Pseudo-stochastic multiple-pulse excitation in dielectric spectroscopy: application to a relaxor ferroelectric

2003 J. Phys.: Condens. Matter 15 S1069

(http://iopscience.iop.org/0953-8984/15/11/328)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **15** (2003) S1069–S1075 PII: S0953-8984(03)58080-8

Pseudo-stochastic multiple-pulse excitation in dielectric spectroscopy: application to a relaxor ferroelectric

O Kircher[1,3], **R Böhmer**[1] **and G Hinze**[2]

[1] Experimentelle Physik III, Universität Dortmund, 44221 Dortmund, Germany
[2] Institut für Physikalische Chemie, Johannes Gutenberg-Universität, 55099 Mainz, Germany

E-mail: Roland.Bohmer@udo.edu

Received 27 September 2002
Published 10 March 2003
Online at stacks.iop.org/JPhysCM/15/S1069

Abstract

The nonlinear dielectric response of a lead titanate-doped lead magnesium niobate relaxor ferroelectric was studied using pseudo-stochastic binary electrical field excitation. The polarization was recorded for various pulse spacings and electrical field amplitudes. The decay of the field-polarization cross-correlation function could be accelerated by increasing the amplitude of the pulse fields. The extension of these experiments in order to record multidimensional dielectric spectra is illustrated.

1. Introduction

Noise is often annoying when trying to acquire experimental data. On the other hand, fluctuations arising from thermally agitated molecular or ionic motions in condensed matter, sometimes also referred to as noise, can be exploited to characterize the dynamics of liquids and solids. Spectroscopy based on this type of intrinsic 'noise' enjoys widespread application, e.g. in correlation spectroscopy [1] as well as for the monitoring of the spectral densities in magnetic [2] and dielectric materials [3]. Another way to employ noise is to subject the system under study to a pseudo-random perturbation and to record its response. This type of extrinsic noise is used quite successfully in the field of magnetic resonance [4], e.g. in order to enhance the experimentally accessible excitation bandwidth sometimes necessary in the context of solid-state NMR [5]. In the field of relaxation spectroscopy the application of stochastic excitation is however quite scarce [6].

White noise excitation is particularly useful for nonlinearly responding systems, since it allows one to characterize their response

$$y(t) = \sum_{i=0}^{\infty} y_i(t) \tag{1}$$

[3] Present address: Institut für Nanotechnologie, Forschungszentrum Karlsruhe, 76021 Karlsruhe, Germany.

0953-8984/03/111069+07$30.00

in a systematic manner. For increasing powers of the excitation $x(t)$, the response can be written via the Wiener–Volterra series [4]

$$\begin{aligned} y_0(t) &= h_0 \\ y_1(t) &= \int_0^\infty h_1(\tau)x(t-\tau)\,\mathrm{d}\tau \\ y_2(t) &= \int_0^\infty \int_0^\infty h_2(\tau_1,\tau_2)x(t-\tau_1)x(t-\tau_2)\,\mathrm{d}\tau_2\,\mathrm{d}\tau_1 \\ &\vdots \end{aligned} \tag{2}$$

Here the τ_i are time shift arguments and the h_i designate ith-order Volterra kernels, also called multidimensional response functions. In linear systems all h_i (for $i \geqslant 2$) vanish. Other ways to characterize nonlinear systems are the generation of higher harmonics as driven by periodic fields [7].

Nonlinear relaxation spectroscopies are still not in widespread use. This is probably due to the fact that a general theoretical framework, analogous to linear response theory [8], simply does not exist for the nonlinear case, despite various attempts that have been made [9]. Notwithstanding the fact that the problem can be formulated in general terms, solutions relevant for nonlinear spectroscopy can obviously only be given for specific models [10, 11].

In the present paper we investigate the nonlinear response of the relaxor ferroelectric $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) doped with 10% $PbTiO_3$ (PMN–10PT). From previous ageing studies we have argued that the nanopolar domain structure existing in this material can be manipulated by temperature jumps and by temperature cycles [12]. Also large electrical field perturbations were employed for this purpose, e.g. using nonresonant hole-burning (NHB) studies carried out for temperatures between 275 and 295 K [13, 14]. Lower temperatures were not accessible via the NHB technique due to the increasingly long recycle times necessary to carry out such experiments. One of the motivations of the current work was to see whether modification of the polarization response can be achieved for large field excitations at lower temperatures also. In this paper we show that this is indeed the case.

