Broadband dielectric spectroscopy of 0.4PMN-0.3PSN-0.3PZN ceramics

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Abstract. In this paper, results of the broadband dielectric spectroscopy of 0.4PbMg1/3Nb2/3O3-0.3PbZn1/3Nb2/3O3-0.3PbSc1/2Nb1/2O3 (0.4PMN-0.3PZN-0.3PSN) are presented. Dielectric spectra of these solutions were investigated in a broad frequency range from 20 Hz to 100 GHz. Very strong and broad dielectric relaxation was analyzed in terms of distribution of relaxations times, using Tichonov regularization method. It revealed slowing down of the longest relaxation and the mean relaxation times in the agreement with the Vogel-Fulcher law and the Arrhenius law, respectively.

1. Introduction
Relaxor ferroelectrics have attracted considerable attention in recent years due to their unusual physical behaviour and excellent dielectric and electromechanical properties. Dielectric measurements of relaxors are very important for both fundamental investigations and applications. However most of such investigations are performed only in narrow frequency range [1]. Often only increasing temperature of the dielectric permittivity maximum with increasing frequency is analyzed. As a rule, such investigations are based on various predefined formulas of distribution of relaxation times. Most popular predefined distribution of relaxation times is the Cole-Cole function [2], however this model is good enough only for narrowband dielectric data of relaxors. On the other hand, two or more Cole-Cole functions describe better dielectric dispersion in relaxors, however a further drawback of such an approach is the inherent difficulty of separating processes with comparable relaxation times. Other predefined distribution functions: Davidson-Cole [3], Havriliak-Negami [4], Joncher, Kolraush-Wiliams-Watts and Curie-von Schweidler [5] also frequently are used for analysis of dielectric data of relaxors, however such analysis can not explain dynamics of polar nanoregions.

Broadband dielectric spectroscopy from Hz to THz region is needed for investigation of very wide dielectric relaxations in relaxors and because the broadband and THz technique is rather rare, only few relaxor ferroelectric systems PMN [6], PST [7] and PLZT [8] were investigated in microwave and THz range simultaneously. However, most of such investigations in frequency range between several GHz and several hundred GHz are performed with thin films at or below room temperature. On the other hand, in literature there are many speculations about relaxor dynamics based on hypothesis about the dielectric dispersion between several GHz and several hundred GHz. The authors of [9] discovered two dielectric dispersions in relaxors, one from low frequencies to 1.8 GHz
and another between 1.8 GHz and several hundred GHz, however no any data they have between 1.8 GHz and 100 GHz. We can predicate that dielectric dispersion of bulk relaxors at higher temperatures (near and below $T_B$) is rather unknown, because the dielectric dispersion at higher temperatures is reveals mainly in microwave and THz region.

Dielectric and piezoelectric studies of solid solutions of relaxor ferroelectrics like PMN and PSN with normal ferroelectric PbTiO$_3$ revealed giant piezoelectricity (one order of magnitude larger than in the best classical ferroelectrics like PbZr$_{1-x}$Ti$_x$O$_3$) for compositions near morphotropic phase boundary [10]. The paper of Park and Shrout [10] turned the attention of many physicists to the study of solid solutions of relaxor ferroelectrics with ferroelectrics. Monoclinic phase was observed on the morphotrophic phase boundary between the tetragonal and rhombohedral phases and it was proposed that the easy rotation of polarization in the monoclinic phase is responsible for the giant piezoelectric coefficient in these systems [11].

Solid solutions of two relaxor ferroelectrics were investigated, although it was intuitively expected that such solid solutions will exhibit again a relaxor behaviour. The best-investigated system is PMN - PSN solid solution [12, 13]. The relaxor behaviour was observed in both ordered and disordered forms of (1-x)PMN-(x)PSN for $x \leq 0.64$. At higher levels of substitution, the dielectric response was dependent on the degree of order: disordered samples were relaxors and ordered samples exhibited normal ferroelectric behaviour. Such behaviour was explained within a Bragg-Wiliams approach by employing the random layer model.

Ternary solid solutions of PSN-PZN-PMN relaxor ferroelectrics were first synthesized and investigated by [14]. The system was very easily soluble and the dielectric data showed high values of permittivity 7000–30 000 with a diffuse peak typical for relaxor ferroelectrics. Preliminary dielectric spectra of 0.2PMN-0.4PSN-0.4PZN [15] and 0.4PSN-0.3PMN-0.3PZN [16] ceramics already were published. It was shown that the dielectric relaxation is so broad in these systems that the Cole-Cole model only above room temperature can describe it. The aim of this paper is to investigate dielectric dispersion of 0.4PMN-0.3PZN-0.3PSN ceramics in wide frequency range (20 Hz – 100 GHz) on order to explain dynamics of polar nanoregions in ferroelectric relaxors.

