OPEN ACCESS
JOURNAL OF ADVANCED DIELECTRICS
(2022) 2250021 (5 pages)

DOI: 10.1142/S2010135X22500217

Electric field-induced phase transition from the glasslike to paraelectric phase and dielectric spectra hardening in PMN single crystal

E. Koroleva*, A. Molokov and S. Vakhrushev
Ioffe Institute, Polytekhnicheskaya 26, 194021, St.-Petersburg, Russia
*e.yu.koroleva@mail.ioffe.ru

Received 22 September 2022; Revised 21 October 2022; Accepted 24 October 2022; Published 18 November 2022

One of the key points in the physics of the relaxors is their response to the applied DC field. Many studies of this topic were made, in particular on the influence of the field on the dielectric properties. However, practically, in all the cases, the measurements were performed at a fixed frequency and usually with the change in the temperature at the fixed field strength. In this paper, we report the evolution of the dielectric spectra at low frequencies (0.1 Hz < ω < 1 kHz) at fixed temperature 246 K on changing the DC electric field applied in (111) from 1 kV to 7 kV. Cole–Cole function was used to describe the spectra and the field dependences of the mean relaxation time τ, the oscillation strength $\Delta\varepsilon$ and the width parameter α were determined. The obtained $\tau(E)$ and $\Delta\varepsilon(E)$ provide evidence of the field-induced transition from the nonpolar glass-like phase to the nonpolar paraelectric phase at around 1.5 kV/cm. In the paraelectric phase, very fast hardening of the spectra was observed with τ changing from 10 s to about 10^{-4} s. The performed analysis demonstrated that the earlier reported positive C-V effect is completely determined by the spectra hardening, while $\Delta\varepsilon$ does not show any change in the glass-like phase and monotonously decreases with a field increase in the paraelectric state. For complete understanding of the microscopic origin of the observed phenomena, a detailed study on the short- and long-range structures at the same condition is necessary.

Keywords: Relaxor; ferroelectrics; dielectric spectroscopy; phase transition; lead magnoniobate.

1. Introduction

Relaxor ferroelectrics are widely used for ultrasonic transducers, electrostrictive actuators and electrostatic energy storage devices. Lead magnoniobate $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) can be considered as an archetypal relaxor. It was discovered more than 60 years ago, but still the nature of its physical properties is not completely understood. Instead of the sharp peak in the temperature dependence of the dielectric susceptibility $\varepsilon(T)$ PMN demonstrates the broad frequency-dependent maximum attaining at low frequencies to about tens of thousands.[1] Originally, this maximum was attributed to the diffuse ferroelectric phase transition, but no real transition took place and PMN remained cubic down to 4K.[2] The PMN can be transformed to a macroscopic polar ferroelectric state either by mixing with a normal ferroelectric, such as lead titanate (PT) (PMN–PT solid solutions[3]) or by applying an external electric field. It was shown for the first time in Refs. 4 and 5 that when PMN is cooled in electric fields above the threshold value, applied in the (111) or (110) directions (for PMN in the (111) direction, Etr ≈ 2.2 kV/cm), phase transition to the ferroelectric state takes place. Based on the obtained results, an E-T phase diagram was proposed.[5] Subsequently, the field-induced phase transition in PMN under various conditions of field application was actively studied by many groups, phase diagrams were refined for different crystallographic directions, and lines inside the glassy phase (ergodic and nonergodic phases) were added.[6–8] All these studies were carried out with a change in the temperature at E = const typically at fixed frequencies. Main attention was paid to the induced transition itself. At the same time, the behavior of the permittivity in the region of the smeared maximum was less discussed, although it was noted in some papers that the application of an external field can lead both to an increase in ε' ($\Delta\varepsilon = \varepsilon'(E) - \varepsilon'(E = 0) > 0$) and to its decrease. Dec *et al*.[9] noted an increase in ε' in large AC-field at 1 kHz. In Ref. 10, ε' was studied when the field was applied in different directions and it was shown that the application of the field in the (100) direction leads to a decrease of permittivity near the maximum, while when the field is applied in the (111) direction, ε can either increase or decrease in, depending on the temperature and measuring frequency. In Ref. 11, the influence of the DC field applied in different directions on the permittivity of PMN single crystals and ceramics in the region of a diffuse maximum was studied in detail. In single crystals at 100 Hz, when a field was applied in the (111) direction, $\Delta\varepsilon$ was found to be positive, while in the case of the field in the (100) direction, it was negative. At the same time, an essentially different situation was observed in ceramics: Positive $\Delta\varepsilon$ was observed up to the maximum temperature, and negative $\Delta\varepsilon$ above. Guerra[12] and Lima[13] also studied the dielectric response of PMN ceramics

