Distribution of Relaxation Times in 0.5PMN-0.5PSN Ceramics

R. Grigalaitis¹, J. Banys¹, A. Brilingas¹, A. Sternberg², K. Bormanis², V. Zauls²
¹Faculty of Physics, Vilnius University, Sauletekio 9, 10222 Vilnius, Lithuania
²Institute of Solid State Physics, University of Latvia, 8 Kengaraga str., 1063 Riga, Latvia
robertas.grigalaitis@ff.vu.lt

Abstract. Dielectric properties of chemically ordered and disordered 0.5PbMg₁/₃Nb₂/₃O₃-0.5PbSc₁/₂Nb₁/₂O₃ (0.5PMN-0.5PSN) ceramics were investigated in frequency range from 20 Hz to 3 GHz by dielectric spectroscopy. The broad dielectric dispersion, similar to this typically obtained for relaxor ferroelectrics (RFE), was observed in both ceramics below 350 K. The frequency dependence of dielectric permittivity of these ceramics were analyzed in terms of the distribution of relaxation times and showed the splitting into two components at lower temperatures. The longest relaxation times part slows down following Vogel-Fulcher law with lower freezing temperature compare with typical RFE like PbMg₁/₃Nb₂/₃O₃.

1. Introduction
Pb(Mg₁/₃Nb₂/₃)O₃ (PMN) and Pb(Sc₁/₂Nb₁/₂)O₃ (PSN) compounds belongs to a wide class of materials owing perovskite structure. Due to the excellent piezoelectric properties especially when doped with PbTiO₃ both materials attracts a great technological interest [1] despite the attempts to change these by lead-free compounds. On the other hand not fully explained RFE behaviour in these materials causes a big scientific attention.

PMN is probably most documented RFE since 1958 when it was initially studied [2]. It is well known that this material remains macroscopically cubic down to ~5K temperatures without an external electric field, higher than critical, applied [3]. However the observed broad maxima of real and imaginary parts of dielectric permittivity which shift to higher temperatures with frequency increase [4,5] needs an explanation. Now it is widely accepted that the cubic structure of PMN is locally broken at nanoscale and forms polarized areas called polar nano regions (PNR). Discovered by Burns and Dacol [6] PNR appear at sufficiently high temperature (e.g. ~620 K for PMN), causing a damping of soft phonon modes which can be monitored e.g. by inelastic neutron scattering [7] and are growing on cooling thus making noticeable influence on microwave and low-frequency dielectric response of RFE.

PSN belongs to different kind of RFE which can be transformed to an ordered state by proper thermal annealing. It was shown in [8] that by thermal annealing the so-called spontaneous relaxor to normal ferroelectric phase transition in PSN can occur. Such a highly ordered PSN shows typical ferroelectric phase transition as was observed by dielectric permittivity and differential scanning calorimetry measurements [9,10] while disordered PSN shows typical RFE behaviour [9-11]. The difference between PMN and PSN arises due to the different charge of Mg²⁺ and Sc³⁺ ions. While in 1:1 ordered PSN Sc³⁺ and Nb⁵⁺ cations displaced on the opposite sides along the [111] direction
preserves the charge neutrality 1:1 ordered PMN regions become negatively charged. Considering the mixed (1-x)PMN-(x)PSN solid solutions it was shown that substitution of PMN by PSN and subsequent ordering can induce a normal ferroelectric behaviour when x>0.5 [12] while disordered samples remain typical RFE. In order to deeper understanding of dielectric behaviour of mixed PMN-PSN solid solutions we examined the chemically ordered and disordered 0.5PMN-0.5PSN ceramics in a broad frequency range. To show the dynamic of systems with a wide distribution of PNR the simple formulas like Cole-Cole or Havriliak-Negami usually not properly describe the dielectric dispersion at all temperatures, so we calculated the real distribution of relaxation times for both ceramics [13].

