

Phenomenological Model of Dynamic Nonlinear Response of Relaxor Ferroelectrics

A. E. Glazounov

Institute for Ceramics in Mechanical Engineering, University of Karlsruhe, D-76131 Karlsruhe, Germany

A. K. Tagantsev

Ceramics Laboratory, Swiss Federal Institute of Technology in Lausanne (EPFL), CH-1015 Lausanne, Switzerland

(Received 14 March 2000)

A phenomenological model was proposed which describes frequency dispersion of nonlinear dielectric response of relaxor ferroelectrics (relaxors) as a result of dispersion of their linear dielectric permittivity. The model was applied to $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) relaxor. It provided a good qualitative description of temperature and frequency dependence of the third harmonics of PMN. Analysis within the model yielded a frequency independent nonlinear coefficient corresponding to static nonlinear dielectric susceptibility. The model explained the recently reported for PMN data on the Vogel-Fulcher law for frequency dependence of the temperature at which the third harmonics passes a maximum.

PACS numbers: 77.84.Dy, 77.22.Gm, 77.80.-e

Recently, there has been a strong interest in studying nonlinear dielectric properties of relaxor ferroelectrics (relaxors), since it has been recognized that nonlinear dielectric data could be used to discriminate between existing models of relaxors, and thus lead to the development of the understanding of these materials.

At present, there remain only two concepts which are consistent with the key features of relaxors, such as (i) frequency dispersion within giga- to millihertz range [1,2] with a freezing of the relaxation time spectrum [2,3], (ii) nonergodic behavior at low temperatures [4,5] as a result of the freezing, and (iii) phase transition into a long-range ferroelectric phase induced by a dc electric field around the freezing temperature T_f [4,6]. One concept describes relaxors as analogs of dipolar glasses where random fields and random interactions between polar regions lead to the freezing transition into the glassy state [2,4,7–9]. The second concept describes the freezing as a phase transition to ferroelectric state broken into nanodomains due to quenched random fields [5,10,11].

The current discussion suggests that the controversy between the dipolar glass and nanodomain concepts of relaxors can be solved by measuring the temperature dependence of the ratio χ_{n1}/ϵ_s^4 in the vicinity of T_f , which should contain information about the type of freezing [12]. ϵ_s and χ_{n1} are the static linear permittivity and static nonlinear susceptibility, respectively, defined from $P = \epsilon_0[\epsilon_s E - \chi_{n1} E^3 + \dots]$, where P is the polarization, E is the electric field, and $\epsilon_0 = 8.854 \times 10^{-12}$ F/m. It is recommended to determine χ_{n1} from the third harmonic component of the polarization measured in the limit of the very small ac field, instead of using the dc nonlinear effect [13], in order to avoid a possibility of inducing the phase transition into a long-range ferroelectric phase near T_f [4,6,12]. So far, it has been impossible to obtain conclusive information on the behavior of χ_{n1}/ϵ_s^4 vs T for any of the relaxors. The reason is that in relaxors the frequency dispersion of both linear permittivity and third harmonics

starts far above T_f [2,14], and thus hinders determination of ϵ_s and χ_{n1} around the freezing temperature.

Since dielectric properties of relaxors exhibit strong frequency dispersion, it is highly desirable to have a dynamic theory of nonlinear response, which would allow one to either model the dynamic response and compare it with experimental data, or to analyze the data and obtain the temperature dependence of χ_{n1}/ϵ_s^4 . To our knowledge, no dynamic theory of nonlinear response is available either for the dipolar glass [2,4,7–9] or for the nanodomain [5,10,11] concept of relaxors. Recently, a spherical random bond-random field (SRBRF) model [9,13] was developed for the static case of the dipolar glass concept. It predicted that χ_{n1}/ϵ_s^4 should have a maximum at T_f , instead of diverging behavior observed in classical dipolar glasses [15,16], due to the presence of random fields. However, because of the difficulties related with obtaining χ_{n1}/ϵ_s^4 near T_f , this static case could not be validated experimentally.

