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Mamadou D. Coulibaly,<sup>a)</sup>  Caroline Borderon,<sup>b)</sup>  Raphaël Renoud,<sup>c)</sup>  and Hartmut W. Gundel<sup>d)</sup>

## AFFILIATIONS

IETR UMR CNRS 6164, University of Nantes, 2 Rue de la Houssinière, 44322 Nantes, France

<sup>a)</sup> Author to whom correspondence should be addressed: [mamadoucoulibalypro1@gmail.com](mailto:mamadoucoulibalypro1@gmail.com)

<sup>b)</sup> E-mail: [caroline.borderon@univ-nantes.fr](mailto:caroline.borderon@univ-nantes.fr)

<sup>c)</sup> E-mail: [raphael.renoud@univ-nantes.fr](mailto:raphael.renoud@univ-nantes.fr)

<sup>d)</sup> E-mail: [hartmut.gundel@univ-nantes.fr](mailto:hartmut.gundel@univ-nantes.fr)

## ABSTRACT

In antiferroelectric  $\text{PbZrO}_3$  thin films, a weak residual ferroelectric phase is often observed on the double hysteresis loop and it is important to know its impact on the dielectric properties. To study this residual phase, a low and homogeneous electric field can be used because antiferroelectric domain walls are not sensitive to homogeneous fields; thus, contributions of ferroelectric domain wall motions to permittivity and dielectric losses can be isolated. In this paper, the hyperbolic law characterization is used on lead zirconate thin films, which present a residual ferroelectric phase. The study shows that domain wall contributions of the ferroelectric phase are small (less than 2% of the total permittivity), but their impacts are very important in the overall dielectric losses ( $\approx 26\%$ ). These losses are, however, lower than those obtained in pure ferroelectric materials due to a residual state composed of well distributed ferroelectric clusters of small size with no interactions between domain walls.

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In a lead zirconate cell, the polar direction of the antiparallel dipoles is along the [110] direction of the orthorhombic primitive cell.<sup>1</sup> The origin of antiferroelectricity is attributed to the antiparallel displacements of lead atoms along this direction.<sup>2</sup> These shifts resulted in a zero net polarization in the  $a$ - $b$  plane. However, antiparallel shifts of oxygen atoms along the [001] direction remained unbalanced, which induce a permanent dipolar moment along the  $c$  axis,<sup>3</sup> thus explaining the existence of weak ferroelectricity in the antiferroelectric state of lead zirconate. This ferroelectricity has then an impact on the dielectric properties and on applications like energy storage or negative tunability devices.

In this study, we investigate the influence of ferroelectric domain walls caused by the weak ferroelectricity on  $\text{PbZrO}_3$  dielectric properties. The  $\text{PbZrO}_3$  thin films are prepared by a sol-gel process. Lead acetate trihydrate [ $\text{Pb}(\text{CH}_3\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}$ ] with 10% molar excess is dissolved in de-ionized water and acetic acid. An excess of lead is used in order to compensate the loss during the annealing treatment due to the formation of the volatile  $\text{PbO}$ .<sup>4</sup> Zirconium isopropoxide [ $\text{Zr}(\text{O}(\text{CH}_2)_2\text{CH}_3)_4$ ] is then added to the solution. In addition, ethylene glycol [ $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$ ] is used for reducing the appearance of micro-cracks in the films<sup>5</sup> and improves the solution stability.<sup>6</sup> The

solution (concentration of 0.5 M) is then deposited on an alumina substrate precoated with titanium and platinum layers, at 4000 rpm during 25 s by a multi-step spin coating process. 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.<sup>7</sup> Each layer is 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. Square platinum electrodes of 0.5 mm broad are deposited by RF magnetron sputtering 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. The capacitance and the dielectric losses ( $\tan\delta$ ) were measured with an Agilent 4294A from 100 Hz to 1 MHz with a low AC field  $E_{AC}$  from 6 mV/ $\mu\text{m}$  to 1.3 V/ $\mu\text{m}$ . The real and imaginary parts of the relative permittivity were calculated from the measured capacitance and the dielectric losses ( $\tan\delta$ ). A hyperbolic law<sup>8</sup> is then used to study ferroelectric domain wall movements. This law permits us to distinguish the contribution from domain wall vibration (reversible contribution), domain wall pinning/unpinning (irreversible contribution), and the contribution from the lattice, which is similar to

the Rayleigh law.<sup>8–10</sup> According to the hyperbolic law, the dielectric permittivity is described as a function of the amplitude of the exciting electric field ( $E_{AC}$  is very low compared to the transition field  $E_{AF}$ ),<sup>11</sup>

$$\epsilon_r = \epsilon_{rl} + \sqrt{\epsilon_{r-rev}^2 + (\alpha_r E_{AC})^2}, \quad (1)$$

where  $\epsilon_{rl}$  corresponds to the lattice contribution,  $\epsilon_{r-rev}$  represents the contribution due to domain wall vibrations, and  $\alpha_r$  is the contribution due to domain wall pinning/unpinning (jump).