2. Pseudo-white noise and cross-correlation functions

In order to excite a system uniformly with an external perturbation $x(t)$ (e.g. an electrical field $E(t)$) it should be exposed to white noise, i.e., the power spectrum of the perturbation $x(t)$ as given by $S(\omega) = \lim_{\theta\to\infty} \frac{2}{\theta}\{(\int_0^\infty x(t)\sin(\omega t)\,\mathrm{d}t)^2 + (\int_0^\infty x(t)\cos(\omega t)\,\mathrm{d}t)^2\}$ has to be constant over the relevant frequency range. In other words, the normalized autocorrelation function should obey

$$a(\tau) = \langle x(t)x(t+\tau)\rangle / \langle x(t)^2\rangle = \delta(\tau). \tag{3}$$

Here the $\langle\cdots\rangle$ brackets indicate a time average over all times t and $\delta(\tau)$ is a delta distribution. For a finite time series, which is unavoidable in the experimental situation, this requirement can of course only be fulfilled approximately. There are several possibilities for achieving this goal. We have used irreducible polynomials in binary (i.e., $n = 2$) Galois fields, GF(n) [15]. This means that only $n = 2$ different electrical field amplitudes are used in a given experiment, e.g. $+E$ and $-E$. Usually it may be necessary to employ irreducible polynomials of relatively high orders r in order to generate long binary sequences with $2^r - 1$ elements. This is because for finite values of τ the autocorrelation function then is relatively small, $a_{\mathrm{GF}(2)}(\tau \neq 0) = -E^2/(2^r - 1)$, while for $\tau = 0$ one has $a_{\mathrm{GF}(2)}(\tau = 0) = E^2$. The negative value is due to the fact that a Galois series contains $2^r/2$ negative (e.g., $-E$) and

$2^r/2 - 1$ positive (e.g., $+E$) values. However, the negative sign does not have an impact on the experiments.

The simplest way to extract information under these conditions is to calculate the cross-correlation function

$$c(\tau) = \langle P(t)E(t-\tau)\rangle_\theta. \tag{4}$$

Here the index θ is introduced in order to emphasize that the averaging is carried out for a finite time interval. Furthermore, $P(t)$ denotes the polarization response to the perturbing field $E(t)$. In the linear regime, $c(\tau)$ can be identified with the impulse response function, corresponding to $y_0 + y_1(t)$ in equation (2) [4]. We briefly sketch how this comes about: starting from Boltzmann's superposition principle $P(t) = \varepsilon_0\chi_s \int_{-\infty}^{t} \varphi(t-t')E(t')\,\mathrm{d}t'$ and with $t' \to t-\sigma$, one obtains $c(\tau) = \varepsilon_0\chi_s\langle\int_0^\infty \varphi(\sigma)E(t-\sigma)\,\mathrm{d}\sigma\, E(t-\tau)\rangle_T$. Here $\varphi(\tau)$ denotes the impulse response function. When carrying out the time average $\varepsilon_0\chi_s \int_t^{t+T} \int_0^\infty \varphi(\sigma)E(t-\sigma)\,\mathrm{d}\sigma\, E(t-\tau)\,\mathrm{d}t = \varepsilon_0\chi_s \int_0^\infty \varphi(\sigma) \int_t^{t+T} E(t-\sigma)E(t-\tau)\,\mathrm{d}t\,\mathrm{d}\sigma$ via equation (3), the inner integral for a binary sequence reduces to $E_0^2\delta(\sigma-\tau)$. Here E_0 designates the field amplitude. This finally shows that $c(\tau) = \varepsilon_0\chi_s E_0^2 \int_0^\infty \varphi(\sigma)\delta(\sigma-\tau)\,\mathrm{d}\sigma = \varepsilon_0\chi_s E_0^2\varphi(\tau)$.

If one does not operate in the linear response regime, then $\varphi(\tau)$ cannot be identified with the impulse response but in general denotes a memory function.

3. Experimental details

For the experimental implementation of a binary pseudo-random excitation, a relatively high order r of the Galois polynomials is desired. By using pulse widths t_p of about 1 ms or less the length of a single cycle of an experiment could be kept below 30 min, even with, e.g., $r = 20$ (roughly corresponding to 10^6 pulses). It should be mentioned that due to the excitation with a *finite* pulse train, a broad but nevertheless spectrally limited time or frequency range is covered (for $t_p = 300\ \mu$s and $r = 20$, one has 3.3 mHz $\leqslant \nu \leqslant$ 1.67 kHz). To generate voltage pulses of up to 200 V with rise times of less than 10 μs, we used commercial voltage modules (CPS series from ISEG Spezialelektronik) that were triggered by a computer-controlled DA/AD converter [16]. A fragment of a pulse train is sketched in figure 1(a). Polarization readings are taken in the middle of each pulse plateau. The experimental set-up is shown schematically in figure 1(b).

