, we observe in the same experiment the whole electric polarization response, which adds the electric polarizations of both AFM2 and AFM4 phases. The sharp anomaly around 24 K corresponds very clearly to the onset of the AFM4 phase, polar along the \(c\)-axis, and the broad anomaly corresponds to the onset of the AFM2 phase, polar along the \(a\)-axis. From the shape of the current density curves, metastability at the merging border of those two phases is expected. Figure 9(b) shows the electric polarization obtained by time integration of \(J(T)\), depicted in figure 9(a). The saturation value of the electric polarization increases as the poling electric field increases, except for \(E > 918 \text{ kV m}^{-1}\). For \(E = 1224 \text{ kV m}^{-1}\), the value of the saturation polarization is 380 \(\mu\text{C m}^{-2}\).

The inset of figure 9(b) shows a comparison between the remanent polarization recalled from figure 5, and the polarization obtained from the time integration of the displacement current, measured after cooling the sample under a polarizing electric field of 10 \(\text{kV m}^{-1}\). We have used this field intensity because the induced component does not totally mask the spontaneous polarization. Despite the different magnitudes of both results, there is a clear similarity between the overall temperature dependence of the two curves. This feature yields two main conclusions. First, the measurement of the spontaneous polarization obtained from the time integration of displacement currents has actually to be done in zero-field conditions or with a very small polarizing field. Secondly, for higher values of the field a very strong induced component emerges, much larger than the spontaneous polarization, and thus preventing the actual ferroelectric nature of the phase from being firmly settled.

In order to study to what extent the dipolar relaxation above 50 K could modify the properties of the ferroelectric phases, we have used a peak cleaning technique as follows [17]: the sample was cooled from 200 to 40 K under
an applied electric field of 408 kV m\(^{-1}\); at 40 K the field was removed and the electrodes short-circuited; then, the current was measured in a cooling run from 40 to 10 K, and afterwards in a heating run from 10 to 200 K, with a temperature rate of 2 K min\(^{-1}\). Figure 10(a) shows the experimental results obtained. On cooling, a double peak appears at \(T_2 = 23\) K indicating the building up of an electric polarization, even in the absence of an applied electric field between 40 and 10 K. The time integration of this current density gives a polarization of 200 \(\mu\)C m\(^{-2}\) at 10 K, well above the value of the remanent polarization obtained from hysteresis loops. So, by cooling the sample, between 200 and 40 K under a 408 kV m\(^{-1}\) electric field, electric dipoles associated with the high temperature relaxations of the sample are oriented, giving rise to an internal electric field, which determines the direction of alignment of both spontaneous and induced dipoles below \(T_2\), which have the opposite direction to the one revealed at high temperatures. In a heating run, below 50 K, as expected, the sign of the current density is reversed, and presents only a well defined peak at \(T_2\), associated with the transition from the AFM4 to the AFM1 phases. Above 50 K, the results obtained are very similar to those displayed in figure 6, as expected.

Figure 10(b) shows the current density as a function of the temperature, measured in a heating run with a temperature rate of 2 K min\(^{-1}\), after cooling the sample with an applied electric field of 408 kV m\(^{-1}\), between 40 and 10 K, and short-circuiting the sample at 10 K during 30 min. Above \(T_2 = 24\) K, as expected, there is no spontaneous polarization, in good agreement with the results obtained from polarization reversal.

3.4. Polar and dielectric properties under magnetic fields

To check for the existence of a magnetodielectric effect in Eu\(_{0.4}\)Y\(_{0.4}\)MnO\(_3\), a measurement of the dielectric constant \(\varepsilon'(T)\) was carried out under magnetic fields of 20, 50, and 90 kOe, parallel to the direction of the measuring ac electric field, at a frequency of 100 kHz. The results are displayed
Figure 11. (a) Temperature dependence of the real part of the complex dielectric constant measured at 100 kHz under different magnetic fields. (b) Magnetic field induced change in the real part of the complex dielectric constant as a function of the temperature. The dielectric peak becomes smaller, and is shifted towards higher temperatures under an external magnetic field. Similar behaviour has been observed for other magnetoelectric compounds and is linked to the effect of a magnetic field on the spin configuration, responsible for the electric polarization phenomenon [18].

