Piezoelectricity in NaNbO$_3$ ceramics

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L A Reznitchenko[1], A V Turik[2], E M Kuznetsova[1] and V P Sakhnenko[1]

[1] Institute of Physics, Rostov State University, Stachki 194, 344090 Rostov-on-Don, Russia
[2] Department of Physics, Rostov State University, Zorge 5, 344090 Rostov-on-Don, Russia
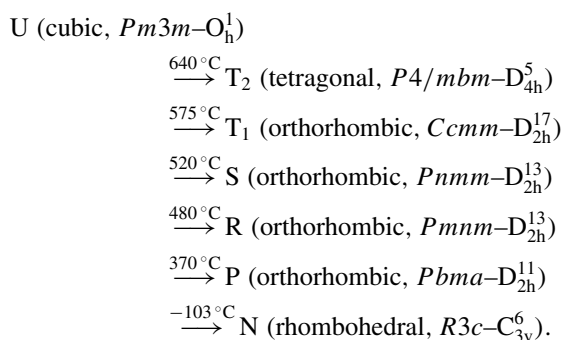
Abstract
Piezoelectric and dielectric measurements were performed on different batches of polarized NaNbO₃ ceramics. It has been established that, as a result of polarization, in these ceramics there appears a metastable ferroelectric phase existing for a long time. The presence of this phase manifests itself as a piezoelectric effect accompanied by a piezoresonance dispersion of the dielectric permittivity. The magnitudes and temperature dependencies of the piezoelectric coefficients d_{33} of the NaNbO₃ ceramics were measured for the first time.

1. Introduction

Sodium niobate NaNbO₃ has claimed the attention of researchers and designers of equipment owing to its unique physical properties and as a basis for a class of ecologically benign active materials. An intriguing feature of NaNbO₃ is that it shows the largest—among the oxygen-octahedral perovskites—number of structural phase transitions (PT) between nonferroelectric, antiferroelectric (AFE) and ferroelectric (FE) phases. The presence of six PT in the temperature range from $T = 650\,°C$ to $T = -120\,°C$ is generally accepted [1]:

U (cubic, $Pm3m$–O_h^1)

$$\xrightarrow{640\,°C} T_2 \text{ (tetragonal, } P4/mbm\text{–D}_{4h}^5)$$

$$\xrightarrow{575\,°C} T_1 \text{ (orthorhombic, } Ccmm\text{–D}_{2h}^{17})$$

$$\xrightarrow{520\,°C} S \text{ (orthorhombic, } Pnmm\text{–D}_{2h}^{13})$$

$$\xrightarrow{480\,°C} R \text{ (orthorhombic, } Pmnm\text{–D}_{2h}^{13})$$

$$\xrightarrow{370\,°C} P \text{ (orthorhombic, } Pbma\text{–D}_{2h}^{11})$$

$$\xrightarrow{-103\,°C} N \text{ (rhombohedral, } R3c\text{–C}_{3v}^6).$$

The symmetries and space groups of the phases formed are indicated in parentheses. Three successive high-temperature PT were initiated by the rotation of oxygen octahedra (crumpling-type PT) only, and the others were initiated also by the ordering of the displacements of cations from the octahedral centres (AFE and FE PT).

At room temperature, $NaNbO_3$ is AFE, of orthorhombic symmetry type P (*Pbma*). Application of an electric field to the crystal can induce the different FE phases in it. So, at room temperature, a sufficiently strong electric field perpendicular to the pseudocubic direction [101] induces a FE phase Q (*P2₁ma*) [2] that may coexist with the P phase for rather a long time. At temperatures below 80 °C, an electric field applied parallel to the direction [101] results in the appearance of a FE phase N (*R3c*) which may stay metastable at $T \approx 55$ °C for an infinitely long time, and upon heating to higher temperatures the crystal returns to the AFE phase P (*Pbma*) [3]. Above and in the vicinity of the Curie temperature $T_c \approx 370$ °C, in $NaNbO_3$ crystals and ceramics, one can observe a dispersion of the dielectric permittivity [4, 5], and below T_c, one can observe dielectric hysteresis loops [6, 7] and a piezoelectric effect (with thickness electromechanical coupling factor $K_t \approx 0.28$ in the temperature range from 25 °C to 250 °C [8–10]). However, quantitative estimates of the piezoelectric coefficients and their temperature dependence in $NaNbO_3$ were not made.