In this study, only the effects of ferroelectric domain wall movements are investigated. Antiferroelectric domain walls cannot move under the action of a homogeneous electric field<sup>12</sup> and do not contribute to the permittivity. Thus, no term related to the presence of antiferroelectric domain walls appears in the hyperbolic law.

The polarization  $P$ - $E$  and the switching current  $I$ - $E$  hysteresis loop of the lead zirconate thin film are shown in Fig. 1. The  $\text{PbZrO}_3$  sample presents a double  $P$ - $E$  hysteresis loop, indicating its antiferroelectric nature and has a slim hysteresis loop, which is characteristic of a material with low dielectric losses. The switching current curve has four peaks corresponding to the antiferroelectric-ferroelectric fields  $E_{AF}$  and to ferroelectric-antiferroelectric  $E_{FA}$  field transitions ( $|E_{AF}| = 490 \text{ kV/cm}$  and  $|E_{FA}| = 350 \text{ kV/cm}$ ). The peak present around zero electric field ( $I$  increases from 0.2 to 0.32 mA) shows the existence of a residual ferroelectric phase (weak ferroelectricity) in the antiferroelectric state. This phenomenon is common for pure lead zirconate ( $\text{PbZrO}_3$ )<sup>13,14</sup> due to an unbalanced antiparallel shift of oxygen atoms along the  $[001]$  direction.<sup>3</sup>

In order to determine the different contributions to the real and imaginary parts of the permittivity and the influence of the residual ferroelectric phase on dielectric properties, the complex permittivity as a function of a low AC field has been analyzed at different frequencies. The dependence of the material's real part of the relative permittivity on the alternative field at 1 kHz is shown in Fig. 2. The evolution corresponds to the ferroelectric domain wall motion as the electric field is very low compared to  $E_{AF}$  and  $E_{FA}$ . Thus, no switching polarization occurs and no more ferroelectric domain walls appear (the domain wall density remains constant).<sup>8</sup> The evolution of the imaginary part of the permittivity is similar to the real part curve.

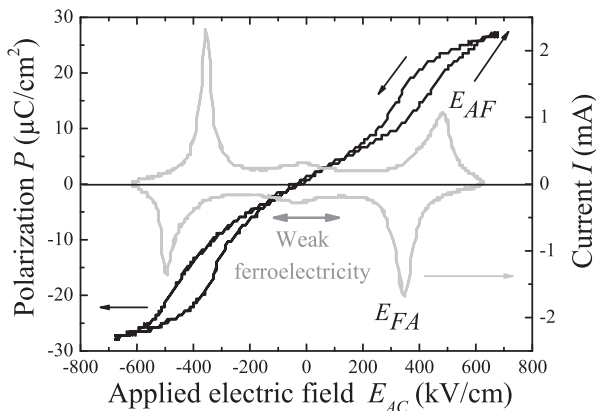


FIG. 1. Polarization and switching current hysteresis loops of the lead zirconate thin film at 1 kHz.  $E_{AF}$  and  $E_{FA}$  are the field transitions.

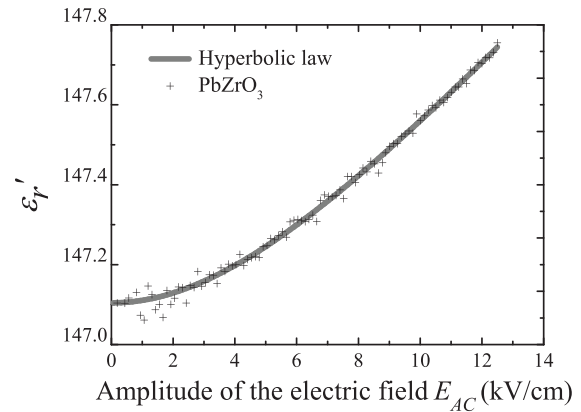


FIG. 2. The real part of relative permittivity is plotted against the applied AC electric field (black crosses). The solid gray line is a fit to the hyperbolic law [Eq. (1)] at 1 kHz.

