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1 Study of the long time relaxation of the weak ferroelectricity
2 in PbZrO_3 antiferroelectric thin film using Positive Up
3 Negative Down and First Order Reversal Curves
4 measurements

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10 **Abstract**

The weak ferroelectric contribution to the polarization of antiferroelectric lead zirconate (PZO) thin films has been investigated using PUND (Positive Up Negative Down) pulse measurements and hysteron decomposition by First Order Reversal Curves (FORC) technique. The PUND allows decomposing the measured current, obtained from the polarization-electric field loop measurements, into a switching and a non-switching contribution. We show that the weak ferroelectric phase is enhanced when a large electric field has been previously applied to the material, in order to switch from the antiferroelectric to the ferroelectric phase. Using the PUND measurement at fields below the antiferroelectric to ferroelectric phase transition, the polarization loop corresponding only to the ferroelectric switching contribution has been determined revealing that this contribution to the overall polarization is small. FORC measurements, however, indicate that the ferroelectric phase is present at different fields. At low fields, a quite homogeneous distribution of hysterons exists and at large field, a high concentration of hysterons at a field near to the antiferroelectric to ferroelectric phase transition can be seen. Moreover, when changing the delay between pulses of the PUND and the FORC measurements, we show that this weak ferroelectricity contribution is metastable and decreases with time.

11 *Keywords:* Anti-ferroelectric; Thin film; Residual ferroelectricity; Positive up negative

13 1. Introduction

14 Antiferroelectric materials present an important interest for energy storage applica-
15 tions [1–3] due to the double hysteresis in the polarization versus electric field loop.
16 When a high electric field is applied to an antiferroelectric material, a large increase of the
17 polarization is obtained at the antiferroelectric (AFE) to ferroelectric (FE) phase transition,
18 which permits a much higher stored energy compared to the case of linear dielectrics or
19 relaxor ferroelectrics like $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ [4]. Compared to hard fer-
20 roelectrics (PbZrTiO_3) a better efficiency due to a considerably larger released energy
21 can be obtained. In antiferroelectric materials, however, a residual ferroelectric contri-
22 bution, called weak ferroelectricity, may be present which increases the overall material's
23 losses. This has been largely mentioned in the literature and widely studied using various
24 methods such as low field hysteresis measurement [5–7] or impedance spectroscopy [8–
25 10]. Understanding the influence of the residual ferroelectric phase of antiferroelectrics
26 is mandatory in order to increase the stored energy and the efficiency of the AFE energy
27 storage devices.

28 Pulse switching of ferroelectric materials has been described by Merz [11] in the fifties
29 of the last century, especially in order to show the stable or not stable partial switching
30 behavior of those materials. Also called PUND (Positive Up Negative Down) method [3,
31 12–14], and when applied to antiferroelectrics, this technique allows detecting a possible
32 residual ferroelectric phase in the AFE material.

33 An initial pulse (here of negative polarity, rectangular, trapezoidal or triangular) is
34 applied in order to switch all existing ferroelectric domains in a given direction (Fig. 1a).
35 Then, two pulses of opposite polarity (P and U, here positive) are successively applied

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36 and finally, the application of the pulses N and D, again of opposite polarity (here nega-
37 tive) allows obtaining the full hysteresis cycle. The current signal of the respective pulses
38 is recorded.

39 In the case of the pulses P and N (so-called switching pulses), the measured current
40 is the sum of the contributions (i) leakage current, (ii) capacitive charging, (iii) possible
41 ferroelectric phase switching as the previous pulse was of opposite polarity, and (iv) po-
42 larization changes for fields higher than the AFE-FE phase transition field. In the case
43 of a purely capacitive behavior, a triangular applied voltage should result in a constant
44 current: positive if the voltage is increasing and negative if the voltage is decreasing. A
45 deviation of this behavior indicates a polarization change at this particular field, which
46 may include FE switching and AFE-FE phase transition depending on the field ampli-
47 tude. The example of the current signals obtained for fields below the AFE-FE transition
48 and for a small residual ferroelectric phase in the AFE material is shown in Fig. 1b, which
49 can be used for representing the obtained global $I(E)$ cycle (Fig. 1c). For the pulses U
50 and D (non switching pulses), no FE phase switching should occur as already switched
51 by the previous pulses of the same polarity, and hence the current is the sum of only the
52 three other contributions. By subtracting the non switching currents from the switching
53 currents ($i_P - i_U$ and $i_N - i_D$), it is possible to extract the pure switching contribution for
54 both polarities to compute the respective $I(E)$ loop (Fig. 1d).

55 In order to obtain a sufficient signal to noise ratio, the switching contribution needs
56 to be high as compared to the capacitive and the leakage contributions. Otherwise, some
57 current subtraction prior to the amplification and acquisition can be used [15]. This
58 method has been widely used for ferroelectric materials in order to remove excessive
59 capacitive and leakage contributions and to study the switching times of the different
60 contribution to the polarization [3, 12–16] To the best of our knowledge, however, it has
61 never been used for studying the weak ferroelectricity in antiferroelectrics.

62 Ferroelectric materials can also be investigated by First Order Reversal Curves (FORC)
63 measurements which permit the decomposition of the $P(E)$ loop into elementary hystere-
64 sis contributions called hysterons [13, 17–20]. This method also gives information on the

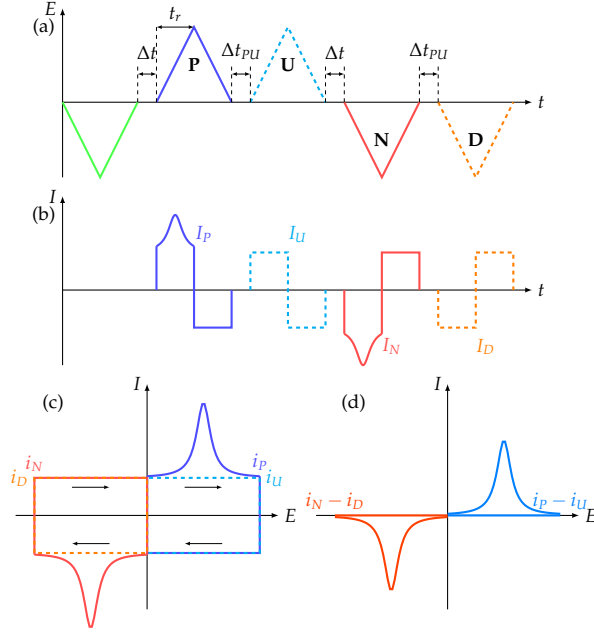


Figure 1: Applied PUND signal (a) and measured current (b), as function of time for fields below the AFE-FE transition. Global $I(E)$ cycle (c) and $I(E)$ cycle of only the ferroelectric switching contribution (d). t_r is the raise time of the pulse and Δt the delay between the orientation pulse and the PUND measurement, and Δt_{PU} the delay between the pulses P and U as well as N and D. Arrows indicates the sense of the cycle.

65 degradation of the material and the presence of a possible residual ferroelectric phase
 66 in AFE materials which otherwise is difficult to see from the $P(E)$ loops [8, 18, 21–23].
 67 The standard implementation of this method is to vary the electric field from one satu-
 68 ration state to another[18–20] but it is also possible to use a bipolar waveform with an
 69 increasing amplitude[8, 24]. The advantage of the bipolar waveform approach is the ex-
 70 isting delay between the different pulses allowing to investigate temporal relaxation of
 71 the switching processes which can reach several tens of second in ferroelectric [25] and
 72 in antiferroelectric [26, 27] materials.