*Corresponding author.

in external fields and observed both positive and negative $\Delta\varepsilon$. There are no models explaining the behavior of ε' PMN in electric fields. In our opinion, this situation could be clarified by studies in a wide frequency range, and especially at low measuring frequencies, since it is known that in the low-temperature state, PMN has a wide range of relaxation times and very long characteristic times exceeding the measuring frequencies. It should also be noted that most of the measurements were performed with a change in temperature at fixed electric field. The exceptions are two papers by Kutnjak *et al.*,[14,15] in which the studies were carried out at several temperatures with a change in the field and it was shown that, in this regime, the line corresponding to the phase transition from the relaxor phase to the ferroelectric phase in the phase diagram changes significantly. We carried out synchronous measurements of the piezoresponse signal and electrical impedance to study the processes of switching the polarization of PMN at a constant temperature with a change in the external electric field in the (111) direction.[16] At 203 K, we observed a pronounced "positive capacitance-voltage effect" $\Delta\varepsilon > 0$. The aim of our present work was to obtain information on the possible transformation of the dielectric spectra with a change in the external electric field applied to a PMN single crystal in the (111) direction, which can provide the reason for the observed $\Delta\varepsilon$ sign at different measuring frequencies and about the behavior of the static permittivity of PMN in an external field. These studies can also provide new information about the nature of the glasslike state of relaxors and the processes of their destruction.