2. Experimental

The ternary 0.2PSN-0.4PMN-0.4PZN solid solution was synthesized by solid state reactions from high grade oxides PbO$_3$, Nb$_2$O$_5$, MgO, ZnO, Sc$_2$O$_3$. Detailed forming and sintering conditions are presented in [14].

The low-frequency dielectric response in the range of 20 Hz – 1 MHz was measured using a HP 4284 LCR meter. Dielectric measurements in the high-frequency range of 10 MHz – 1.25 GHz were performed using a computer controlled HF dielectric spectrometer. The dielectric parameters were calculated taking into account the electromagnetic field distribution in the sample [17]. In the frequency range 8 –100 GHz the waveguide automatic dielectric spectrometers have been used. In all measurements the silver paste have been used for contact.

3. Results and discussion

The temperature dependences of complex dielectric permittivity $\varepsilon^*$ of presented ceramics at various frequencies show typical relaxor behaviour in all investigated ceramics (figure 1). There is a broad peak in the real part of dielectric permittivity as a function of temperature. With increasing frequency in the wide frequency range, $T_m$ increases, while the magnitude of the peak decreases. Static permittivity of this ceramics is very high; the peak value is about 6,000 at frequencies lower than 0.1 kHz. There is a strong dielectric dispersion in the radio frequency region around and below $T_m$ at 1 kHz. At temperatures around and above its peak temperature ($T'_m$) of the dielectric absorption, the dielectric losses exhibit strong frequency dependence. The value of $T'_m$ is much lower than that of $T_m$ at the same frequency, the difference between $T_m$ and $T'_m$ increase on increasing frequency, that this difference is about 10 K at 129 Hz and about 100 K at 53 GHz. With increasing frequency, $T_m$ shifts
to higher temperature and the magnitude of the dielectric absorption peak increases till about 1 GHz and then decrease. At frequencies below 1 GHz, with decreasing temperature, the dielectric absorption increases rapidly in the temperature region around $T_m$. At higher (above 1 GHz) frequencies the absorption temperature dependence is almost symmetric. The dielectric absorption is nearly independent of the frequency (in fact, the dielectric absorption shows a very diffuse dependence on the frequency) at a temperature much lower than $T_m$. Permittivity remains of the order of 1,000 even in microwave range and losses are also very high ($\tan \delta \approx 1$) at microwaves. It indicates that the main dielectric dispersion occurs in the microwave range.

The Vogel-Fulcher behaviour for the temperatures of the permittivity peaks, which is known to be one of the typical peculiarities of relaxors [18], is also observed in our samples. From this Vogel-Fulcher analysis follows that $\varepsilon(0)$ have maximum nearly at room temperature, however such analysis is not absolutely correct for relaxors as it is described below. On the other hand, the maximum of $\varepsilon(0)$ indicates some phase transition, which is really not observed in prototypical relaxors PMN. More appropriate assumption is that $\varepsilon(0)$ does not decrease on cooling.

For understanding the dielectric relaxation, it is more convenient to use frequency plot of the complex permittivity at various representative temperatures (see figure 2). One can see a huge change of dielectric dispersion with temperature in all investigated ceramics. At higher temperatures ($T \geq 400$ K), the dielectric loss dispersion it is clearly symmetric and is observed only at higher frequencies (more than 1 GHz). On cooling, the relaxation slows down and broadens. At temperatures around 300 K the relaxation becomes strongly asymmetric and very broad. On further cooling, the dielectric dispersion becomes so broad that we can see only part of this dispersion in our frequency range.

![Figure 1](image1.png)  
**Figure 1** Temperature dependence of complex dielectric permittivity of 0.4PMN-0.3PSN-0.3PZN measured at different frequencies.

![Figure 2](image2.png)  
**Figure 2** Frequency dependence of complex dielectric permittivity of 0.4PMN-0.3PSN-0.3PZN ceramics measured at different temperatures. The solid lines are the best fit according to (3).
The symmetric dielectric dispersion at high temperatures can be easily described by the Cole-Cole formula

\[ \varepsilon^* = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{1 + (i\omega\tau)^{\alpha}} \, , \]  

(1)

which reduces to the Debye type formula with \( \alpha = 0 \). In this equation \( \Delta\varepsilon \) represents the strength of relaxator, \( \tau \) is the mean Cole-Cole relaxation time, \( \alpha \) is the relaxation time distribution parameter, \( \varepsilon_{\infty} \) is the contribution of all phonon modes and electronic polarization.