To fill the existing gap between theory and experiment, in this work we develop a phenomenological model of a dynamic nonlinear response of relaxors. It aims at describing the frequency dependence of the third harmonics of the polarization, in order to expand the temperature interval, necessary to study freezing phenomena in relaxors [2], toward freezing temperature T_f . The model employs a series expansion of the free energy of the material in terms of macroscopic polarization: $G_1 = \alpha P^2 + \beta P^4 + \dots$, where α and β are temperature dependent coefficients. This expansion describes macroscopically centrosymmetrical cubic material, which is the case of most of the relaxors, including the “classical” example $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) [1,6]. The expansion (and the following formulas) is written in the scalar form, which corresponds to the case of either a single crystal where field and polarization are directed along the $\langle 100 \rangle$ crystal axis, or ceramics with a random orientation of the grains. The term βP^4 in this expansion controls the nonlinear dielectric

properties of the material, and higher order nonlinear terms are omitted. This assumption may be the case of experiment where the amplitudes of polarization harmonics, P_k , satisfy inequality: $P_1 \gg P_3 \gg P_5 \dots$, which was observed in PMN [14,17].

For the system where the dynamic response is controlled by a single relaxation time, such as “normal” ferroelectrics, the equation of motion corresponding to the above expansion can be written as [18] $E = \alpha P + \beta P^3 + \eta dP/dt$, or in the following form:

$$\tau \frac{dP}{dt} + P = \varepsilon_0 \varepsilon_s [E - \beta P^3], \quad (1)$$

where relaxation time, $\tau = \eta \alpha^{-1}$, and static linear permittivity, $\varepsilon_s = \varepsilon_0 \alpha^{-1}$, were introduced. From Eq. (1), the nonlinear component of the polarization can be found by using response function, $f_P(t) = e^{-t/\tau}/\tau$, and iterating the following integral equation:

$$P(t) = \varepsilon_0 \varepsilon_s \int_{-\infty}^t f_P(t-t') [E(t') - \beta P^3(t')] dt', \quad (2)$$

which directly follows from Eq. (1). This method can also be applied to relaxors, if one takes into account their broad spectrum of relaxation times [2,3]. The solution of Eq. (1) can be generalized in the case of the spectrum by using the response function in the form [19]: $f_P(t) = \int_{-\infty}^{+\infty} G(\ln\tau) (e^{-t/\tau}/\tau) d(\ln\tau)$, where the spectrum $G(\ln\tau)$ has a normalizing condition: $\int_{-\infty}^{+\infty} G(\ln\tau) d(\ln\tau) = 1$. With a generalized response function, the nonlinear component of the polarization can still be found by iterating Eq. (2).

If an ac field, $E(t) = E_m \sin\omega t$, is applied to the cubic material, the induced polarization is given as a sum of odd frequency harmonics. Since in the model being considered the nonlinear properties are given by the term βP^3 in Eq. (1), we limit ourselves to the first and third harmonics: $P(t) = P_1' \sin\omega t + P_1'' \cos\omega t + P_3' \sin 3\omega t + P_3'' \cos 3\omega t$, where the amplitudes of their real, P_1', P_3' , and imaginary, P_1'', P_3'' , parts satisfy inequality $P_3', P_3'' \ll P_1', P_1''$. The first iteration of Eq. (2) gives well-known expressions for the real and imaginary parts of linear permittivity [19]:

$$\varepsilon_1'(\omega) = \varepsilon_s \int_{-\infty}^{+\infty} G(\ln\tau) \frac{1}{[1 + (\omega\tau)^2]} d(\ln\tau)$$

and $\varepsilon_1''(\omega) = \varepsilon_s \int_{-\infty}^{+\infty} [G(\ln\tau) (\omega\tau)] / [1 + (\omega\tau)^2] d(\ln\tau)$, which are defined from the amplitudes of the first harmonics as $P_1' = \varepsilon_1' \varepsilon_0 E_m$ and $P_1'' = -\varepsilon_1'' \varepsilon_0 E_m$, respectively. The second iteration yields the amplitudes of the third harmonics as [17]

$$P_3' = \frac{\beta}{4} [\varepsilon_1'^3(\omega) \varepsilon_1'(3\omega)] \varepsilon_0^4 E_m^3, \quad (3)$$

$$P_3'' = \frac{\beta}{4} [\varepsilon_1''(3\omega) \varepsilon_1'^3(\omega) + 3\varepsilon_1''(\omega) \varepsilon_1'(3\omega) \varepsilon_1'^2(\omega)] \varepsilon_0^4 E_m^3. \quad (4)$$

Note that in these equations, β , the permittivity, and the third harmonics also depend upon temperature T ; however, this argument is omitted to make the reading of the formulas easier.