In order to evaluate the maximum dynamic range of our apparatus we measured the autocorrelation function for $r = 20$. For this purpose the sample capacitor shown in figure 1(b) was replaced by a short. The magnitude of $a(\tau \neq 0)$ turned out to be $\approx 10^{-5}$ which is about one order of magnitude larger than for ideal conditions.

For the measurements, trains of $2^{20} - 1$ pulses were applied at least three times. No significant differences could be found when comparing the results from the first with those from the third cycle, implying that transient effects do not play a major role.

We used the PMN–10PT samples previously investigated using nonlinear dielectric spectroscopy [14]. The thickness of our samples was 0.8 mm. We checked that the cross-correlation functions $c_{t_p}(\tau)$ did not depend on the pulse width in the range 100 μs $\leqslant$ $t_p \leqslant$ 3 ms, i.e. the normalized functions $c_{t_p}(\tau)/c_{0.1\mu\mathrm{s}}(t_p)$ were found to be identical within experimental error.

4. Results and discussion

In figure 2 we present the cross-correlation function as measured for PMN–10PT at $T = 250$ K using different pulse field amplitudes. At the lowest fields, $c(\tau)$ roughly follows a power law, $t^{-0.72}$. An important result of our investigation is that when increasing the amplitude of the

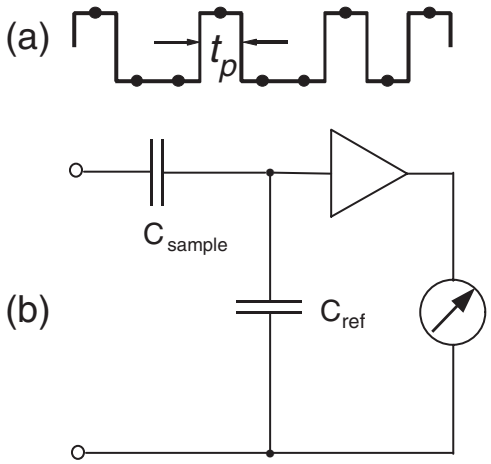

Figure 1. (a) A sketch of the electrical field sequence used for the binary excitation experiments using pulses of width t_p. The dots indicate the times at which the polarization was recorded using the circuit depicted in (b). Here the reference capacitance (C_{ref}) was chosen much larger than that of the sample (C_{sample}). The voltage across the reference capacitor, which is proportional to the polarization of the sample, was monitored using a high-impedance amplifier.

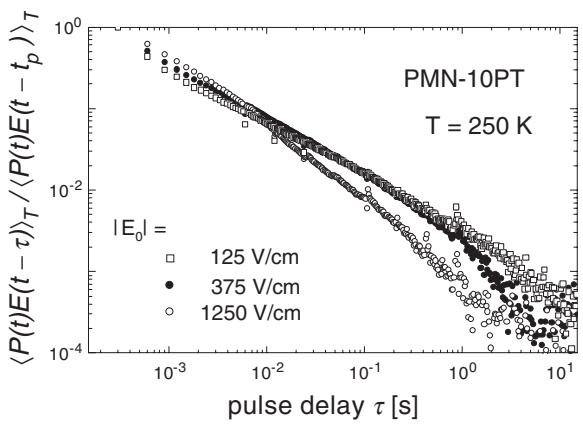

Figure 2. Normalized cross-correlation functions of PMN–10PT for different pulse field amplitudes. The pulse width was 300 μs.

pulse field, the decay of the cross-correlation functions becomes faster. This shows the presence of nonlinear effects.

In order to understand these measurements, let us note that there is increasing evidence that the polarization response of relaxor ferroelectrics is not only due to the on-site reorientation of dipolar moments but also involves an important contribution from the growth and reconformation of domain walls. It has been suggested that the typical size R of a domain after a temperature perturbation should evolve in time roughly as $R(t) = R_C(1 + \frac{a}{R_0}\frac{\Gamma}{k_B T}\ln\frac{t}{\tau_C})$ [17]. Here a denotes the lattice constant, R_C the characteristic domain size at time τ_C, and Γ an effective energy barrier. Similarly, growth and reconformation processes will be initiated by electrical field perturbations. The latter can be inferred from field-induced ageing measurements on relaxor ferroelectrics [18] and is also consistent with results from NHB [14].

