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Polar properties and phase sequence in $Eu_{0.8}Y_{0.2}MnO_3$

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Abstract

In this work, we have studied in detail the temperature dependence of the electric polarization of $Eu_{0.8}Y_{0.2}MnO_3$ aimed at clarifying the controversial issues concerning the ferroelectric nature of the lower temperature magnetic phases and hence its multiferroic character. The existence of a spontaneous polarization in 30 K $< T <$ 22 K, provides clear evidence for the ferroelectric character of the re-entrant non-collinear spiral-antiferromagnetic phase, stable in that temperature range. Contrary to results published in previous works, our experimental data clearly show that the weak-ferromagnetic, canted antiferromagnetic phase stable below 20 K is not intrinsically ferroelectric. The misinterpretation, regarding the polar character of the lower temperature magnetic phases, stems from the existence of an induced polarization occurring below 30 K. The mechanisms associated with polar and magnetic properties, and their correlation with both spin and lattice structures are also discussed.

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

1. Introduction

Two years ago, Hemberger *et al* [1] published a work about the structural, thermodynamic, magnetic and dielectric properties of the orthorhombic Y-doped $EuMnO_3$ system ($Eu_{1-x}Y_xMnO_3$, with $0 \leqslant x < 1$). Based on their experimental results and on theoretical arguments, these authors proposed a phase diagram (x, T) for $Eu_{1-x}Y_xMnO_3$, in the $0 \leqslant x \leqslant 0.55$ range [1], more detailed than the one proposed by Ivanov *et al*, the year before [2]. The compound $Eu_{0.8}Y_{0.2}MnO_3$ has been reported by Hemberger *et al* [1] as the only magnetoelectric multiferroic system among the rare-earth perovskite manganites, which means that both ferroelectricity and ferromagnetism coexist and are coupled with each other in the same thermodynamic phase. In the following, we shall summarize some of the main features of the phase sequence of $Eu_{0.8}Y_{0.2}MnO_3$ presented in figure 8 of [1]. The paramagnetic and paraelectric phase of $Eu_{0.8}Y_{0.2}MnO_3$ transforms into an antiferromagnetic phase (AFM-1) at $T_N = 48$ K, presumably with an incommensurate sinusoidal collinear arrangement of the Mn^{3+} spins. The anomalies detected in both specific heat and electric permittivity have revealed another phase transition at $T_{AFM-2} = 30$ K. Double magnetic hysteresis loops at 25 K were reported, revealing the antiferromagnetic character of the phase below T_{AFM-2}, hereafter called AFM-2 [1]. Based on the anomalous behaviour observed in the electric permittivity and magnetization curves, a canted antiferromagnetic phase (AFM-3) below $T_{AFM-3} = 22$ K has been proposed [1]. According to Hemberger *et al* [1], $Eu_{0.8}Y_{0.2}MnO_3$ becomes ferroelectric below $T_{AFM-2} = 30$ K. The electric polarization was obtained from the time integration of a pyroelectric current, after polarizing the sample under an electric field of 1 kV cm^{-1} [1]. The ferroelectric character of both low temperature AFM-2 and AFM-3 magnetic phases was also found by Valdés *et al* in $Eu_{0.75}Y_{0.25}MnO_3$ [3]. Taking into account the weak-ferromagnetic character of the AFM-3 phase, as well as the electric polarization below $T_{AFM-2} = 30$ K, Hemberger *et al* [1] have proposed a non-collinear spiral order for the AFM-2 phase, and a spin-canting cone-like structure, for the AFM-3 one. The actual magnetic structure of the low temperature phases, however, remains still unknown.

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More recently, Yamasaki *et al* [4] reported a structural, dielectric, magnetic and polarization study done in $Eu_{1-x}Y_xMnO_3$ single crystals ($x = 0$, 0.1, 0.2, 0.3 and 0.4). The temperature dependence of the electric polarization was obtained by measuring the pyroelectric current, after cooling the sample, provided with silver paste painted electrodes, under rather high electric fields (2 kV cm^{-1}) [4]. For the particular case of $x = 0.2$, Yamasaki *et al* [4] reported the absence of a ferroelectric phase, and they attributed the discrepancy in the results reported in [1] and [4] to the non-stoichiometry of the samples.