To verify the model, our experiments included measurements of $\varepsilon_1', \varepsilon_1'', P_3'$, and P_3'' of the PMN single crystal as a function of temperature and frequency [17]. An ac field was applied along the $\langle 100 \rangle$ axis and had an amplitude of $E_m = 40$ V/cm, which is considered to be small enough to probe “true” nonlinear properties of relaxors [2]. The permittivity was measured within the frequency interval 20 Hz to 1 MHz using a HP 4284A LCR meter, and the third harmonics was measured within the interval 1 Hz to 10 kHz using a SR 830 lock-in amplifier. All the experiments were performed upon cooling from 380 to 180 K with a rate of 0.5 K/min.

The temperature and frequency dependence of the third harmonics measured in the experiment are plotted in Figs. 1(a) and 1(b). Imaginary part, P_3'' , and the absolute value of the real part, $|P_3'|$, exhibit similar behavior: They have a maximum as a function of temperature, which shifts to higher temperatures and becomes smaller in magnitude with increasing frequency. At high temperatures, P_3'' and the frequency dispersion of $|P_3'|$ disappear simultaneously: above $T \approx 270$ K, P_3' coincides for different frequencies within the experimental uncertainty and $P_3'' = 0$.

Figures 1(c) and 1(d) show P_3' and P_3'' calculated within the proposed model using Eqs. (3) and (4). The curves were calculated from the data on linear permittivity using $P_3' \propto \varepsilon_1'^3(\omega) \varepsilon_1'(3\omega)$ and $P_3'' \propto [\varepsilon_1''(3\omega) \varepsilon_1'^3(\omega) + 3\varepsilon_1''(\omega) \varepsilon_1'(3\omega) \varepsilon_1'^2(\omega)]$, which differ from Eqs. (3) and (4) only by a factor of $\beta \varepsilon_0^4 E_m^3 / 4$. As one can see, the model reproduces qualitatively the experimentally measured dispersion of the third harmonics, shown in Figs. 1(a) and 1(b). The only disagreement is a nonmonotonical behavior of $P_3''(T)$ measured around 270 K at 1 Hz, Fig. 1(b). This deviation represents the contribution from higher polarization harmonics. When the ac field amplitude was increased, it developed into a well-defined minimum in $P_3''(T)$, which exhibited a regular frequency dependence, as shown in Fig. 2.

If the model is correct, the nonlinear coefficient β should be frequency independent. Figure 3 demonstrates β calculated from P_3' using Eq. (3) and the data from Figs. 1(a) and 1(c). To the most part β appears to be frequency independent: above 280 K (obviously, here the response is quasistatic), and below 250 K, where the values of β corresponding to different frequencies coincided to within the experimental uncertainty. $\beta(T)$ shows some frequency dependence only in the temperature interval 260–280 K. Two possible reasons can be indicated: either this is a true dispersion of β itself, or the dispersion comes from higher order harmonics. We gravitate towards the latter option, because in this temperature interval, 260–280 K, the third harmonics of PMN exhibited deviation from the dependence expected from Eq. (3): $P_3' \propto E_m^3$, even at small values of the ac field [14,17].

