Local polar order in the ferroelectric-relaxor $Na_{1/2}Bi_{1/2}TiO_3$ as studied by ^{23}Na NMR

Yu.E.Yablonskaya, I.P.Aleksandrova, A.A.Sukhovsky, Yu.N.Ivanov

L.V.Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences, 660036 Krasnoyarsk, Russia

^{23}Na NMR spectra have been measured in a very low magnetic field at temperatures between 293 K and 729 K. The achieved spectral resolution is sufficient to test various models of short-range order in the $Na_{1/2}Bi_{1/2}TiO_3$ structure using computer simulations of the spectral line shape. The best agreement between experimental and calculated spectra has been obtained for the inhomogeneous structure where the polar nanoscale areas with Na displaced along the pseudo-cubic directions $[111]_P$ coexist in the 293 K–580 K temperature region with the tetragonal phase insertions with Na displaced along $[100]_P$ and the "matrix" having very small deviations from the cubic structure.

Проведены измерения спектров ЯМР ^{23}Na в очень низком магнитном поле при температурах между 293 К и 729 К. Достигнутое разрешение достаточно для тестирования различных моделей ближнего порядка в структуре $Na_{1/2}Bi_{1/2}TiO_3$ при использовании компьютерной симуляции формы спектральной линии. Наилучшее согласие между экспериментальными и расчетными спектрами было достигнуто для неоднородной структуры, где полярные нанообласти со смещениями Na вдоль псевдокубических направлений $[111]_P$, включения тетрагональной фазы со смещениями Na вдоль направлений $[100]_P$ и "матрица", имеющая очень малые отклонения от кубической структуры, сосуществуют в температурном интервале 293 К–580 К.

Ferroelectrics-relaxors are complex perovskites with the general formula $A'A''BX_3$ and $A'B'B''X_3$. Within a certain temperature region, nanoscale regions with ordered polar structure (polar clusters) embedded into a disordered cubic matrix were revealed in these compounds. A specific feature of the relaxors consists in anomalous dielectric relaxation, which is observed in a broad frequency range. When frequency increases, the peak in the dielectric permittivity curve is lowered and shifts towards higher temperatures. The relaxors are attractive to solid state physics as partially disordered systems with uncommon structure arrangement and outstanding dielectric properties ($\varepsilon' \sim 20000$ at $f = 1$ kHz), strong piezoelectric coefficients and giant electrostriction.

Interrelations between composition, structure, and properties of relaxors are among the most actively developing areas of modern solid state physics. There are numerous researches of local and average structures of relaxors carried out using neutron and X-ray scattering methods. Nevertheless, various authors present quite different interpretations of the data on both elastic and diffuse scattering. This is due to certain specifics of the relaxor structures. Those are: (i) small values of atomic displacements which determine the difference between local and average structures; and (ii) low-frequency tilts of the oxygen octahedrons and fluctuations of the local polarization directions of polar clusters in certain temperature region. In such cases, the Wyckoff atomic positions may depend con-

siderably on the refinement procedure. That permits various interpretations of the anomalous large thermal factors. In certain cases, NMR allows to eliminate the above mentioned indefinites at the structure determination.

The compound under investigation, $Na_{1/2}Bi_{1/2}TiO_3$ (NBT), belongs to the ferroelectrics-relaxors of the ABX_3 perovskite type with substitution in the A-position. In contrast to "true" relaxors, remaining to be cubic till the lowest investigated temperature, NBT exhibits a sequence of spontaneous phase transitions from the cubic phase ($Pm\bar{3}m$) to the tetragonal phase ($P4bm$, $Z = 2$) at 813 К (T_{C1}) and then to the trigonal phase ($R3c$, $Z = 6$) at approximately 600 К (T_{C2}) [1–3]. The cubic and tetragonal phases are long-range ordered structures. In the trigonal phase, the long-range order is lost, the space group $R3c$ describes the average structure.

The measurements of the second-order quadrupole interactions in very low magnetic fields made it possible to improve considerably the spectral resolution. The achieved resolution has been found to be sufficient for testing various models of short-range order in the NBT structure using the computer simulations of the spectral line shape.

The ^{23}Na NMR spectra of NBT single crystal were measured at Larmor frequency 15.7 MHz. The dependences of the line shape on the crystal orientation in the magnetic field were obtained at the rotation about the $[110]_P$ direction of the pseudo-cubic cell at 293 К, 350 К, 400 К, 450 К, 475 К, 500 К, 540 К, 580 К, 640 К, and 729 К. The continuous wave technique with a signal accumulation was used.

