MAGNETISM
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^{23}Na NMR Study of the Local Order in the Na$_{1/2}$Bi$_{1/2}$TiO$_3$ Structure in a Weak Magnetic Field

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Abstract—The orientation dependences of the second-order quadrupole shifts of the central component in the ^{23}Na NMR spectrum were studied in the temperature range 293–760 K. The profile of the spectral distribution is calculated using various models of the Na$_{1/2}$Bi$_{1/2}$TiO$_3$ structure. The calculations agree with the experimental data for the monoclinic structure of a polar cluster with two Na displacement components: a displacement along the $[111]_P$ direction and a small displacement statistically or dynamically disordered over six equally probable $[100]_P$-type directions. Tetragonal-phase nuclei and monoclinic clusters with a very small displacement component along the $[111]_P$ direction are found to coexist and have close energies over the temperature range 580–610 K. The results obtained provide new information concerning the character of the diffuse phase transition at 610 K.

1. INTRODUCTION

To date, numerous neutron and x-ray diffraction investigations of the local and average structure of relaxor ferroelectrics have been performed. Nevertheless, both the elastic- and diffuse scattering data for the same compounds are variously interpreted in the literature. The reason for this is that some specific features of the structure of relaxor ferroelectrics are combined. Among them are small ion displacements responsible for the deviation of the local polar structure from the average structure. Small displacements are combined with the existence of a number of equally probable orientations of locally ordered regions with respect to the symmetry axes of the average structure. Over the temperature range in which a wide dielectric anomaly and dielectric relaxation (relaxor region) are observed, the structure is very dynamic. The vibrational degrees of freedom and the position mobility of some ions cause anomalously large thermal factors that can be ambiguously interpreted when determining the structure.

These relaxor peculiarities hamper the use of nuclear magnetic resonance (NMR). However, using complementary methods for studying the local structure allows one to expand and refine information.

Earlier, the NMR method was used in studying Pb-containing crystals retaining the average cubic structure over the entire region of existence. The studies have been performed under high magnetic fields [1, 2].

The situation with Na$_{1/2}$Bi$_{1/2}$TiO$_3$ (NBT) is more complex, because, along with relaxor properties, this compound exhibits phase transitions from the cubic $Pm\bar{3}m$ to tetragonal $P4bm$ ($Z = 2$) structure at 813 K (T_{c1}) and to trigonal $R3c$ ($Z = 6$) structure at a temperature of about 600 K (T_{c2}) [3–5]. We performed measurements under very weak magnetic fields, which permit us to significantly increase the NMR spectrum resolution when studying the second-order quadrupole effects. The resolution was sufficient to test various structural models by modeling the shape of the observed spectral distribution.

2. RESULTS AND DISCUSSION

2.1. Experimental

The orientation dependence of the shape of the central component in the ^{23}Na NMR spectrum was measured at a Larmor frequency of 15.7 MHz by rotating the NBT single crystal around the $[110]_P$ axis of the pseudocubic unit cell. The orientation dependence was measured at 293, 350, 400, 450, 475, 500, 540, 580, 640, 729, and 780 K using continuous wave method. To increase the signal-to-noise ratio, the signal was accumulated.

2.2. Models and Spectra

In complex perovskites $A'B''BX_3$ and $AB'B''X_3$, the main contribution to the polar-cluster dipole moment comes from the displacement of the cation A from the equilibrium position in the cubic phase. An NBT single crystal is convenient for NMR study of the displacement of cation A, since the ^{23}Na nucleus ($I = 3/2$) has a quadrupole moment. From studying the quadrupole interactions, one can determine the quadrupole coupling constant $q = eQV_{zz}/h$, where V_{zz} is the principal value of the electric-field gradient (EFG) tensor at a nucleus, Q is the nucleus quadrupole moment, e is the electron charge, and h is the Planck constant. The sensitivity of the quadrupole coupling constant to cation shifts from the equilibrium position in the high-temperature cubic phase is fairly high (about 10^{-3} Å). As we established in [6, 7], for relaxor ferroelectrics, the studies of the second-order quadrupole shifts under a weak magnetic field are most informative. The determination of the EFG tensor parameters from the orientation dependences of the frequency shift of the central spectral components in crystals with a long-range order is a standard procedure, since the spectral lines from the structurally and magnetically nonequivalent positions of the nucleus under study are usually resolved sufficiently well. In relaxor structures, there are several equally probable orientations of the electric dipole moments of polar regions. These regions have different orientations of the principal axis of the EFG tensor with respect to the direction of a magnetic field. As a result, the NMR spectrum contains lines from numerous magnetically nonequivalent positions of a ^{23}Na nucleus. According to our previous data, in a wide temperature range, the NBT spectrum also reveals structurally nonequivalent ^{23}Na positions in coexisting polar clusters and tetragonal-phase regions. The total spectrum is an unresolved ^{23}Na line, whose shape can be represented as the convolution of the frequency distribution function of the spectral components $f(\nu)$ and a broadening function $L(\nu'-\nu)$.

