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## THE DISPERSION OF STRONG FIELD DIELECTRIC PERMITTIVITY IN (1-x)PMN-(x)PT CERAMICS

### DYSPERSJA PRZENIKALNOŚCI DIELEKTRYCZNEJ W SILNYCH POLACH ELEKTRYCZNYCH W CERAMICE (1-x)PMN-(x)PT

We propose the method of analysis of the dielectric permittivity measured in very strong electric fields. The method is based on the numeric calculations of derivative from  $P - E$  hysteresis loop. Such investigations have been performed for PMN-PT ceramics at various temperatures and frequencies. As a result we analyze the low frequency dispersion of the strong field dielectric permittivity.

*Keywords:* dielectric permittivity, ceramics, hysteresis, dispersion, ferroelectric relaxor

Artykuł przedstawia propozycję metody analizy przenikalności elektrycznej mierzonej w bardzo wysokich polach elektrycznych. Metoda opiera się na obliczeniach numerycznych pochodnych z pętli histerezy  $P - E$ . Przedstawiono badania tą techniką ceramiki PMN-PT dla różnych temperatur i częstotliwości. Praca prezentuje analizę dyspersji przenikalności dielektrycznej w silnych polach elektrycznych o niskiej częstotliwości.

### 1. Introduction

Relaxor materials are the object of interest from many years. The properties of the relaxors locate them between ferroelectrics and normal dielectrics. One of main differences between relaxors and normal ferroelectrics is the shape of the  $PE$  hysteresis loop and its changes vs. temperature. In ferroelectrics the  $P - E$  hysteresis loop is square and decreases rapidly during heating at the temperature close to  $T_c$  while in relaxors the  $PE$  hysteresis loop is very slim and decreases gradually in the very wide temperature range. In many papers (for example [1-3]) other properties of relaxors are described.

For understanding the properties of relaxors the investigations of solid solutions relaxor-normal ferroelectrics are very important for understanding the nature of relaxors. The example of such compounds is  $(1-x)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3 - (x)\text{PbTiO}_3$  i.e. (1-x)PMN-(x)PT. On the other hand such materials are very important for practical applications. In PMN-PT at the room temperature the continuous transition from relaxor to ferroelectric properties take place with increasing  $x$ . Phase diagram of PMN-PT was investigated in works [4-6]. It has been stated that for  $x < 0.2$  the symmetry is rhombohedral  $R3m$  for  $0.2 < x < 0.4$  monoclinic  $Cm/Pm$  for  $x < 0.4$  tetragonal. For  $x \approx 0$  (i.e. in PMN) the model re-

laxor properties are observed while for  $x > 0.25$  PMN-PT become normal ferroelectric.

Usually, the term "dielectric permittivity" is used for measurements in a.c. electric field with low amplitude ( $\sim 1\text{kV/m}$ ). At first approximation we can assume that in normal ferroelectrics the weak a.c. electric field leads to small vibrations of the domain walls but  $180^\circ$  reorientations of domains are absent. Such vibrations of domain walls lead to the dispersion of dielectric permittivity of relaxation type within the frequency range  $10^2 - 10^6$  Hz [7]. Some RLC meters allow to measure dielectric permittivity with applied additional d.c. voltage but the field is still lower than coercive field. On the other hand it is observed also the influence of frequency of the strong a.c. field on the shape of  $PE$  hysteresis loop which can be attributed to the fact that some frequency is too high to switch domains (in ferroelectric) or polar regions (in relaxors). Lente and Picinin [8] stated that in the ferroelectric ceramics the frequency dependence of the polarization revealed a strong relaxation of the  $90^\circ$  domain walls at about 100 Hz strongly influenced by defects and their distribution. Also in the case of relaxors (for example PMN-PT) the influence of frequency on the shape of slim hysteresis loop was observed [9-11].