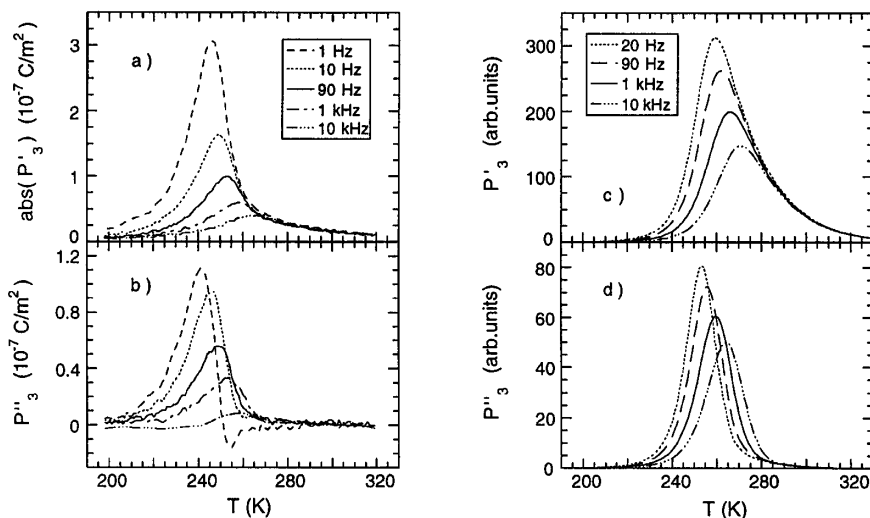


FIG. 1. (a) and (b) Temperature and frequency dependence of the real, P'_3 , and imaginary P''_3 , parts of the third polarization harmonics of PMN single crystal, measured using ac field amplitude of 40 V/cm. (c) and (d) P'_3 and P''_3 calculated within the proposed phenomenological model using the data for linear dielectric permittivity measured at the same ac field amplitude, as $P'_3 \propto \epsilon_1'^3(\omega)\epsilon_1'(3\omega)$ and $P''_3 \propto [\epsilon_1''(3\omega)\epsilon_1'^3(\omega) + 3\epsilon_1''(\omega)\epsilon_1'(3\omega)\epsilon_1'^2(\omega)]$.

Nevertheless, the results presented above lead to the following conclusions: (i) there is a good qualitative agreement of calculations, Figs. 1(c) and 1(d), with the experiment, Figs. 1(a) and 1(b), (ii) the nonlinear coefficient β is frequency independent in the temperature interval where both linear permittivity and third polarization harmonics exhibit frequency dispersion, and, in particular, (iii) upon cooling from 260 to 200 K, β shows the same steep increase by 2 orders of magnitude for all the frequencies. Taken together, (i)–(iii) let us conclude that the proposed phenomenological model provides a good description of the dynamics of the nonlinear response of PMN.

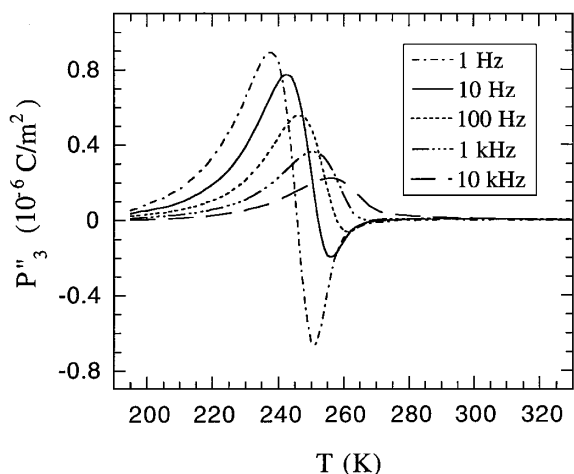


FIG. 2. Temperature and frequency dependence of the imaginary part, P''_3 , of the third harmonics of PMN measured at higher ac field amplitude, 100 V/cm. The nonmonotonic deviation in $P''_3(T)$ seen in Fig. 1(b) for 1 Hz is now developed into a well-defined minimum, which shows a regular change with frequency. Thus, this corresponds to the contribution from higher polarization harmonics.

The fact that β , derived from the dynamic experiment, does not show a frequency dependence, even around the freezing temperature, $T_f = 220$ K [2,3], may imply that β corresponds to the true static nonlinear susceptibility of PMN [20]: $\beta \propto \chi_{nl}/\epsilon_s^4$. Thus, one can compare $\beta(T)$ from Fig. 3 with the microscopic SRBRF model [9,13]. To the larger part, $\beta(T)$ seems to be consistent with model calculations [9,13]. It exhibits a minimum around 270 K in Fig. 3, which was also observed in Ref. [21], and a strong