Figure 3 shows the real and imaginary parts of the lattice contribution  $\epsilon_{rl}$  to the permittivity as a function of frequency, calculated from the Eq. (1). The evolution of the permittivity (real and imaginary parts) is fitted using the “universal power law,” which described any dielectric relaxation in solids as demonstrated by Jonscher.<sup>15,16</sup> In our case, two relaxation phenomena are superposed, one occurring at higher frequencies than the other,<sup>17</sup>

$$\epsilon_{rl} = \epsilon_{hf} \omega^{S_{hf}} + \epsilon_{lf} \omega^{S_{lf}}, \quad (2)$$

where  $\epsilon_{hf}$  and  $\epsilon_{lf}$  are the permittivity contribution at “high” and “low” frequencies, respectively, and  $\epsilon_{hf} \omega^{S_{hf}}$  and  $\epsilon_{lf} \omega^{S_{lf}}$  represent the high frequency relaxation and the low frequency diffusion, respectively.<sup>15,16</sup> Fitting of the experimental data (least squares method) is presented in Fig. 3, and the coefficients are given in Table I. According to the Kramer-Kronig relations (invariance of a power law by Hilbert transformation), the exponents of the two contributions are the same for the real and the imaginary part of the permittivity,<sup>17</sup> and only the weighting coefficients vary.

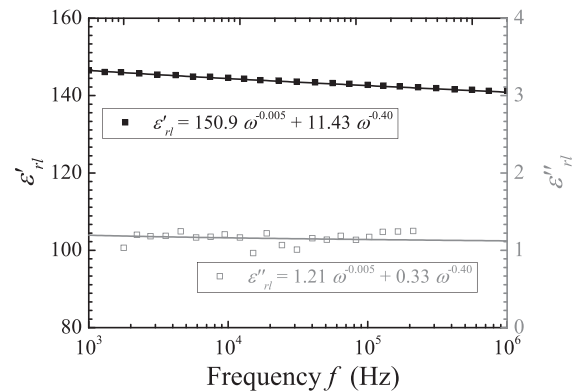


FIG. 3. Real and imaginary parts of the lattice contribution to the permittivity as a function of frequency, decomposed according to the hyperbolic law [Eq. (1)]. Evolution of the lattice contribution is fitted with Eq. (2). The increase in the losses above  $10^5$  Hz is due to a resonance of the impedance analyzer.

TABLE I. Exponents, weighting coefficients, and dissipation factors of the lattice contribution to the permittivity.

	High frequency relaxation				Low frequency diffusion			
	$S_{hf}$	$\epsilon'_{hf}$	$\epsilon''_{hf}$	$\tan \delta_{hf}$	$S_{lf}$	$\epsilon'_{lf}$	$\epsilon''_{lf}$	$\tan \delta_{lf}$
PbZrO <sub>3</sub>	$-0.005 \pm 0.001$	$150.9 \pm 0.1$	$1.21 \pm 0.01$	$0.008 \pm 0.001$	$-0.40 \pm 0.01$	$11.43 \pm 0.01$	$0.33 \pm 0.01$	$0.029 \pm 0.001$

In all cases, the exponents of the power law fitting curves are negative. The characteristic frequency of the concerned relaxations is, therefore, much lower than the minimum measurement frequency (1 kHz).

The exponent  $S_{lf}$  ( $-0.40$ ) is identical to those obtained for ferroelectric oxides.<sup>17</sup> Jonscher indicated that  $S_{lf}$  exponent values between  $-0.2$  and  $-0.4$  are often associated with hopping conduction.<sup>16</sup> In ferroelectric oxides, oxygen vacancies leave dangling bonds,<sup>18,19</sup> which allows hopping of electrons from vacancies to vacancies as shown by Morozov and Damjanovic in the case of PZT (lead zirconate titanate).<sup>19</sup> This mechanism, due only to the presence of oxygen vacancies, explains why the exponent  $S_{lf}$  takes the same value for different ferroelectric oxides.

The exponent  $S_{hf}$  ( $-0.005$ ) is attributed to the relaxation of the dipole present in the lattice cells. Its value is low compared to those obtained in the literature for ferroelectric oxides ( $S_{hf} > -0.009$ ).<sup>17</sup> According to Jonscher,<sup>15,16</sup> the absolute value of the exponent  $S_{hf}$  accounts for the importance of the correlations between the dipoles. Indeed, tunnel effect transitions can occur to lead to a new (but similar) configuration of the dipole system. These transitions are favored if correlations between the dipoles are important, i.e., if the mutual influence due to the electric field generated by dipoles is important. We go from a completely correlated system, therefore, very “rigid,” when  $|S_{hf}| = 1$ , while the system does not admit any correlation when  $|S_{hf}| = 0$ . Thus, the dipoles of our antiferroelectric sample have less correlation than those of a ferroelectric sample. This could be related to the head-to-tail dipole configuration found in antiferroelectrics, which is less favorable to the mutual influence.

