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Evolution of weak ferroelectricity dielectric response in $PbZrO_3$ antiferroelectric thin films

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ABSTRACT

In this study, the ferroelectric domain wall contributions to the permittivity is investigated in a $PbZrO_3$ antiferroelectric thin film far from its antiferroelectric-ferroelectric field transition E_{AF} ($E \leq 150$ kV/cm). The lattice contribution to the permittivity increases as function of polarization electric field E_{DC} but also presents two additional small peaks. The increase is due to the antiparallel dipoles reoriented along the electric field direction (antiferroelectric contribution) and the two peaks correspond to a ferroelectric butterfly loop. The two phenomena are added to the permittivity, which make it difficult to decorrelate them. The vibration and pinning/unpinning contributions of the domain walls present only a ferroelectric butterfly loops but they do not tend to zero at infinite fields, which suggests that the ferroelectricity does not disappear completely. Dielectric losses decrease as a function of the polarization (Lorentzian function) due to a reduction of the ferroelectric domain walls density.

1 Introduction

Antiferroelectric thin films have been investigated the last few years for energy storage applications, which need, large polarization at high electric fields, high efficiency and no polarization at zero field. Unfortunately, antiferroelectric materials have sometimes a weak ferroelectric phase with a remnant polarization. The losses associated to this ferroelectric phase also leads to an opening of the *P-E* loop and the polarization at zero field is non-null. "Weak ferroelectricity" is a common phenomenon in lead zirconate ($PbZrO_3$) thin films [1, 2] due to an unbalanced antiparallel shifts of oxygen atoms [3], which break the polarization neutrality in the antiferroelectric state by inducing a permanent dipolar moment along the *c* axis of the orthorhombic primitive cell [3]. The ferroelectric domain walls contribution of the residual phase (weak ferroelectricity) is small (less than 2% of the permittivity) but its impact is important in the overall dielectric losses ($\approx 26\%$) [4]. However, the evolution of the weak ferroelectricity has only been investigated at zero electric field and at our knowledge, there is no study of the weak ferroelectricity as a function of the polarization state. Due to the dissipative character of domain walls in the weak ferroelectric state [4], evolution of dielectric losses as function of polarization is a critical parameter for

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optimizing devices such as energy storage capacitor or nonvolatile memories, whose efficiencies are related to the dielectric losses. A Lorentzian function is used in this study, which allows to predict dielectric losses as function of the polarization state, enabling the determination of an optimal working state.

In this study, far from the antiferroelectric-ferroelectric field transition E_{AF}, the evolution of the ferroelectric domain walls contributions to the permittivity in the weak ferroelectricity range ($E \leq 150$ kV:cm) is investigated. A hyperbolic law [5] is used to determine the lattice contributions, the domain walls vibration and the domain walls pinning/unpinning. The hyperbolic law describes dielectric permittivity as a function of the amplitude of the low exciting electric field [6] ($E_{AC} < < E_{AF}$):

$$\varepsilon_r = \varepsilon_{rl} + \sqrt{\varepsilon_{r-rev}^2 + (\alpha_r E_{AC})^2} \tag{1}$$

where ε_{rl} corresponds to the lattice contribution, ε_{r-rev} represents the domain walls vibrations and α_r quantified the pinning/unpinning of domain walls. Antiferroelectric domain walls are not sensitive to the action of a homogeneous electric field [7]. Thus, only ferroelectric domain wall dynamics are investigated.

1.1 Experimental procedure

A sol–gel route is used for the synthetization of $PbZrO_3$ thin films, details on the fabrication can be found in [8]. Twelve layers have been deposited by a spin coating process at 650 °C, which permits to have the perovskite structure with a [100] preferential orientation [8]. Platinum electrodes are deposited by magnetron sputtering in order to realize a Metal–Insulator-Metal capacitor. The cross section image of the $PbZrO_3$ sample (obtained with a JEOL 7600 scanning electron microscope) is shown in Fig. 1A. The $PbZrO_3$ films have a uniform microstructure and show a columnar structure. Due to the multi-step deposition of $PbZrO_3$ films, layer interfaces are visible.