73 In this paper, the complementary PUND and FORC measurements are used in order
 74 to obtain a better understanding of the weak ferroelectricity in antiferroelectric PbZrO_3 ,
 75 visible at low fields and to study especially its temporal relaxation and the dependence
 76 on the applied electric field amplitude. In the first part, conventional $P(E)$ -loops (at low
 77 and large fields) are used in order to show the weak ferroelectric phase enhancement
 78 in the material after the realization of a $P(E)$ major loop. The ferroelectric switching

79 contribution to the polarization is studied by PUND measurements, for different ampli-
80 tudes of the electric field and with different delay time between the pulses, in the second
81 and third part, respectively. Using these measurements, the $P(E)$ loop of the switching
82 contribution has been extracted in order to see the effect of amplitude and delay and to
83 study the evolution of the antiferroelectric-ferroelectric transition fields. In the last part,
84 FORC measurements are presented in order to gain better understanding of the phenom-
85 ena that appear at low and high fields, and to correlate them to the results of the PUND
86 measurements.

87 2. Experiments

88 Antiferroelectric lead zirconate (PbZrO_3) thin films are prepared by a sol-gel process
89 using multi-step spin coating[1, 8, 9]. Firstly, lead acetate trihydrate [$\text{Pb}(\text{CH}_3\text{CO}_2)_2 \cdot 3 \text{H}_2\text{O}$]
90 is dissolved in de-ionized water and acetic acid. Zirconium isopropoxide [$\text{Zr}(\text{O}(\text{CH}_2)_2\text{CH}_3)_4$]
91 is then added in the solution, as well as ethylene glycol [$\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$] used
92 for reducing the appearance of micro-cracks[28] in the films and improves the solution
93 stability[29]. The solution has been deposited on alumina substrates precoated with a
94 titanium and platinum layers in order to form the bottom electrode. Twelve layers re-
95 sult in an overall film thickness of 800 nm. Square platinum electrodes of 0.1 mm width
96 are deposited by RF magnetron sputtering in order to realize a Metal-Insulator-Metal
97 (MIM) capacitor and to allow the dielectric characterizations of the fabricated thin films.
98 Structural characterizations reveal the studied thin film presents the (100) and (111) crys-
99 tallographic orientations [1] and presents a columnar structure [8, 30].

100 The electric measurements have been performed with an AixACCT TF2000 ferroelec-
101 tric analyzer. The conventional $P(E)$ loops, presented in the first part, have been mea-
102 sured using a sine waveform and the applied voltage has been varied from 2 V to 40 V
103 with a step of 2 V. The AFE-FE transition fields correspond to the maxima of the re-
104 spective current waveforms. In the case of the PUND pulse measurements, a triangular
105 waveform with a voltage sweep from 10 V to 70 V, corresponding to an electric field from
106 125 kV cm^{-1} to 875 kV cm^{-1} , and a step of 10 V have been applied, with the sequence de-

107 scribed Fig. 1. The delay between the pulses Δt has been varied from 1 μs to 1000 s and
108 the duration of the pulses $2t_r$ has been adjusted for a constant slew rate of 4 V ms^{-1} . For
109 the construction of the $P(E)$ loops of the pure switching contribution, the non-switching
110 current is subtracted from the switching current signal and integration as a function of
111 time to obtain the polarization.

112 The waveform used for the FORC measurements correspond is similar to this PUND
113 method, except that only the switching pulses P and N are applied. The delay between
114 the positive and negative pulses has been varied from 1 μs to 1000 s and the duration of
115 the pulse slew rate has been kept constant. The FORC distribution extraction method is
116 presented elsewhere [8, 24]. The applied voltage has been swept from 2 V to 70 V with
117 a step of 2 V corresponding to an electric field varying from 25 kV cm^{-1} to 875 kV cm^{-1} .
118 Reduction of the step voltage permits increasing of FORC distribution resolution and
119 hence to better discern the residual ferroelectric phase.

120 3. Results and discussions

121 In the first part, conventional $P(E)$ loops are presented in order to show the current
122 peaks associated to the weak ferroelectricity in the studied PZO thin films. In the second
123 and third parts, a precise characterization of this weak ferroelectricity has been done
124 using the PUND method by varying respectively the electric field amplitude and the
125 delay between pulses. Each time, the PUND measurements are presented separately for
126 low and high fields. Finally, the FORC measurements are used in order to show the effect
127 of the delay between pulses on the high field ferroelectric contribution.

128 3.1. Large field $P(E)$ loops

129 The polarization has been measured as a function of voltage with an amplitude swept
130 from 2 V to 70 V with a step of 2 V, corresponding to an electric field of 25 kV cm^{-1} and
131 875 kV cm^{-1} applied to the 800 nm thick sample.

132 The polarization versus electric field loops obtained from a virgin sample are shown
133 in Fig. 2a. The typical double hysteresis of an antiferroelectric material is well visible.
134 The maximum value of polarization is 26 $\mu\text{C cm}^{-2}$ which is close to the value reported