The present paper is devoted to a systematic study of the piezoelectric properties of $NaNbO_3$ (including the NaO nonstoichiometry) using different techniques for measuring the dynamical (d), direct (d_d) and quasistatic (d^{qs}) piezoelectric coefficients.

2. Ceramic preparation

To obtain the stoichiometric and nonstoichiometric $NaNbO_3$ samples having compositions with the formula $Na_{1-x}NbO_{3-x/2}$ ($0 \leqslant x \leqslant 0.2$) we used pure Na_2CO_3 for analysis (p.f.a.) and Nb_2O_5 of two types: 'Nbo' of special purity (sp.p.) and 'Nbo-pt' of 'technical' type (distinguished by the qualitative/quantitative impurity content). The niobates were synthesized by the method of solid-phase reactions using two-stage annealing at $T = 800$–850 °C, and kept for four hours at each stage. The components were mixed in alcohol to avoid hydrolysis and milled in water. Two batches of samples were fabricated. Granulation of the powders is carried out to give them fluidity; this was done in synthesizing batch 1 and not done in synthesizing batch 2. Granulation resulted in a substantial increase of density of the ceramic samples and was carried out by rubbing the pressed blocks in two stages: through a screen with 0.7–0.9 mm meshes and, after retention for more than four hours in a closed vessel, through a screen with 0.25–0.30 mm meshes. As a binder, we used a 5% aqueous solution of polyvinyl alcohol. To obtain samples of 12 mm diameter and 2.5 mm thickness, the powders were subjected to two-sided pressing under a pressure of 2×10^8 Pa. Sintering was carried out by the conventional ceramic technique in a closed alundum boat at $T = 1220$–1240 °C for two hours. Silver paste was fired by the usual technique for use as electrodes. The polarization was performed in a polyethylene–siloxane liquid in the following way. The samples were loaded into a chamber at room temperature, and then the temperature was smoothly elevated to 140 °C for 15–20 min; this procedure was accompanied by the increase of a poling field from 0 to 5×10^5 V m^{-1}. The samples were kept under these conditions for 20–25 min and then cooled under the field down to 60 °C over at least 20 min.

3. Experimental procedure

The following characteristics of the polarized $NaNbO_3$ ceramics were determined at room temperature: dielectric permittivities of the mechanically free ($\varepsilon_{33}^\sigma/\varepsilon_0$) and mechanically clamped ($\varepsilon_{33}^\xi/\varepsilon_0$) samples ($\varepsilon_0$ is the dielectric permittivity of vacuum); the electromechanical coupling factors of thickness (K_t) and planar (K_p) vibration modes (by the resonance–antiresonance method); the dynamical piezoelectric coefficients d_{33} (from the factor K_t) and

d_{31} (for a few samples, from the factor K_p); and the direct piezoelectric coefficients d_{33d} and d_{33}^{qs} in the static and quasistatic regimes. In addition, the temperature dependencies of the dielectric permittivities $\varepsilon/\varepsilon_0$ (only for the unpolarized samples), the loss tangent $\tan\delta$, the quasistatic direct piezoelectric coefficients d_{33}^{qs} and the electromechanical coupling factors K_t were measured.

The direct piezoelectric coefficients d_{33d} were measured by means of an abrupt drop of the mechanical load of $\sim$60 N applied to the sample and by determining the electric charge appearing on a parallel-connected capacitor of large capacitance. The quasistatic piezoelectric coefficients d_{33}^{qs} were measured with a Berlincourt d_{33}-meter as an electric response of the samples to the mechanical load, pulsating with a frequency of 150 Hz, of $\sim$20 N applied in the direction of the remanent polarization.