The relative value of the magnetodielectric effect determined as $\varepsilon'(B = 0 \text{T}) - \varepsilon'(B = 9 \text{T})$, which is generally proportional to the magnetoelectric susceptibility, shows a characteristic maximum slightly above $T_2$ and it also shows a discontinuity in its slope with a sign change (see figure 11(b)). This behaviour confirms that magnetodielectric effect may be present even in the non-polar antiferromagnetic region $T > T_2$.

The behaviour of the dielectric constant of Eu$_{0.6}$Y$_{0.4}$MnO$_3$ under a magnetic field applied along the $a$-axis is associated with a new orientation of the spin configuration that determines a change of the direction of the polarization from the $a$-axis to the $c$-axis [9]. This means that the AFM2 phase is gradually replaced by the AFM4 phase as the magnetic field increases. As the dielectric constant in the AFM2 phase is much higher than that in the AFM4 one, a decrease of the dielectric constant is expected, as is observed in figure 11(a). Moreover, the small shift of the maximum of the dielectric constant towards higher temperatures under a magnetic field is consistent with the behaviour of the dielectric constant in the AFM4 phase.

The existence of an electric polarization in Eu$_{0.6}$Y$_{0.4}$MnO$_3$ samples associated with the magnetic transition at $T_2$, and together with the observed large magnetodielectric effect, suggests the existence of an intrinsic magnetoelectric coupling in the polycrystalline samples. Consequently, we have studied for Eu$_{0.6}$Y$_{0.4}$MnO$_3$ the magnetic field dependence of the electric polarization. Figure 12(a) depicts the time dependence of the electric polarization of Eu$_{0.6}$Y$_{0.4}$MnO$_3$, recorded at 14 K (left scale), and magnetic field as a function of time (right scale). (b) Electric polarization as a function of magnetic field, measured at 14 K. (c) Transverse magnetostriction as a function of magnetic field, measured at 14 K.
dependence of both the electric polarization and the magnetic field. Figure 12(b) shows the magnetic field dependence of the electric polarization, measured at 14 K, obtained from figure 12(a). As the magnetic field starts to increase, the electric polarization first goes up, and reaches its maximum value around 40 kOe, after which it decreases continuously up to 90 kOe. The oscillation of the magnetic field with the amplitude of 90 kOe induces oscillation of the electric polarization with a maximum amplitude of about 1.5 μC m⁻² at a double frequency, suggesting the existence of a quadrupole magnetoelectric coupling in Eu⁰.₆₂Y⁰.₄₄MnO₃. The magnetic field dependence of the polarization can be well represented by a butterfly loop shape, as shown in figure 12(b). In fact, the sign of the polarization does not change, but the magnitude of the effect is much smaller than the one reported recently for Ba₃Mg₂Fe₁₂O₁₂ by Ishiwata et al [19]. The decrease of the polarization observed for magnetic fields higher than 40 kOe is due to the onset of the AFM4 phase. The magnetoelectric effects, whose mechanism is related to the modulation of the crystal structure, as was observed for EuMnO₃ [20], TbMnO₃ and DyMnO₃ [21, 22], are probably induced by magnetoeelastic interactions, which can be associated with the magnetic field induced transition from the commensurate to the incommensurate modulated structure [8]. In order to work out the validity of such an assertion, we have measured the magnetostriuction effect from −90 to 90 kOe, using a modified capacitance dilatometer technique and a PPMS cryostat [23]. To keep the same configuration as was used for magnetopolarization measurements, the magnetic field was applied perpendicularly to the direction along which the change of dimension was measured. Figure 12(c) shows the strain ΔL/L as a function of the magnetic field, measured at 14 K. Although a correlation exists between the magnetic field induced polarization changes and the ΔL/L magnetic loops, the magnetostriuction effect is of the order of 10⁻⁵, which is much lower than the order of the magnetodielectric effect, whose value, calculated from our results, is ~2 × 10⁻⁴. Therefore, in Eu⁰.₆₂Y⁰.₄₄MnO₃, the effect of a magnetic field on both the dielectric constant and the polarization is genuine.

4. Conclusions

From the results presented in this work, we can conclude that Eu⁰.₆₂Y⁰.₄₄MnO₃ is very easily polarizable under an electric field, and the polarization obtained from integration of the displacement currents, after cooling the sample under an electric field, corresponds to the sum of spontaneous and induced polarizations. This assertion is supported by the study of polarization reversal, which yields a remanent polarization of ~40 μC m⁻², which is much lower than the value reported in the current literature. The study of hysteresis loops and pyroelectric current obtained by polarization reversal and displacement current measurements, respectively, yields unambiguously that Eu⁰.₆₂Y⁰.₄₄MnO₃ is ferroelectric between 23 and 7 K.

