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Broadband dielectric spectroscopy of $PbMg_{1/3}Nb_{2/3}O_3$–$PbSc_{1/2}Nb_{1/2}O_3$ ceramics

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Abstract

Broadband dielectric spectroscopy results of various ordered and disordered $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$(x)Pb(Sc_{1/2}Nb_{1/2})O_3$ (PMN–PSN) ceramics are investigated in the temperature range from 80 K to 300 K and frequency range from 20 Hz to 2 THz. Dielectric dispersion is very broad and in the ferroelectrics case ($x = 1$, 0.95) consists of two parts: low-frequency part caused by ferroelectric domains and higher frequency part caused by soft mode. The relaxational soft mode exhibits pronounced softening close to phase transition temperature, as it is typical for order–disorder phase transitions. By substituting Sc^{3+} by Mg^{2+} in PMN–PSN ceramics relaxation slows down, and for relaxors ($x = 0.2$) the most probable relaxation frequency decreases on cooling according to Vogel–Fulcher law.

Keywords: Perovskites; Ferroelectric properties; Spectroscopy; Niobates

1. Introduction

The broadband dielectric spectroscopy of relaxors showed that the dielectric relaxations appear below Burns temperature[1] in the THz frequency range, anomalously slows down and splits into two parts close to freezing temperature.[2] Dielectric dispersion in order–disorder ferroelectrics slows down close to phase transition temperature.[3] Very interesting problem is to investigate dielectric dispersion in various disordered solids, which demonstrate intermediate properties between ferroelectrics and relaxors.

Nowadays, it is generally accepted that the complex dielectric properties of relaxors are related to the chemical disorder of ions with different valency at the B perovskite sites. For example, B sites of PSN contain 50% of Sc^{3+} and 50% of Nb^{5+} ions and, if these ions are statistically disordered, PSN exhibits relaxor ferroelectric behaviour.[4–7] If the ions are 1:1 chemically ordered (it can be achieved by proper annealing) PSN shows only a sharp ferroelectric transition at $T_C = 340$ K.[4–7] Relaxor behaviour was observed in both ordered and disordered forms of $(1-x)$PMN–(x)PSN for $x \geq 0.6$. At higher levels of substitution, the dielectric response was dependent of the degree of order: disordered samples were relaxors and ordered samples exhibited normal ferroelectric behaviour.[8–10] However, differently from PMN in disordered $(1-x)$PMN–(x)PSN for $x > 0.6$ at low temperatures relaxor-to-ferroelectric phase transition has been observed.[8–10] Experimental results of dielectric spectroscopy (up to 1 GHz) of ordered PSN[6] and 0.05PMN–0.95PSN[11] and disordered 0.8PMN–0.2PSN[12] ceramics are discussed in terms of distributions of relaxation times. One must note, however, that its temperature dependence is less expressed, since ferroelectric dispersion mainly appears in the region of several GHz and several tens of GHz, the main dielectric dispersion of relaxors is also in the region of GHz.[2] There are still open questions: what is the nature of ferroelectrics phase transition in PMN–PSN ceramics; what is the dynamics of the phase transition; what is the behaviour of relaxations in PMN–PSN ceramics by substitution Sc^{3+} by Mg^{2+}?

The aim of this paper is to investigate various ordered and disordered $(1 \times x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPb(Sc_{1/2}Nb_{1/2})O_3$ (PMN–PSN) ceramics by broadband (20 Hz to 2 THz) dielectric spectroscopy and to try to answer these questions.

