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Ferroelectricity in antiferromagnetic phases of $Eu_{1-x}Y_xMnO_3$

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ABSTRACT

This work reports an experimental investigation of the ferroelectric character of magnetic phases of the orthorhombic $Eu_{1-x}Y_xMnO_3$ system at low temperatures. The temperature dependence of the polarization curves clearly reveals the existence of a re-entrant improper ferroelectric phase for $x = 0.2$, 0.3 and 0.5. A ferroelectric phase is also stable for $x = 0.4$, and we have no experimental evidence for its vanishing down to 7 K. From these and early results obtained using other experimental techniques, the corresponding (x, T) phase diagram was traced, yielding significant differences with regard to the ones previously reported.

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1. Introduction

The orthorhombic $Eu_{1-x}Y_xMnO_3$, with $0 \leq x \leq 0.5$, is a very interesting system, allowing the possibility of tuning the magnetic and polar phases through the manipulation of the *A*-site size, which can be achieved by the isovalent substitution of the trivalent Eu^{3+} ion by the smaller Y^{3+} ion, without increasing the magnetic complexity. The solid solutions allow for a continuous variation of the Mn–O1–Mn bond angle, which is associated with the development of the complex magnetic ground states and ferroelectric phases, which underlies the magnetoelectric properties exhibited by this system [1–3].

All compositions undergo a transition from a paramagnetic to an incommensurate antiferromagnetic phase (AFM-1) at T_N, ranging monotonously from 52 K ($x = 0$) to 45 K ($x = 0.50$) [4,5]. For $x < 0.1$, a transition from the AFM-1 to a canted A-type antiferromagnetic phase occurs at 43 K ($x = 0$) to 33 K ($x = 0.1$), following Ref. [4], whilst it emerges for $x < 0.25$, as the results from Ref. [5] suggest. For the compositions $0.25 < x < 0.35$, a cycloidal modulated antiferromagnetic, and ferroelectric phase (AFM-2) becomes apparent. For $0.35 < x < 0.55$, a re-entrant magnetic phase is detected, corresponding to two successive magnetic transitions, associated with the rotation of the cycloidal plane from the *ab* to the *bc* plane [4,5]. This rotation implies that the spontaneous electric polarization changes from the *c*-axis to the *a*-axis [5]. Contrarily to Yamasaki et al. [5], Hemberger et al. [4] considered for $0.15 < x < 0.35$, a further low temperature modulated conical magnetic, and ferroelectric phase (AFM-3).

Notwithstanding numerous studies, the phase diagram of this system, for the *Y*-concentration range $0 \leq x \leq 0.5$, is still not unambiguously established (for more details, see Refs. [6,4,5,7]). Particularly, the ferroelectric character of the low temperature magnetic phases remains a controversial issue. The ferroelectric properties of the $Eu_{1-x}Y_xMnO_3$ have been studied by measurement of the displacement current after cooling the sample under high applied electric fields ($E > 1$ kV/cm). As it was shown in Refs. [8,9], $Eu_{1-x}Y_xMnO_3$ exhibits a very rather high polarizability, which can make it difficult to ascertain the actual spontaneous polarization. In this case, a special experimental procedure has to be adopted. In fact, the detection of electric current in a heating run, obtained after applying an unusually high electric field in a cooling run, does not allow the identification of a phase as ferroelectric [10]. It is also necessary to perform hysteresis loop measurements in the same phase [10]. Besides two reports concerned the ferroelectric properties of the compounds with $x = 0.2$ and 0.4 [8,9], a systematic and careful study regarding the polarization reversal in a set of representative compounds of the system $Eu_{1-x}Y_xMnO_3$ is still missing. These aspects are very important both from an experimental and a theoretical point of view.

In this work, we report a detailed and systematic study of the polar domain reversal in $Eu_{1-x}Y_xMnO_3$ ceramics, with $x = 0$, 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5, in order to search for the ferroelectric character of the magnetic phases at low temperatures, and thus to establish a more adequate phase diagram of the system.

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2. Experimental details

High quality $Eu_{1-x}Y_xMnO_3$ ceramics were prepared by the sol–gel urea combustion method [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 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 in both systems a typical ceramic microstructure with regular shaped crystal grains ranging from 3 up to 10 μm in diameter. The valence of the europium ion was checked through XPS technique, and no evidences of the existence of oxidation states other than Eu(III) in the sample could be detected. As the samples were fast cooled from 1350 °C down to room temperature, significant deviations of the oxygen occupancy from the expected stoichiometric $Eu_{1-x}Y_xMnO_3$ are not expected, excluding the existence of significant amount of Mn(IV) ion [11].

Rectangular shaped samples were prepared from the ceramic pellet, and gold electrodes were deposited using the sputtering method. The $P(E)$ relation was recorded between 50 and 8 K, using a modified Sawyer–Tower circuit [12]. 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 enough low 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 $P(E)$ curves were measured by changing the temperature in small steps, namely in the ferroelectric phases, where a 0.3 K was chosen, in order to follow in detail any changes on the coercive electric field. The electric voltage maximum applied to the sample was 1000 V. On this regard, the corresponding electric field maxima amplitude (10–15 kV/cm) is large enough to assure the full orientation of the ferroelectric domains. No visible changes in the shape of the $P(E)$ curves, even for higher values of the electric field maximum, are expected.

3. Experimental results and discussion

Fig. 1 shows the $P(E)$ relations at several fixed temperatures, for the compositions $x = 0.2$, 0.3, 0.4, and 0.5. The analysis of all available $P(E)$ relations allows us to determine the temperature dependence of the remanent polarization, which is displayed in Fig. 2.