The structure of the films was analyzed using a Bruker D8 X- ray diffractometer (XRD) with CuKα radiation. According to the indices of the pseudocubic perovskite structure, the lead zirconate sample has a preferential orientation along the (100) crystallographic plane (Fig. 1B). This preferential orientation is due to a most thermodynamically favorable growth direction on a lowest surface energy [9, 10].

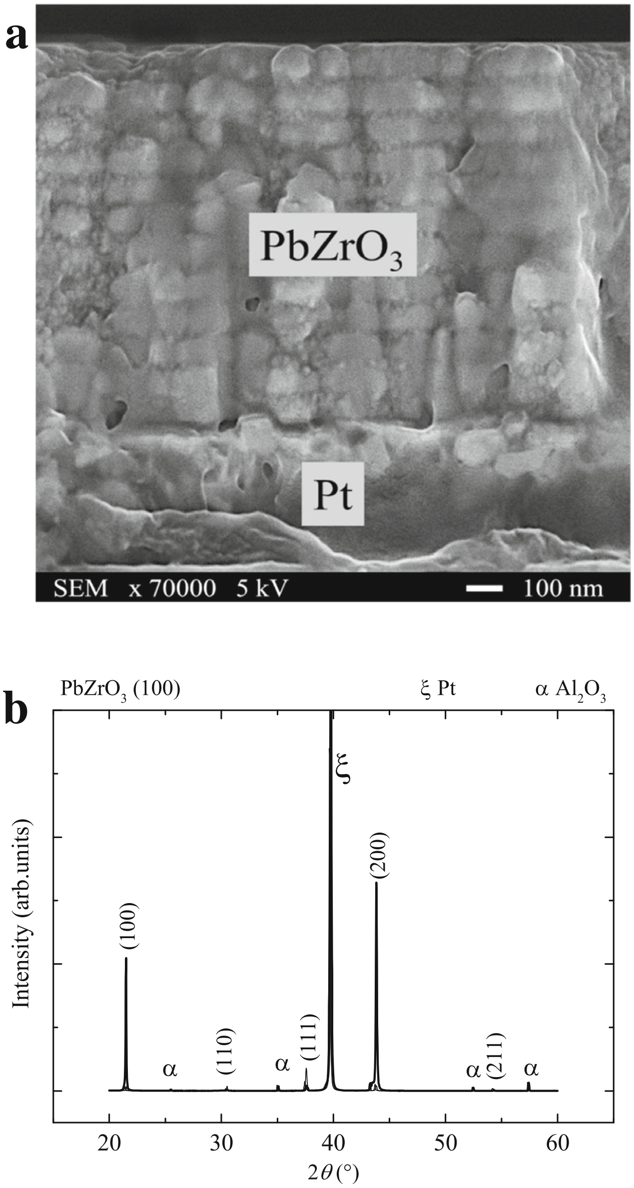

Fig. 1 **a** Cross-sectional SEM image of the lead zirconate thin films. **b** X-ray diffraction patterns of the lead zirconate sample

Polarization and current hysteresis were measured with an alternative electric field $E(t)$ at 1 kHz using a Sawyer–Tower circuit. Capacitance and dielectric losses are measured with an *Agilent 4294A*. In order to change the polarization state of the material in the weak ferroelectricity range, a DC bias electric field (E_{DC}) is added to the alternating electric field used for the measure. Then, in order to study domain walls contributions, for a fixed DC field, the AC field amplitude (E_{AC}) sweeps from 0.06 to 12 kV/cm.

2 Results and discussion

The polarization and current hysteresis of the lead zirconate thin film are shown in the Fig. 2. A double polarization hysteresis loop is shown, indicating $PbZrO_3$ antiferroelectric nature. Switching current has four peaks corresponding to the antiferroelectric-ferroelectric transition ($|E_{AF}| \approx$ 450 kV/cm) and to the ferroelectric-antiferroelectric transitions fields ($|E_{FA}| \approx$320 kV/cm). The peak around zero electric field shows the existence of weak ferroelectricity in the antiferroelectric state [4]. This ferroelectricity is not visible on the P-E loop but can be responsible of an opening of the loop at zero electric field.