To extract information on the temperature evolution of the NBT local structure from the NMR spectrum, we developed a computer program. The program allows one to calculate the spectral line shape for any crystal orientation in a magnetic field using a proposed structural model and can be employed to simulate the NMR spectra of both homogeneous structures with a long-range order and inhomogeneous structures containing various types of shifts of the nucleus under study.

Since there is a fairly direct relation between the ^{23}Na quadrupole coupling constant and the displacement making the main contribution to the cluster dipole moment, one can use fairly simple models.

In model 1, a Na displacement in a polar cluster is assumed to occur equally probably along a $[111]_P$-type direction of the pseudocubic unit cell coinciding with a C_3 axis of the rhombohedral $R3c$ unit cell. The Na
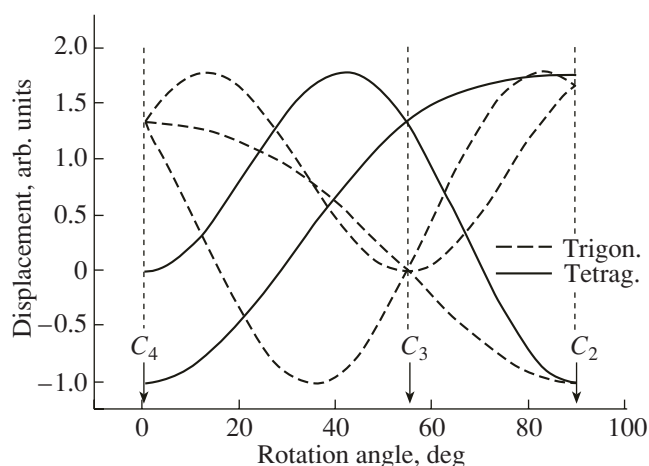

Fig. 1. Orientation dependences of the second-order Na ion shift showing the total number of spectral lines and their mutual positions for any crystal orientation with respect to the rotation axis. The calculation is carried out for $Kq^2 = 1$ in Eq. (1).

potential relief in the cluster has eight minima. The displacements in the tetragonal structure occur equally probably along $[100]_P$-type directions of the pseudocubic unit cell coinciding with a C_4 symmetry axis of space group $P4bm$. The character of displacements in model 1 is chosen in accordance with the neutron and x-ray diffraction data obtained for NBT in [5, 8]. Bragg scattering data are well known to give information on the average structure. The model allows for the coexistence of independent Na displacements along the $[111]_P$ and $[100]_P$ directions. In the calculations, we used the dependence of the second-order quadrupole shift $\delta\nu$ on the crystal orientation in a magnetic field for an axially symmetric EFG tensor [9]

$$\delta\nu = -\frac{9}{64}\frac{(I(I+1)-3/4)q^2}{(I(2I-1))^2}\frac{q^2}{\nu_L}(1-\cos^2\theta)(9\cos^2\theta-1)$$
$$= Kq^2(1-\cos^2\theta)(9\cos^2\theta-1),$$
(1)