In the complex perovskites $A'A''BX_3$ and $AB'B''X_3$, it is just the displacement of A-cation from its equilibrium position in the cubic phase that causes the main contribution to the electric dipole moment of polar clusters. The same displacement defines the quadrupole coupling constant (QCC) value on the ^{23}Na nucleus, $q = e \cdot Q \cdot V_{zz}/h$ (V_{zz} is the main value of the electric field gradient tensor (EFG) on the nucleus; Q, the nuclear quadrupole moment; e, the electron charge; h, the Planck constant). The quadrupole coupling constant sensitivity to the cation displacement from the equilibrium position in the high-temperature cubic phase is relatively high, about 10^{-3} Å.

In relaxors, the electric dipole moment of the polar regions has several equiprobable orientations in the structure. Consequently, there are several different orientations of the EFG tensor axes with respect to the magnetic field direction. Thus, in the NMR spectrum there appear signals coming from quite a large number of magnetically non-equivalent lattice sites. In addition, according to our previous measurements [4, 5], appear structurally nonequivalent positions of ^{23}Na, which belong to the coexisting regions of the polar clusters and the tetragonal phase. As a result, the NMR ^{23}Na spectrum consists of one broad non-resolved line with a shape depending on the crystal orientation in the magnetic field. The line shape can be presented as the convolution of frequency distribution function, $f(\nu)$, and of the spectral broadening function $L(\nu'-\nu)$:

$$F(\nu) = \int f(\nu')L(\nu' - \nu)d\nu. \qquad (1)$$

A computer program has been developed which allows to calculate the line shape for any crystal orientation in the magnetic field for various structural models. Two version of the NBT structure arrangement were tested.

The Model 1: in the polar cluster, Na is displaced equiprobably along one of the eight equivalent directions $[111]_P$ of the pseudo-cubic cell. The Na atom is supposed to be located in a multi-welled (8-positions) potential around its special Wyckoff position. In the tetragonal structure, the Na displacements occur with an equal probability along one of six $[100]_P$ directions, coinciding with the C_4 symmetry axis of the $P4bm$ space group. The Model 1 permits a coexistence of independent Na displacements along $[111]_P$ and $[100]_P$ directions.

The second-order quadrupole shift, $\delta\nu$, of the central component ($+1/2 \to -1/2$) for an axially symmetric tensor is [6]:

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

Here, θ is the angle between the magnetic field direction and the principal z axis of EFG tensor; ν_L, the Larmor frequency; I, the nuclear spin ($I = 3/2$ for ^{23}Na).

In Fig. 1, the angular dependences of $\Delta\nu$ (for $Kq^2 = 1$) for eight "trigonal" displacements along the directions of $[100]_P$ type in the tetragonal twins are presented. The fre-

quency distribution function $f(\nu)$ in Eq.(1) is actually determined by the dependences presented in Fig. 1 for any crystal orientation.

When simulating the spectral shapes, the variable parameters are as follows: the values of q for the clusters and for the tetragonal phase; the peak intensity A and half-width W of the Gaussian broadening functions. The model also assumes the existence of regions within the trigonal phase with a very small deviation from the cubic structure, so-called "matrix". The position of the corresponding line is varied within narrow limits around the Larmor frequency, the peak intensity and the line width are also variable parameters. The relative phase volumes X of the regions with different structures are determined by integral intensities of the related lines. The data array for each temperature consists of 10 spectra corresponding to the angles (θ) varying from 0° to 90° with a step of 10°. The least square method for data array containing 10 spectra was used when the experimental spectra were compared with the calculated shapes. Table represents the most important variables corresponding to the minimal deviation Δ between the experimental and simulated line shapes. As an example, the experimental and calculated spectra at 350 K are shown in Fig. 2.

The data presented in Table show that the best agreement is attained when the inhomogeneous structure where the regions
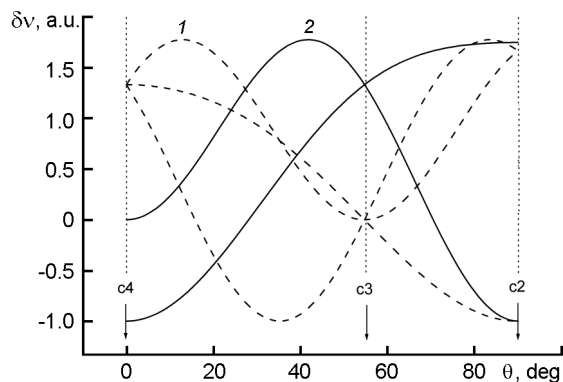

Fig. 1. Angular dependences of second order quadrupole shifts for magnetically equivalent positions in trigonal (*1*) and tetragonal (*2*) NBT phases, at crystal rotation around $[110]_P$ direction.

with the Na displacements along the directions of types $[111]_P$, $[100]_P$ and the matrix coexist in the temperature range 293 K–580 K. Table also illustrates how the phase volumes X of the regions with different distortions of the ^{23}Na nuclei nearest surrounding are changed with temperature. The phase volumes as a function of temperature are shown in Fig. 3.