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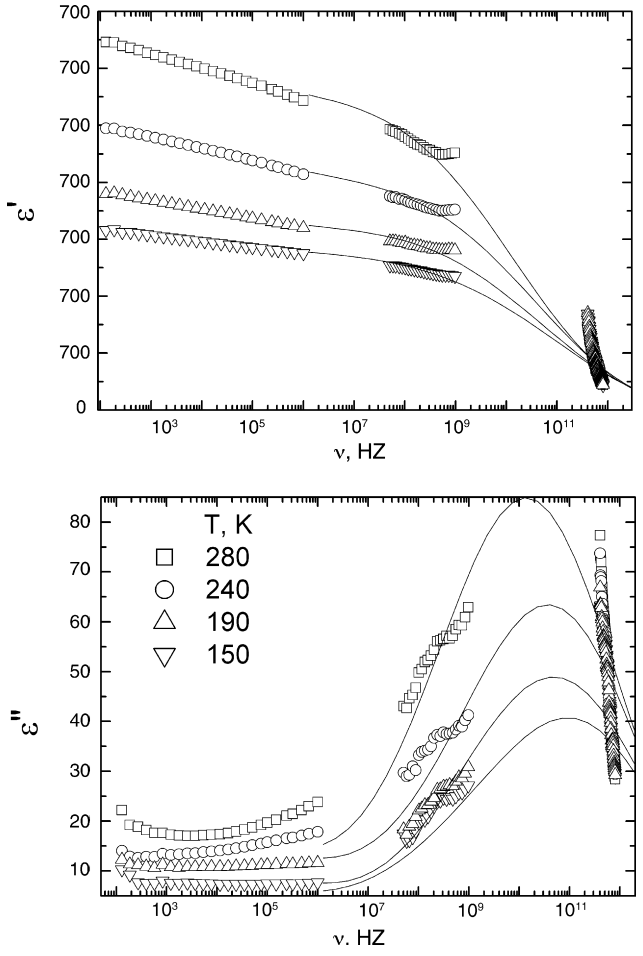

Fig. 1. Frequency dependence of complex dielectric permittivity ε^* of PSN ordered ceramics.

2. Experimental

The binary PMN–PSN solid solution was synthesized by solid-state reaction from high-grade oxides PbO_3, Nb_2O_5, MgO, and Sc_2O_3. The primary ingredients were homogenized and milled in an agate ball mill for 20–24 h in ethanol and dried at 250 °C. The dried mixture was fired in platinum crucibles. To obtain a sufficient homogeneous mixture of perovskite structure, the synthesis was repeated two times: first at 900 °C, the second between 1000 °C and 1250 °C. Detailed processing and sintering conditions are given in Ref. [13]. The complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ was measured using the HP4284A capacitance bridge in the frequency range 20 Hz to 1 MHz. In the frequency region from 1 MHz to 3 GHz measurements were performed by a coaxial dielectric spectrometer. Silver paste has been used for contacting. Measurements at THz frequencies from 100 GHz to 3 THz were performed in the transmission mode using a time-domain THz spectrometer based on a femtosecond laser system. A polished plane-parallel 40 μm thick plates with a diameter of 4 mm were investigated. More details about used spectrometers and dielectric permittivity calculations technique are given in Ref. [14].

3. Results and discussion

Below room temperature the dielectric dispersion of PMN–PSN ceramics is very broad (Figs. 1–3) and for ferroelectrics consists of two parts: at lower frequencies (below 1 MHz) ferroelectric domains cause the dispersion and at higher frequencies (1 MHz to 2 THz) relaxational soft mode causes the dispersion. The low-frequency dielectric dispersion of presented ferroelectrics is very broad and part of it is below our low-frequency limit (20 Hz). In this paper we have analyzed only the high-frequency dispersion of ferroelectric PMN–PSN ceramics. The dielectric dispersion of 0.8PMN–0.2PSN shows typical relaxor behaviour[15]: on cooling, the relaxation slows down and broadens; at very low temperature, the dielectric dispersion becomes so broad that we can see only part of this dispersion in our frequency range (Fig. 3). At very low temperatures the nearly frequency-independent imaginary part of dielectric permittivity is observed below THz frequencies. The dielectric dispersion of 0.8PMN–0.2PSN is very similar to pure PMN.[16]