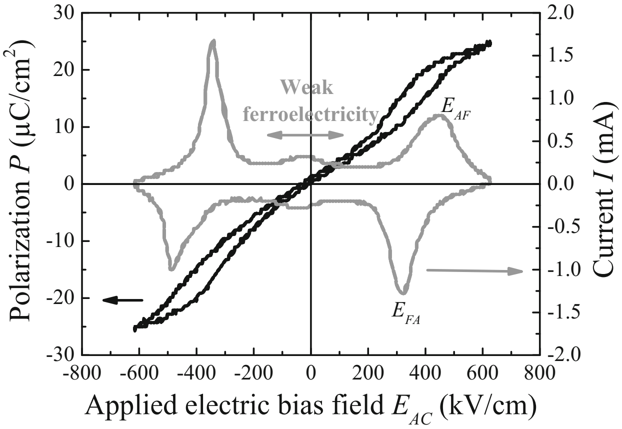

Fig. 2 Polarization and current hysteresis of the lead zirconate thin film as a function of the electric field. E_{AF} and E_{FA} are, respectively, the antiferroelectric-ferroelectric and ferroelectric-antiferroelectric fields transitions

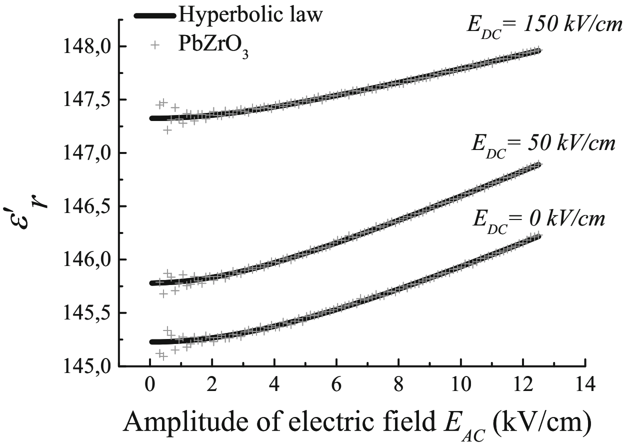

Fig. 3 The real part of relative permittivity is plotted against the amplitude of applied AC electric field (grey crosses) at 10 kHz and for different polarization states by superposing a DC electric field (E_{DC}) in the weak ferroelectric range. The black grey line correspond to the hyperbolic law fit (Eq. 1)

In order to limit our study to the weak ferroelectricity, the evolution of the ferroelectric domain walls are studied with a DC bias field between 0 and ± 150 kV/cm, which is far from the E_{AF} field transition and corresponds to the weak ferroelectric range in the Fig. 2. The complex permittivity has been measured as a function of the amplitude of a low AC field and has been analyzed with the hyperbolic law. The dependence of the material's real part of the relative permittivity on alternative field at different polarization states (by superposing a DC electric field (E_{DC}) in the weak ferroelectric range) is shown in the Fig. 3. Evolution of the relative permittivity shows an antiferroelectric like behavior, as ε'_r increases at zero exciting field as function of E_{DC}. In the antiferroelectric state, application of a DC field leads to the reorientation of the antiparallel dipoles along the electric field direction [11, 12] and the dielectric permittivity increases [13]. The evolution of the relative permittivity shows also a ferroelectric behavior as ε'_r increases as a function of the amplitude E_{AC} of the alternative field. This evolution can be fitted by the hyperbolic law, which permits us to obtain the lattice contribution (Fig. 3).

As determined in a previous work [4], the highest contribution to the permittivity is from the lattice.

($\approx$ 99%). This high contribution can be explained by the low density of ferroelectric domain wall and their weak interactions due to the presence of residual ferroelectric clusters well distributed in the material [4]. As the lattice contribution is driven by atoms displacements (which induce antiparallel dipoles), the lattice contribution increases as function of E_{DC} (Fig. 4). As previously mentioned, this increase is due the reorientation of antiferroelectric dipoles in the direction of the electric field. However, the evolution of the permittivity is not linear and reversible as the curve is not the same for up and down bias field evolution. Two additional small peaks seems to be present at positive and negative fields, which correspond to a ferroelectric butterfly loop. The two phenomena (antiferroelectric and ferroelectric contributions) are added to the permittivity, which make it difficult to decorrelate them. The real and imaginary part of the lattice contribution have the same evolution.