Temperature dependences of the Cole-Cole parameters obtained from the fit of investigated ceramics are presented in figure 3. The parameter \( \alpha_{CC} \) is small (<0.2, however no Debye like dispersion really is observed in presented relaxors) only at higher temperatures. On cooling, this parameter increases (i.e. distribution of relaxation times broadens). The mean Cole-Cole relaxation time on cooling diverges according to the Vogel-Fulcher law

\[ \tau = \tau_0 e^{E_f/(T-T_0)} \, . \]  

(2)

The Vogel-Fulcher law parameters are: \( \tau_0 = 1.5 \times 10^{-14} \) s, \( T_0 = 210 \) K, \( E_f/k_B = 1150 \) K. The maximum of temperature dependences of \( \Delta\varepsilon \) correspond to maximum of dielectric permittivity at lower frequencies, but real temperature dependences of static dielectric permittivity of relaxors cannot be obtained below \( T_m \), because the dielectric dispersion is too broad and part of it appears below our experimental frequency limit. At lower temperatures, the Cole-Cole fit is no more appropriate, because the absorption peak is not symmetric, and even close to the freezing temperature the absorption \( \varepsilon''(\nu) \) does not exhibit any clear maximum, so that the determination of the mean relaxation time \( \tau_{CC} \) is not unambiguous (figure 2, \( T \leq 300 \) K).

Figure 3 Temperature dependence of Cole-Cole parameters a) \( \alpha_{CC} \), b) \( \Delta\varepsilon \), c) \( \tau_{CC} \) of the 0.4PMN-0.3PSN-0.3PZN ceramics.

Figure 4 Distribution of relaxation times \( f(\tau) \) of 0.4PMN-0.3PSN-0.3PZN calculated at different temperatures.
More general approach has to be used for determination of the real and continuous distribution function of relaxation times \( f(\tau) \) by solving Fredholm integral equation

\[
\varepsilon^*(\nu) = \varepsilon_{\infty} + \Delta\varepsilon \int_{-\infty}^{\infty} \frac{f(\tau)d\log\tau}{1 + 2\pi\nu\tau}.
\]

The Tikhonov regularization method has been used. This method and calculation technique is described in detail elsewhere [19].

Calculated distribution of the relaxation times \( f(\tau) \) is presented in figure 4. Symmetric and narrow distribution of relaxation times is observed at higher temperatures. On cooling the \( f(\tau) \) function becomes asymmetrically shaped and a second maximum appears. The shortest and longest limits of the \( f(\tau) \) function were calculated (level 0.1 of the maximum \( f(\tau) \) was chosen for definition of the limits) at various temperatures (figure 5). The longest relaxation time \( \tau_{\text{max}} \) diverges according to the Vogel-Fulcher law (figure 5) and the obtained parameters are \( \tau_0 = 5.1 \times 10^{-12}, T_0 = 297 \text{ K}, E_F/k_B = 334 \text{ K}. \) All the shortest relaxation times have the same values \( 10^{-12} - 10^{-13} \text{ s} \) and are practically temperature independent within the accuracy of our analysis. The most probable relaxation time \( \tau_{\text{mp}} \) obtained from the peak of distributions follows the Arrhenius law (figure 5)

\[
\tau = \tau_0 e^{\frac{E_A}{k_B T}}
\]

with parameters \( \tau_0 = 1.35 \times 10^{-17} \text{ s}, E_A/k_B = 5366 \text{ K}. \)

Distribution function \( f(\tau) \) was determined only at rather high temperatures, when the relaxation time lies within our experimental frequency range. When the \( \tau_{\text{max}} \) appears much below our frequency limit, we could not determine the static permittivity and therefore also \( \tau_{\text{max}} \) unambiguously. Nevertheless, one can expect that \( \tau_{\text{max}} \) does not really diverge below \( T_0 \), because some dispersion remains also below the freezing temperature.

On the other hand, the Arrhenius fit describes good enough the temperature dependence of most probable relaxation time in a temperature range where distributions were calculated. At the same time, the Arrhenius law validity at higher temperatures is unlikely because most probable relaxation time become smaller as \( 10^{-13} \) \text{ s}, more appropriate assumption is that most probable relaxation time alternates only slightly above 400 K. Therefore value of \( \tau_0 \) in Arrhenius law (4) is very low.

The nature of the polar nanoregions and two-component dielectric relaxation is still under debate. Very recently Blinc et al. [20] suggested that \( ^{207}\text{Pb} \) NMR spectra give evidence for the two-component nature of relaxors - glassy matrix (corresponding to spherical displacements of Pb ions) and frozen polar nanoregions (due to the Pb displacements in the [111] directions). These two components could be responsible also for the two-component dielectric relaxation [20]. Xu et al. [21] published recently some evidence that the polar nanoregions have polarizations along [110] directions, and that these clusters persist even in poled ferroelectric PZN with polarization along the [111] directions.
Our opinion is that the two dielectric relaxation regions have origin in the flipping and breathing of the polar clusters, but the subject needs still further investigations.

4. Conclusion

Two dielectric relaxation regions of ferroelectric relaxors PMN-PSN-PZN were successfully separated. The short relaxation times region appears at the Burns temperature in THz spectra and on cooling it heavily slows down according to the Arrhenius law. Breathing of the polar nanoregions causes this region. The long relaxation times region appears close to room temperature and, on cooling it slows down according to the Vogel-Fulcher law and disappears below freezing temperature. Flipping of the polar nanoregions causes this relaxation.

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