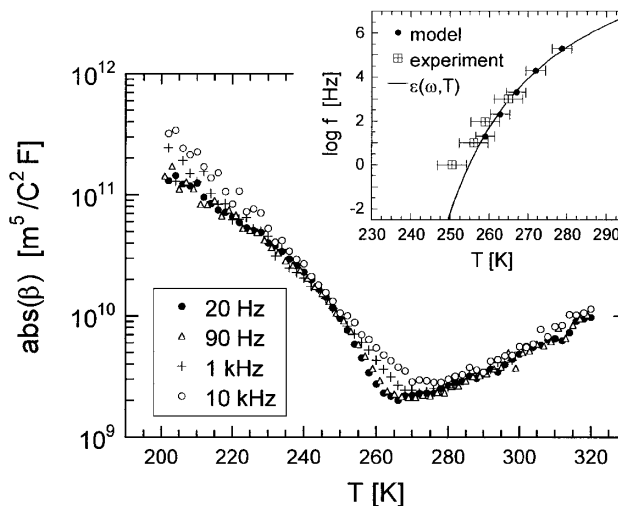


FIG. 3. Temperature dependence of nonlinear coefficient β at different frequencies of the ac field calculated within the phenomenological model from the data on the third harmonics, P'_3 , and linear permittivity, ϵ_1' . The inset shows the relationship between the logarithm of measurement frequency and temperature of the maximum, T_{max} , corresponding to the measured $P'_3(\omega, T)$ (boxes) from Ref. [2] and the model, $\epsilon_1'^3(\omega, T)\epsilon_1'(3\omega, T)$, (closed circles) from Fig. 1(c). The solid line corresponds to the fit of $\omega(T_{max})$ for $\epsilon_1'(\omega, T)$ to the Vogel-Fulcher law within eleven decades of frequency, from Ref. [3].

increase over 2 orders of magnitude at lower temperatures. We find only one discrepancy with the SRBRF model. In Fig. 3, $\beta(T)$ continues to increase monotonically even below the freezing temperature, $T_f = 220$ K, whereas the SRBRF model predicts a maximum of $\beta(T)$ at T_f . This discrepancy may require additional verification. No conclusion can be made now regarding the nanodomain concept of relaxors [5,10,11], because no microscopic theory is available here, even in the static case.

The essential feature of the present phenomenological model is that here the dispersion of the nonlinear response originates from the dispersion of linear permittivity, Eqs. (3) and (4). This may explain the recent data [2] for the frequency dependence of the temperature of the maximum, T_{\max} , of the third harmonics, $P_3'(\omega, T)$. It was shown that $\omega(T_{\max})$ obeyed the Vogel-Fulcher (VF) law: $\omega = \omega_0 \exp[-U_a/k_B(T_{\max} - T_f)]$, and the fit yielded the value of freezing temperature T_f very close to that determined from the similar analysis of the linear permittivity [2]. The inset of Fig. 3 compares the frequency dependence of T_{\max} derived from the results of calculations within the present model, $\varepsilon_l'^3(\omega, T)\varepsilon_l'(3\omega, T)$, and from the measured third harmonics, $P_3'(\omega, T)$. One can see that $\omega(T_{\max})$ for the model (closed circles) and measurements (open circles) agree well with each other. In fact, this result correlates with the data showing that nonlinear coefficient, $\beta(T)$, is frequency independent, Fig. 3, and therefore, the frequency dependence of the third harmonics is due to that of linear permittivity. We did not try to fit $\omega(T_{\max})$ for $P_3'(\omega, T)$ and the model, because the small number of data points available would not produce a reliable fit. Instead, to check if the third harmonics may follow the VF law, in the same plot we compare its data with the curve $\omega(T_{\max})$ for the linear permittivity, which is known to obey the VF law within eleven decades of frequency [3]. The close agreement between data points for the third harmonics (both model and measured) with the solid line corresponding to $\varepsilon_l'(\omega, T)$ let us conclude that most likely $\omega(T_{\max})$ for $P_3'(\omega, T)$ will also follow the VF law, and the values of the parameters will be close to those corresponding to the VF law for $\varepsilon_l'(\omega, T)$, as was observed in Ref. [2].