The ferroelectric character of $Eu_{0.8}Y_{0.2}MnO_3$ below T_{AFM-2} is then an open question. In most of the magnetically induced ferroelectrics, ferroelectricity originates from a variety of spiral magnetic structures [5], and can be explained in terms of the inverse Dzyaloshinski–Morya model, which states that the electric polarization is expected as [6, 7]:

$$\vec{P} = \sum_{i,j} A\vec{e}_{ij} \times (\vec{S}_i \times \vec{S}_j), \tag{1}$$

where $\vec{e}_{ij}$ denotes the unit vector connecting the interacting neighbour $\vec{S}_i$ and $\vec{S}_j$ spins, and A is the coupling constant between electric polarization and magnetic momenta, determined by both spin exchange interaction and spin–orbit coupling [8]. The origin of ferroelectricity in some rare-earth manganites and other magnetic ferroelectrics, such as $Ni_3V_2O_8$ [9] and $CoCrO_4$ [10] has been attributed to that mechanism. So, in the magnetic ferroelectric rare-earth manganites, the ferroelectricity has an improper character, having a completely different origin from that in conventional ferroelectrics, leading, in general, to very small values of the spontaneous electric polarization.

The measurement of the electric polarization reported in the works referred to above was carried out using rather high electric fields, yielding, however, a very small polarization value ($P \approx$ 30–50 nC cm^{-2}, at the lowest measured temperature) [1, 4]. In $Eu_{0.8}Y_{0.2}MnO_3$, the existence of Y-impurities, with a smaller ionic radius than Eu^{3+}, can enhance the polarizable character of the crystal lattice. Thus, induced polarization is expected in this compound. In materials where a small spontaneous electric polarization and an induced electric polarization coexist, understanding experimental data concerning the temperature dependence of the electric polarization, calculated from the time integration of the pyroelectric current, requires a very careful analysis. These aspects are particularly relevant when, after cooling the sample under high electric fields, the pyroelectric currents are measured in heating runs. The induced polarization can then be taken erroneously as a spontaneous one if a polarization reversal study is not undertaken to confirm the obtained results.

In this work, we report a detailed study of the polar properties of $Eu_{0.8}Y_{0.2}MnO_3$ through measurements of the thermally stimulated depolarization current, pyroelectric current and polarization reversal ($P(E)$). As far as we know, a study of the temperature dependence of the $P(E)$ relation has not yet been reported in current literature. Our aim is to clarify the controversial aspects of the phase sequence of the $Eu_{0.8}Y_{0.2}MnO_3$ system, concerning the ferroelectric properties of its lower temperature magnetic phases, and thus its multiferroic character.

2. Experimental details

High quality $Eu_{0.8}Y_{0.2}MnO_3$ ceramics were prepared by the sol–gel combustion method. A detailed study in $EuMnO_3$ and $GdMnO_3$ ceramics prepared in this way, has lead to results very similar to the ones obtained in the corresponding single crystals [11]. The phase purity, the crystallographic and the microstructural characterization of the ceramic samples were checked using x-ray powder diffraction and scanning electron microscopy, equipped with energy dispersion spectroscopy. The Rietveld refinement of 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.