Above Tₐ, the observed dielectric relaxation, which is well described by an energy level of 0.020 ± 0.003 eV, is very probably independent of the yttrium content in Eu₁₋ₓYₓMnO₃. In fact, a dielectric relaxation study carried out in EuMnO₃ ceramics led to a similar value for the activation energy [15]. In contrast, the energy levels revealed through the study of displacement currents in the temperature range 50–180 K are surely due to the yttrium ions. The partial substitution of Eu³⁺ by Y³⁺, and its random distribution probably yield the complex shape of the displacement current in the temperature range 50–180 K. So, the presence of Y³⁺ should be the principal factor determining the high level of the induced polarization in the Eu₁₋ₓYₓMnO₃ system, even at low temperatures.

As expected, the displacement current versus temperature is also rather complex, due to a random orientation of the ceramic grains. So, in this system, we cannot completely separate the contributions from the electric polarization obtained along a- and c-axes. The study of the displacement currents under different poling electric fields clearly show the importance of induced currents that are different in the AFM2 and AFM4 phases.

We have found clear evidence for the influence of a magnetic field in the polar properties of Eu⁰.₆₂Y⁰.₄₄MnO₃. The study of electric polarization of Eu⁰.₆₂Y⁰.₄₄MnO₃ under a magnetic field, at 14 K, yields a value of ~36 μC m⁻², in fact, of the same order of magnitude of the remanent polarization determined from polarization reversal experiments. On increasing the magnetic field we observe an increase of the polarization, which attains its maximum value by 40 kOe, and then, the polarization decreases on further increasing the magnetic field. Qualitatively, these results are similar to those reported by Noda et al [8] and Murakawa et al [9]. The latter authors assumed a cycloidal magnetic structure for Eu⁰.₆₂Y⁰.₄₄MnO₃ crystals, and suggested that the behaviour observed is due to a flexible rotation of the conical spin structure under a magnetic field.

The comparison between the results obtained on polycrystalline samples and single crystals as regards the effect of an applied magnetic field on the electric polarization confirms the threshold magnetic field value for the polarization rotation from the a- to the c-direction, but the shape and magnitude of the response are different. These features can be well understood on the basis of the granular nature of the samples by assuming a random distribution of the directions of crystallographic axes in the sample. Following the results of Noda et al [8] obtained on single crystals (see figures 1b and 1c of [8]), we can see that at 14 K the magnetic field oriented along the a-axis decreases by 15% the magnitude of the electric polarization along the a-direction, up to Bₐ ~ 35 kOe, but around this value, there is a sudden decrease of this polarization component, which takes a very low value, while for B > Bₐ, a sudden increase of the c-component of the electric polarization takes place, reaching a maximum value, which is about eight times lower than the a-component, for B < Bₐ [8, 9].

In the results displayed in figure 12(b), we see that the polarization measured in ceramic samples starts to increase with the magnetic field magnitude, attains a maximum value around 40 kOe and then starts to decrease rather slowly. Moreover, the variation of the polarization in the ceramics is much lower than that in single crystals [8, 9].

Taking into account the results obtained on single crystals for B < Bₐ, we have not found a plausible explanation for
the increase of the electric polarization between 0 Oe and 40 kOe. However, we can understand the slow decrease and the small variation of the electric polarization above 30 kOe. This feature can be well understood if a random distribution of the crystallographic axes in the sample is assumed. If $B_o$ stands for the minimum magnetic field along the $a$-direction that changes the polarization from the $a$-direction to the $c$-direction, and $B$ means the magnitude of the magnetic field in one direction, the change of the $a$-component of the electric polarization ($\Delta P_a$) under the $B$ field is

$$\Delta P_a = \begin{cases} 
0, & \text{for } B < B_o \\
\frac{P_a}{2} \left[ 1 - \frac{B^2}{B_o^2} \right], & \text{for } B > B_o.
\end{cases} \quad (3)$$

The above result means that the electric polarization decreases as $1/B^2$, for $B > B_o$, which describes our results, obtained for $B > 40$ kOe, quite well. As in our experiment we have $B_o = 40$ kOe and $B_{\text{max}} = 90$ kOe, the maximum variation of the polarization is about $2 \mu \text{C m}^{-2}$, which is of the same order of magnitude as is observed in this work. This result evidences clearly the effect of the granular nature of the samples in the magnetic field dependence of the electric polarization. However, for the granular samples, the magnitude of $B_o$ is clearly similar to the one found for single crystals. It is worth stressing that when comparing our results and those previously obtained for the corresponding single crystals no differences could be ascertained for their dielectric, magnetic, and magnetoelectric critical behaviours. Instead, differences could be perceived both in the critical temperature values and in the maximum amplitude values of the physical properties studied. These differences stem actually from the granular nature of the corresponding ceramic samples.