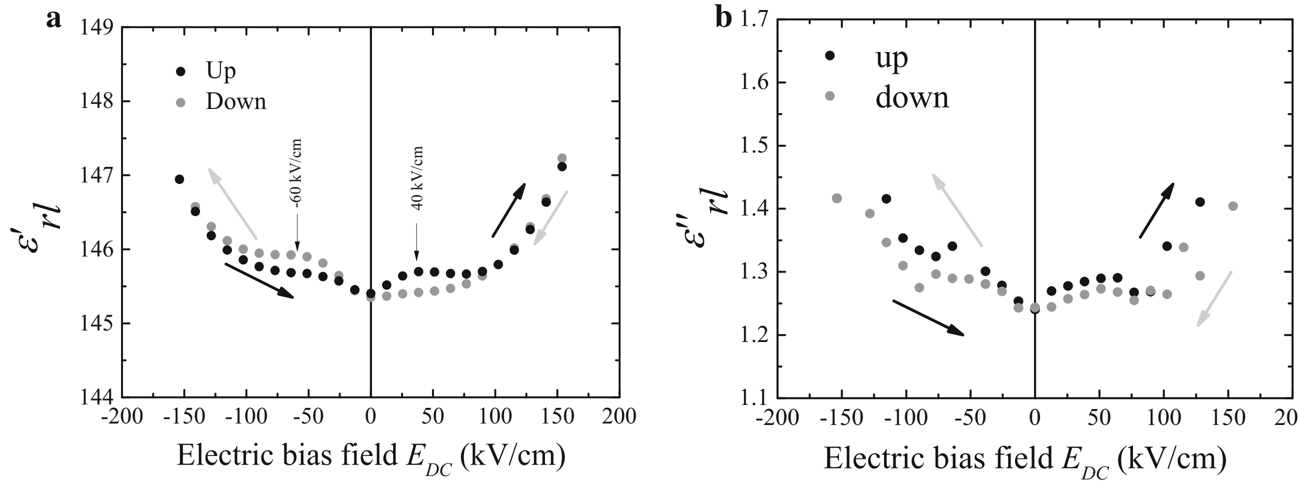

Fig. 4 **a** Real and **b** imaginary parts of the lattice contribution to the permittivity decomposed according to the hyperbolic law (Eq. 1) and measured at 10 kHz as a function of the electric bias field E_{DC} corresponding to different polarization states