Rectangular parallelepipedic shape samples were prepared from the ceramic pellet, and gold electrodes were deposited using the evaporation method. The study of thermally stimulated depolarization currents was carried out in sequential thermal cycles as follows: (i) cooling the sample from 60 to 10 K under a polarizing electric field E_p up to 11.3 kV cm^{-1}; (ii) heating the sample, after short-circuiting it for 30 min, from 10 to 60 K under zero electric field, at the temperature rate 2 K min^{-1}. The thermally stimulated depolarization 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 temperature rate [12]. The temperature dependence of the corresponding polarization was obtained by the time integration of the current density. The sample temperature was measured with an accuracy better than 0.1 K. $P(E)$ was recorded between 45 and 10 K, using a modified Sawyer–Tower circuit [13]. In order to prevent any dynamical response, from masking the actual domain reversal, we have chosen to perform the measurements of the $P(E)$ at low enough operating frequencies. As the $P(E)$ relations do not change with frequency below 1 Hz, we have taken 330 mHz as the operating frequency. The complex dielectric constant was measured with an HP4284A impedance analyzer in the 7–300 K temperature range, under an ac electric field of amplitude 1 V cm^{-1} from 10 kHz to 1 MHz. Low field magnetization measurements were carried out in heating runs, using a Quantum Design SQUID magnetometer, in the temperature range 5–300 K, after cooling the sample for both zero and 0.07 kV cm^{-1} dc electric fields. The resolution in the magnetization measurements is better than 5×10^{-7} emu.

3. Experimental results

Figure 1 shows the hysteresis loops obtained at several selected temperatures, recorded at 330 mHz. Between 40 and 28 K, a linear $P(E)$ dependence is observed. As the temperature decreases from 27 towards 23 K, hysteresis loops can be detected, with an elongated shape. A limited value of the electric polarization could not be achieved, even for electric fields of up to 15 kV cm^{-1}, which shows how easily this material can be polarized. The most remarkable result is the retrieval of the linear $P(E)$ relationship below T_{AFM-3}, which clearly reveals that ferroelectricity is intrinsic in the AFM-2 magnetic phase, and not in the AFM-3 phase, as previously suggested [1].