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The thermodynamic relation between dielectric permittivity and the polarization can be obtained as  $\varepsilon = \frac{\partial P}{\partial E}$ . Comparing with for example LGD theory we obtain the following expressions:

$$g(T, P) = \frac{\alpha(T)P^2}{2} + \frac{\beta P^4}{4} + \frac{\gamma P^6}{6} + \dots \quad (1)$$

$$\frac{\partial g(T, P)}{\partial P} = E(T, P) = \alpha(T)P + \beta P^3 + \gamma P^5$$

$$\varepsilon = \frac{\partial P}{\partial E} = \left( \frac{\partial^2 g(T, P)}{\partial P^2} \right)^{-1} = \frac{1}{\alpha(T) + 3\beta P^2 + 5\gamma P^4} \quad (2)$$

For known  $\alpha$ ,  $\beta$ ,  $\gamma$  we can plot dependency between dielectric permittivity and the electric field. Obtained in such a way dependency  $\varepsilon(E)$  is presented in Fig. 1.

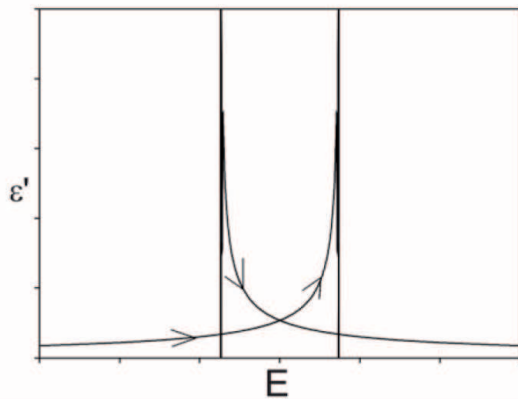


Fig. 1. The dependency  $\varepsilon'(E)$  for ferroelectric material with known  $\alpha$ ,  $\beta$ ,  $\gamma$  parameters

In this work, for such dielectric permittivity we use the name “strong field dielectric permittivity”  $\varepsilon'_H(E)$  (index *H*- means high value of amplitude of a.c. electric field, index *L*- means low value of measuring electric field usually used in RLC meters). In real materials instead two asymptotes presented in Fig. 1, we obtain more or less diffused maxima of  $\varepsilon(E)$ .

Below we try to describe the relaxation processes of domains in the strong electric fields using the formalism from the macroscopic theory of dispersion for low field dielectric permittivity.

## 2. Experiment and calculations

The investigations have been performed for PMN-PT ceramic samples with compositions within the range  $0 < x < 0.25$  (i.e. for which the transition from relaxor to normal ferroelectric properties take place at the room temperature).

Ceramic samples were obtained using sol-gel technology and have been described elsewhere [10]. PMN was got as a result two stages. First, reaction between  $\text{Nb}(\text{OC}_2\text{H}_5)_5$  and  $\text{Mg}(\text{OC}_2\text{H}_5)_2$  with admixture

of ethyl alcohol as a dissolvent. Next, lead acetate (II) and ethylene glycol were added to the mixture. The synthesis of  $\text{PbTiO}_3$  was carried out from lead acetate (II)  $\text{Pb}(\text{CH}_3\text{COO})_2$  and n-titanium propanolate  $\text{Ti}(\text{CH}_3\text{CH}_2\text{CH}_2\text{O})_4$ . The last stage of sol-gel synthesis consisted in connecting both mixtures in order to obtain a mixture of PMN-PT with definite contents of PT. Obtained powders were formed into discs and densification was performed using uniaxial hot pressing method. The pellets were sintered at 1473K for 2 hours under 10MPa pressure in air.

The hysteresis loops within the frequency range 0.1-100 Hz have been presented in [10] and the electrical conductivity measurements in [12]. Calculating the derivative  $\frac{\partial P}{\partial E} = (\varepsilon' - 1)\varepsilon_0 \approx \varepsilon'\varepsilon_0$  we obtain  $\varepsilon'_H(E)$ . The value of  $\varepsilon'_H(E)$  in general depends on the place on the hysteresis loop what is schematically presented in Fig. 2.