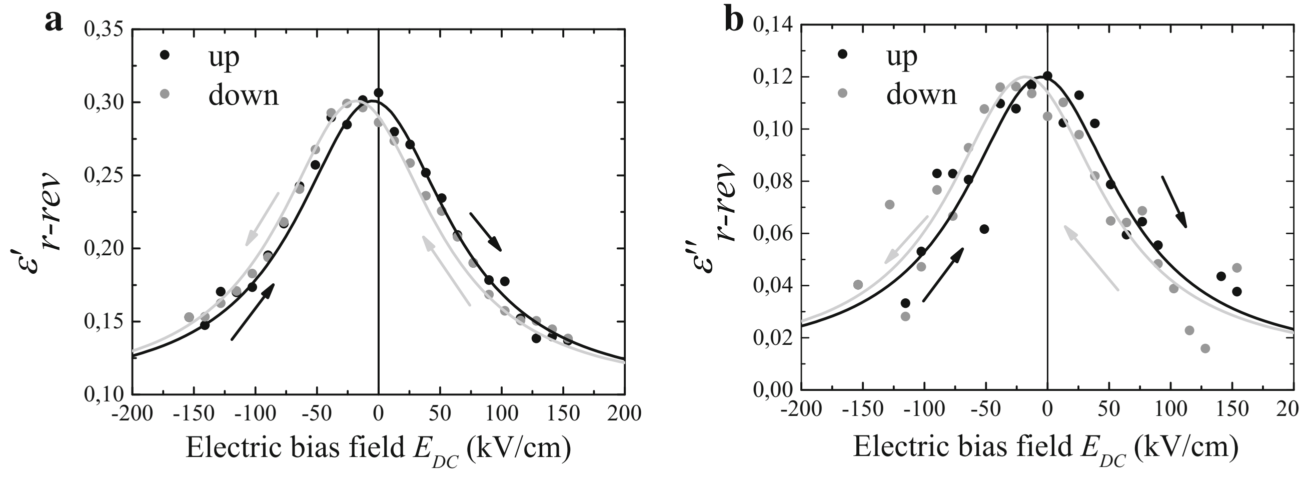

Fig. 5 **a** Real and **b** imaginary parts of domain wall vibration contribution as function of the applied DC electric field at 10 kHz, decomposed according to the hyperbolic law (Eq. 1) and fitted by the Lorentzian function (Eq. 2)

Due to the highly dissipative character of domain walls motions, domains interactions must be monitored in order to reduce dielectric losses. Indeed, previous works have shown that vibration and jump of walls contributed significantly to dielectric losses [4, 10]. However, evolution of this losses as function of the polarization states have not been investigated yet, which is of particular interest for optimizing $PbZrO_3$ operating range.

In order to know the contribution of the ferroelectric phase, the domain wall vibration parameter (ε_{r-rev}) is obtained, thanks to the hyperbolic law, for the real and imaginary parts of the permittivity (Fig. 5a and b). Contrary to the lattice contribution, the vibrational contribution shows a ferroelectric like behavior, as ε_{r-rev} decreases as function of E_{DC} and presents a butterfly loops with two peaks. The decrease of ε_{r-rev} is attributed to the coalescence of the ferroelectric domain walls when a bias field is applied [14] which leads to the reduction of the density of domain walls and of their interactions [15].

To obtain characteristic parameters, evolution of real and imaginary parts of ferroelectric domain walls contributions are described by a Lorentzian distribution, which is an appropriate function according to previous works on ferroelectric domain walls [15, 16]. The function is described as follows:

$$f(E_{DC}) = \frac{A_{max} - A_{\infty}}{1 + \left(\frac{E_{DC} - E_{int} \pm E_C}{w}\right)^2} + A_{\infty}, \tag{2}$$

where E_C is the coercive field of the residual ferroelectric phase, E_{DC} is the applied bias electric field,A_{max} is an amplitude factor corresponding to the maximum value of the permittivity, A_{∞} is the permittivity at an infinite applied electric field and w is the width at half maximum of the Lorentzian function. E_{int} is an internal field, which is due to the formation of a space charge layer at the interface between the platinum bottom electrode and lead zirconate thin films and it is attributed to the differences in the work functions between the top and the bottom electrodes [17]. Due to the multi-step deposition process of thin films at high temperature (650 °C), adsorption of oxygen atoms can occur at the interface between the platinum bottom electrode and lead zirconate thin films (formation of a space charge layer [18]), which induces a change of the platinum bottom electrode work function [19, 20]. In previous research [21], a similar behavior was observed in lead zirconate thin films deposited on platinum electrodes. This asymmetry can be seen in the current hysteresis (Fig. 2), where the weak ferroelectricity peak (around zero electric field) is slightly offset toward negative electric fields, and in the evolution of ε_{rl} where the two ferroelectric peaks are not symmetrical to zero (Fig. 4 a). E_{int} has been found equal to -11.5 kV/cm for all domain wall contributions.