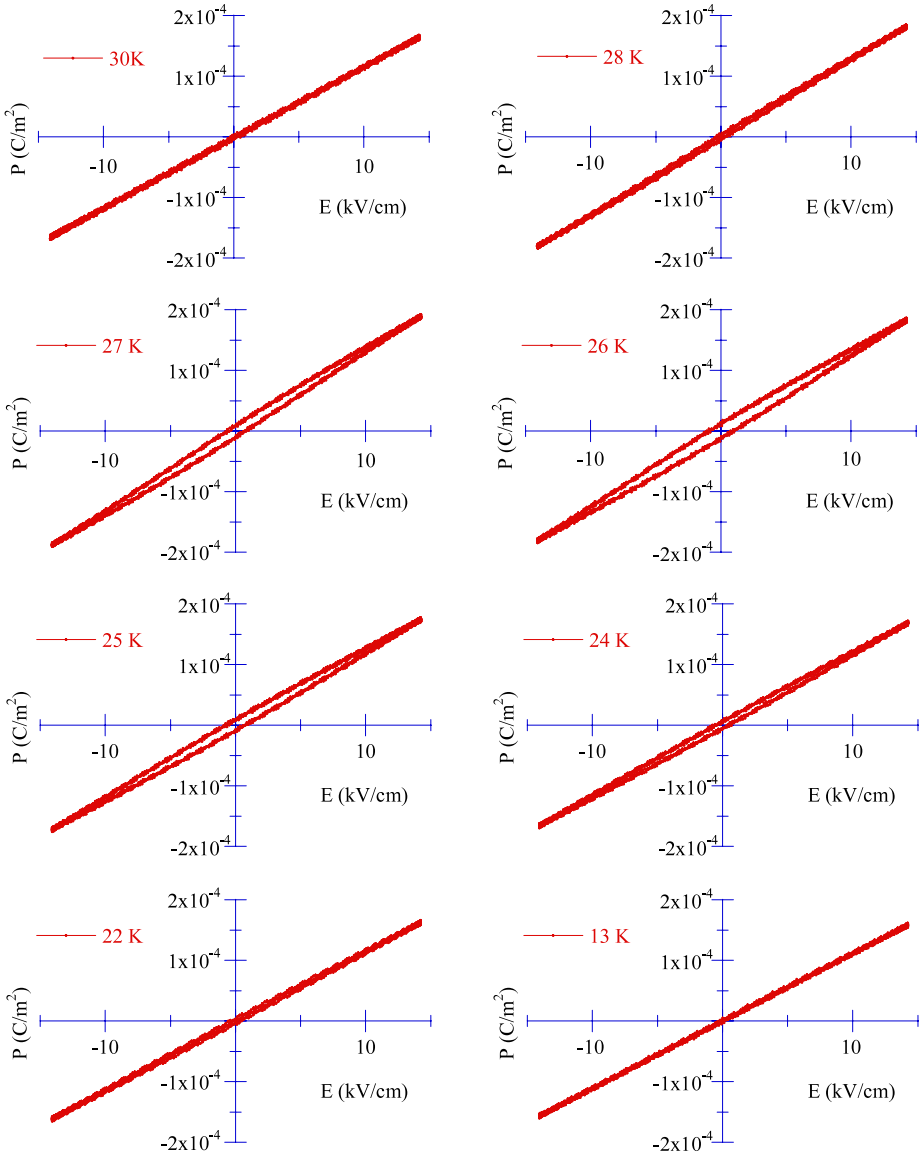

Figure 1. $P(E)$ recorded at 330 mHz, for fixed different temperatures.

The ease of inducing polarization in this material, revealed in the results referred to above, is corroborated by the experimental data obtained from the study of thermally stimulated depolarization currents, as we shall see below. Figure 2(a) shows the temperature dependence of the thermally stimulated depolarization current density $J_{\mathrm{TSDC}}(T)$. In all measurements, $J_{\mathrm{TSDC}}(T)$ curves show anomalies at $T_{\mathrm{AFM-2}}$, and their amplitudes increase as the polarizing field increases, which is, as it is well known, the main characteristic of an electrically induced polarization. The temperature dependence of both real ($\varepsilon'_{\mathrm{r}}$) and imaginary ($\varepsilon''_{\mathrm{r}}$) parts of the dielectric constant, measured in a heating run at several fixed frequencies, is presented in figures 2(b) and (c), respectively. $\varepsilon'_{\mathrm{r}}(T)$ and $\varepsilon''_{\mathrm{r}}(T)$ exhibit a pronounced anomaly at $T_{\mathrm{AFM-2}}$, in good agreement with the reported results in single crystals [1, 2]. No hint of conductive mechanisms in the frequency dependence of both $\varepsilon'_{\mathrm{r}}(T)$ and $\varepsilon''_{\mathrm{r}}(T)$ are detected, excluding the existence of free carriers in the sample. The clear anomaly in $\varepsilon''_{\mathrm{r}}(T)$ at $T_{\mathrm{AFM-3}}$ (see inset of figure 2(b)) marks the AFM-2/AFM-3 phase transition. Figure 2(d) shows the temperature dependence of the electric polarization, which was obtained from time integration of the current density displayed in figure 2(a). All the polarizations emerge below 30 K and their saturation values are strongly dependent on the polarizing electric field. The saturation value of the polarization for $E_{\mathrm{p}} = 2.8$ kV cm^{-1} ($P_{\mathrm{s}} \approx 1 \times 10^{-4}$ C m^{-2}) is lower but of the same order of magnitude as the one along the a-axis reported by Hemberger *et al* [1] for $Eu_{0.8}Y_{0.2}MnO_3$ single crystals ($P_a \approx 5 \times 10^{-4}$ C m^{-2}) under a polarizing electric field of 1 kV cm^{-1}. This difference should be associated with both random orientation of ceramic grains and surface effects, which apparently reduce the actual polarization in granular samples. We should emphasize how easy is to polarize $Eu_{0.8}Y_{0.2}MnO_3$, even for rather small electric fields, below 0.07 kV cm^{-1} (see inset of figure 2(d)).