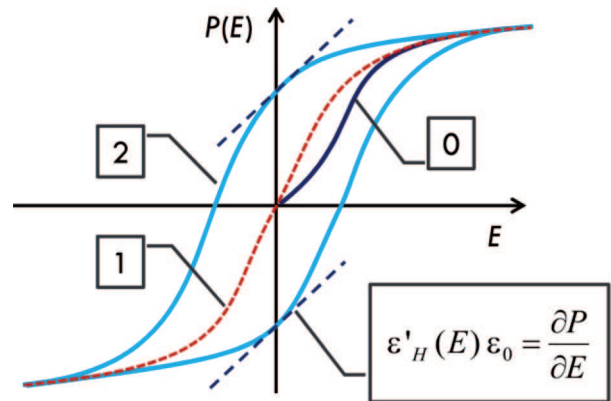


Fig. 2. Schematically presented how  $\varepsilon'_H(E)$  has been calculated from hysteresis loop

In Fig. 2 label 0 is a virgin curve for the sample to which any constant electric field has not been earlier applied, 1 – is the trace of the point of maximal polarization during the increase of the electric field, 2 – the hysteresis loop obtained during alternation of the electric field with the amplitude stronger than coercion field. Below described  $\varepsilon'_H(E)$  has been calculated from the curve 2. Such obtained permittivities for ferroelectrics are schematically presented in Fig. 3a and for relaxors/paraelectrics in Fig. 3b. It is seen that for ferroelectrics dependencies  $\varepsilon'_H(E)$  consists of two symmetrical parts. Below we present only one of these two parts.

First we tried to answer the question how the amplitude of applied a.c. electric field influences the shape of hysteresis loop and  $\varepsilon'_H(E)$  dependency. To answer this question we obtained  $PE$  hysteresis loops for various amplitudes of applied a.c. electric field. The results are presented in Fig. 4.

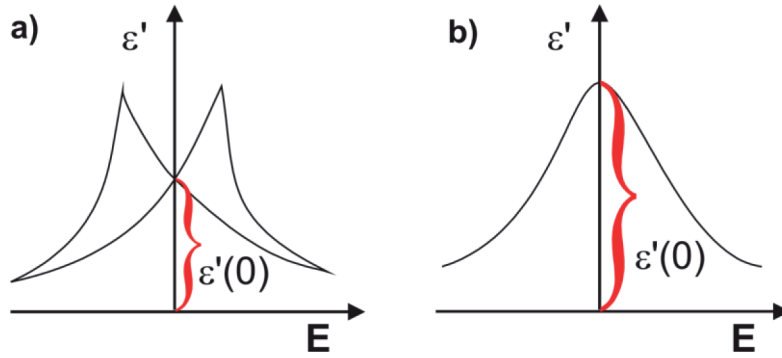


Fig. 3. Schematically presented changes of the dependency  $\varepsilon'(E)$  for a) – ferroelectric material, b) – relaxor

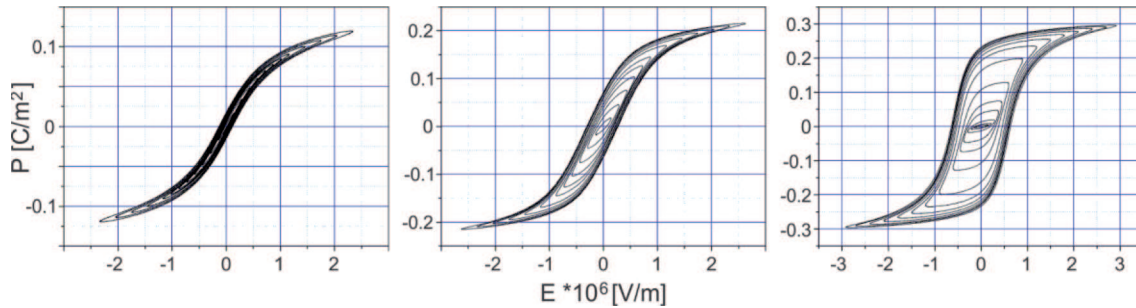


Fig. 4. P-E hysteresis loops obtained for various amplitudes of applied a.c. fields. From left to right – samples with 0.075, 0.150, 0.225 percent PT in PMN-PT solid solution