The evolution of $\varepsilon_{r\text{-}rev}$ is then fitted with the Lorentzian function for the real and imaginary parts and the characteristic parameters are given in Table 1. These two contributions are weak compared to the overall permittivity (only 1%) and the data are noisy but the proposed fit describes well their evolution. Contrary to a ferroelectric material [13], the vibrational contribution does not tend to zero at infinite fields, which suggests that the ferroelectricity does not disappear completely. As $\varepsilon_{r\text{-}rev}$ is essentially proportional to the domain wall density [21], the difference between A'_{max} and A'_{∞} for $\varepsilon_{r\text{-}rev}$ suggests that 1/3 of the domain walls persists at high electric fields. A similarly observation has been done with First-Order Reversal Curves FORC measurements where the ferroelectric phase only disappears at the antiferroelectric-ferroelectric phase transition [22]. For the imaginary part, the ratio$\frac{A''_{\infty}}{A''_{max}}$ is only 8% and is lower than the ratio of the real part. This is due to a reduction of the domain wall interactions when the domain wall density decreases [13]. The residual domain walls at high field are less in interaction and created lower losses. This suggest that they are on ferroelectric clusters well distributed in the material as it has been already suggested in the literature [4, 22]. The vibrational dissipation factor ($m_{rev} = \varepsilon''_{r\text{-}rev}$ / $\varepsilon'_{r\text{-}rev}$) decreases from 0.40 to 0.10, between 0 and the infinite field, the last value corresponds to vibration of one domain wall without any interaction with the other.

Table 1 Characteristic parameters of the Lorentzian function fitting (Eq. 2) for the domain wall vibrations and pinning contributions

	Real part				Imaginary part			
	A'_{max}	A'_{∞}	w'	E_C'	A''_{max}	A''_{∞}	w''	E_C''
ε_{r-rev}	0.301	0.100	76	6.5	0.120	0.010	76	6.5
α_r(cm/kV)	0.109	0.027	87	6.5	0.038	0.007	77	6.5

The contributions of domain wall pinning (α_r) decomposed according to the hyperbolic law and fitted thanks to the Lorentzian function are shown in Fig. 6 and their characteristic parameters are given in Table 1. Pinning contribution of domain walls also shows a ferroelectric like behavior, as α_r decreases as function of E_{DC} and presents two peaks corresponding to a butterfly loop. As stated previously, this decrease is attributed to the reduction of domain walls density due to the coalescence of domains when a bias electric field is applied [14]. Fitting of the experimental data by the Lorentzian function (Table 1) indicates that the pinning contribution does not tend to zero at high applied fields due to a residual ferroelectricity which only switch at E_{AF} [22]. According to the reduction of the domain wall interactions due to the coalescence, between 0 and an infinite field, the pinning dissipation factor ($m_{\alpha} = \alpha_r''$/ α_r') decreases from 0.35 to 0.26, the last value corresponds to a jump of one domain wall without any interaction with the other. The coercive field is similar to the vibration contribution.

Thanks to the determination of the different contribution of the permittivity, evolution of weak ferroelectricity dielectric response is shown in Fig. 7. As mentioned previously, the highest contribution of the relative permittivity is from the lattice (99%), the contribution of ferroelectric domain walls decreases