The electric current density referred to above is not only due to a spontaneous ferroelectric polarization. If it were, the corresponding polarization would have similar

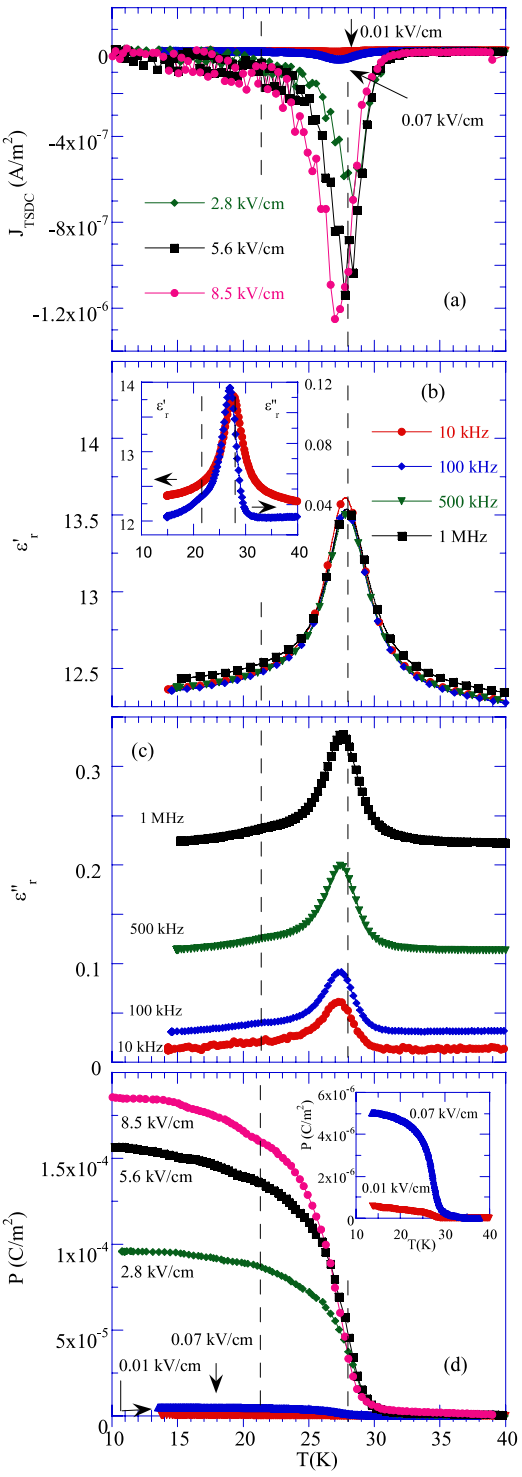

Figure 2. Temperature dependence of: (a) the thermally stimulated depolarization current density, measured in a heating run, after polarizing the sample under several fixed electric fields; (b) the real (ε_r') and (c) the imaginary (ε_r'') parts of the complex dielectric constant measured for different fixed frequencies; (c) the electric polarization, obtained from time integration of the thermally stimulated depolarization current density. Insets: (b) an expanded view of the $\varepsilon_r'(T)$ and $\varepsilon_r''(T)$ measured at 100 kHz; (c) an expanded view of the induced polarization, after poling the sample under 10 and 70 V cm^{-1}.

temperature behaviour to the remanent polarization, obtained from $P(E)$ measurements. In this work, the measurement of pyroelectric current was carried out as follows: a low

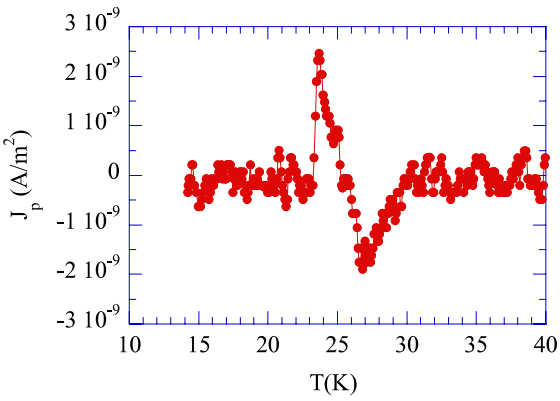

Figure 3. Temperature dependence of the pyroelectric current density, measured in a heating run, after cooling the sample with an applied electric field of 1 V cm^{-1}.