Next calculating numerically derivative  $\frac{\partial P}{\partial E} = (\varepsilon' - 1)\varepsilon_0 \approx \varepsilon'\varepsilon_0$  we obtain dependencies  $\varepsilon'_H(E)$  for increasing amplitude of applied fields. Taking the values of  $\varepsilon'_H(0)$  defined at Fig. 3 we can plot the dependency between  $\varepsilon'_H(0)$  and the amplitude of applied a.c. field. Results are presented in Fig. 5. For high enough amplitude of applied a.c. field obtained value of  $\varepsilon'(0)$  does not increase with increasing amplitude and can be named  $\varepsilon'_H(0)$ . Such values are taken below to investigation of the influence of the frequency on  $\varepsilon'_H(0)$

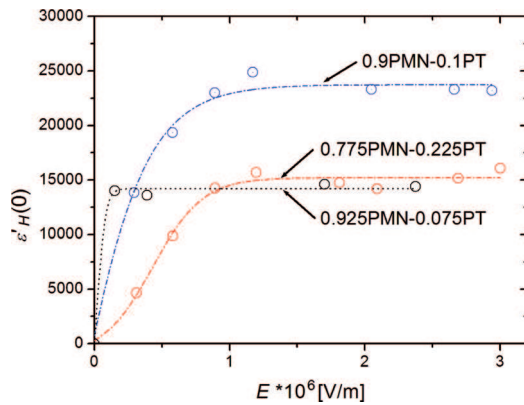


Fig. 5. The dependency between  $\varepsilon'_H(0)$  and the amplitude of applied a.c. field

Dependencies  $\varepsilon'_H(E)$  obtained as described above are presented in Fig. 6 at constant temperature 40°C. In left hand parts of Fig. 6 the dependencies  $\varepsilon'_H(f)$  are presented while at right parts of these graphs the dependencies  $\varepsilon'_L(f)$  are shown for comparison.

The dependencies  $\varepsilon'(f)$  (Fig. 6) have been fitted to the formula:

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + (\omega\tau)^{2\alpha}} \quad (3)$$

which can be obtained from Cole dispersion formula as:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau^{1-\beta}} = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + i\omega\tau^\alpha} \quad (4)$$

The parameters of fitting are presented in Table I for 0.9PMN-0.1PT, 0.85PMN-0.15PT, and 0.775PMN-0.225PT and as solid lines in Fig. 6. For  $T > T_c$  the difference between low and strong field dielectric permittivities gradually disappears.

