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Study of a residual ferroelectric contribution in antiferroelectric lead-zirconate thin films

Caroline Borderon
IETR, UMR CNRS 6164
Université de Nantes
44322 Nantes, France
caroline.borderon@univ-nantes.fr

Kevin Nadaud
GREMAN UMR 7347, CNRS, INSA-CVL Université de Tours,
37071 Tours, France
kevin.nadaud@univ-tours.fr

Mamadou D. Coulibaly
IETR, UMR CNRS 6164
Université de Nantes
44322 Nantes, France
mamadoucoulibalypro1@gmail.com

Raphaël Renoud
IETR, UMR CNRS 6164
Université de Nantes
44322 Nantes, France
raphael.renoud@univ-nantes.fr

Micka Bah
GREMAN UMR 7347, CNRS, INSA-CVL Université de Tours,
37071 Tours, France
micka.bah@univ-tours.fr

Stéphane Ginestar
IETR, UMR CNRS 6164
Université de Nantes
44322 Nantes, France
stephane.ginestar@univ-nantes.fr

Hartmut W. Gundel
IETR, UMR CNRS 6164
Université de Nantes
44322 Nantes, France
hartmut.gundel@univ-nantes.fr

***Abstract*— In this study, First-Order Reversal Curves (FORC) measurements and impedance spectroscopy coupled to hyperbolic law analysis have been used in order to characterize lead zirconate antiferroelectric thin films elaborated by a sol-gel process. The presence of a weak residual ferroelectric behavior has been shown even if this contribution is not clearly visible on the polarization-electric field loops. Moreover, FORC measurements indicate that the weak ferroelectric phase switch only when the antiferroelectric phase state of the cell is modified. On the other hand, impedance spectroscopy reveals a fairly good distribution of small residual ferroelectric clusters in the material as no coalescence of ferroelectric domains has been observed at low fields. This study aims to show that FORC distribution measurements and impedance spectroscopy coupled to the hyperbolic law analysis are very sensitive and complementary methods for the understanding of the polarization switching dynamics in antiferroelectric materials.**

Keywords—antiferroelectric thin films, FORC measurement, hyperbolic law, domain wall motions, ferroelectric phase

I. Introduction

Antiferroelectric $PbZrO_3$ (PZO) thin films have been studied since many years in order to investigate the antiferroelectric-ferroelectric (AFE-FE) transition and more recently also for energy storage applications [1-3]. The advantage of antiferroelectric materials is its high-saturated polarization P_{Sat} and its low remnant polarization P_r. This makes possible to obtain an important recoverable energy W defined by [1]:

$$W = \int_{P_r}^{P_{sat}} E dP \,. \quad (1)$$

However, conventional *P-E* loop measurements and impedance spectroscopy are not sufficient for a complete description of an antiferroelectric material and hence other analysis techniques have been developed for a better understanding of the material's electrical behaviour. Specific characterization methods, like domain wall motion measurements (electric characterization in the Rayleigh domain) can be used for example in order to show a small ferroelectric phase in antiferroelectric materials [4]. This small ferroelectric phase can be undesirable since ferroelectric domain wall motions create supplementary dielectric losses and the ferroelectric phase can also be responsible of an opening of the *P-E* loop at zero field. Thus, the recoverable energy will be decreased.

In this study, First-Order Reversal Curves (FORC) measurements are used in order to characterize the ferroelectric phase of lead zirconate antiferroelectric thin films. The relative permittivity is measured at low field (Rayleigh region) in order to show ferroelectric domain wall motions [5-6]. Moreover, vibration and pinning of those domain walls are studied using the hyperbolic law [7].

II. Experimental

The antiferroelectric $PbZrO_3$ thin films were prepared by a sol-gel process. Lead acetate trihydrate $[Pb(CH_3CO_2)_2,3H_2O]$ with 15% molar excess was dissolved in acetic acid at 100°C. The lead excess is used in order to compensate the loss during the annealing treatment due to the formation of the volatile PbO [8]. The solution was then cooled down and the zirconium isopropoxide $[Zr(O(CH_2)2CH_3)_4]$ was added to the solution. In order to stabilize the solution, deionized