where θ is the angle between the magnetic-field direction and the principal axis of the EFG tensor; ν_L is the Larmor frequency, and I is the nucleus spin. Figure 1 shows the orientation dependences of the second-order shift (for $Kq^2 = 1$) corresponding to eight equally probable trigonal Na displacements in polar clusters and analogous orientation dependences for tetragonal-phase twins with equally probable Na shifts along six $[100]_P$-type directions. These orientation dependences give the frequency distribution function $f(\nu)$ for any crystal orientation. When modeling the spectra, variable parameters are taken to be the values of q for clusters and the tetragonal phase, the peak intensities (A) of the corresponding lines of the NMR spectrum, and the half-width (W) of a Gaussian broadening function for lines of the clusters and the tetragonal phase. The
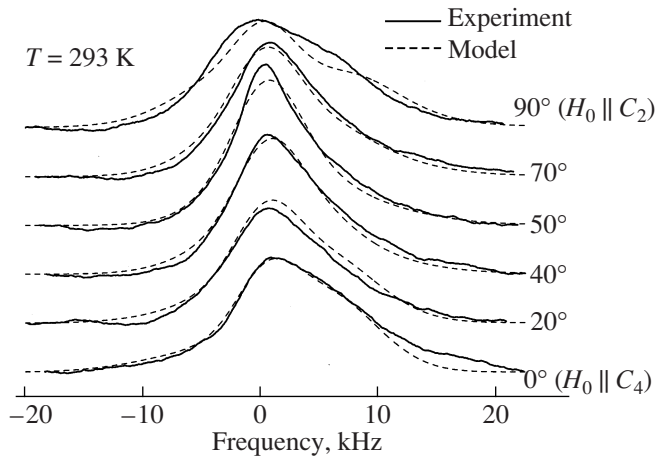
Fig. 2. Orientation dependences of the ^{23}Na NMR line shape at 293 K. The solid curves are experiment, and the dashed lines are calculations.
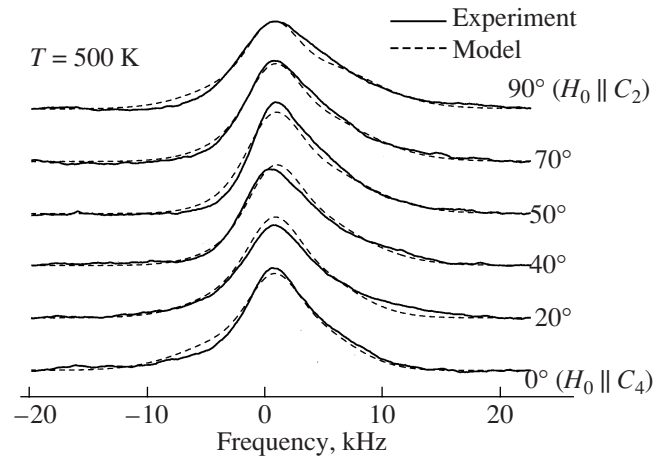

Fig. 3. Orientation dependences of the ^{23}Na NMR line shape at 500 K. The solid curves are experiment, and the dashed lines are calculations.

model also assumes the existence of regions with very small distortions of the cubic structure (matrix) in the trigonal phase. The matrix line position can be varied within narrow limits around the Larmor frequency. The peak intensity and the matrix-line width are also variable parameters. The weight fractions X of the regions differing in structure are determined from the integral intensities of the corresponding spectral lines. The data for each temperature includes ten spectra corresponding to rotation angles varying from 0° to 90° in steps of 10°. A comparison of the calculated and experimental spectra was performed using the least square technique

for all points on the orientation dependence of NMR spectra.

The table lists the main variational parameters corresponding to the minimum difference Δ between the profiles of the calculated and measured spectra for each temperature. Figures 2–5 show the measured and calculated spectra for several temperatures. From the data presented in the table, it follows that, in the temperature range 293–580 K, the best agreement between the calculated and measured spectra is achieved for the structure in which the matrix and regions with shifts along the $[111]_P$- and $[100]_P$-type directions coexist. From the

Results of computer simulations of the orientation dependences of the ^{23}Na NMR spectra in NBT at various temperatures (notation is explained in the text)

Temperature, K	q_{trig}, MHz	q_{tetr}, MHz	W_{trig}, kHz	W_{tetr}, kHz	W_{matr}, kHz	X_{trig}	X_{tetr}	X_{matr}	Δ
				Model 1					
293	1.18	1.13	3.94	6.13	2.6	0.43	0.29	0.28	0.018
350	1.19	1.11	3.68	5.94	2.66	0.45	0.28	0.27	0.013
400	1.17	1.05	3.54	5.49	2.54	0.29	0.35	0.37	0.011
450	1.14	1.03	3.12	5.0	2.42	0.29	0.33	0.38	0.011
475	1.18	1.04	3.08	4.97	2.43	0.2	0.31	0.49	0.012
500	0.93	0.98	3.42	4.71	1.96	0.25	0.5	0.25	0.015
540	1.05	0.91	1.63	4.38	1.91	0.06	0.59	0.35	0.019
580	0.03	1.05	1.37	4.0	1.89	0.01	0.7	0.29	0.019