In order to study the dissipation factor of the low and high frequency components,  $\tan \delta_{hf} = \epsilon''_{hf} / \epsilon'_{hf}$  and  $\tan \delta_{lf} = \epsilon''_{lf} / \epsilon'_{lf}$  are also calculated (Table I). The low frequency dissipation factor is more than 3.5 times higher than the high frequency dissipation, which shows that the diffusion is a very dissipative phenomenon. In ferroelectric oxides, the presence of oxygen vacancies in the lattice is the origin of the high dissipative factor at low frequencies<sup>17</sup> and the compensation of these vacancies leads to the reduction of dissipation factors. However, the low frequency diffusion has a lower weight in the total permittivity ( $\epsilon_{lf} \ll \epsilon_{hf}$ ) and the total losses remain low.

Compared to the lattice contribution, the domain wall contributions to the lead zirconate permittivity are small (Fig. 4). The contribution due to domain wall vibrations,  $\epsilon_{r-rev}$ , are thus difficult to obtain because the portion of the domain wall vibrations is around 0.5% of the permittivity.

Figure 4 show real and imaginary parts of the vibration and domain wall pinning contributions to the permittivity as a function of frequency. The evolution of each coefficient is fitted with a power law,<sup>17</sup>

$$\epsilon_{r-rev} = \epsilon_{f-rev} \omega^{-S_{rev}}, \quad (3)$$

$$\alpha_r = \alpha_f \omega^{-S_z}, \quad (4)$$

where  $\epsilon_{f-rev}$  and  $\alpha_f$  represent the vibration and the pinning/unpinning contributions at  $\omega = 1$  rad/s, respectively, and  $S_{rev}$  and  $S_z$  denote their frequency dependence. The coefficients and dissipation factors of the vibrations and irreversible contributions are given in Table II. The coefficient  $S_z$  is higher than the coefficient  $S_{rev}$ , which indicates that

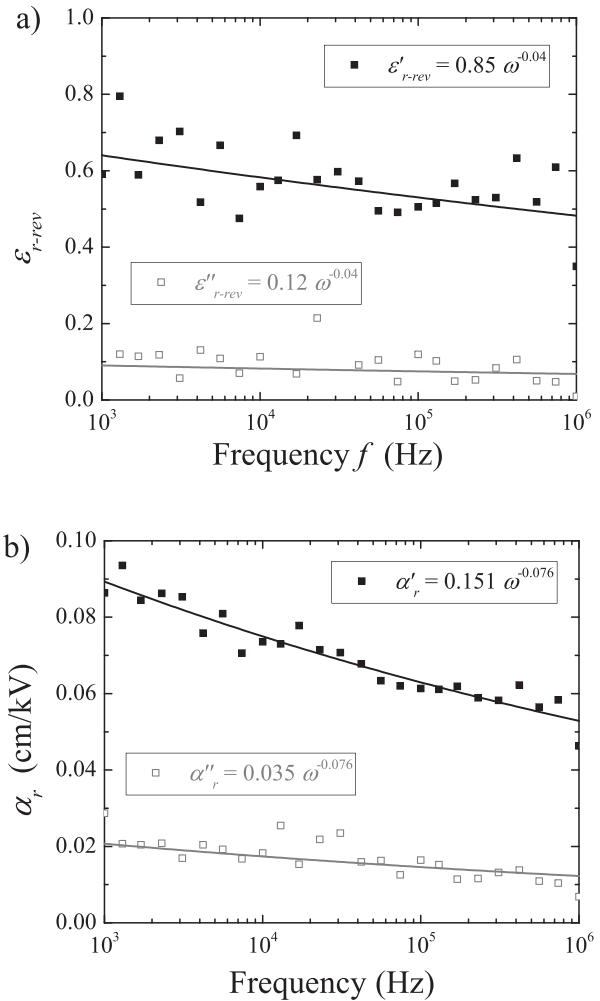


FIG. 4. Real and imaginary parts of (a) the domain wall vibrations and (b) the domain wall pinning contributions to the permittivity as a function of frequency decomposed according to the hyperbolic law [Eq. (1)]. Vibration and domain wall pinning contributions are fitted, respectively, with Eqs. (3) and (4).

TABLE II. Exponents, weighting coefficients, and dissipation factors of the vibrations and domain wall pinning contribution to the permittivity.