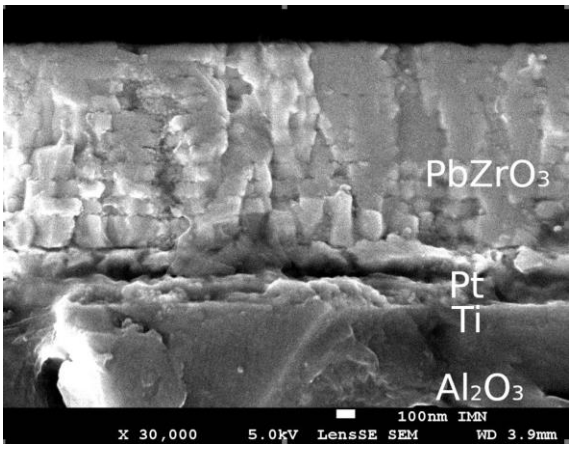


Fig. 1. Cross-section SEM image of the $PbZrO_3$/Pt/Ti/Al_2O_3 sample

water was added with a ratio water/acetic acid of 65/35. In addition, ethylene glycol [HO–CH_2–CH_2OH] is used for reducing the appearance of micro-cracks in the films [9]. The solution was then deposited, at 4000 rpm during 25 s by a multi-step spin coating process on an alumina substrate precoated with a titanium and a platinum layer-. The titanium adhesion layer (40 nm) permits the improvement of the poor adhesion of the platinum layer (300 nm) on a very smooth alumina polished surface. Each individual PZO layer was annealed during 10 min in a pre-heated open air furnace at 650°C in order to obtain the perovskite structure. Twelve layers are deposited, resulting in an overall film thickness of 800 nm (determined with a Jeol 7600 scanning electron microscope, see Fig. 1). Square platinum electrodes of 0.5 mm and 0.1 mm width are deposited by RF magnetron sputtering on the top of the PZO films in order to realize a metal–insulator–metal capacitor. The polarization vs electric field (*P*–*E*) and the current vs electric field (*I*–*E*) hysteresis loops were measured at 1 kHz using a classical Sawyer-Tower circuit and the FORC measurements were performed with a AixACCT TF2000 ferroelectric analyzer at 1 kHz using custom scripts in order to allow automatic data analysis. The capacitance has been measured with an Agilent 4294A at 1 kHz with a low AC field E_{AC}. The relative permittivity was calculated from the measured capacitance.

III. RESULTS AND DISCUSSION

The polarization *P*–*E* and the switching current *I*–*E* hysteresis loop at 1 kHz of the lead zirconate thin film are shown in Fig. 2 for a maximum field of 600 kV/cm. The $PbZrO_3$ sample presents an antiferroelectric double *P*–*E* hysteresis loop. The switching current curve has four peaks corresponding to the antiferroelectric–ferroelectric E_{AF} and the ferroelectric–antiferroelectric E_{FA} transition fields (E_{AF} = ±380 kV/cm and E_{FA} = ±240 kV/cm). Near zero electric field, the switching current *I* increases from 0.2 to 0.36 mA indicating the existence of a residual ferroelectric phase (weak ferroelectricity) in the antiferroelectric state, which is not visible on the *P*-*E* loop. This phenomenon is common for pure lead zirconate ($PbZrO_3$) [10-11] due to an unbalanced antiparallel shift of the oxygen atoms along the [001] direction.

In order to study this weak ferroelectricity, the *P*-*E* loops were measured by applying a maximum positive voltage in order to saturate the material and recording the polarization while decreasing the electric field to E_r and going back to the saturation field (Fig. 3a). A maximum voltage of 70 V has been chosen which corresponds to a maximum field of 875 kV/cm. The FORC distribution ρ is then calculated (Fig. 3b) as the mixed second derivative [12-13]:

$$\rho(E_r, E) = \frac{1}{2}\frac{\partial^2 P(E_r, E)}{\partial E_r \partial E} \quad (2)$$

A great value of ρ indicates a large number of cells which have a backswitching field between E_r and $E_r + \Delta E_r$ and a switching field in the interval [E, $E + \Delta E$]. The resolution of the FORC distribution in Fig 3b is 1V, corresponding to a step field ΔE_r = 12.5 kV/cm. The slew rate is 1 V/ms. Two peaks at positions (E,E_r) = (−310 kV/cm, −630 kV/cm) (yellow dash lines in Fig.3) and (520 kV/cm, 250 kV/cm) (red dash lines in Fig.3) are visible, corresponding to the antiferroelectric switching behavior. The two maxima are not exactly symmetrical to the $E_r = -E$ axis which can be attributed to an internal field. The four fields found from the FORC measurements are in good agreement with the E_{AF+}, E_{FA+}, E_{AF-} and E_{FA-} transition fields determined by the $I(E)$ loops measurement. In addition to the two antiferroelectric switching maxima, a less pronounced peak is visible at (E,E_r) = (630 kV/cm, −610 kV/cm) which corresponds to a small ferroelectric switching polarization (see hypothetic loop in green in Fig 3a). This low proportion of ferroelectric domains switches at a field near E_{AF+} and E_{AF-} suggesting that switching of this ferroelectric phase occur when the antiferroelectric cells modify their phase. The antiferroelectric cells seem to create a strain on the ferroelectric phase and the global switching of the ferroelectric polarization is only possible when the