For all of the samples under study, one could observe a strong damping of the thickness vibration mode, that manifested itself in a small value of the mechanical quality factor $Q_m = 4$–7 and increase of the difference between the antiresonance and resonance frequencies $f_a - f_r$. Therefore, for the precise determination of the thickness electromechanical coupling factors K_t and dynamical piezoelectric coefficients d_{33} at room temperature, we used the static ($\varepsilon_{33}^{\sigma}/\varepsilon_0$) and high-frequency ($\varepsilon_{33}^{\xi}/\varepsilon_0$) dielectric permittivities measured with a BM-508 ('Tesla') impedance meter at frequencies much smaller and much higher than the thickness piezoelectric resonance ones, respectively. K_t was calculated from the formula

$$K_t^2 = (\pi/2)(f_s/f_p)\cotan(\pi/2)(f_s/f_p)$$

where the ratio of frequencies of the series and parallel resonances of the thickness vibrations was defined as $f_s/f_p = (\varepsilon_{33}^{\xi}/\varepsilon_{33}^{\sigma})^{1/2}$. Because of the almost complete absence of the planar mode of piezoelectric vibrations in most of the polarized samples, in calculating the dynamical piezoelectric coefficients d_{33} we used the equation

$$d_{33}^2 = K_t^2(\varepsilon_{33}^{\sigma}/c_{33}^D)/(1 - K_t^2)$$

where c_{33}^D is the stiffness coefficient measured at the antiresonance frequency.

4. Results and discussion

The x-ray measurements were carried out with a DRON-3 diffractometer using Fe Kα radiation incident through a Mn filter on the powdered objects (powdered ceramic samples). The x-ray data for the batches of both stoichiometric and nonstoichiometric NaNbO$_3$ evidence the obtaining of practically 'pure' samples with a perovskite-type structure up to $x < 0.1$. The unit-cell symmetry is quadruple, doubled or with a mixed multiplicity. The observed negligible amount of the NaNb$_3$O$_8$ impurity is related to the effect of crystallographic shifting in NaNbO$_3$ (Magneli phases) and, as a result, to the elimination of some of the Na–O positions, which leads to an excess of Na [11]. The established region of NaNbO$_3$ homogeneity ($x < 0.1$) is consistent with the results reported in [12]. Exceeding this limit leads to a drastic increase of the impurity content, growing with the increase of x. The samples from the two batches had close unit-cell parameters. However, the density of the batch-2 samples appeared to be higher than that of the batch-1 samples.

The main results of the piezoelectric and dielectric measurements at room temperature are listed in table 1. For all compositions of NaNbO$_3$ ceramic studied (both stoichiometric and nonstoichiometric), polarization resulted in the appearance of a piezoelectric effect accompanied by a piezoresonance dispersion of the dielectric permittivity: $\varepsilon_{33}^{\xi}/\varepsilon_{33}^{\sigma} = 0.90$–0.95. This fact, together with the observed dielectric hysteresis loops [6, 7], indicates the presence of polar nanodomains (FE clusters) in the AFE phase, the sizes of which may increase in the process of polarization of the ceramics.

Table 1. Mean values of the density ρ (g cm^{-3}), piezoelectric coefficients d_{33} (pC N^{-1}), electromechanical coupling factors K, dielectric permittivities ε_{33} and stiffness coefficients c_{33} (GPa) for polarized NaNbO$_3$ ceramics at room temperature.

Series number	Batch number	x	ρ	d_{33d}	d_{33}^{qs}	d_{33}	K_t	K_p	$\varepsilon_{33}^{\sigma}/\varepsilon_0$	$\varepsilon_{33}^{\xi}/\varepsilon_0$	c_{33}^{D}
1	1 'sp.p.'	0	3.1	50	38	30	0.30	0	70	65	54
	1 'Nbo-pt'	0	3.1	33	30	25	0.26	0	90	85	65
	2 'sp.p.'	0	4.31	49	36	31	0.31	0.10	190	175	130
								$d_{31} = 7.35$			
2	1*	0.02	4.27		17						
	2	0.02	4.25		17	14	0.15	0.04	168	165	172
3	1	0.04	4.16		12						
	2	0.04	4.38		22	26	0.18	0.1	291	283	123
4	1	0.06	4.18		16						
	2	0.06	4.28		16	18	0.16	0.1	173	169	129
5	1	0.08	4.08		19						
	2	0.08	4.15		23	26	0.23	0.06	192	184	135
6	1	0.10	3.74		11						
	2	0.10	4.35		27	29	0.25	0.07	180	170	131
7	1	0.12	3.09		9				102	97	
8	1	0.14	3.40		17	18	0.17		78	76	68
9	1	0.16	3.18		24	23	0.17		99	95	83
10	1	0.18	3.18		23	24	0.22		97	93	82

* The nonstoichiometric NaNbO$_3$ in both batches was prepared from Nb$_2$O$_5$.