From dielectric spectra the distribution of relaxation times $f(\tau)$ have been calculated by solving Fredholm equations:

$$\varepsilon'(\nu) = \varepsilon_\infty + \Delta\varepsilon \int_{-\infty}^{\infty} \frac{f(\tau) d\lg\tau}{1 + (\omega\tau)^2}, \quad (1.a)$$

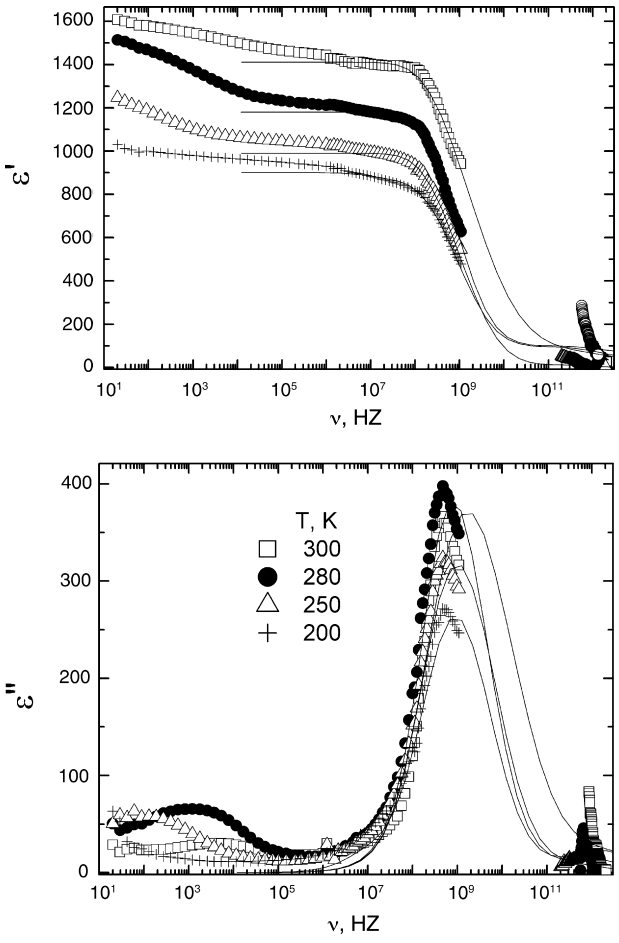

Fig. 2. Frequency dependence of complex dielectric permittivity ε^* of 0.05PMN–0.95PSN ordered ceramics.

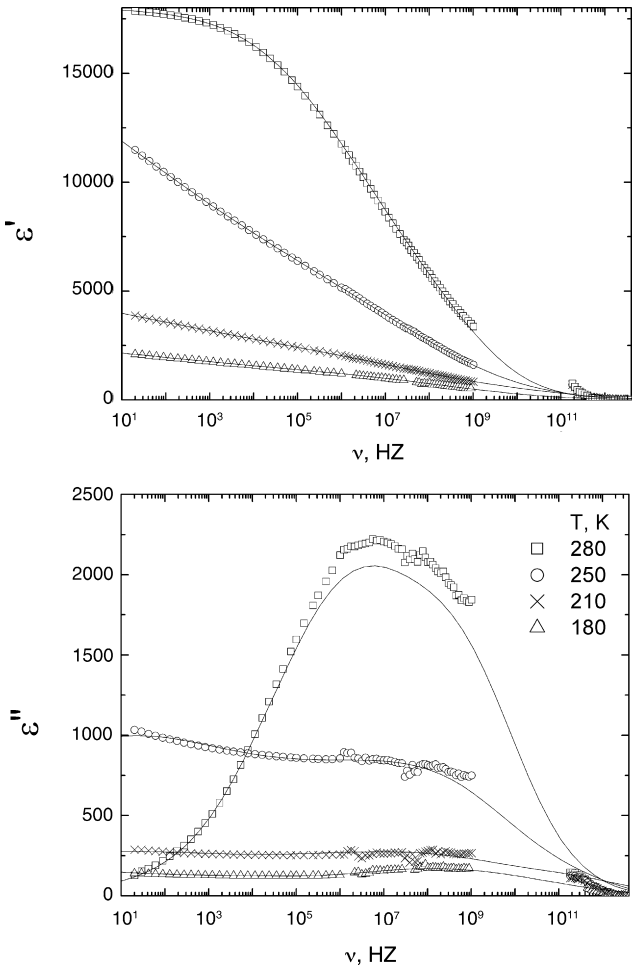

Fig. 3. Frequency dependence of complex dielectric permittivity ε^* of 0.8PMN–0.2PSN ceramics.