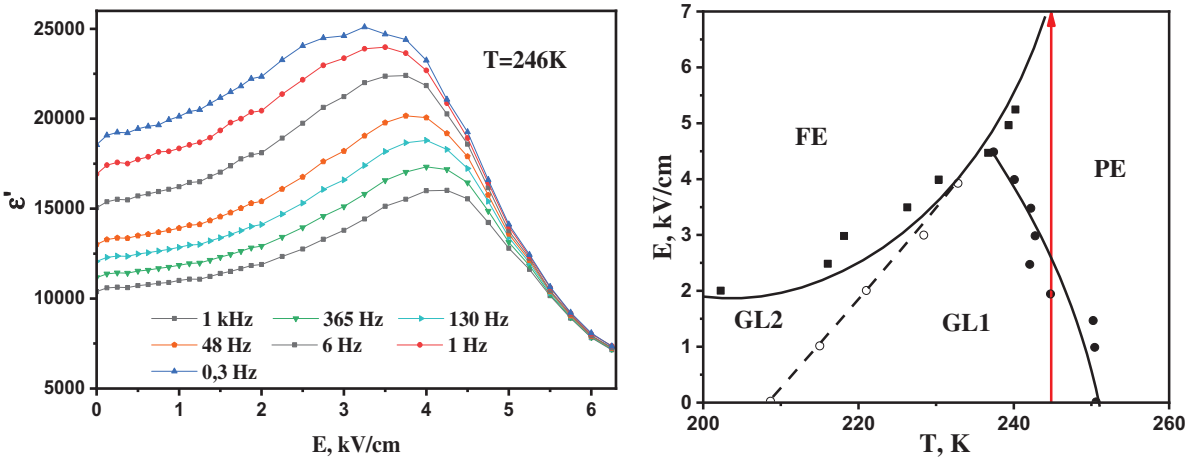
2. Experimental Procedure

All studies were carried out on a platelet-shaped single crystal sample of about 5*5*1 mm in size, the large faces were perpendicular to the (111) direction sample was cut from the large single crystal, grown in the Institute of Physics of the Southern Federal University. It was then polished with a diamond paste. Gold electrodes with a chromium sublayer were deposited on the larger surfaces. The dielectric studies were carried out on the ultra-broadband dielectric spectrometer with a cryosystem Novocontrol BDS80 with a high electric field application system HVB1000 and a high-voltage sample cell (Novocontrol Technologies GmbH & Co. KG). The AC measuring field was 10 V/cm, the DC field varied from 0 to 7 kV/cm. The measuring frequency range was from 0.1 Hz to 1 kHz. Before each measurement, the sample was annealed for 30 min at a temperature of 450 K in the ergodic phase to eliminate memory effects, and then cooled to a given temperature without a DC field. Measurements were carried out at 246 K (in the region of maximum $\varepsilon(T)$), since in this region the greatest frequency dispersion is observed and the most significant and rapid changes in the spectrum can be expected.

3. Results and Discussion

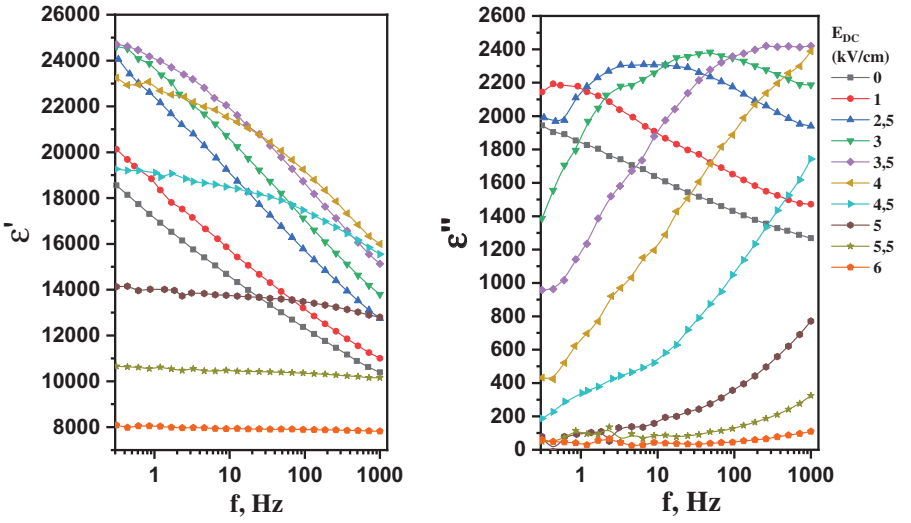
Figure 1(a) shows the field dependences of the dielectric permittivity of PMN at 246 K at several measuring frequencies. E-T phase diagram of PMN for the DC-field in (111) direction based on data from Ref. 5 is shown in Fig. 1(b). The red line marks the trajectory along which the measurements were carried out.

At low fields, a clear positive change of ε' is seen, however, on the field increase, $\varepsilon'(E)$ dependence passes through the maximum at some E_{max}, with E_{max} monotonously increasing and $\varepsilon'(E_{max})$ decreasing with the frequency increase. Upon transition to the ferroelectric phase (E~ 6 kV/cm), the dispersion disappears. To observe the changes in the spectrum, we analyzed the frequency dependences of ε' and ε'' for all studied external fields. Figure 2 shows the frequency dependences of ε' and ε'' for several applied fields. It can be



(a) (b)

Fig. 1. (a) (Color online) Field dependences of the dielectric permittivity (ε') of PMN at 246 K at several measuring frequencies. Applied and measuring fields are in (111) direction. (b) E-T phase diagram of PMN.[5] The red line marks the trajectory along which the measurements were carried out.



(a) (b)

Fig. 2. Dispersion dependences of the dielectric permittivity (ε') (a) and losses (ε'') (b) of PMN at 246 K for several DC fields.