polarizing electric field ($E_p \approx 0.001$ kV cm^{-1}) was applied inside the ferroelectric phase ($T = 25$ K). It is convenient to stress that we have used a low enough electric field intensity, which enables both enhancing the alignment of the spontaneous ferroelectric dipoles, and minimizing the induced electric polarization. Afterwards, the sample was cooled to 10 K, when the electric field was removed and the sample short-circuited for 30 min. The measurement of the electric current was then carried out in a heating run without applied electric field. Figure 3 shows the pyroelectric current density (J_p) as a function of the temperature. Anomalies are detected at both T_{AFM-2} and at T_{AFM-3}, with opposite signs, yielding a spontaneous component for the electric polarization (P_s) between T_{AFM-3} and T_{AFM-2}. We calculated the electric polarization (P_s) by time integrating the pyroelectric current density presented in figure 3. The analysis of the data displayed in figure 1 enables us to determine the temperature dependence of the remanent polarization (P_r). Figure 4(a) shows the temperature dependence of both P_s and P_r. As is generally the case, the amplitude of P_r obtained from hysteresis loops is larger than P_s obtained from the analysis of the pyroelectric current. Leaving out the tail of $P_s(T)$ observed below T_{AFM-3}, which is apparently associated with the induced polarization component already observed just below T_{AFM2}, as is clear from figure 2, the occurrence of both P_s and P_r between T_{AFM-2} and T_{AFM-3} provides evidence for the ferroelectric character of the AFM-2 phase. It is worth stressing that to classify a phase as a ferroelectric one, observing just one of the two aforementioned quantities is not enough; both of them have to occur in the same phase [14].

We have also studied the effect of a polarizing electric field on the induced magnetization below 60 K, maintaining the same experimental procedures used in the measurement of the thermally stimulated depolarization currents. The measuring magnetic field was fixed at 50 Oe. We have taken into account the effect on the magnetization of both parallel and perpendicular orientations of applied electric field and measuring magnetic field. In both cases, an effect on the magnetization is observed, though it is larger for the parallel configuration. Only this one will be further studied in this work.

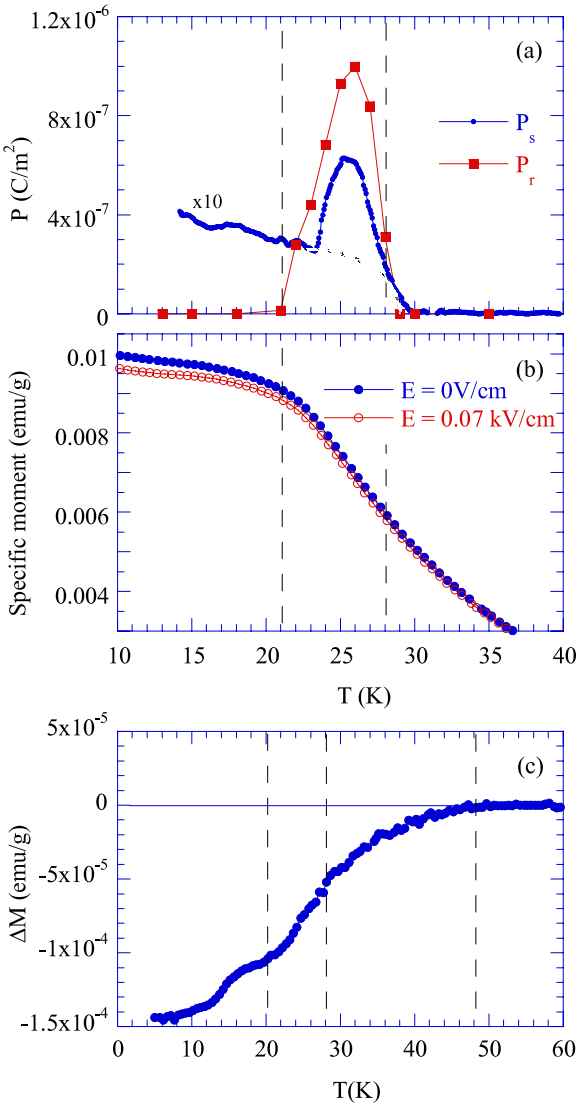

Figure 4. (a) Temperature dependence of the electric polarization (P) obtained from the time integration of the pyroelectric current and of the remanent polarization (P_r), obtained from $P(E)$. (b) Temperature dependence of the specific magnetization measured in the heating run after cooling the sample under an electric field of 0 and 0.07 kV cm^{-1}. (c) Temperature dependence of the difference of the magnetization measured under electric field and zero-electric-field cooling conditions.