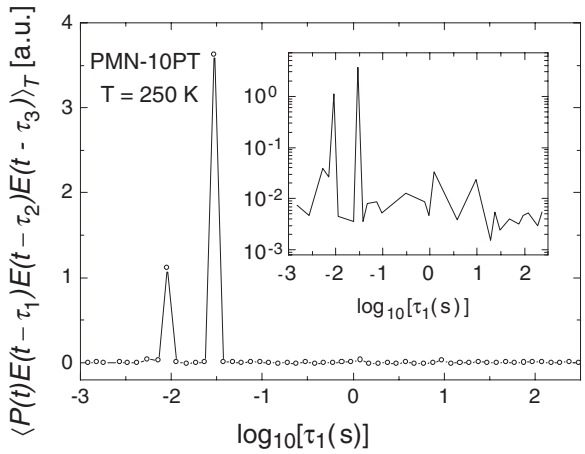

Figure 3. A cut along τ_1 through the three-dimensional correlation function $c(\tau_1, \tau_2, \tau_3)$ of PMN–10PT. The data were recorded at 250 K with $\tau_2 = 9$ ms and $\tau_3 = 30$ ms and an electrical pulse field strength of ± 375 V cm^{-1}. The line connects the data points. The inset gives a double-logarithmic representation.

We interpret the accelerated decay of the correlation function as seen in figure 2 as a consequence of an electrical field-assisted depinning of domain walls. This is in harmony with results that we obtained for this sample using NHB at higher temperatures [14]. Thus the current data support this conclusion also for lower temperatures.

However, the main advantages of experiments using pseudo-stochastic excitation arise from their potential to yield multidimensional cross-correlation functions of the type implicit in equation (2). This fact has been exploited in the generation of multidimensional NMR spectra [19]. Recently, a host of other two-dimensional (2D) correlation techniques have been developed, such as 2D Raman [20] or 2D electrical birefringence spectroscopy [21]. In the present context, a 2D dielectric experiment can be based on the third-order function

$$c(\tau_1, \tau_2, \tau_3) = \langle P(t)E(t-\tau_1)E(t-\tau_2)E(t-\tau_3)\rangle_T. \tag{5}$$

In order to obtain a 2D frequency domain spectrum, it has to be Fourier transformed, e.g. with respect to the first and third time shift arguments. Similarly to what is done in 2D NMR exchange spectroscopy, one can keep τ_2 (then called the mixing time) fixed for each spectrum.

We have carried out some preliminary experiments in order to record such multiple-time correlation functions. A cut through $c(\tau_1, \tau_2, \tau_3)$ along τ_1 with $\tau_2 = 9$ ms and $\tau_3 = 30$ ms is shown in figure 3. For time shifts of $\tau_1 = \tau_2 = 9$ ms and $\tau_1 = \tau_3 = 30$ ms, prominent peaks show up. Since $E(t-\tau)E(t-\tau) = E_p^2$ (for all τ), these intensities do not yield additional information as compared to the one-dimensional cross-correlation function $c(\tau)$. In other words, for two equal time delays (e.g., $\tau_1 = \tau_2$) the correlation function over the third time (then τ_3) shows a decay which is equivalent to that of the one-dimensional function $c(\tau)$.

Unfortunately our efforts to acquire more extensive sets of data were cut short by the fatigue of our samples. This effect, which degrades the sample properties, is known to show up after a sufficiently large number of switching cycles [22]. In our experiments, more than 10^8 pulses were applied. Fatigue was recognized in the course of our studies from a decreasing polarization of the samples and from an increase in their electrical conductivity.

5. Summary

In the present paper we have applied a binary pseudo-random electrical field sequence to the relaxor ferroelectric PMN–10PT. This enabled us to record field-polarization cross-correlation functions. We observed an accelerated decay of these response functions when the pulse field amplitude increases. This observation is consistent with an electrical field-induced domain wall depinning in PMN–10PT. In order to obtain further insights into the relaxation dynamics of this material, we carried out some preliminary work aimed at recording higher-order cross-correlation functions.

Acknowledgments

We thank Gregor Diezemann for stimulating discussions as well as L E Cross and S E Park for supplying the samples. The Deutsche Forschungsgemeinschaft supported this project financially under grant No 1301/4.