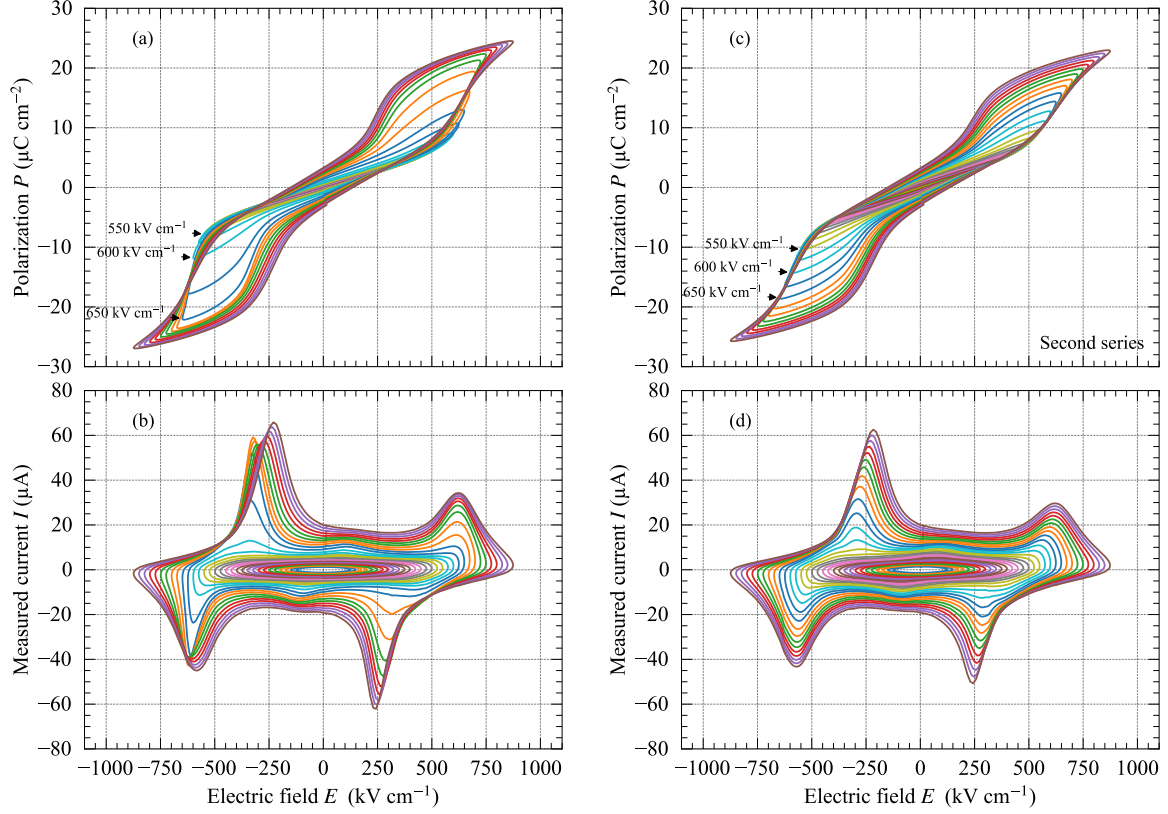


Figure 2: $P(E)$ loops of the first (a) and second (b) series of cycles and corresponding current of the first (c) and second (d) series.

135 for PZO thin films [31]. The antiferroelectric to ferroelectric and ferroelectric to antiferro-
 136 electric transition fields are respectively $E_{AF}^+ = 628 \text{ kV cm}^{-1}$ and $E_{FA}^+ = 244 \text{ kV cm}^{-1}$ for
 137 the positive and $E_{AF}^- = -580 \text{ kV cm}^{-1}$ and $E_{FA}^- = -229 \text{ kV cm}^{-1}$ for the negative polarity.
 138 In the case of this first measurement, the significant increase of the polarization is visible
 139 at field above $\pm 575 \text{ kV cm}^{-1}$, indicating the onset of a rapid antiferroelectric to ferroelec-
 140 tric phase transition. The current loops corresponding to these first applied electric fields
 141 cycles are shown Fig. 2c When repeating the measurement for a second time, similar val-
 142 ues of the maximum polarization and transition fields are obtained (Fig. 2b), however,
 143 the curves are more regularly spaced and the sharp increase of the polarization at driv-
 144 ing fields between 575 kV cm^{-1} and 650 kV cm^{-1} is not visible (Fig. 2d). This difference
 145 is attributed to the enhanced weak ferroelectricity and will be detailed below, discussing

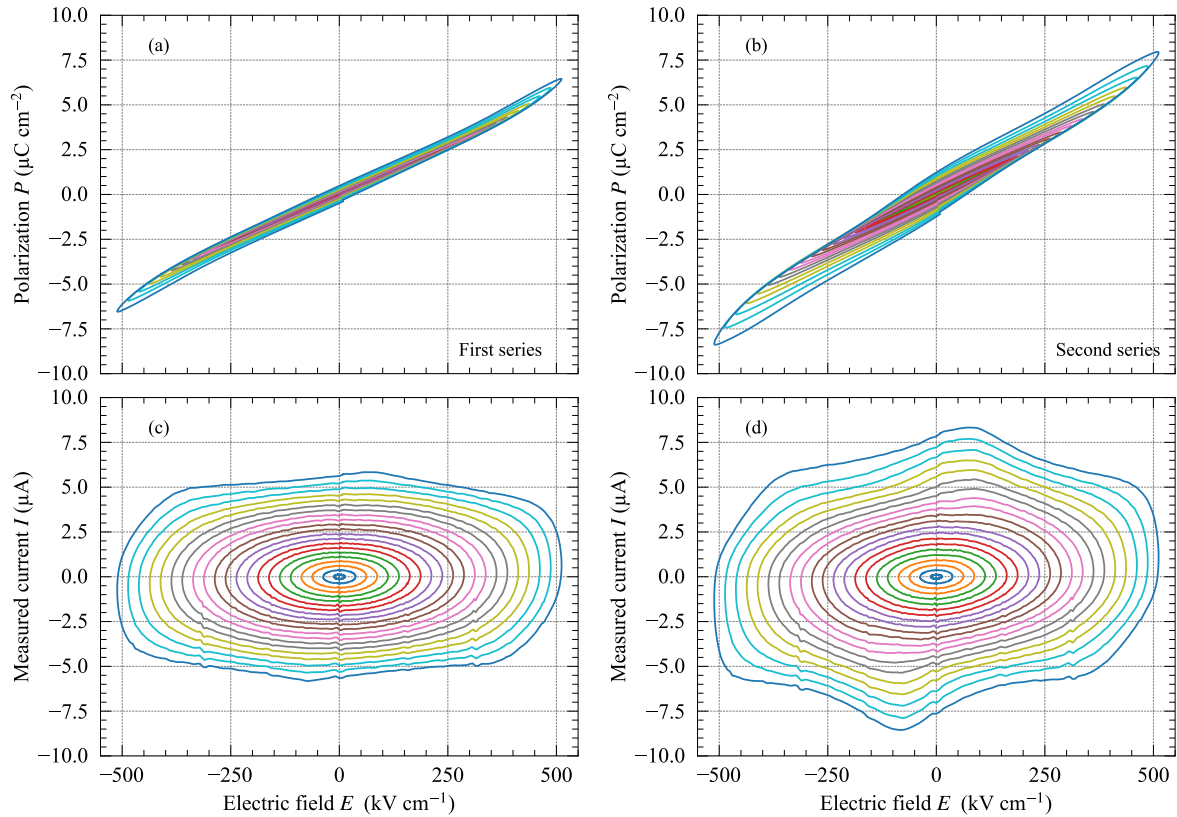


Figure 3: Polarization (a)(b) and current (c)(d) for the first series of measurement (a)(c) and for the second series of measurement, after a major loop with a driving field amplitude of 875 kV cm^{-1} (b)(d).

146 the low field $P(E)$ -loops.

147 3.2. Low fields $P(E)$ -loops

148 The polarization and current loops of Fig. 2 for electric fields below 500 kV cm^{-1} are
 149 shown in Fig. 3a and 3c for the first applied cycles (i.e. new sample) and in Fig. 3b
 150 and 3d for the second cycles (i.e. after the exposition of the sample to the maximum
 151 electric field of 875 kV cm^{-1}). At low electric fields, and especially for the first applied
 152 cycles (Fig. 3c), the current describes an ellipse with the principal axis near to the x -
 153 axis, which is typical for a capacitive behavior when using a sinewave excitation and
 154 indicates a low leakage current. In the case of the cycles after a major loop with a driving
 155 field amplitude of 875 kV cm^{-1} had been applied, a more open $P(E)$ loop, (Fig. 3b) and a
 156 current peak at $\pm 100 \text{ kV cm}^{-1}$ (3d) are observed, less visible but already existing for the

157 first cycles. This current peak is attributed to the weak ferroelectric contribution [5–7] in
158 the AFE thin film. This indicates that the ferroelectricity is present into the material, even
159 before the application of the large electric field of 875 kV cm^{-1} and is largely enhanced
160 by the application of a large electric field. The opening of the $P(E)$ -loops in the case of
161 the second series indicates higher losses, which can be attributed to the more important
162 switching contribution.