Figure 4(b) shows the temperature dependence of the induced magnetization measured under zero electric field and electric field cooling conditions, respectively. In order to gain a deeper knowledge of the effect of the electric field on the magnetic system, we have determined the temperature dependence of the difference of the magnetization (ΔM), measured under electric field and zero-electric-field cooling conditions, which is displayed in figure 4(c). The effect of the polarizing electric field on the magnetization starts to be visible only in the ordered magnetic phases. It decreases as the temperature decreases, sensing the phase transitions both at T_{AFM-2} and T_{AFM-3}, by either small steps or changes in curvature. As can be seen, an electric field as low as 0.07 kV cm^{-1} yields a significant decrease of the induced magnetization magnitude below T_{AFM-2}, reaching a 5% reduction at the lowest temperature. The temperature dependence of ΔM can be well understood from the ordering of the magnetic structure occurring below T_N, along with the spin–lattice coupling mechanism already present below 100 K [3, 15]. This result is still in good agreement with the interpretation presented in [16], wherein it is ascertained that a clear anticorrelation exists between weak ferromagnetism and ferroelectricity in this compound.

4. Discussion and conclusions

We have investigated the ferroelectric character of the low temperature magnetic phases of $Eu_{0.8}Y_{0.2}MnO_3$. The absence of both spontaneous and induced electric polarization in the AFM-1 phase corroborates its incommensurate collinear spin and lattice structures, which prevent electric polarization from emerging, even after poling the samples with high electric fields.

Unlike AFM-1, AFM-2 is a ferroelectric phase, exhibiting very small values of the spontaneous polarization, arising from lattice deformations underlined by the microscopic mechanisms associated with the phase transition at T_{AFM-2}.

As opposed to the AFM-2 phase, the AFM-3 phase is not intrinsically ferroelectric, since its polar nature could not be simultaneously ascertained by both pyroelectric and $P(E)$ measurements. The decrease of the remanent polarization observed as the temperature decreases towards T_{AFM-3}, can be in fact associated with changes of both spin and lattice structures. Following the interpretation, forwarded in [16], such a polarization decrease is a consequence of the enhancement of the weak-ferromagnetic ordering in AFM-3 at the expense of the cycloidal-antiferromagnetic one, which in turn yields ferroelectric ordering through the inverse Dzyaloshinski–Morya interaction. Although in this work, no history-dependent ground state character was induced by cooling the sample under a polarizing magnetic field, the explanations provided in [16] can still be invoked to understand our results. Since the main mechanism is very likely associated with Néel domain wall dynamics, the role of the polarizing magnetic field is basically played by the granular nature of the samples. Indeed, grain microstructure can prevent, like polarizing magnetic fields do, Néel domain walls acting as nuclei towards the growth of polar domains, enhancing weak-ferromagnetic ordering rather than the polar ordering, as actually occurs in the AFM-3 phase.

A polarizing electric field can induce an electric polarization in both AFM-2 and AFM-3 phases, which, of course, is associated with further lattice deformations. As a consequence of the spin–lattice coupling mechanism, existing already below ∼100 K, and the emerging ordering of the magnetic structure below the Néel temperature, the lattice deformations induce changes in the spin arrangement, enhancing the modulated spin structure, while suppressing the weak-ferromagnetic ordering. This interpretation is in very good agreement with the decrease of $M(T)$, and the appearance of an induced electric polarization, when the sample is cooled down under even a low polarizing electric field.

The experimental results presented in this work prove that ferroelectricity and ferromagnetism do not coexist in the same phase. Consequently, $Eu_{0.8}Y_{0.2}MnO_3$ is not a multiferroic material.

Acknowledgments

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