As shown in table 1, the dielectric permittivities and stiffness coefficients of the stoichiometric NaNbO$_3$ ceramics increased considerably with the increase of the density. However, there was not much influence of density on the piezoelectric properties. The measured values of the piezoelectric coefficients d_{33} for the stoichiometric ceramics were 25–50 pC N^{-1} and the dynamical and direct coefficients were different. The direct piezoelectric coefficients d_{33d} were especially large: they were found to be close to d_{33d} for the (Pb, Ca)TiO$_3$-type FE ceramics [13, 14]. The K_t-values of 0.26–0.31 are close to those measured in [8, 9].

It is of interest to note that all of the compositions under study had very small planar electromechanical coupling factors K_p ($K_p^2 \leqslant 0.015$) and, hence, very large magnitudes of the anisotropy of the electromechanical coupling factors K_t/K_p and the piezoelectric coefficients $d_{33}/|d_{31}|$. The same situation was observed previously and studied in detail [13, 14] for some PbTiO$_3$-based FE ceramics. Therefore, the reason for the large piezoelectric anisotropy in NaNbO$_3$ can be expected to be the same as the reason for that in PbTiO$_3$: small values and a small anisotropy of the components of the tensor of dielectric permittivities of single-domain NaNbO$_3$ crystals in a metastable FE phase and, also, the peculiarities of the domain structure and distribution of clusters of the FE phase. The increase of the porosity (decrease of density) of the ceramics led to the decreased K_p-values and had not much influence on K_t. This seems to be related to the more ordered structure of clusters (and domains) in denser ceramics. Qualitative differences between the piezoelectric properties of stoichiometric and nonstoichiometric NaNbO$_3$ ceramics were not observed.

An important distinguishing feature of the polarized NaNbO$_3$ ceramics is the inequality of the magnitudes of the direct static and dynamical piezoelectric coefficients $d_{33d} > d_{33}$, which is typical of FE ceramics too. Moreover, the direct static coefficients d_{33d} are slightly larger than the quasistatic ones, d_{33}^{qs}. One can expect the measured d_{33d}-values to contain contributions from both reversible and irreversible displacements of the domain walls, but

the d_{33}-values to contain only reversible ones. It is interesting to see that the quasistatic piezoelectric coefficients d_{33}^{qs} of the stoichiometric NaNbO$_3$ ceramics are also greater than d_{33}: a value of $\Delta d_{33}/d_{33} = (d_{33}^{qs} - d_{33})/d_{33} \approx 20\%$ was obtained at room temperature. The same situation arises for Pb(Zr, Ti)O$_3$-based (PZT) FE ceramics. So, our room temperature measurements of some soft and hard PZT (PCR in our notation) materials, which were carried out at Rostov University, gave the following results:

- PCR-7M (soft, $d_{33} = 718$ pC N^{-1} [15]): $\Delta d_{33}/d_{33} \approx 50\%$;
- PCR-8 (hard, $d_{33} = 250$ pC N^{-1} [15]): $\Delta d_{33}/d_{33} \approx 25\%$;
- PCR-1 (hard, $d_{33} = 221$ pC N^{-1} [15]): $\Delta d_{33}/d_{33} \approx 30\%$.

The difference between d_{33}^{qs} and d_{33} was less for the nonstoichiometric NaNbO$_3$ compositions with $x \geqslant 0.08$. It is evident that the piezoelectric properties of the polarized NaNbO$_3$ ceramics are close to those of the hard PZT ones.

The x-dependencies of d_{33}^{qs} and K_t were of irregular character. A study of aging has shown that the electromechanical coupling factors and piezoelectric coefficients of the NaNbO$_3$ ceramics varied by no more than 10% during a year.