$$\varepsilon''(\nu) = \Delta\varepsilon \int_{-\infty}^{\infty} \omega\tau \frac{f(\tau) d\lg\tau}{1+(\omega\tau)^2}, \tag{1.b}$$

where $\Delta\varepsilon$ is the contribution of the relaxation process to the static permittivity, ε_∞ is the contribution of the phonon modes and electronic polarization. The regularization parameter has been selected according to recommendations published in Ref. [17]. Symmetric and narrow distributions of relaxation times of ordered PSN ceramics are typical for order–disorder ferroelectrics (Fig. 4). Similar distributions have been obtained also for 0.05PMN–0.95PSN ceramics. Additionally, hardening of the relaxational mode on cooling below the phase transition of ordered PSN ceramics confirms order–disorder nature of this phase transition. However, the distributions of relaxations times of 0.8PMN–0.2PSN exhibit typical relaxor behaviour (Fig. 5): symmetric and narrow distribution of relaxation times is observed only at higher temperatures; on cooling the $f(\tau)$ function becomes asymmetrically shaped and a second maximum appears, which shifts to longer relaxation time with decrease of the temperature. From the distributions of relaxation times the most probable relaxation frequency $\nu_{mp} = 1/\tau_{mp}$ has been obtained. Usually for the order–disorder phase transitions ν_{mp}

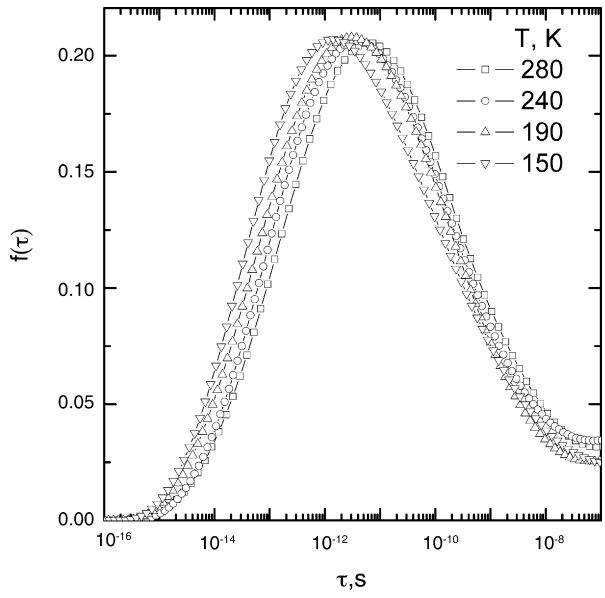

Fig. 4. Distribution of relaxation times of PSN ordered ceramics.

must have linear dependence:

$$\nu_{mp} = A(T - T_C), \tag{2}$$

where A is a constant and T_C is Curie–Weiss temperature. Such behaviour of ν_{mp} is observed in the case of ordered PSN ceramics (Fig. 6), with parameters $A = 262$ MHz/K, $T = 391$ K. In the case of ordered 0.05PMN–0.95PSN ceramics the most probable relaxation time slows on approaching antiferroelectric phase transition temperature 286 K[11] from higher temperatures side, and below the phase transition stays nearly constant. Our investigations of dielectric dispersion below 2 THz confirm order–disorder nature of transitions in PMN–PSN ferroelectrics. However, the evidence for resonant soft mode existence in PMN–PSN was already presented in Ref. [18]. Therefore, the nature of ferroelectric transitions in ordered PMN–PSN ceram-