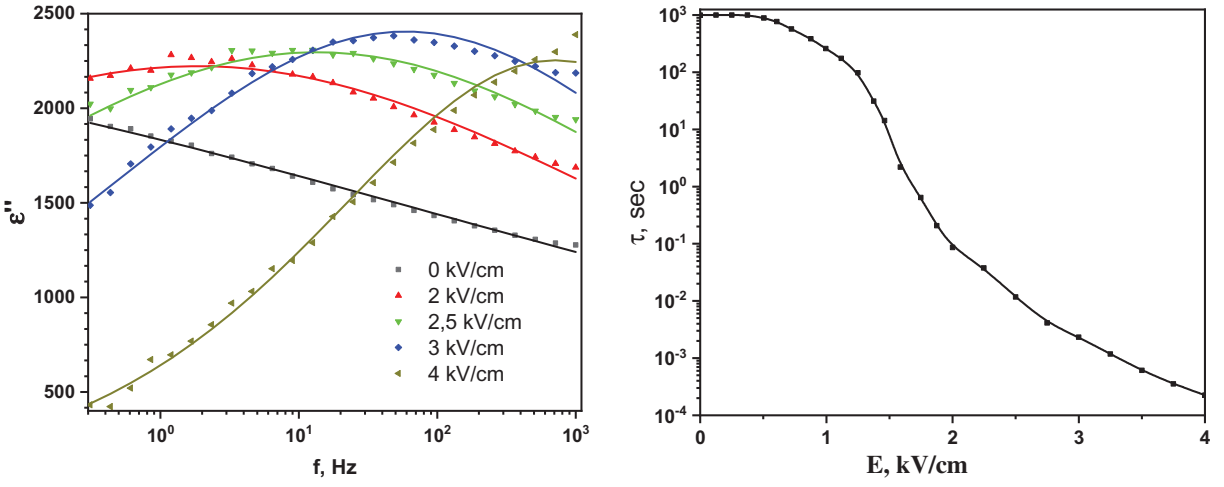
seen that the shape of the dependences substantially changes with a change in the external field.

To describe the corresponding change of the dielectric spectra, we used the Cole–Cole distribution function, which makes it possible to describe the spectra that are symmetrically broadened compared to the Debye spectrum. Only the low-frequency component from the bimodal distribution falls into our measurement frequency window,[17] but it is this component that is responsible for the low-temperature dielectric response of the PMN. The sum of the high-frequency permittivity (ε_∞) and the Cole–Cole function was used as a model:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \Delta\varepsilon/(1+(i\omega\tau)^\alpha). \quad (1)$$

Here, $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$ is the dielectric strength of the process, ε_0 is the static permittivity, τ is the characteristic relaxation time, α is the spectrum broadening coefficient of the relative Debye spectrum and ω is the cyclic frequency. The data fit was made using the Levenberg–McGwart algorithm.[18] ε' and ε'' were adjusted simultaneously, which made it possible to significantly increase the accuracy of fitting and reduce the error.

Figure 3(a) shows the experimental frequency dependences of ε'' (points) and the results of their fit with Eq. (1) (lines) for several bias fields from 0 to 4 kV/cm. It can be seen that with an increase in the external field, the position of the loss peak shifts to the high-frequency region, the relaxation time spectrum becomes sharper. In Fig. 3(b), the field dependence of the relaxation time is shown. τ is nearly constant up to 1.5 kV/cm while from 1.5 to 4 kV/cm, it decreases for nearly six orders of magnitude. To our knowledge, such striking hardening of the spectra was never observed either



(a) (b)

Fig. 3. (a) Loss spectra of PMN for several bias fields. Points - the experimental frequency dependences of ε'', lines - the results of their fitting by model function (1). (b) Field dependence of the characteristic relaxation time τ.