Figures 1 and 2 show the temperature dependencies of the dielectric permittivities $\varepsilon/\varepsilon_0$ of the unpolarized samples (the temperature behaviour of $\varepsilon_{33}^\sigma/\varepsilon_0$ for the polarized samples was not recorded because of the growth with temperature of the dc electric conductivity), the quasistatic piezoelectric coefficients d_{33}^{qs} and the electromechanical coupling factors K_t of the
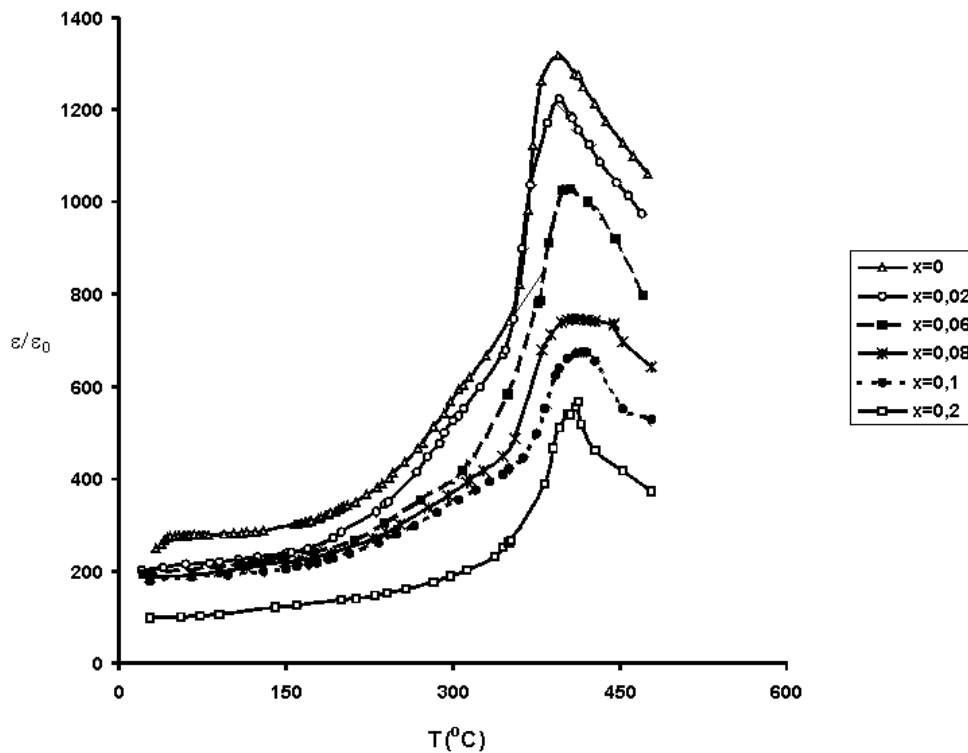

Figure 1. The temperature dependencies of the dielectric permittivity $\varepsilon/\varepsilon_0$ of stoichiometric and nonstoichiometric Na$_{1-x}$NbO$_{3-x/2}$ ceramics measured at the frequency 20 kHz.
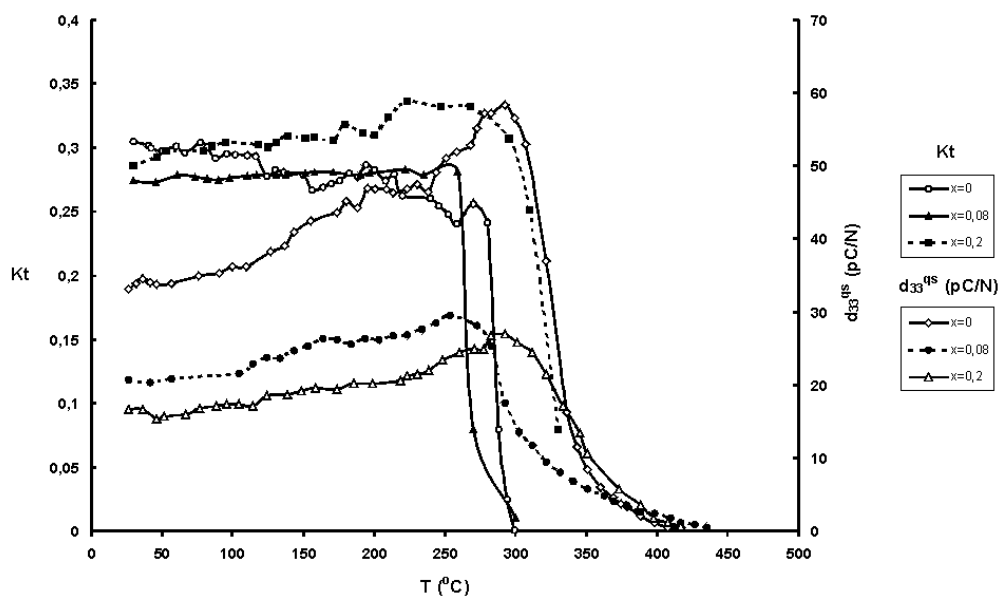
Figure 2. The temperature dependencies of the electromechanical coupling factors K_t and piezoelectric coefficients d_{33}^{qs} of stoichiometric and nonstoichiometric $Na_{1-x}NbO_{3-x/2}$ ceramics.