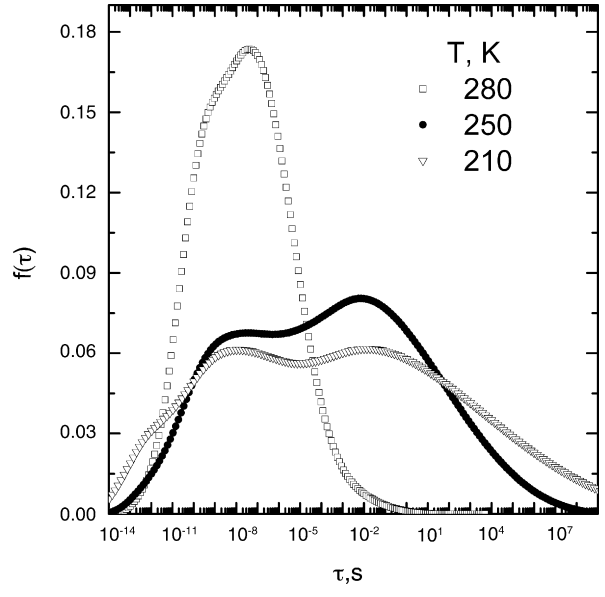

Fig. 5. Distribution of relaxation times of 0.8PMN–0.2PSN ceramics.

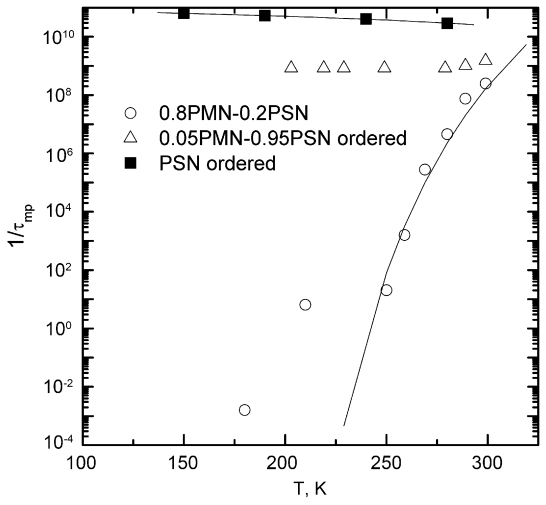

Fig. 6. Temperature dependence of the most probable relaxation frequency $\nu_{mp} = 1/\tau_{mp}$ of PMN–PSN ceramics.

ics is mixed between displacive and order–disorder types. The most probable relaxation frequency of 0.8PMN–0.2PSN relaxor slows down on cooling according to Vogel–Fulcher law:

$$\nu = \nu_0 e^{-E_A/k_B(T-T_0)} \quad (3)$$

with parameters $\nu_0 = 4.1 \times 10^{20}$ Hz, $E_A/k_B = 4136$ K, $T_0 = 154$ K. The high value of ν_0 appears here, because Vogel–Fulcher law is applied for the mean relaxation time, but we must keep in mind that we have different polar nanoregions, which freeze at different temperatures and have different relaxation times.[2,19]

4. Conclusions

Below room temperature dielectric dispersion in PMN–PSN ceramics is very broad and for ferroelectrics composition ($x = 1$, 0.95) consists of two parts: at lower frequencies ferroelectric domains cause the main dielectric dispersion and at higher frequencies relaxational soft mode causes dielectric dispersion. The relaxational soft mode exhibits pronounced softening on approaching the phase transition temperature, as is typical for other order–disorder phase transitions. However, in other paper[16] the evidence for resonant soft mode existence in PMN–PSN was presented. Therefore, the nature of phase transition in these ceramics is mixed between displacive and order–disorder type. In the relaxor ($x = 0.2$) case the most probable relaxation time increases on cooling according to Vogel–Fulcher law.

Acknowledgments

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