163 For certain compounds of PZO-based antiferroelectric materials [32–36], the whole
164 material stays in the ferroelectric phase when the electric field applied during the initial
165 AFE-FE phase transition is released, and the transition is hence irreversible. In our case,
166 the phase transition is reversible and the major part of material goes back to the antiferro-
167 electric phase, giving rise to the typical double hysteresis loop. One part of the material,
168 however, stays in the ferroelectric phase thus enhancing the weak ferroelectricity.

169 One can note that the weak ferroelectricity is only visible around $E = \pm 100 \text{ kV cm}^{-1}$
170 if a larger electric field is applied during the cycle. This suggests that the weak ferro-
171 electricity switching depends on the electric field amplitude previously applied and has
172 a time relaxation.

173 In order to better study the influence of the weak ferroelectric contribution to the
174 overall properties, the PUND method has been used which allow separating the switch-
175 ing and the non-switching contributions. To begin with (section 3.3), the measurements
176 have been done for different electric field amplitudes and a given delay between pulses
177 to determine the minimum electric field necessary to enhance the weak ferroelectricity.
178 After that, the delay between the pulses has been varied in order to discern stable and
179 unstable ferroelectric switching (section 3.4).

180 3.3. PUND measurement with fixed delay between pulses

181 To begin with, the delay Δt between the negative orientation pulse and the PUND
182 measurements as well as the delay Δt_{PU} between the PUND pulses has been set to $250 \mu\text{s}$.
183 The measured current is plotted as a function of the electric field for fields below the AFE-
184 FE phase transition field ($E_{max} \leq 500 \text{ kV cm}^{-1}$) and for fields above ($E_{max} > 500 \text{ kV cm}^{-1}$)

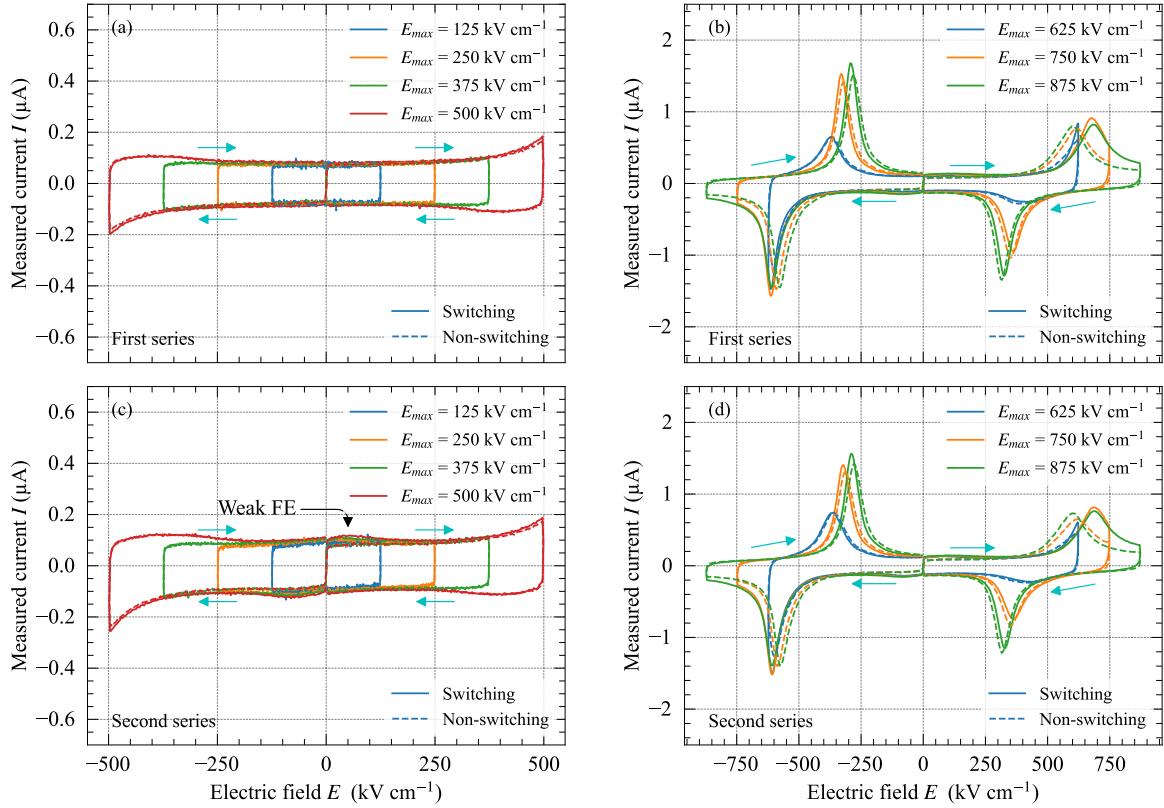


Figure 4: PUND current measurements as a function of the applied electric field of the first series (a),(b) and of the second series (c),(d). For fields below (a),(c) and above (b),(d) the AFE-FE phase transition. The switching pulses are shown in full line and the non-switching pulses in dashed lines.

185 in Figs 4a and 4c and Figs. 4b and 4d, respectively.

186 Below the AFE-FE phase transition and in the case of the first series of applied fields,
 187 no notable difference between the switching and the non switching current is visible
 188 (Fig. 4a) suggesting that switching of the residual ferroelectric phase does not occur. At
 189 electric fields above the AFE-FE phase transition (Fig. 4b), the switching current exceeds
 190 the non switching current, well visible for the highest applied fields. In the case of the
 191 second series, even below the phase transition, a small difference between the switching
 192 and the non switching current appears, visible around $\pm 100 \text{ kV cm}^{-1}$ (Fig. 4c). The broad
 193 current peak indicates that there does not exist a sharp but a rather distributed coercive
 194 field.

195 For fields above the AFE-FE transition, switching of the ferroelectric residual phase

196 is hardly visible due to the much more important amplitude of the phase transition cur-
 197 rent. There is no significant difference between the first and the second measurement
 198 series since, for field above the AFE-FE transition, the sample has already been exposed
 199 to a large field and changes the phase structure of the material (a part of the material stays
 200 in the ferroelectric phase). For both series, the maximum of the phase transition current
 201 appears at higher fields for the switching pulses, particularly well visible in the case of
 202 the positive pulses P and U (after initial orientation by application of a negative pulse).
 203 The shift of the current maximum is 100 kV cm^{-1} (from 700 kV cm^{-1} to 600 kV cm^{-1}) for
 204 the E_{AF}^+ field and 35 kV cm^{-1} for the E_{AF}^- field while small for the ferroelectric to antiferro-
 205 electric transitions E_{FA}^+ (below 10 kV cm^{-1}). The antiferroelectric to ferroelectric transition
 206 hence seems to depend on the initial polarization orientation of the material, which cor-
 207 respond to a memory effect in antiferroelectric materials [37]. The residual ferroelectric
 208 cells that switch below the antiferroelectric to ferroelectric transition [8] may also influ-
 209 ence and thus lower the transition field when initially orientated favorably.

210 3.4. Influence of the delay between the pulses of the PUND measurement

211 In the previous section, the delay between pulses has been kept constant ($250 \mu\text{s}$). The
 212 delay between the initial orientation pulse and the PUND measurement pulses however
 213 influences the switching behavior. We have hence varied this delay from $1 \mu\text{s}$ to 1000 s
 214 using a homogeneous repartition in the logarithmic scale. All measurements presented
 215 in this section have been performed on an enhanced ferroelectric behavior sample that
 216 has already been exposed to an electric field of 875 kV cm^{-1} . As before, we study (i)
 217 ferroelectric switching at low fields and (ii) the AFE-FE transition at high fields.