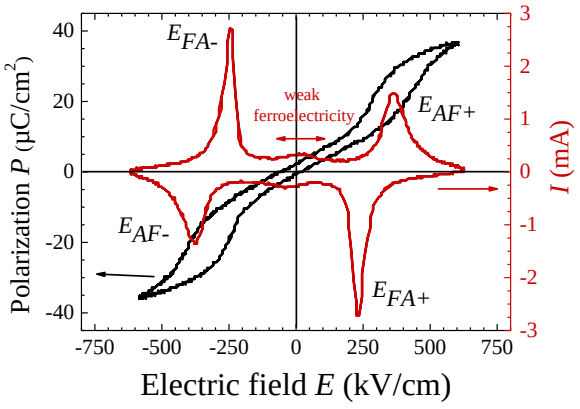


Fig. 2. *P*-*E* and *I*-*E* loops of the $PbZrO_3$ sample at 1 kHz. The *I*-*E* loop shows a slight increase at zero field corresponding to a weak ferroelectricity

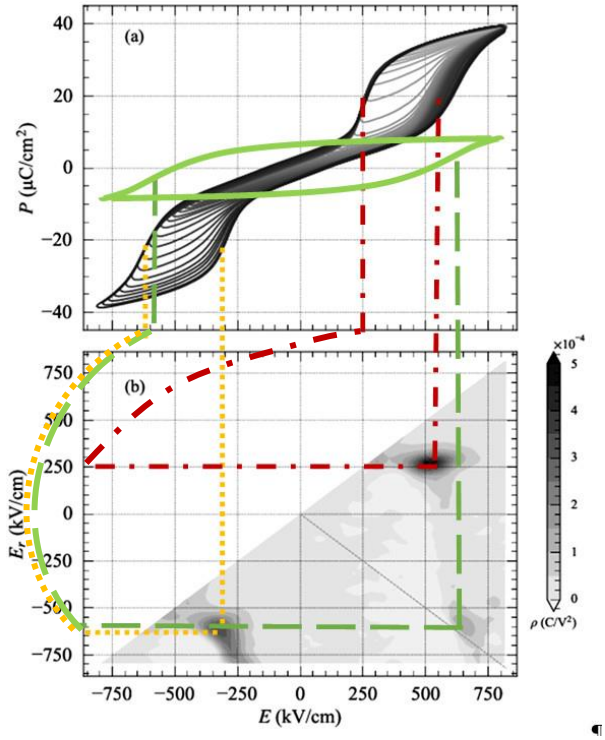


Fig. 3. *P*(*E*) loops and FORC distribution of the PZO antiferroelectric thin films. The different lines show the switching fields and the green loop is hypothetic.

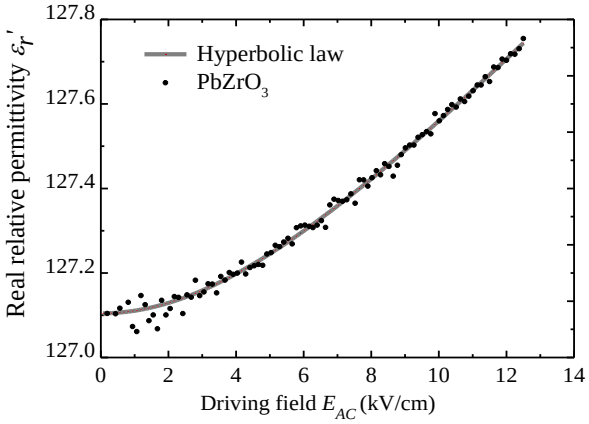


Fig. 4. The real part of relative as the function of the applied AC electric field (black circles). The solid gray line is a fit to the hyperbolic law (1) at 1 kHz.

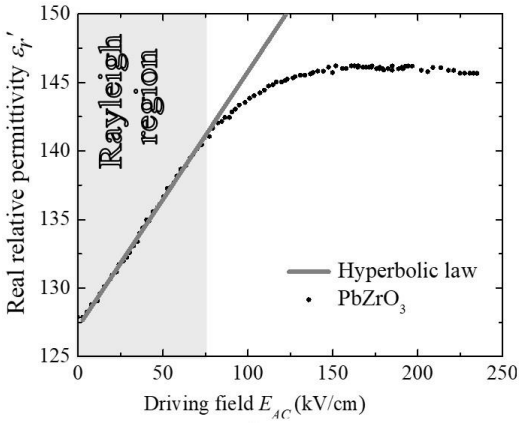


Fig. 5. The Real part of the relative permittivity as the function of the driving field E_{AC}. The solid gray line correspond to the hyperbolic fit.

antiferroelectric cells change to the ferroelectric state.