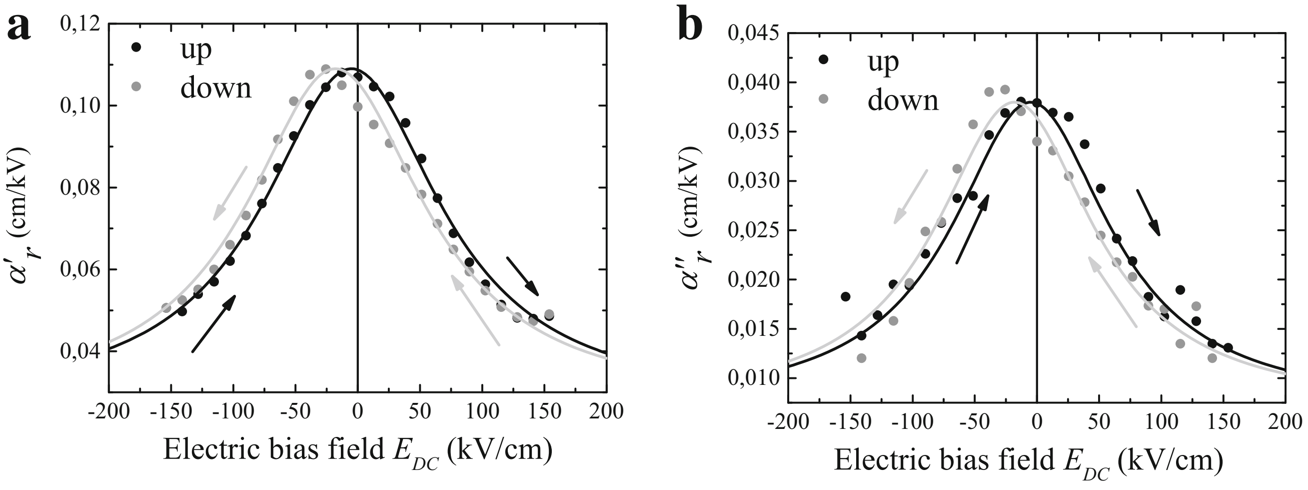

Fig. 6 **a** Real and **b** imaginary parts of domain walls pinning contribution as a function of the applied DC electric field at 10 kHz, decomposed according to the hyperbolic law (Eq. 1) and fitted by the Lorentzian function (Eq. 2)

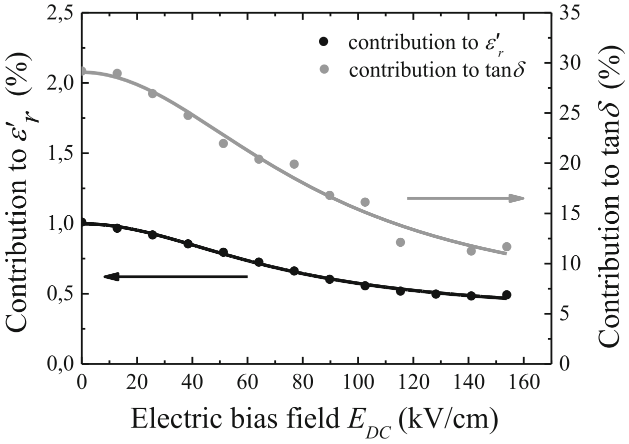

Fig. 7 Evolution of the ferroelectric domain walls contribution to the relative permittivity and to the dielectric losses fitted according to the Lorentzian function (Eq. 2)

according to a Lorentzian function from 1 to 0.5% between 0 and 150 kV/cm. Nevertheless, the contribution of ferroelctric domain walls movements is high in the overall dielectric losses despite a low participation in the permittivity. The contribution to dielectric losses decreases according to a Lorentzian function from 29 to 11% between 0 and 150 kV/cm. This result shows that by choosing the right operating range, dielectric losses can be significantly reduces, which is an important result for enhancing dielectric properties of lead zirconate thin films.

3 Conclusion

In this study, far from the antiferroelectric-ferroelectric field transition E_{AF} (in the weak ferroelectricity range ($E \leq 150$ kV/cm)) the ferroelectric domain wall contributions to the permittivity is investigated thanks to the hyperbolic law. This permits us to understand the weak ferroelectric contribution on the classical antiferroelectric *P-E* loops. The highest contribution to the permittivity is from the lattice, which presents two superposed phenomena. The lattice contribution increases as function of the polarization because the antiparallel dipoles are reoriented along the electric field direction. Two additional small peaks is also present at positive and negative fields, which correspond to a ferroelectric butterfly loop. The two phenomena (antiferroelectric and ferroelectric contributions) are added to the permittivity, which make it difficult to decorrelate them. The vibration and pinning/unpinning contributions of the domain walls present only a ferroelectric butterfly loops and decrease as function of the polarization. Contrary to a ferroelectric material, the domain wall contributions do not tend to zero at infinite fields, which suggests that the ferroelectricity does not disappear completely. These ferroelectric domain walls are important as they correspond to 29% of the overall dielectric losses but represent only 1% of the permittivity. Dielectric losses decrease as a function of the polarization (Lorentzian function) due to the reduction of the ferroelectric domain walls density.

Author contributions

MDC: Conceptualization, Methodology, Writing—review & editing. CB: Supervision, Visualization, Writing—review & editing. RR: Supervision, Visualization. HWG: Supervision, Visualization.

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Data availability

Data will be made available on reasonable request.

Declarations

Conflict of interest The authors have not disclosed any competing interests.

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