	$S_{rev}$	$\epsilon'_{f-rev}$	$\epsilon''_{f-rev}$	$m_{rev}$	$S_x$	$\alpha'_f$ (cm/kV)	$\alpha''_f$ (cm/kV)	$m_x$	$E_{th}$ (kV/cm)
PbZrO <sub>3</sub>	$-0.04 \pm 0.01$	$0.85 \pm 0.01$	$0.12 \pm 0.01$	$0.14 \pm 0.01$	$-0.076 \pm 0.005$	$0.151 \pm 0.005$	$0.035 \pm 0.005$	$0.23 \pm 0.04$	$5.6 \pm 0.2$

the irreversible phenomenon cannot follow the switching field when the frequency is too high. Therefore, there is no comparison in the literature for these two coefficients.

The real part of the vibration coefficient  $\epsilon'_{f-rev}$  proportional to the domain wall density, is low compared to a ferroelectric Pb(Zr<sub>x</sub>Ti<sub>1-x</sub>)O<sub>3</sub> thin film but higher than a c-domain epitaxial ferroelectric with a very low domain wall density.<sup>5</sup> This low value indicates a low domain wall density in agreement with the residual ferroelectric phase. The coefficient  $\alpha_f$  is also proportional to the density of the domain wall<sup>11</sup> and, consequently, has a low value compared to coefficients of ferroelectric Pb(Zr,Ti)O<sub>3</sub> thin films.<sup>9,20</sup>

The threshold field of domain wall pinning ( $E_{th}$ ) can also be calculated by<sup>6</sup>

$$E_{th} = \frac{\epsilon'_{f-rev}}{\alpha'_f}. \quad (5)$$

At  $\omega = 1$  rad/s, the threshold field is 5.6 kV/cm, which seems higher to what observed in the literature for ferroelectric PZT thin films.<sup>21</sup> The little size of the residual ferroelectric clusters avoids the domain wall motions and, consequently, the walls are pinned in the material.<sup>7</sup>

Even if there are only a few domain walls, their motion can produce high losses. The vibrational dissipation factor ( $m_{rev} = \epsilon''_{f-rev}/\epsilon'_{f-rev} = 0.14$ ) is lower than those reported in the literature ( $m_{rev} \geq 0.35$ ).<sup>11-17</sup> This low value can be explained not only by the low density of domain wall<sup>22</sup> but also by the weak interaction between domain walls due to the presence of the residual ferroelectric cluster well distributed in the material. The pinning dissipation factor ( $m_x = \alpha''_f/\alpha'_f = 0.23$ ) is, consequently, also lower than what is reported in the literature ( $m_x \geq 0.31$ ).<sup>11-23</sup>

In order to estimate the influence of the residual ferroelectric phase (weak ferroelectricity), we calculate contributions of lattice and domain walls in comparison to the overall permittivity and the dielectric losses. As we mentioned previously, the highest contribution of the permittivity is from the lattice (98.4%) and the contribution of ferroelectric domain walls is less than 2% of the total permittivity. Nevertheless, the contribution of ferroelectric domain wall movements is very important in the overall dielectric losses ( $\approx 26\%$ ) despite a low participation in the permittivity ( $\approx 1.5\%$ ). This comes from the extremely dissipative nature of the domain wall movements.

In this study, an antiferroelectric lead zirconate thin film presents a weak ferroelectricity phase visible on the  $I-E$  loop. This residual ferroelectricity has been studied using the hyperbolic law, and contributions of ferroelectric domain wall motions to permittivity and dielectric losses have been obtained.

The analysis of the lattice contribution indicates a low frequency conduction identical to what is obtained for ferroelectric oxides in the literature.<sup>17</sup> This phenomenon is attributed to the presence of oxygen vacancies, which created dangling bonds and high dielectric losses (16% of the total losses). A compensation of

these vacancies, by doping, for example, can lead to the reduction of the dissipation factors.<sup>17</sup>

However, the study of ferroelectric domain wall contributions shows that despite a low participation in the permittivity ( $\approx 1.5\%$ ) due to a low domain wall density, the contribution of ferroelectric domain wall movements is very important in the overall dielectric losses ( $\approx 26\%$ ). These losses are lower than in a pure ferroelectric material due to a residual state composed of well distributed ferroelectric clusters of small size with no interaction between domain walls. In addition, the small size of the clusters implies an important pinning of the domain wall (high threshold field). It will be interesting to reduce the ferroelectric cluster size to minimize domain wall motion and interaction in order to lower dielectric losses.

## DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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