218 3.4.1. Low field measurements

219 The full switching and non switching current waveforms for different delay are shown
 220 in Fig. 5a and 5b, respectively for a field of 500 kV cm^{-1} . The non switching current
 221 almost does not depend on the delay Δt_{PU} between the pulses P and U, although it is
 222 possible to subtract the non-switching from the switching current in order to amplify the
 223 difference.

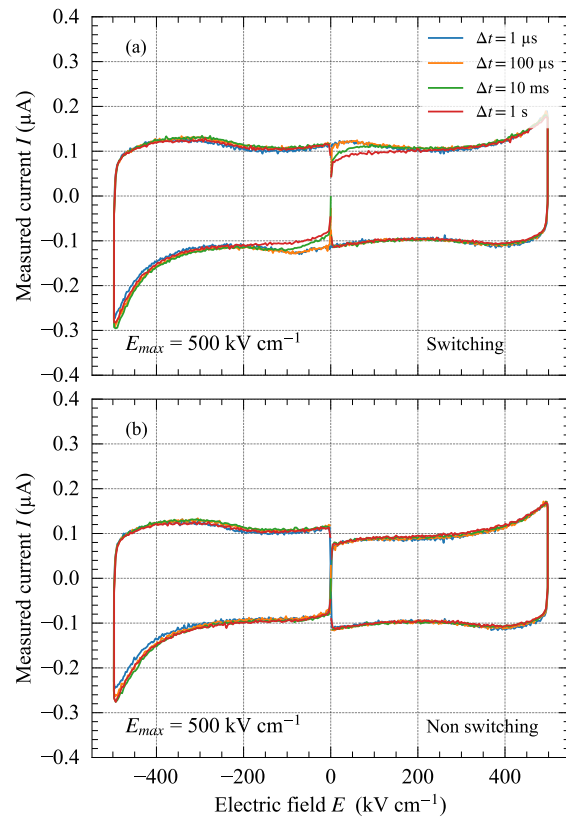


Figure 5: Measured switching current (a) and non switching current (b), at 500 kV cm^{-1} , for various delay Δt_{PU} between the pulses P and U as well as N and D of the PUND measurement.

224 The differential current waveforms for various delay times Δt between the initial ori-
225 entation pulse and the PUND measurement pulses and for different applied field are
226 shown in Fig. 6. As the delay between the orientation pulse and the PUND measure-
227 ment evolves, the differential current signal changes, showing that the orientation of the
228 residual ferroelectric phase is not stable. Independent of the applied field, a maximum
229 of polarization switching is obtained for delay times $\Delta t \leq 100 \mu\text{s}$. As the delay is getting
230 longer, the differential switching current signal decreases, indicating a partial relaxation
231 of the initial domain orientation. For delay times longer than 100 s, the differential current
232 signal disappears. This indicates that the influence of the negative orientation pulse prior
233 to the PUND measurements has become negligible and that the ferroelectric domains are
234 completely relaxed. A similar behavior has been observed for all applied electric fields.

235 Integration with time of the differential current waveform signals allows obtaining
236 the $P(E)$ loop of the residual ferroelectric phase which is shown in Fig. 7a for a driving
237 field amplitude of 500 kV cm^{-1} and for different delay times Δt . The straight horizontal
238 lines of the $P(E)$ cycles when the applied field decreases to zero are typical for corrected
239 PUND loops[12, 14].

240 The maximum value of the weak ferroelectric contribution $P = 0.7 \mu\text{C cm}^{-2}$ for a field
241 $E_{max} = 500 \text{ kV cm}^{-1}$ is very small compared to the typical values of polarization for fer-
242 roelectric or antiferroelectric materials. In accordance to the broad current peaks of Fig. 6,
243 a rather wide distribution of the coercive field (with a mean value around 150 kV cm^{-1})
244 has been found, confirming the poly-crystalline structure of the thin film.

245 The difference between the maximum and the minimum polarization, ΔP_m has been
246 calculated for each delay time between pulses and is reported on Fig. 7b, showing that the
247 switched polarization depends on the delay between the orientation pulse and the PUND
248 measurement. At shortest delay times Δt , the switched polarization slightly increases
249 and achieves a maximum value for several tens of microseconds. Complete switching of
250 the residual ferroelectric phase hence can be supposed at the maxima of the respective
251 polarization versus delay curves of Fig. 7b. For further increasing delay, however, the
252 switched polarization ΔP_m decreases and tends to zero at delay times of the order of