References

[1] The most prominent example is photon correlation spectroscopy (PCS); see
Berne B J and Pecora R 1976 *Dynamic Light Scattering* (New York: Wiley)
A recent development is x-ray PCS; see, e.g.,
Thurn-Albrecht T, Steffen W, Patkowski A, Meier G, Fischer E W, Grübel G and Abernathy D L 1996 *Phys. Rev. Lett.* **77** 5437
[2] Weissman M B 1996 *Annu. Rev. Mater. Sci.* **26** 395
[3] O'Brien K P, Weissman M B, Sheehy D and Viehland D D 1997 *Phys. Rev.* B **56** R11365
Musevic I, Kityk A, Skarabot M and Blinc R 1997 *Phys. Rev. Lett.* **79** 1062
Israeloff N E and Grigera T S 1998 *Europhys. Lett.* **43** 308
Bellon L, Ciliberto S and Laroche C 2001 *Europhys. Lett.* **53** 511
[4] Ernst R R, Bodenhausen G and Wokaun A 1987 *Principles of Nuclear Magnetic Resonance in One and Two Dimensions* (Oxford: Clarendon)
[5] For recent examples, see
Yang D K and Zax D B 1998 *J. Magn. Reson.* **135** 267
Hirsch O, Weingarten K, Blümich B and Jäger C 2000 *Solid State NMR* **16** 123
[6] Husimi Y and Wada A 1975 *Rev. Sci. Instrum.* **47** 213
Köhler W and Schäfer R 2000 *Adv. Polym. Sci.* **151** 1
[7] For recent applications, see, e.g.,
Hemberger J, Böhmer R and Loidl A 1998 *Phase Transit.* **65** 233
De Smet K, Hellemans L, Rouleau J F, Courteau R and Bose T K 1998 *Phys. Rev.* E **57** 1384
Rzoska S J and Ziolo J 1999 *Phys. Rev.* E **59** 2460
Kimura Y, Hara S and Hayakawa R 2000 *Phys. Rev.* E **62** R5907
[8] Kubo R, Toda M and Hashitsume N 1985 *Statistical Physics* vol 2 (Berlin: Springer)
[9] e.g.,
Nakada O 1960 *J. Phys. Soc. Japan* **15** 2280
Morita A 1986 *Phys. Rev.* A **34** 1499
Morita A and Watanabe H 1987 *Phys. Rev.* A **35** 2690
Dyre J C 1989 *Phys. Rev.* A **40** 2207
Fulton R L 1983 *J. Chem. Phys.* **78** 6856
Fulton R L and Lim R 1988 *J. Chem. Phys.* **89** 3181
[10] For recent examples, see
Glazounov A E and Tagantsev A K 2000 *Phys. Rev. Lett.* **85** 2192
Diezemann G 2001 *Europhys. Lett.* **53** 604
Bobnar V, Kutnjak Z, Pirc R, Levstik A, Dec J and Kleemann W 2001 *Ferroelectrics* **261** 759
Roling B 2002 *J. Chem. Phys.* **117** 1320
Richert R 2003 *Physica* A at press

[11] The relation to the Kerr effect seems to be particularly well studied:
Rosato V and Williams G 1981 *Trans. Faraday Soc.* II **77** 1761
Rosato V and Williams G 1982 *Mol. Interact.* **3** 273
Cole R H 1982 *J. Phys. Chem.* **86** 4700
Hellemans L and de Maeyer L 1986 *Chem. Phys. Lett.* **129** 262
Dejardin J L and Debiais G 1995 *Adv. Chem. Phys.* **91** 241
[12] Kircher O and Böhmer R 2002 *Eur. Phys. J.* B **26** 329
[13] Kircher O, Schiener B and Böhmer R 1998 *Phys. Rev. Lett.* **81** 4520
[14] Kircher O, Diezemann G and Böhmer R 2001 *Phys. Rev.* B **64** 054103
[15] Lüke H D 1992 *Korrelationssignale* (Berlin: Springer) ch 3
[16] Kircher O 2001 *Dissertation* Universität Mainz
[17] Doussineau P and Levelut A L 2002 *Phys. Rev.* B **66** 024105 and references cited therein
[18] Colla E V, Yushin N K and Viehland D 1998 *J. Appl. Phys.* **83** 3298
Doussineau P and Levelut A 2001 *Europhys. Lett.* **55** 739
[19] Blümich B 1987 *Prog. NMR Spectrosc.* **19** 331
Paff J, Blümich B and Kaiser R 1992 *Adv. Magn. Opt. Reson.* **17** 1
[20] Noda I and Marcott C 2002 *J. Phys. Chem.* A **106** 3371
[21] Hosokawa K, Shimomura T, Frusawa H, Kimura Y, Ito K and Hayakawa R 1999 *J. Chem. Phys.* **110** 4101
[22] Depending on the system, crystal orientation and temperature fatigue can show up even after just 10^4 switching cycles; see, e.g.
Levstik A, Bobnar V, Kutnjak Z, Filipic C and Kosec M 1999 *J. Eur. Ceram. Soc.* **19** 1233
Ozgul M, Takemura K, Trolier-McKinstry S and Randall C A 2001 *J. Appl. Phys.* **89** 5100