In order to verify and quantify the presence of the ferroelectric phase, the dielectric permittivity was measured as a function of the magnitude of the driving field E_{AC} (Fig. 4 and Fig. 5). At low field, the permittivity increases when the driving electric field increases indicating domain wall motion [7,14]. This correspond to motions in the center of the FORC distribution, inside the triangle with corners (E,E_r) = (−250 kV/cm, −250 kV/cm), (250 kV/cm, −250 kV/cm) and (250 kV/cm, 250 kV/cm) where no important hysteron distribution is visible (no global switching polarization). Only ferroelectric domain walls contribute to this increase since an antiferroelectric domain wall motion cannot appear under the action of a homogeneous electric field [15]. At low fields, in the Rayleigh region, the real part of the permittivity have been fitted using the hyperbolic law [7,16]:

$$\varepsilon_r = \varepsilon_{rl} + \sqrt{\varepsilon_{r-rev}{}^2 + (\alpha_r E_{AC})^2}\,, \qquad (3)$$

where ε_{rl} is the lattice contribution to the permittivity, ε_{r-rev} and α_r correspond respectively to domain wall vibrations and domain wall pinning/unpinning (jump). The two last parameters depend on the domain wall density. The coefficients are extracted using the Levenberg-Marquat method by minimizing the quadratic error. For $PbZrO_3$ thin films, the Rayleigh parameter α_r is equal to 0.086 cm/kV, which is smaller than the one of ferroelectric $PbZr_{1-x}Ti_xO_3$ (PZT) [5-6] but almost of the same order as in a soft ferroelectric thin film $Ba_{1-x}Sr_xTiO_3$ [16]. Nevertheless, the parameter α_r is also one hundred times higher than for a constrained PZT thin film with almost no domain walls [17]. The parameter representing the domain wall vibration contribution has also a small value (ε_{r-rev} = 0.69), confirming the low ferroelectric domain wall density [16]. The two parameters ε_{r-rev} and α_r allow us to calculate the threshold field of domain wall pinning E_{th} by [7,17]:

$$E_{th} = \frac{\varepsilon_{r-rev}}{\alpha_r} \qquad (4)$$

This field represents the degree of wall pinning in the material [18] and indicates the facility for a ferroelectric domain wall to jump from one pinning center to another. The threshold field for the antiferroelectric thin film is E_{th} = 6.8 kV/cm which is higher than what is observed in the literature [19] indicating deep pinning centers for the studied material. This may be due to a strain induced by the antiferroelectric matrix on small ferroelectric clusters, which limits the domain wall motions [4].

For higher field (Fig 5), the permittivity deviates from a Rayleigh behavior (above 75 kV/cm) and the permittivity becomes constant for fields above 150 kV/cm. The driving field has almost no more influence on the permittivity, proving that the domain wall jumps occur with a similar distance regardless to the force of the exciting field. Thus, the density and the displacement distance of the domain walls are constant from 150 kV/cm to 250 kV/cm. This means that there is no interaction between domain walls (no coalition of domain) also signifying that they are well distributed in the material forming small ferroelectric clusters, which limits the domain wall distance traveled and the possible interactions between domains.

IV. CONCLUSIONS

In antiferroelectric materials, a residual ferroelectric phase may exist (weak ferroelectricity) in the antiferroelectric state. This is a common phenomenon for pure lead zirconate $PbZrO_3$ and is due to an unbalanced antiparallel shift of the oxygen atoms along the [001] direction. In order to characterize this ferroelectric phase, this study proposes two specific characterization methods: the First-Order Reversal Curves (FORC) measurements, which allows decomposition of the full polarization loop $P(E)$ into elementary hysteresis elements, and the hyperbolic law, which permit us to study ferroelectric domain wall motions.

In this study, the $PbZrO_3$ thin films present a low ferroelectric phase, which switches only when the antiferroelectris cells modify their own phase. At low fields, the ferroelectric domain wall density is low comparing to hard ferroelectric materials and the threshold field of domain wall pinning is high, indicating deep pinning centers. At moderate fields (150 kV/cm < E < 250 kV/cm), the permittivity remains constant indicating that the domain walls density and the distance of the domain wall jumps are constant. Therefore, there is no interaction between domain walls and no coalition of domains occurs. The ferroelectric phase hence seems to be well distributed into small clusters, which limits the domain wall motion and avoids domain wall coalescence. Moreover, the strain due to the antiferroelectric matrix increases the threshold field of the

domain wall pinning/unpinning and the switching polarization can only occurs when the antiferroelectric matrix changes to a ferroelectric one.

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