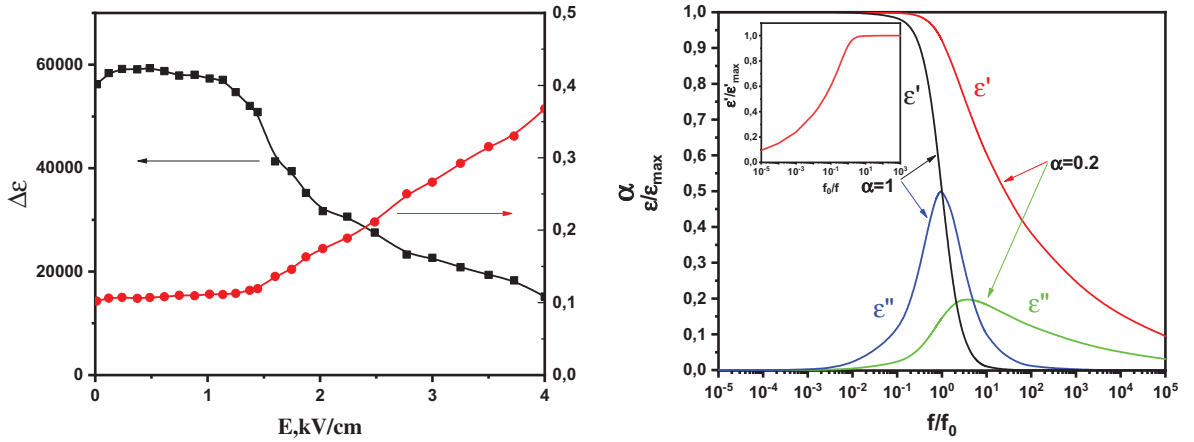


Fig. 4. (a) Field dependencies of $\Delta\varepsilon$ and α. (b) Model spectrum of Cole–Cole relaxation process for $\alpha = 1$ (Debye spectrum) and 0.2. The inset shows the dependence $\varepsilon'/\varepsilon'\max(f_0/f)$ for $\alpha = 0.2$ – application of an external field leads to an increase in f_0, respectively, at a frequency f ε' will increase.

in normal ferroelectrics (displacive or order–disorder) or in relaxors. Experimentally, field-induced changes of the dielectric spectra were studied in the glass forming liquids, where substantial hardening of the spectra was found [19] In the review paper of Richert,[20] both hardening and softening of the spectra were reported. On the other hand, Déjardin *et al*. theoretically considered two-mode approximation, originating in the large separation of the time scales of the fast intra-well and slow inter-well relaxation modes and demonstrated hardening of the loss spectra.[21,22] A similar result, showing the softening of the spectra, was theoretically predicted for the case of the superparamagnetic nanoparticles by Ambarov.[23] The freezing of the glass-like phase PMN and relaxors in general can be regarded as superparaelectrics with the polar nanoregions (PNRs) playing the role of the pseudospins (PS). In such a case, the dynamical properties of the material are related to the angular oscillations of the PNRs. Application of the external DC field results in the preferable orientation of the PSs and narrows the angular range of such oscillations making them faster. Such tentative approach needs to be checked by the precise measurements of the XRAN or (and) neutron diffuse scattering that is planned for the future.

In Fig. 4, the obtained field dependence of $\Delta\varepsilon$ and α is shown. Up to the field $E_{gl} \approx 1.5$ kV/cm, $\Delta\varepsilon$ also changes slightly. The relaxation times are of the order of thousands of seconds, $\alpha \sim 0.1$, i.e., the spectrum is very wide compared to the Debye spectrum, $\Delta\varepsilon \sim 60000$. We can attribute E_{gl} to the field-induced transition from the glass-like to the paraelectric phase. It looks like the obtained E_{gl} value is lower compared to the point of the crossing glass/paraelectric (G/P) line in Fig. 1(b), but we should keep in mind that the phase diagram taken from Ref. 4 was obtained with a different experimental setup and at a different crystal. The glass/ferroelectric line is very steep and the difference is about 0.7 kV/cm which corresponds to only about 2 K difference in temperature. $\Delta\varepsilon$ gives us information about the static permittivity and we see that, in contrast to ε', no increase in the static permittivity (positive capacitance-voltage effect) is observed. In weak fields, $\Delta\varepsilon$ is practically independent of the field strength, and at fields greater than 1.5 kV/cm, it starts to decrease. The observed increase in ε' at a fixed frequency with an increase in the field is determined by hardening of the spectrum and a shift in the loss peak to the high-frequency region. It can be easily illustrated using the model frequency dependences of the permittivity and losses shown in Fig. 4(b) for the Debye relaxation and the Cole–Cole relaxation (the figure shows the dependence for $\alpha = 0.2$, which corresponds to our case). A decrease in α leads to a "smearing" of the step on the dependences ε'. In the zero field, the characteristic frequencies are very low, less than mHz, therefore, in our frequency window, we are on the right slope of the dependences for ε' and ε'' ($f/f_0 > 100$) rather far from the maximum. When the field is applied, the characteristic frequencies increase, the ratio f/f_0 correspondingly decreases, and ε' increases. As long as our measuring frequency is less than the characteristic frequency of the relaxation spectrum, the application of an external field will lead to an increase in the permittivity (see inset in Fig. 4(b)). When the field changes from 0 to 4 kV/cm, the characteristic frequency changes by almost six orders of magnitude, i.e., the external field suppresses the slow dynamics of polar clusters.