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References

[1] Bibes M and Barthelemy A 2007 IEEE Trans. Electron. Devices 54 1033
[2] Nan C-W, Bichurin M I, Dong S, Vichland D and Sriniyasan G 2008 J. Appl. Phys. 103 031101
[3] Hemberger J, Schrettle F, Pimenov A, Lunkenheimer P, Ivanov V Yu, Mukhin A A, Balbashov A M and Loiold A 2007 Phys. Rev. B 75 035118
[4] Ivanov V Yu, Mukhin A A, Travkin V D, Prokhorov A S, Kadomtseva A M, Popov Yu F, Vorob’ev G P, Kamilov K I and Balbashov A M 2006 J. Magn. Magn. Mater. 300 e130
[5] Yamasaki Y, Miyasaka S, Goto T, Sagayama H, Arima T and Tokura Y 2007 Phys. Rev. B 76 184418
[6] Sigienko I A and Dagotto E 2006 Phys. Rev. B 73 094434
[7] Mostovoy M 2006 Phys. Rev. Lett. 96 067601
[8] Noda K, Akaki M, Kikuchi T, Akahoshi D and Kuwahara H 2006 J. Appl. Phys. 99 085905
[9] Murakawa H, Onose Y, Kagawa F, Ishiwata S, Kaneko Y and Tokura Y 2008 Phys. Rev. Lett. 101 197207
[10] Kimura T, Lawes G, Goto T, Tokura Y and Ramirez A P 2005 Phys. Rev. B 71 224425
[11] Lines M E and Glass A M 2001 Principles and Applications of Ferroelectrics and Related Materials (Oxford Classic Texts in Physical Sciences) (Oxford: Oxford University Press)
[12] Agostinho Moreira J, Almeida A, Ferreira W S, Chaves M R, Araújo J E, Pereira A M, Vilela S M F and Tavares P B 2009 submitted
[13] Mori T, Kamegashira N, Aoki K, Shishido T and Fukuda T 2002 Mater. Lett. 54 238
[14] Agostinho Moreira J, Almeida A, Ferreira W S, Chaves M R, Oliveira J B, Machado da Silva J M, Sá M A, Vilela S M F and Tavares P B 2009 submitted
[15] Ferreira W S, Agostinho Moreira J, Almeida A, Chaves M R, Araújo J P, Oliveira J B, Machado da Silva J M, Sá M A, Mendonça T M, Siméão Carvalho P, Kreisel J, Ribeiro J L, Vieira L G, Tavares P B and Mendonça S 2009 Phys. Rev. B 79 054303
[16] Böttcher C J F and Bordewijk P 1978 Theory of Electric Polarization vol II (Amsterdam: Elsevier)
[17] Vandershueren J and Gasiot J 1979 Thermally Stimulated Relaxation in Solids (Topics in Applied Physics vol 37) ed P Bräulich (Berlin: Springer)
[18] Kimura T, Lawes G, Goto T, Tokura Y and Ramirez A P 2005 Phys. Rev. B 71 224425
[19] Ishiwata S, Taguchi Y, Murakawa H, Onose Y and Tokura Y 2008 Science 319 1643
[20] Kadomtseva A M, Popov Yu F, Vorob’ev G P, Ivanov V Yu, Mukhin A A and Balbashov A M 2005 JETP Lett. 81 590
[21] Kimura T, Goto T, Shintani H, Ishizaka K, Arima T and Tokura Y 2003 Nature 426 55
[22] Goto T, Kimura T, Lawes G, Ramirez A P and Tokura Y 2004 Phys. Rev. Lett. 92 257201
[23] Kundys B, Bukhantsev Yu, Kundys D, Berlowski M and Dyakonov V 2004 Rev. Sci. Instrum. 75 2192