In conclusion, the phenomenological model was developed which describes frequency dispersion of the third polarization harmonics in relaxors as a result of the dispersion of their linear response. The model was supported by the following results: (i) good qualitative description of the temperature and frequency dependence of the third harmonics of PMN relaxor; (ii) the nonlinear coefficient $\beta \propto \chi_{nl}/\varepsilon_s^4$ derived from the analysis of experimental data within the model was frequency independent; and (iii) the model explained the VF law for the frequency dependence of the temperature of the maximum of the third harmonics reported recently [2].

The model deals with the frequency dependence of nonlinear response and, therefore, expands the temperature interval necessary to study the freezing phenomena in relaxors toward freezing temperature. To make use of this advantage, $\beta(T)$ derived from our experimental data was compared with microscopic SRBRF model near T_f [9,13]. To the larger part, $\beta(T)$ agreed with the SRBRF model, but it did not exhibit the maximum at the freezing temperature which is predicted by the model.

We would like to thank Mr. A. Titov of the State Optical Institute (Russia) for the supplied PMN crystals, and our colleagues from the Jozef Stefan Institute (Slovenia): Professor R. Blinc, Professor A. Levstik, and Professor R. Pirc, and Dr. V. Bobnar, Dr. C. Filipic, and Dr. Z. Kutnjak for helpful discussions. The work of the EPFL was supported by the Swiss National Science Foundation.

-
- [1] G. A. Smolensky, J. Phys. Soc. Jpn. **28**, 26 (1970).
 - [2] A. Levstik *et al.*, Phys. Rev. B **57**, 11 204 (1998).
 - [3] A. E. Glazounov and A. K. Tagantsev, Appl. Phys. Lett. **73**, 856 (1998).
 - [4] E. V. Colla *et al.*, Phys. Rev. Lett. **74**, 1681 (1995).
 - [5] V. Westphal, W. Kleemann, and M. D. Glinchuk, Phys. Rev. Lett. **68**, 847 (1992).
 - [6] R. Sommer, N. K. Yushin, and J. J. van der Klink, Phys. Rev. B **48**, 13 230 (1993).
 - [7] D. Viehland *et al.*, J. Appl. Phys. **68**, 2916 (1990).
 - [8] B. E. Vugmeister and H. Rabitz, Phys. Rev. B **57**, 7581 (1998).
 - [9] R. Pirc and R. Blinc, Phys. Rev. B **60**, 13 470 (1999).
 - [10] A. E. Glazounov, A. K. Tagantsev, and A. J. Bell, Phys. Rev. B **53**, 11 281 (1996).
 - [11] A. K. Tagantsev and A. E. Glazounov, Phys. Rev. B **57**, 18 (1998).
 - [12] Z. Kutnjak *et al.*, Phys. Rev. B **59**, 294 (1999).
 - [13] R. Pirc and V. Bobnar, in Proceedings of the 9th European Meeting on Ferroelectricity [Ferroelectrics (to be published)].
 - [14] A. E. Glazounov and A. K. Tagantsev, J. Phys. Condens. Matter **10**, 8863 (1998).
 - [15] M. Maglione, U. T. Höchli, and J. Joffrin, Phys. Rev. Lett. **57**, 436 (1986).
 - [16] J. Hemberger *et al.*, Phys. Rev. Lett. **76**, 2330 (1996).
 - [17] A. E. Glazounov, Ph.D. thesis, EPFL, Lausanne, 1997.
 - [18] This equation was employed for the calculation of the frequency dependence of the third polarization harmonics in the case of a single relaxation time by Y. Ishibashi, J. Korean Phys. Soc. **32**, S407 (1998).
 - [19] C. J. F. Böttcher and P. Bordewijk, *Theory of Electric Polarization* (Elsevier, Amsterdam, 1978), Vol. 2, 2nd ed.
 - [20] In the static case, Eq. (3) transforms into $P_3' = \beta \varepsilon_s^4 \varepsilon_0^4 E_m^3 / 4$, which gives $\chi_{nl} = \beta \varepsilon_s^4 \varepsilon_0^3$, according to the expansion: $P = \varepsilon_0[\varepsilon_s E - \chi_{nl} E^3 + \dots]$. Thus, $\beta \propto \chi_{nl} / \varepsilon_s^4$.
 - [21] V. Bobnar *et al.*, Phys. Rev. Lett. **84**, 5892 (2000).