2. Experiment
The binary 0.5PMN-0.5PSN solid solution was synthesized by solid state reaction from high-grade oxides PbO, Nb2O5, Sc2O3, MgO. The mean grain size of synthesized ceramics was about 1µm. The details of sample preparation and characterization can be found e.g. in [14]. The samples for dielectric measurements were cut from a plate of ceramics. The frequency range from 20 Hz to 3 GHz was covered by using HP 4284 precision LCR meter in low frequency (20 Hz – 1 MHz) and Agilent 8714 network analyzer in high frequency (1 MHz – 3 GHz) part. The silver paste electrodes were applied on the each sample to produce good electrical contact. The samples were annealed to 500 K before each measurement to avoid memory effects. The measurements were performed in cooling cycle down to 200 K with the temperature change rate 1 K/min. monitored within 0.1 K accuracy.

3. Results and discussion
Dielectric spectra of ordered 0.5PMN-0.5PSN ceramic are presented in Figure 1 and show typical RFE behaviour. The pronounced dispersion in real and imaginary parts of dielectric permittivity is observed in all investigated frequency region. As a consequence of this, peaks of $\varepsilon'$ and $\varepsilon''$ shift towards higher temperatures on increasing frequency. Dielectric dispersion takes place in a broad temperature region below 350 K. Apparently this dispersion will extend to higher temperatures with increasing measuring frequency. The frequency dependences of dielectric permittivity of ordered 0.5PMN-0.5PSN ceramic (Figure 2) exhibit a large dispersion below 310 K, which broadens and shifts toward lower frequencies on cooling. It is clearly seen that this dispersion consists of at least two non Debye-type processes which overlaps in several MHz region. The lower frequency process becomes anomalous broad on cooling and moves out of our spectral range toward to lower frequencies. In this case the simple models like Cole-Cole, Cole-Davidson or Havriliak-Negami are unable to predict the behaviour of dielectric dispersion (see for instance [15]) and more realistic models should be used e.g. the distribution of relaxation times [13].

![Figure 1. Temperature dependences of dielectric permittivity of ordered 0.5PMN-0.5PSN ceramic at different frequencies.]
But, because the two different processes in this material are separated well enough, we tried to fit frequency dependences of ordered 0.5PMN-0.5PSN ceramic as two Cole-Cole processes:

\[ \varepsilon^* = \varepsilon_\infty + \sum_{i} \frac{\Delta \varepsilon_i}{1 + (i \omega \tau_i)^{\alpha_i}} \quad i = 1, 2; \]

where \( \Delta \varepsilon_i \) is the strength of a relaxator, \( \tau_i \) is the mean relaxation time, \( \varepsilon_\infty \) is the contribution of all higher frequency modes and electronic polarization and \( \alpha_i \) is the relaxation times distribution parameter. Index \( i \) there represents the high and low frequency processes respectively.

This fit allowed us to estimate the mean relaxation times of above mentioned processes and make at least qualitative assumptions about the dynamics of this material. The calculated mean relaxation time of low frequency process diverges according to the Vogel-Fulcher relationship with the dipole freezing temperature \( T_f \approx 199K \) (Inset in Figure 5) while the high frequency process remains almost stable at \( \sim 10^{-11} \) s.

The temperature dependence of disordered 0.5PMN-0.5PSN ceramic looks similar to the ordered one (Figure 3) except that the values of dielectric permittivity at the same frequency are much larger. The frequency dependences (Figure 4) differ much more at higher temperatures (above 300K). In disordered 0.5PMN-0.5PSN we can observe only one broad dispersion region instead of two ones as it was in ordered sample. The reason for this apparently is the different size distribution of PNR in these ceramics. PSN-rich regions in ordered sample form a larger PNR than in disordered one which are surrounded by non polar “matrix” preventing to form long range order. Disordered 0.5PMN-0.5PSN, due to random arrangements of Mg\(^{2+}\), Sc\(^{3+}\) and Nb\(^{5+}\) ions, has a variety of PNR much more equally distributed in size thus leading in a more uniform dispersion. This is the reason why frequency dependences of disordered 0.5PMN-0.5PSN can be fitted with single Cole-Cole process rather well especially at higher temperatures where dielectric dispersion is not very asymmetrical and broad. Obtained mean relaxation time in this case also follows Vogel-Fulcher relationship with the dipole freezing temperature \( T_f \approx 202K \).
The one of most important characteristic of RFE is the distribution of relaxation times which can give us information about the most probable relaxation times, enable us to separate the influence of soft phonon modes from PNR to the total dielectric spectrum as it was shown recently for PMN-PSN-PZN RFE [15] and correlate with the size distribution of PNR. As it was mentioned already, models with one mean relaxation time cannot properly describe the dynamic of RFE so it were the attempts to define this distribution function in advance e.g. uniform, rectangular shaped function [16]. The more realistic idea was introduced to treat the relaxation time distribution as a sum of independent Debye-like processes. This method, described in detail in Ref. 13, allows us to extract the relaxation time distribution without any a priori assumptions and was successfully proved for PLZT, SBN, PMN, PMN-PSN-PZN relaxors [5,16-18] etc. The distributions of relaxation times at various temperatures in ordered and disordered 0.5PMN-0.5PSN are presented in Figure 5 and Figure 6 respectively.