4. Conclusion

We have studied the behavior of the dielectric response of a PMN single crystal in the applied external electric field in (111) direction range from 0 to 7 kV/cm at 246 K crossing the G/P and paraelectric/ferroelectric (P/F) lines. The evolution of the dielectric spectra in the frequency range of 0.1 Hz–1 kHz was followed. For the first time, the measurements were

made by scanning the E-T phase diagram along the line of constant temperature. The analysis of the frequency response within the framework of the Cole–Cole model was carried out. We ignored the fast relaxation process, since it was out of the studied frequency range. The field dependences of the characteristic relaxation frequency and the oscillator strength of the slow relaxation process were obtained. A clear indication of the G/P transition was found. In our knowledge, it is the first observation of the field-induced transition from one nonpolar (glass-like) to the other nonpolar (paraelectric) phase. In the paraelectric phase, the field increases from 1.3 kV/cm to 4 kV/cm which results in strong fastening of the relaxation with relaxation time changing from about 10 s to nearly 10^{-4} s. The obtained results allow us to explain the contradiction between different papers about the sign of the C-V effect. It is shown that the "positive capacitance-voltage effect" (an increase in ε' with an increase in the amplitude of the applied field) is associated with a hardening of the dielectric loss spectrum and a shift of its maximum (the reciprocal of the relaxation time) to higher frequencies. Thus, the external field suppresses the slow dynamics of polar clusters. The static permittivity practically does not change in the glass-like phase, and decreases in the fields above 1.5 kV/cm.

Acknowledgment

The study was supported by Russian Science Foundation grant no. 22-12-00328, https://rscf.ru/en/project/22-12-00328/.

References

[1]E. V. Colla, E. Y. Koroleva, N. M. Okuneva and S. B. Vakhrushev, Low-frequency dielectric response of $PbMg_{1/3}Nb_{2/3}O_3$, *J. Phys. Condens. Matter* **4**, 3671 (1992).

[2]N. De Mathan *et al*., A structural model for the relaxor $PbMg_{1/3}Nb_{2/3}O_3$ at 5 K, *J. Phys. Condens. Matter*, **3**, 8159 (1991).

[3]Z.-G. Ye *et al*., Development of ferroelectric order in relaxor $(1-x)$ Pb $(Mg_{1/3}Nb_{2/3})O_3$–x $PbTiO_3$ ($0 < \sim x < \sim 0.1\,5$), *Phys. Rev. B* **67**, 104104 (2003).

[4]R. Sommer, N. K. Yushin and J. J. Van der Klink, Polar metastability and an electric-field-induced phase transition in the disordered perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$, *Phys. Rev. B* **48**, 13230 (1993).

[5]E. V. Colla, S. B. Vakhrushev, E. Yu. Koroleva and N. M. Okuneva, Properties of the field-induced ferroelectric phase in single-crystal lead magnoniobate, *Phys. Solid State* **38**, 1202 (1996).

[6]Z. Kutnjak, R. Blinc and Y. Ishibashi, Electric field induced critical points and polarization rotations in relaxor ferroelectrics, *Phys. Rev. B* **76**, 104102 (2007).

[7]R. Sommer, N. K. Yushin and J. J. Van Der Klink, Dielectric susceptibility of PMN under DC bias, *Ferroelectrics* **127**, 235 (1992).