Before starting the analysis of the results obtained for the compositions referred to in Fig. 1, it is worth noting that for lower compositions, i.e., $x = 0$, 0.05, 0.10 and 0.15, only linear $P(E)$ relations were obtained in the $7\ \text{K} < T < 50\ \text{K}$ temperature range. This result reveals that no polar domain reversal exists in these compositions, suggesting that these compounds do not exhibit ferroelectric phases, in good agreement with earlier reported results [6,4,5].

In the following, we will discuss only the experimental results obtained for the compositions with $0.2 \leq x \leq 0.5$. As a general feature, it was revealed that only linear $P(E)$ relations are observed for $T > T_{\text{AFM-2}}$.

We start analysing the results obtained for the $Eu_{0.8}Y_{0.2}MnO_3$ sample (Fig. 1(a)). As the temperature decreases from $T_{\text{AFM-2}} = 27$ K to $T_{\text{AFM-3}} = 23$ K, hysteresis loops can be detected, with an unusual elongated shape. A limited value of the saturation of the electric polarization could not be achieved, even for electric fields up to 15 kV/cm, due to the high polarizable character of the composition with $x = 0.2$ [7]. On further temperature decreasing, linear $P(E)$ relationships are retrieved. This result reveals that ferroelectricity in $Eu_{0.8}Y_{0.2}MnO_3$ is intrinsic in the AFM-2 magnetic phase, and not in the AFM-3 phase, as previously suggested. It is worth noting that this outcome is also corroborated by the temperature dependence of the spontaneous polarization obtained through the time integration of the pyroelectric current [7].

Fig. 1(b) shows the $P(E)$ relations obtained in $Eu_{0.7}Y_{0.3}MnO_3$. Hysteresis loops appear just below $T_{\text{AFM-2}} = 26$ K. However, the most remarkable result is the retrieval of linear $P(E)$ relations below 18 K suggesting a further phase transition, which to the best of our knowledge has not yet been reported for this composition below $T_{\text{AFM-2}}$. A careful analysis of the dielectric loss as a function of temperature shows a tiny anomaly at 18 K, reinforcing the possibility of a third and new phase transition in $Eu_{0.7}Y_{0.3}MnO_3$.

For the $Eu_{0.6}Y_{0.4}MnO_3$ compound, hysteresis loops are observed between $T_{\text{AFM-4}} = 24$ and 6 K (Fig. 1(c)), but the temperature behaviour of the remanent polarization is not monotonous (Fig. 2). As the temperature decreases from $T_{\text{AFM-4}}$, the remanent polarization increases, reaching a local maximum at around 21 K, as expected due to the rise of the electric polarization along the c-axis [4,5]. On further cooling, $P_r(T)$ decreases, attaining a minimum at 19 K, and then, an increase of $P_r(T)$ is observed down to 15 K. The increase of electric polarization just below 19 K is associated with the appearance of the component of the electric polarization along the a-axis, which is larger than the c-component [4,5]. Cooling the sample from 15 K down to 6 K, a decrease of the $P_r(T)$ is observed. These results show that $Eu_{0.6}Y_{0.4}MnO_3$ is ferroelectric below $T_{\text{AFM-4}}$, as previously reported, but the temperature dependence of the remanent polarization has no counterpart in the temperature behaviour of the electric polarization reported in current literature [4,5].

A remarkable result is obtained for $Eu_{0.5}Y_{0.5}MnO_3$ (Fig. 1(d)). In fact, hysteresis loops are only visible between $T_{\text{AFM-4}} = 20$ and 12 K, contrarily with that has been published, which yields this composition as ferroelectric below $T_{\text{AFM-4}}$ [4]. Like the compositions with $x = 0.2$ and 0.3, $Eu_{0.5}Y_{0.5}MnO_3$ exhibits a re-entrant ferroelectric phase. For $x = 0.5$, the remanent polarization attains its maximum value at 16 K, which is the smallest value among the maxima values for the other samples. In order to confirm the phase transition temperatures referred to above, we have checked for possible anomalies in the temperature behaviour of other physical properties of this compound. Therefore, we have analysed carefully the data concerning the temperature dependence of the specific heat divided by temperature, the induced molar magnetization divided by the magnetic field strength (M/H), measured in zero-field cooling and field cooling conditions ($H = 20$ Oe), and the real (ε') and imaginary (ε'') parts of the complex dielectric constant measured at 500 kHz in heating run, which are displayed in Fig. 3. Both specific heat and induced molar magnetization exhibit anomalous behaviour at $T_{\text{AFM-4}}$, just above the temperature from which hysteretic $P(E)$ relations start to be observed. Moreover, both a clear anomaly in the temperature dependence of $\varepsilon''(T)$, and a small but distinctive change of slope of C_p/T (see inset of Fig. 3(a)) are detected at 12 K, below which linear $P(E)$ relations are again observed. The derivative maximum of $\varepsilon'(T)$ at ∼15 K can be tentatively assigned to $T_{\text{AFM-2}}$, where $P_r(T)$ peaks. The assignment of the anomalies of the temperature dependence of ε' and ε'' is better understood if one considers the way the dielectric constant evolves from the composition with $x = 0.40$ to $x = 0.50$. The low temperature anomaly in $\varepsilon'(T)$ and $\varepsilon''(T)$ for $x = 0.40$ transforms into the anomaly at lower temperature of the composition with $x = 0.50$, while the higher one decreases in amplitude for $x = 0.50$, and is only visible by the change of slope of $\varepsilon'(T)$.

As ferroelectricity in rare-earth manganites has an improper character, small amplitude anomalies in both $\varepsilon'(T)$ and $\varepsilon''(T)$ are actually expected. The last result is consistent with the existence of a transition from the ferroelectric to a low temperature non-polar

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