Figure 3. Temperature dependences of dielectric permittivity of disordered 0.5PMN-0.5PSN ceramic at different frequencies.

Figure 4. Frequency dependences of dielectric permittivity of disordered 0.5PMN-0.5PSN ceramic at different temperatures. Solid lines are distribution of relaxation times fits.
Figure 5. Distribution of relaxation times in ordered 0.5PMN-0.5PSN ceramic at different temperatures. Lines are guides for eyes. Inset shows the lowest relaxation time behaviour of the distribution of relaxation times (squares) and the mean relaxation time from Cole-Cole formula (circles) fitted with Vogel-Fulcher relationship (solid lines).

Figure 6. Distribution of relaxation times in disordered 0.5PMN-0.5PSN ceramic at different temperatures. Lines are guides for eyes. Inset shows the lowest relaxation time behaviour of the distribution of relaxation times (squares) and the mean relaxation time from Cole-Cole formula (circles) fitted with Vogel-Fulcher relationship (solid lines).

The short relaxation times maxima for both ceramics stay nearly stable at $10^{-10}$ and represent the dynamic of non polar “matrix” i.e. the overdamped mode. The longest relaxation times part is caused by dynamic of PNR and is different for disordered and ordered samples as it already was expected from the analyze of frequency dependences (Figures 3 and 4). Above 300 K this part is more pronounced in ordered 0.5PMN-0.5PSN however on cooling the situation changes dramatically. While in ordered ceramic the influence of PNR to the total distribution of relaxation times increases mainly by broadening of the distribution toward to the longest relaxation times, in disordered one this influence is growing by shifting of the longest relaxation times part of distribution to longest relaxation times as well as by tremendous increase of number of such PNR. This is clearly seen in 290K-270K curves. Similar situation has been observed in RFE of the same family namely PMN and 0.8PMN-0.2PSN ceramics [19,20]. To analyze the behaviour of biggest PNR we plotted the temperature dependence of longest relaxation times edge for ordered and disordered ceramics (Insets in Figures 5 and 6 respectively). Both curves follow the Vogel-Fulcher relationship with the dipole “freezing” temperature $T_f\approx193K$ for ordered and $T_f\approx189K$ for disordered samples.

4. Conclusions
Summarizing the results presented above we should say that dielectric dispersion in both ceramics is similar to that typically observed for RFE. The differences arising during more careful analyze of dielectric spectra revealed that the thermal ordering of 0.5PMN-0.5PSN affects the size and distribution of PNR and consequently the dielectric properties of these ceramics. Ordered samples contain larger PNR thus causing more asymmetric the distribution of relaxation times and making analyze of the dielectric spectra by Cole-Cole formula inconvenient. The distribution of relaxation times consists of two parts. One of them, clearly seen as a peak at short relaxation times, stays nearly stable and represents the dynamic of non polar “matrix”. The another one, appearing as a second peak or even tail at longest relaxation times, broadens and shifts to sufficiently long relaxation times when temperature lowers describes the behaviour of PNR which grow in size and also in number on cooling. The behaviour of longest relaxation times part follows the Vogel-Fulcher relationship with the freezing temperature lower than in pure PMN ceramic [19] what means that PNR in 0.5PMN-0.5PSN ceramics are smaller than in PMN. In contrast to the other RFE like PMN single crystal [5] and
ceramic [19] the dipole freezing temperature obtained from Cole-Cole formula is higher for both ordered and disordered samples as this obtained from the distribution of relaxation times. This shows that Cole-Cole formula is not applicable to analyze the dielectric spectra of 0.5PMN-0.5PSN ceramics in details.

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