[8]Z.-G. Ye and H. Schmid, Optical, dielectric and polarization studies of the electric field-induced phase transition in $Pb(Mg_{1/3}Nb_{2/3})O_3$ [PMN], *Ferroelectrics* **145**, 83 (1993).

[9]J. Dec, S. Miga, W. Kleemann and B. Dkhil, Nonlinear dielectric properties of PMN relaxor crystals within Landau-Ginzburg-Devonshire approximation, *Ferroelectrics* **363**, 141 (2008).

[10]X. Zhao, W. Qu, X. Tan, A. A. Bokov and Z.-G. Ye, Electric field-induced phase transitions in (111)-, (110)-, and (100)-oriented $Pb(Mg_{1/3}Nb_{2/3})O_3$ single crystals, *Phys. Rev. B* **75**, 104106 (2007).

[11]A. E. Glazounov and A. K. Tagantsev, Comparison of DC and AC field effects on dielectric properties of lead magnesium niobate relaxor: Study of single crystals and ceramics, *Ferroelectrics* **201**, 305 (1997).

[12]J. de Los S. Guerra, M. H. Lente and J. A. Eiras, Non-linear dielectric properties in based-PMN relaxor ferroelectrics, *J. Eur. Ceram. Soc.* **27**, 4033 (2007).

[13]E. C. Lima, J. D. S. Guerra and E. B. Araujo, Description of electric field-dependent dielectric permittivity in PMN ceramics, *Ferroelectrics* **545**, 127 (2019).

[14]Z. Kutnjak, B. Vodopivec and R. Blinc, Anisotropy of electric field freezing of the relaxor ferroelectric $Pb(Mg_{1/3}Nb_{2/3})O_3$, *Phys. Rev. B* **77**, 054102 (2008).

[15]V. Bobnar, Z. Kutnjak, R. Pirc, R. Blinc and A. Levstik, Crossover from glassy to inhomogeneous-ferroelectric nonlinear dielectric response in relaxor ferroelectrics, *Phys. Rev. Lett.* **84**, 25 (2000).

[16]A. F. Vakulenko, S. B. Vakhrushev and E. Yu. Koroleva, Combined real-time study of dielectric response and piezoresponse of $Pb(Mg_{1/3}Nb_{2/3})O_3$ relaxor in an electric field, *Phys. Solid State* **62**, 1873 (2020).

[17]A. Vakulenko, S. Vakhrushev and E. Koroleva, *International Youth Conference on Electronics, Telecommunications and Information Technologies*, eds. E. Velichko, M. Vinnichenko, V. Kapralova and Y. Koucheryavy, Springer Proceedings in Physics Vol. 255, (Springer, Cham, 2021), https://doi.org/10.1007/978-3-030-58868-7_6

[18]J. J. Moré, The Levenberg-Marquardt algorithm: Implementation and theory, *Numerical Analysis* (Springer, Berlin, Heidelberg, 1978), pp. 105–116.

[19]A. R. Young-Gonzales, K. Adrjanowicz, M. Paluch and R. Richert, Nonlinear dielectric features of highly polar glass formers: Derivatives of propylene carbonate, J. Chem. Phys. 147, 224501 (2017).

[20]R. Richert, Dielectric Spectroscopy at High Electric Fields, *Broadband Dielectric Spectroscopy: A Modern Analytical Technique* January 1, 2021, 91–104 doi:10.1021/bk-2021-1375.ch004

[21]P. M. Déjardin *et al*., Nonlinear dielectric relaxation in AC and DC electric fields, *Nonlinear Dielectric Spectroscopy* (Springer, Cham, 2018), pp. 35–74.

[22]N. Wei, P.-M. Déjardin, Y. P. Kalmykov and W. T. Coffey, External dc bias-field effects in the nonlinear ac stationary response of dipolar particles in a mean-field potential, *Phys. Rev. E* **93**, 042208 (2016).

[23]A. V. Ambarov, Dynamical susceptibility of interacting superparamagnetic particles in a static magnetic field, *Izvestiya of Sarat. Univ. Phys.* **22**, 131 (2022).