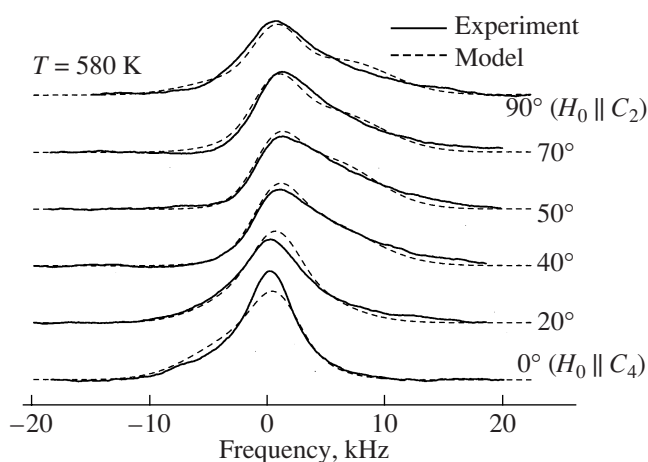| Temperature, K	q_{trig}, MHz	q_{tetr}, MHz	W_{trig}, kHz	W_{tetr}, kHz	$W_{trig}(1)$, kHz	$W_{tetr}(1)$, kHz	X_{trig}	Δ
				Model 2				
640	0.01	1.03	1.34	2.74	2.42	0.01	0.08	0.038
729	0.03	0.87	2.39	0.419	1.94	0.05	0.0	0.031

Fig. 4. Orientation dependences of the ^{23}Na NMR line shape at 580 K. The solid curves are experiment, and the dashed lines are calculations.
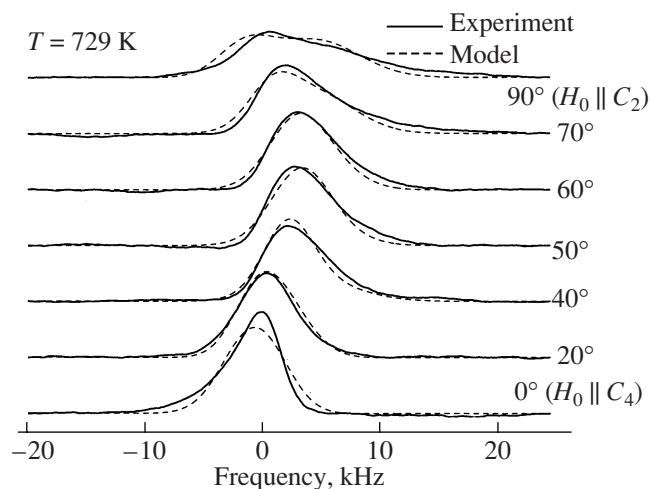

Fig. 5. Orientation dependences of the ^{23}Na NMR line shape at 729 K. The solid curves are experiment, and the dashed lines are calculations.

table, one can also see how the weight fractions X of regions with different types of distortion of the nearest surroundings of the ^{23}Na nucleus vary with temperature.

The temperature dependence of the quadrupole coupling constants q_{trig} and q_{tetr} is of particular interest. The quantity q_{trig} corresponding to polar clusters varies over the temperature range 500–580 K, while the constant q_{tetr} corresponding to tetragonal displacements remains practically unchanged (to within the accuracy of its determination) over the entire temperature range up to 729 K. Above 500 K, the widths of the lines corresponding to polar clusters change noticeably. The spectral lines belonging to the tetragonal phase narrow only slightly as the temperature rises. It should be noted that the decrease in the value of q_{trig} below 500 K causes the corresponding spectral lines to approach the center, where these lines overlap with the matrix line near the Larmor frequency as the temperature increases. This factor decreases the accuracy in determining the relative fractions of the trigonal phase and the matrix at temperatures at which the constant q_{trig} is small. Attempts to fit the orientation dependences using model 1 for temperatures above T_{c2} (~610 K) lead to noticeably increased values of Δ.

For the orientation dependences at 640 and 729 K, we used model 2, in which the matrix is absent, which is natural for the tetragonal structure with a long-range order. When simulating the spectra of the tetragonal phase, we revealed a broadening proportional to the second-order shift. We cannot clearly explain the origin of this broadening associated with the quadrupole interaction; however, the introduction of an appropriate correction $W(1)$ for the lines of the trigonal and tetragonal phases substantially improves the agreement between

of the calculated and measured spectra. The results obtained using model 2 are also given in the table.