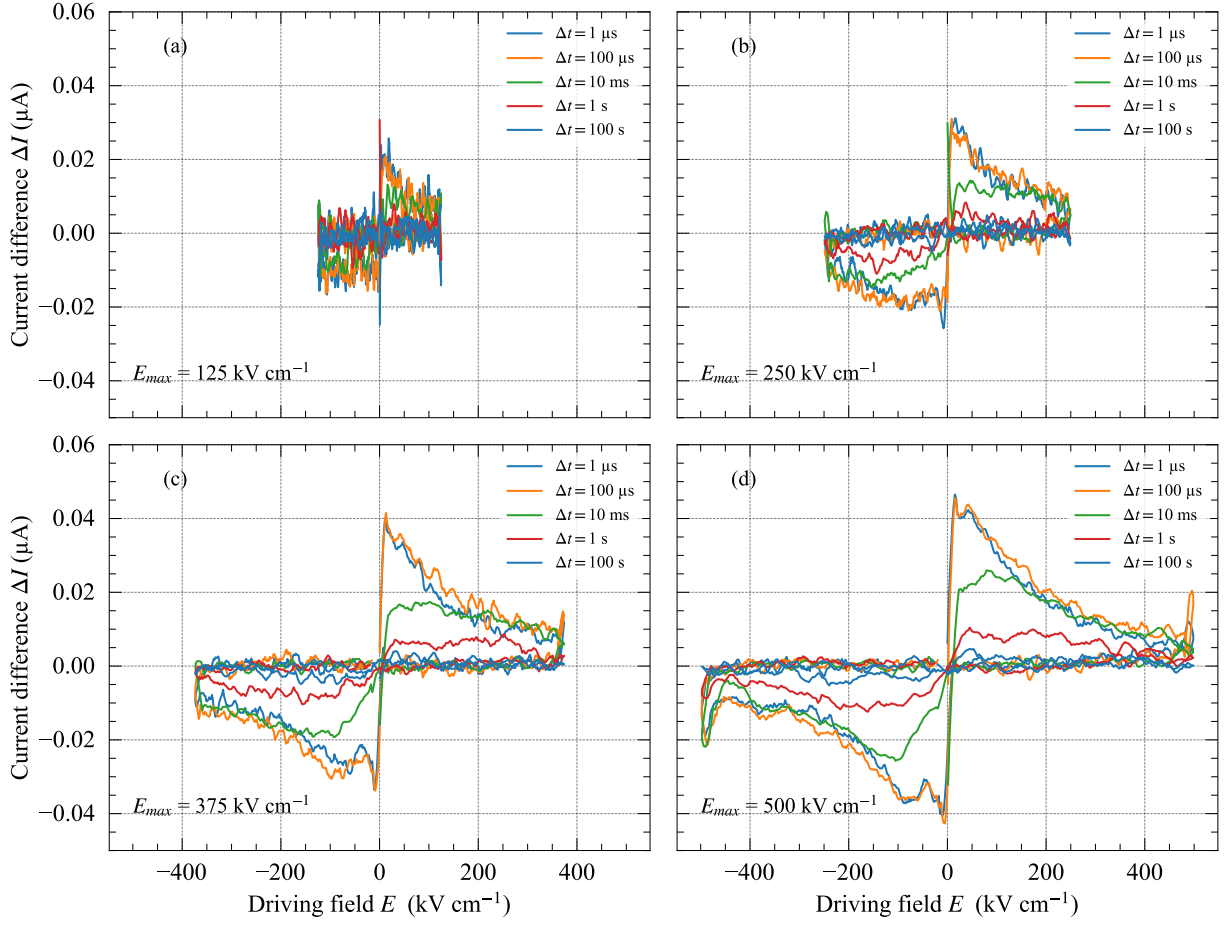


Figure 6: Differential current waveforms $I_{\text{SW}} - I_{\text{NS}}$ for different applied fields and various delay times Δt between the negative orientation pulse and the PUND measurements.

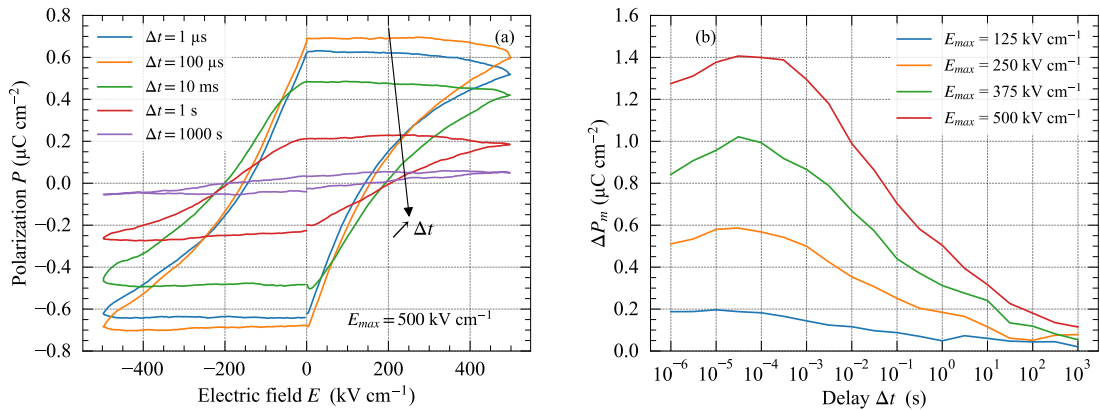


Figure 7: Reconstructed $P(E)$ loops concerning only the switching contribution for difference value of the delay between pulses and for a maximum electric field of 500 kV cm^{-1} (a). Difference between maximum and minimum polarization as a function of the delay between pulses for the reconstructed $P(E)$ loops (b).

253 several seconds, indicating that the orientation of the weak ferroelectricity is not stable.
254 The existence of small ferroelectric clusters in antiferroelectric materials has been shown
255 previously[8, 9], the dimension of those ferroelectric domains however seems to be too
256 small in order to allow self-maintaining of oriented polarization. The mean coercive field
257 value increases with increasing delay Δt indicating that the ferroelectric cells which do
258 not go back to the antiferroelectric phase need a higher electric field to switch. The poly-
259 crystalline structure of the film and the small grain size create different local clamping
260 conditions for each ferroelectric cluster. Each ferroelectric cluster thus has a different
261 polar orientation with respect to the electric field and surrounding environment implying
262 a distribution of coercive field and delay to go back to the antiferroelectric phase.

263 3.4.2. High field measurements

264 The current as a function of an applied electric field above 625 kV cm^{-1} is shown in
265 Fig. 8 for various delay times between the orientation pulse and the PUND measurement.
266 While successive application of the two positive P and U pulses should result in an iden-
267 tical phase transition current, it can be more particularly noticed that the phase transition
268 field E_{AF}^+ is approximately 100 kV cm^{-1} higher for the P-pulse (switching pulse), espe-
269 cially when the delay time Δt is short (Fig. 8a). This difference decreases with increasing
270 delay Δt and disappears at longest delay times (Fig. 8d). Only a much smaller difference
271 (around 30 kV cm^{-1}) of the phase transition field E_{AF}^- between the respective N and D
272 pulse is observed. The ferroelectric to antiferroelectric relaxation (field E_{AF}^-) seems not to
273 be affected, neither by the type of pulse (switching or non-switching) nor by the delay Δt .

274 As shown in Fig. 7, switching of the residual ferroelectric phase at low fields is visible.
275 The electric field amplitude does not increase the low field switching current, indicating
276 that the ferroelectric phase can be fully orientated already by the fields employed for the
277 low field measurements. As already seen before, increasing of the delay time Δt leads to
278 less switching of the residual ferroelectric phase.

279 For a better visibility, the phase transition fields E_{AF} and E_{FA} have been extracted for
280 each delay Δt and are reported Fig. 9. For a delay times between pulses between up to