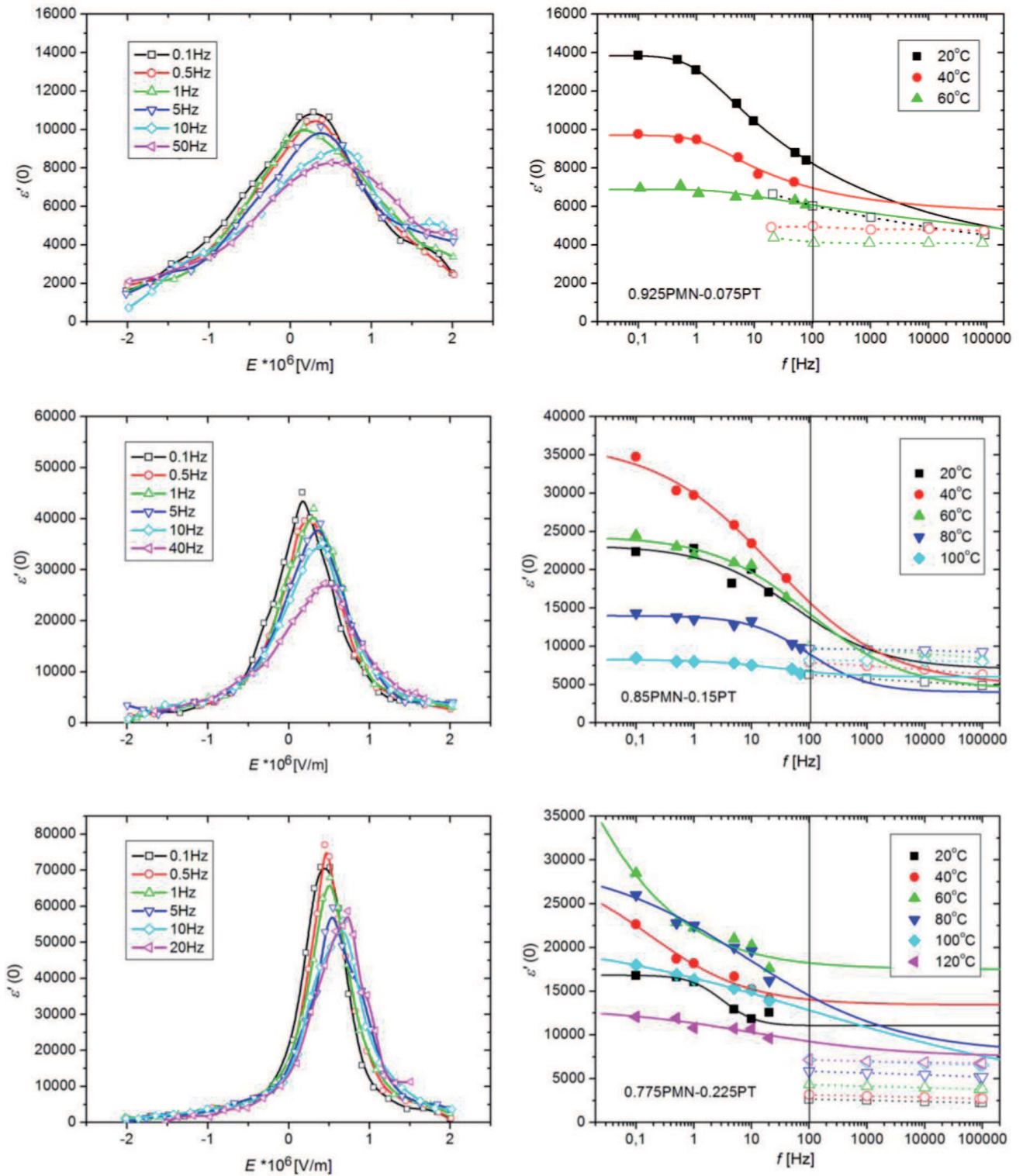


Fig. 6. Dependencies  $\epsilon'_H$  (calculated derivatives from hysteresis loops) for 0.925PMN-0.075PT, 0.85PMN-0.15PT and 0.775PMN-0.225PT. Left column – dependencies  $\epsilon'_H(E)$  for particular frequencies in temperature 40°C. Right column – dependencies  $\epsilon'_H(f)$ ; left part of the graphs – values  $\epsilon'_H(E = 0)$ ; right part –  $\epsilon'_L = \epsilon'$  dotted lines, data from RLC meter measurements (for comparisons)

### 3. Conclusions

Though at temperatures close to  $T_c$  the results of fitting are obtained with rather big errors we think that

proposed method allows to distinguish between strong field relaxation related with domain switching and weak field relaxation related with vibration of domain walls.

For better understanding the mechanism in ferroelectrics and relaxors should be necessary to construct the model which connect the dynamic of domain reversal with dispersion of strong field dielectric permittivity.

#### Acknowledgements

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