At temperatures above 700 K, the second-order shift in the spectrum of the tetragonal phase is gradually averaged over all positions in the tetragonal structure due to diffusion of ^{23}Na nuclei [6]. The effect of diffusion on the width and shape of the tetragonal-phase lines becomes noticeable even at 640 K. In analyzing the shape of the observed spectral distribution, our model is applicable only up to 729 K.

At 780 K, the asymmetry of the observed spectral distribution due to the superposition of the lines from the tetragonal-phase domains and the orientation dependence of the second-order shift practically disappear. The quadrupole constant q_{tetr} is noticeably averaged due to diffusion (see also [6]). These data indicate the approach to the fast-motion limit recovering the cubic symmetry.

The known model of the relaxor structure with A ions in the polar clusters shifted along eight equally probable $[111]_P$-type directions is not the only model based on the diffraction data. For example, for PMN/PT, a model was proposed [10] in which the total shift of the A ion in the polar cluster occurs approximately along $[100]_P$-type directions. The Ti, Mg, and Nb ions are shifted along the $[111]_P$ directions. The local symmetry of the polar regions is monoclinic in this case, but the average structure has trigonal symmetry due to the existence of six possible $[100]$-type directions. Various interpretations of the diffraction data are possible due to anomalously large thermal factors for the oxygen atoms and A ions. In order to test the model proposed in [10], we applied it to NBT using our computer program. We chose a temperature of 293 K, at which transitions between possible Na ion displacements along the six tetragonal directions are frozen out.
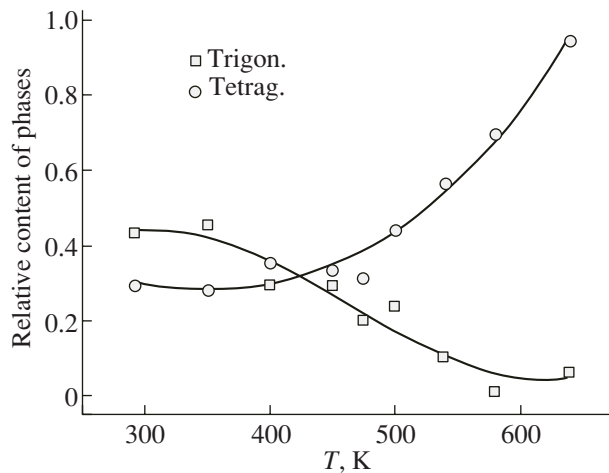
Fig. 6. Temperature dependences of the weight fractions of the trigonal and tetragonal phases of NBT (the weight fraction of the matrix is not shown).

The result for this simplest situation showed dramatic disagreement between the measured and calculated spectra.

2.3. Model 1 and the Local Structure of BNT

Model 1 describes fairly well the shape of the measured ^{23}Na NMR spectrum over a wide temperature range of the existence of the average trigonal structure. However, some of our data [6, 7] indicate that the local symmetry of the polar regions is lower than that of the average structure. Indeed, the transitions of the Na ion between the eight minima of the potential relief that occur in the relaxor region should cause its average position to become cubic. However, the average structure of NBT is trigonal in this temperature range. The dynamical averaging that recovers the cubic structure in the tetragonal phase is observed at temperatures higher than 780 K as a result of the Na diffusion over all positions on the tetragonal lattice.

Equation (1) used in the computer program applies only to axially symmetric EFG tensors. This condition breaks down if the Na ion is shifted from the threefold axis of symmetry. However, when the orthogonal displacement component is small, the axially symmetric approximation is applicable. We assume that, in the clusters, there is a small orthogonal displacement component, which is disordered (statistically or dynamically) over six equally probable $[100]_P$-type directions. At room temperature, the reorientation of the cluster dipole moments does not occur [6, 11]. In the ordered structure of a particular polar cluster, the orthogonal displacement component is oriented along one of $[100]_P$ directions. On the average, the crystal trigonal structure remains. Above 500 K, the narrowing of the NMR lines belonging to the polar clusters indicates that transitions between the Na positions occur with a fre-

quency corresponding to the frequency "window" of the technique. The reorientations of the orthogonal displacement component are correlated within the polar region, which corresponds to significantly lower frequencies than those we can expect for independent Na ion hops between the potential-relief minima. At high temperatures, the reorientations are averaged in time and the average position of the Na ion is on the C_3 axis. However, the reorientations cannot cause q_{trig} to decrease abruptly by more than an order of magnitude, which is observed in the range 540–580 K (see table). The spontaneous decrease in the displacement of Na or Bi ions along the $[111]_P$ direction in the polar clusters is fairly unexpected. However, we can refer to an abrupt increase in the level of optical second harmonic generation revealed in a close temperature range in [5].