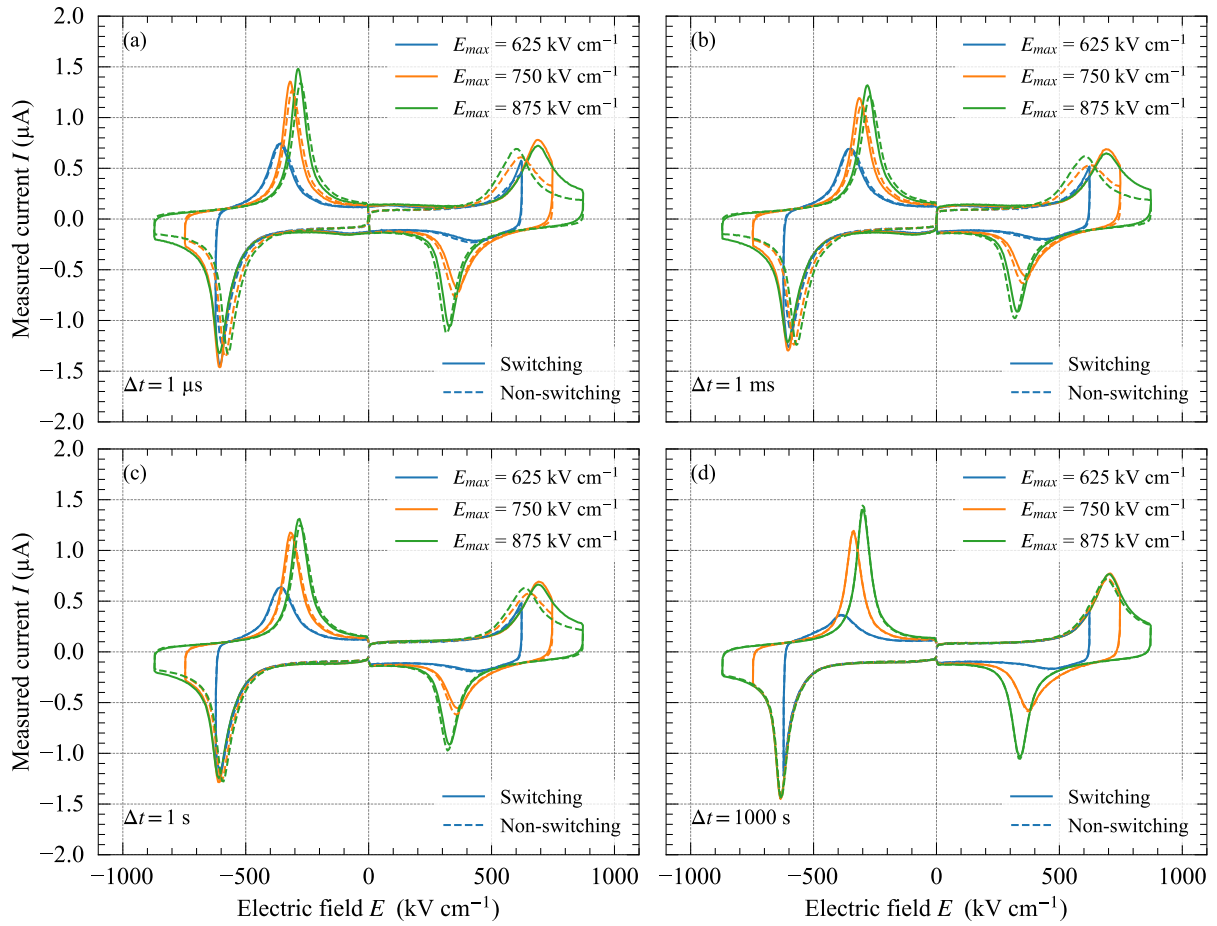


Figure 8: Measured current as a function of the applied electric field for the PUND measurement for various delay times between pulses, for electric field above 625 kV cm^{-1} . Switching pulses are in full line and non-switching pulses are in dashed lines.

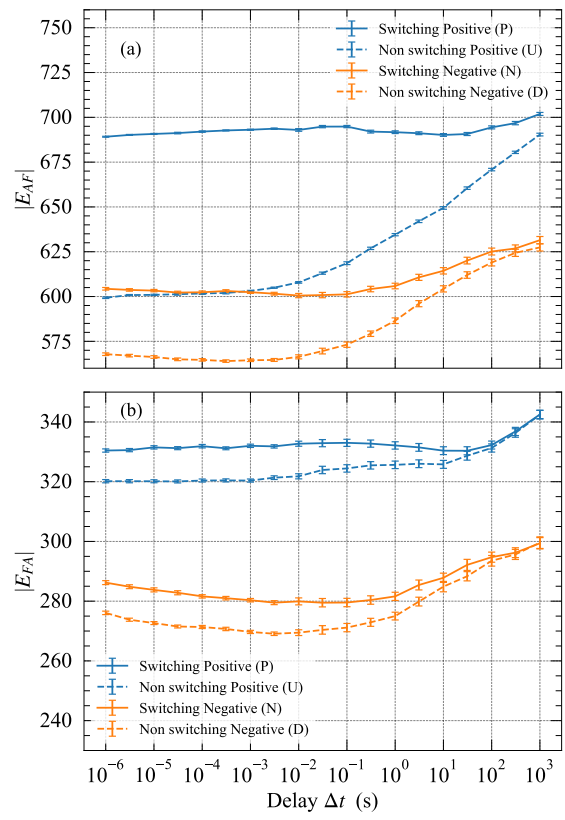


Figure 9: AFE-FE (a) and FE-AFE (b) transition fields as a function of the delay Δt for switching and non-switching pulses of positive and negative polarity obtained by PUND measurement.

281 several milliseconds, the transition fields are rather constant and the difference between
282 switching and non-switching is well visible, with an antiferroelectric to ferroelectric tran-
283 sition field which is 90 kV cm^{-1} higher for the positive pulse and 35 kV cm^{-1} higher for
284 the negative pulse. The difference of the ferroelectric to antiferroelectric transition fields
285 is much smaller (about 10 kV cm^{-1}) and does not depend on the polarity of the pulses.
286 An asymmetry of the switching and non-switching transition fields has already been re-
287 ported for $\text{Pb}_{0.99}\text{Nb}_{0.02}[(\text{Zr}_{0.6}\text{Sn}_{0.4})_{0.95}\text{Ti}_{0.05}]_{0.98}\text{O}_3$ ceramics [37]. In the present case, the
288 observed asymmetry also may come from the asymmetry of the sample, i.e. the number
289 of annealing steps for each layer. The last layer has been annealed only one time whereas
290 the first one has been annealed twelve times and the following layers have a successively
291 decreasing number of heat treatments. Annealing in air atmosphere may create oxygen
292 vacancies in the structure which are known to be responsible of imprint and internal bias
293 for ferroelectric materials [38, 39].

294 For a delay between pulses above several milliseconds, the difference between the
295 switching and the non-switching transition field progressively weakens due to an in-
296 crease of the non-switching field, while the switching field rather remains constant. Sim-
297 ilar to what has been observed for the switching of the weak ferroelectric phase, the
298 transition between the antiferroelectric and the ferroelectric phase is influenced by the
299 delay time Δt , too. Switching of the residual ferroelectric phase seems to lower the AFE-
300 FE transition field for the successively applied pulse of the same polarity as long as the
301 delay Δt is sufficiently short to maintain the orientation of the weak ferroelectricity. The
302 AFE-FE transition is hence favored by the previous orientation of the residual ferroelec-
303 tric phase. The influence of the delay Δt on the ferroelectric to antiferroelectric relaxation
304 electric field is similar but less pronounced since switching of the ferroelectric phase al-
305 ready has been established by the first pulse (switching-pulse). The internal fields hence are
306 less modified, also limiting the change of the AFE-FE relaxation electric field.

307 3.5. FORC measurement

308 In order to further study the ferroelectric contribution into the PZO thin film, FORC
309 measurements with increasing delay time between the positive and the negative pulse
310 have been done. The FORC distributions for various delay between the pulses are shown
311 Fig. 10, the $P(E)$ loops which were used for the FORC extraction are given in the supple-
312 mentary material. The two peaks visible at $(E; E_r) = (-350 \text{ kV cm}^{-1}; -650 \text{ kV cm}^{-1})$ and
313 $(700 \text{ kV cm}^{-1}; 350 \text{ kV cm}^{-1})$ correspond to the antiferroelectric-ferroelectric transitions.
314 When the delay between pulses changes, the peaks keep its position and the respective
315 intensity is only slightly affected. The width of the peaks is due to the distribution of the
316 transitions fields.

317 Further to the phase transition peaks, an additional ferroelectric contribution is visible
318 in the bottom-right corner of the FORC distribution at the position $(E; E_r) = (700 \text{ kV cm}^{-1};$
319 $-650 \text{ kV cm}^{-1})$, highlighted by the red arrow. This ferroelectric contribution can not be
320 discerned by the high field PUND measurements because the switching current peaks
321 occur for the same field than the antiferroelectric to ferroelectric transitions: for positive
322 fields, the ferroelectric phase switches at $E^+ = 700 \text{ kV cm}^{-1}$, same field than E_{AF}^+ and
323 for negative field, it switches at $E^- = -650 \text{ kV cm}^{-1}$ same field than E_{AF}^- . Switching
324 of this ferroelectric phase is correlated to the antiferroelectric phase transition [8] since
325 the field values correspond to the sharp increases of the polarization which occurs for
326 the first measurement series (See section 3.1 Large field $P(E)$ loops) and which is related
327 to the irreversible antiferroelectric to ferroelectric transition. As the delay time between
328 the pulses increases, the position of this ferroelectric contribution remains unchanged,
329 the magnitude of the peaks, however, decreases and finally disappears, indicating relax-
330 ation with time of this contribution. This is consistent to what has been found from the
331 high field PUND measurements and indicates that the difference between switching and
332 non-switching transition fields is influenced by this high field ferroelectric contribution.
333 The very sensitive FORC measurement technique allows evidencing this contribution al-
334 though not visible from the $P(E)$ loop.