NaNbO$_3$ ceramics. As can be seen in figure 1, with the increase of x the maxima of $\varepsilon/\varepsilon_0$ decreased and slightly shifted to the high-temperature side. The Curie temperature $T_c \approx 370$–400 °C; piezoelectric properties were observed at $T \leqslant T_c$, i.e. in the initially orthorhombic *Pbma* phase (see figure 2). For all compositions studied, tan δ for unpolarized ceramics passed through diffuse maxima at temperatures of 300–360 °C. These temperatures were a little smaller than the ones for maxima of $\varepsilon/\varepsilon_0$. An unusual and as yet unclarified feature of the tan $\delta(T)$ behaviour is the appearance of additional maxima at low temperatures of 50–80 °C. At high $T > 400$ °C, the tan δ dependences were monotonically increasing temperature functions, reaching values of tan $\delta = 0.3$–0.6 at $T = 500$ °C. The values and character of the tan $\delta(T)$ dependences for the unpolarized and polarized ceramics did not differ substantially at low temperatures, $T < 250$ °C. At higher temperatures, measurements of tan δ for the polarized ceramics become difficult to execute owing to the sharp increase of the dc conductivity.

The main peculiarity of the temperature dependencies shown in figure 2 is an abrupt lowering of K_t (and, hence, the dynamical piezoelectric coefficients d_{33}) as $T \rightarrow 300$ °C, whereas the diffuse maxima (especially at $x \rightarrow 0$) and 'tails' extending to $T \approx 400$ °C are typical of the dependencies $d_{33}^{qs}(T)$. The first peculiarity was observed previously [8, 9], and is certain to be related to a drastic decrease of the remanent polarization of the NaNbO$_3$ ceramics as $T \rightarrow 300$ °C. The second peculiarity is due to FE hardness of the polarized NaNbO$_3$ ceramics, which manifests itself in small values of the piezoelectric coefficients d_{33} (tens of pC N^{-1}). The dynamical coefficients d_{33} measured at the very low levels of excitation are, mainly, internal coefficients by their nature, and stemmed from the intrinsic piezoelectric coefficients of the polarized FE clusters with an additional contribution due to the reversible displacements of the non-180° domain walls [16]. Both of these contributions decrease rapidly as the temperature approaches T_c. At the same time, the coefficients d_{33}^{qs} are measured at higher levels of excitation (10^5–10^6 Pa) and contain a contribution due to the irreversible displacements of the non-180° domain walls, which increases near T_c as a result of a decrease

of the coercive fields of the domain (cluster) reorientations. Therefore, as $K_t \rightarrow 0$ and the dynamical coefficients $d_{33} \rightarrow 0$ in a temperature range near T_c, the d_{33}^{qs}-values are maintained, though at a diminished (but finite) level ('tails' of d_{33}^{qs} up to $T \approx 400\,^\circ$C). An additional factor causing the inequality $d_{33} < d_{33d}$ is a greater ease of reversible displacement of the non-180° domain walls in mechanical fields compared to the corresponding displacement in electric fields [16]. As a result, even above T_c, in a small temperature range, $d_{33}^{qs} \neq 0$, whereas $K_t = 0$ and $d_{33} = 0$.

5. Conclusions

Polarization of the initially orthorhombic AFE NaNbO$_3$ ceramics leads to the appearance of a metastable FE phase existing for several years. The presence of the FE phase manifests itself as a piezoelectric effect accompanied by a piezoresonance dispersion of the dielectric permittivity. The values of the direct static and dynamical piezoelectric coefficients d_{33} at room temperature and the temperature dependencies of the quasistatic piezoelectric coefficients d_{33}^{qs} of the NaNbO$_3$ ceramics are measured for the first time. It is shown that piezoelectric properties are observed at $T \leqslant T_c$, i.e. in the polarized orthorhombic $Pbma$ phase, and at high temperatures a major contribution to the quasistatic piezoelectric coefficients d_{33}^{qs} comes from the processes of irreversible displacements of the non-180° domain walls.

Acknowledgment

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