From the table, it can be seen that the increase in the weight fraction of the tetragonal phase above 500 K occurs mainly due to the decrease in the polar-cluster fraction. The monoclinic regions exhibiting a "tetragonal" displacement along $[100]_P$-type directions can act as tetragonal-phase nuclei when the Na ion displacement along the $[111]_P$ direction decreases as the temperature T_{c2} is approached. Near 580 K, the energy of the monoclinic regions with a very small displacement along the $[111]_P$ direction and the energy of tetragonal-phase nuclei become close in magnitude and heterogeneous fluctuations become possible. As the temperature increases further, nuclei of the tetragonal phase grow rapidly and the transition occurs to the tetragonal phase with a long-range order. This transition does not require a complete reconstruction of the local structure of clusters, in contrast to the trigonal–tetragonal phase transition.

In NBT, the range between 580 K and T_{c2} is close in some respects to morphotropic boundaries existing when the trigonal phase transforms to a tetragonal phase via an intermediate monoclinic phase in compounds such as $PbZr_{1-x}Ti_xO_3$ ($x \sim 0.5$) (PZT) [12] and $PbMg_{0.3}Nb_{1-x}Ti_xO_3$ ($x \sim 0.35$) (PNM/PT) [10]. This is a very dynamic labile structure wherein the cluster dipole moments are reoriented, heterogeneous fluctuations are probable, and nucleation processes occur. A long-range monoclinic order does not appear in NBT even in a narrow temperature range near the transition point, as well as in the low-temperature trigonal phase.

Due to very small Na ion displacements in the polar clusters above 580 K, the energy barriers between equally probable orientations of the dipole moments are low. It is possible that this factor is responsible to a large measure for the wide maximum of the dielectric susceptibility (typical for relaxors) observed below T_{c2} = 610 K over a 30-K-wide temperature range.

According to the NMR data, the weight fraction of the tetragonal phase is about 30% at the lowest temperature studied (293 K) and remains at this level up to approximately 475 K (Fig. 6); This value of the weight

fraction is significantly higher than that obtained earlier from the temperature dependences of the superstructural reflections [5, 11]. It should be noted that, in the tetragonal phase with a long-range order and below T_{c2}, the values of the tetragonal-phase quadrupole constant and the width of the corresponding spectral line differ in magnitude only slightly. It is possible that the NMR data reveal regions of the high-temperature tetragonal phase with a long-range order that persist in the range of existence of the average trigonal structure. This fraction does not participate in the processes of nucleation and growth of the tetragonal phase above 475 K.

3. CONCLUSIONS

(i) In [13], the asymmetric diffuse x-ray scattering observed in NBT was explained in terms of the presence of small flat islands of monoclinic structure with ordered components of displacement along [100]-type directions in the randomized trigonal matrix. While both diffuse x-ray scattering and NMR reveal a local order, they differ in terms of their physical nature. The fact that the results are in agreement in this case confirms the validity of the proposed interpretations.

(ii) It has been well established that the record-breaking piezoelectric properties and the giant electrostriction of the abovementioned Pb-containing compounds are associated with the existence of the monoclinic phase near the morphotropic boundary [14]. The distinctive feature of NBT is that the monoclinic long-range order does not arise even in a narrow temperature range. However, the fairly good electromechanical characteristics of NBT are likely related to the monoclinic structure of the polar clusters and possible rotation of the local spontaneous cluster polarization with varying temperature in the range 580–610 K.

(iii) The measurements under a very weak magnetic field have allowed us to increase significantly the spectral resolution as compared with the previous NMR studies of Pb-containing relaxors (see, e.g., [1, 2]). The ^{23}Na NMR line shape in NBT has a clearly pronounced orientation-dependent substructure. This substructure agrees well with the calculations based on the position model with six equally probable orientations of the electric dipole moment of the polar cluster. The isotropic glass model with numerous orientations of the local polarization used in [2] disagrees with the experimental spectra, at least for NBT.

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