335 A more subtle evolution in the FORC distribution in area around the $E_r = -E$ axis

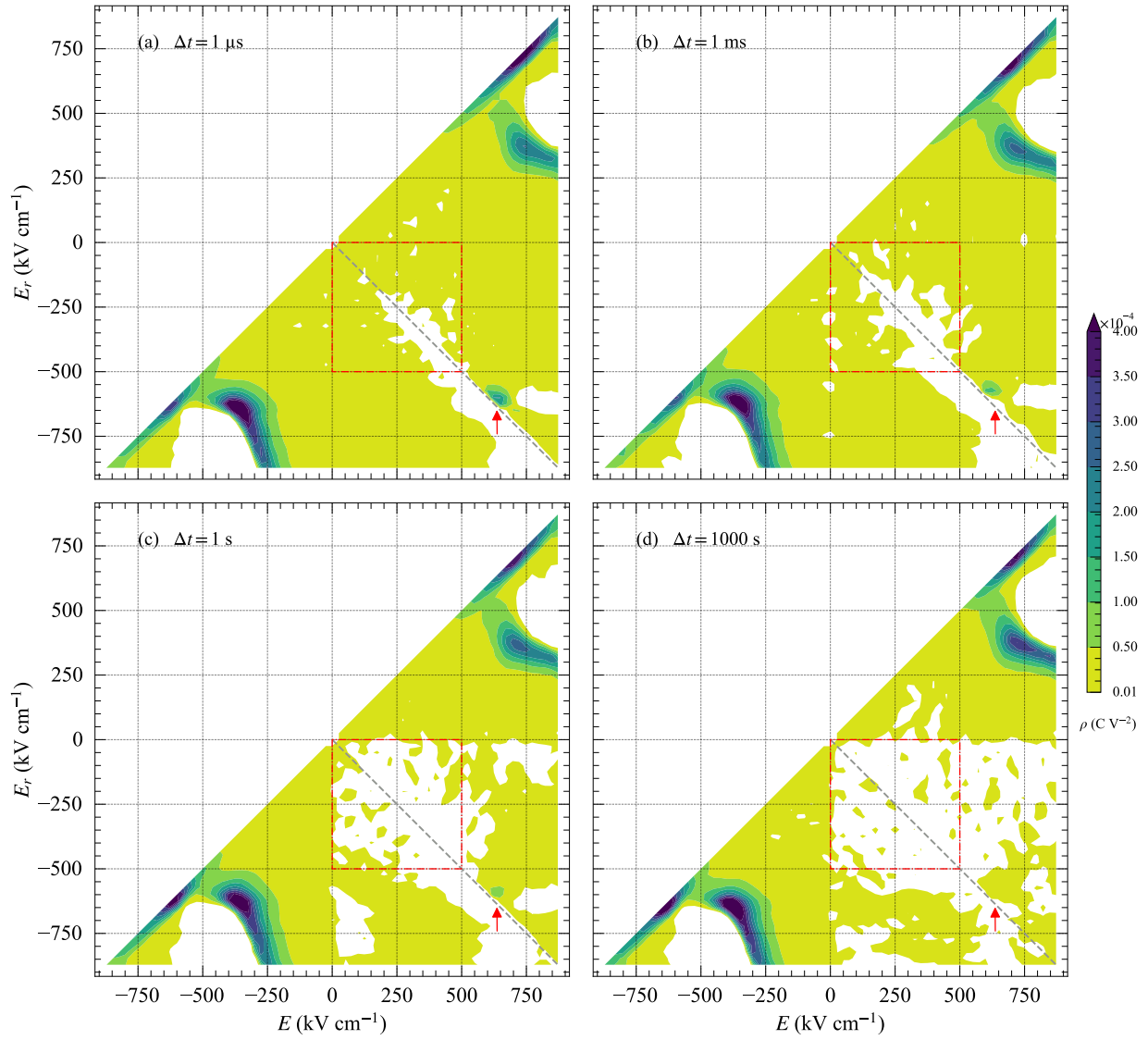


Figure 10: FORC distributions for different delay between the positive and the negative pulse. The dashed gray line shows the $E_r = -E$ axis. The red arrows point toward the position of the high field ferroelectric contribution peak and the red square indicates the low field hysterons. Density values below $1 \times 10^{-6} \text{ C V}^{-2}$ are displayed in white.

336 (dotted line in Fig. 10), delimited by the red square can be seen. When the delay between
337 pulses increases, the hysteron density in this area progressively decreases, correspond-
338 ing to a decrease of the switching polarization contribution studied in the low field sec-
339 tion 3.4.1 (decrease of ΔP_m with time). In this area, a homogeneous low hysteron density
340 is visible indicating that switching of the weak ferroelectric phase does not appear at a
341 precise coercive field but with rather distributed values, as already seen from the broad
342 current peak of Fig. 6.

343 4. Conclusion

344 In this paper, using the complementary PUND and FORC methods, we study the time
345 and field dependency of the ferroelectricity contribution to the polarization in antiferro-
346 electric PZO thin film. The PUND measurement permits us to show that some residual
347 ferroelectric phase is present in the antiferroelectric thin film and can be switched at low
348 fields. By varying the delay time between the pulses, we show that this weak ferroelec-
349 tric contribution is not stable and disappears with time. This might be due to orientation
350 relaxation of the ferroelectric domains in the antiferroelectric matrix. Using the FORC
351 measurements, we show that this ferroelectric contribution, visible at low fields, has a
352 quite homogeneous hysteron distribution, corresponding to the observed broad distribu-
353 tion of the coercive field.

354 The high field PUND measurements reveal that the delay between pulses also af-
355 fects the antiferroelectric to the ferroelectric phase transition fields which is higher for
356 the first pulse of identical polarity, especially when the delay time is short. This indicates
357 that the previously oppositely oriented ferroelectric phase hinders the antiferroelectric-
358 ferroelectric transition. As the delay between pulses is getting longer, the difference be-
359 tween the switching and non-switching phase transition field vanishes.

360 The high field FORC measurements show that there exist a further ferroelectric con-
361 tribution, which can be switched at fields of the order of the phase transition electric
362 field. When the delay between the pulses increases, the magnitude of this ferroelectric
363 peak decreases, again indicating that switching of this ferroelectric contribution is not

364 stable. This ferroelectric switching contribution, not visible on the $P(E)$ loops, shows the
365 sensibility of the FORC method and its complementarity with the PUND measurements.

366 **Data availability**

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

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372 croelectronics technological research and development center) of French region Centre
373 Val de Loire.

374 **Conflict of interest**

375 The authors declare that they have no known competing financial interests or personal
376 relationships that could have appeared to influence the work reported in this paper.

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