The temperature behavior of the quadrupole coupling constants q_{trig} and q_{tetr} is of a special interest. While the constant q_{trig} related to polar clusters is changed in the temperature interval 500–580 K, q_{tetr} remains nearly constant in the whole tempera-

Table. The most important variables corresponding to the minimal deviation Δ between the experimental and simulated line shapes at different temperatures

Model 1									
T, K	q_{trig}, MHz	q_{tetr}, MHz	W_{trig}, kHz	W_{tetr}, kHz	W_{matr}, kHz	X_{trig}	X_{tetr}	X_{matr}	Δ
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

Model 2							
T, K	q_{trig}, MHz	q_{tetr}, MHz	W_{trig}, kHz	W_{tetr}, kHz	$W_{trig}(1)$, kHz	$W_{tetr}(1)$, kHz	X_{trig}	Δ
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

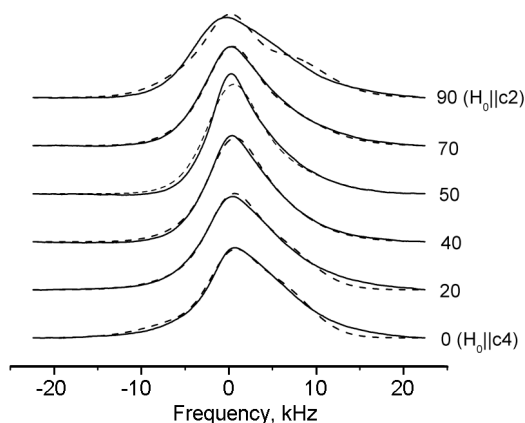Fig. 2. Angular dependences of ^{23}Na NMR spectra at 350 K. Solid line shows the experimental shape, dashed line, the simulated one.
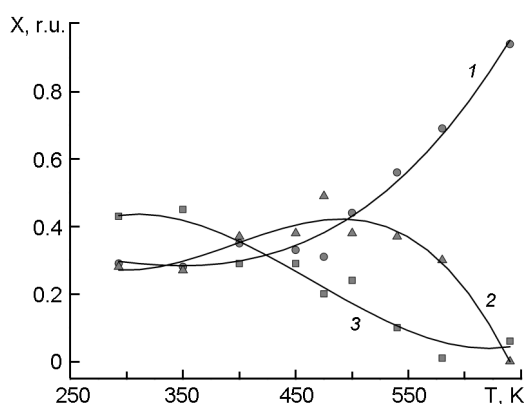

Fig. 3. The phase volumes X as a function of temperature: *1*, tetragonal; *2*, matrix; *3*, trigonal.

ture range up to 729 K. Above 500 К, a noticeable change is detected in the width W_{trig} of the lines, corresponding to polar clusters. The spectral lines related to the tetragonal phase undergo only small, smooth narrowing as the temperature increases.

An attempt to simulate the spectra at the temperatures above T_{C2} using Model 1 results in an appreciable increase of Δ. For the temperatures 640 К and 729 К, the Model 2 was used. There is no matrix in this model, which looks to be natural for the tetragonal long-range ordered structure. When simulating, the broadening of spectral lines proportional to the second order quadrupole shift has been revealed. To date, we do not know the origin of this broadening. Nevertheless, taking into account the corresponding broadening, $W(1)$, one can improve sufficiently the Δ factor. The result is shown in Table. We have also tested Model 2 for trigonal phase temperature region. However Δ in this case shows 2–3

time increase in comparison with Model 1. The Model 2 seems to be more applicable in the high temperature tetragonal phase.

Model 1 describes rather well the shape of the ^{23}Na spectra in a wide temperature range where the average trigonal structure exists. Nevertheless, our previous data [4, 5] allow to assume that local symmetry of the polar regions is lower than the trigonal one. So, Na hops between 8 positions of the multi-welled potential give the cubic Na position as an average. However, it does not agree with the *R3c* space group. Besides, the Na dynamic restoring the cubic symmetry is observed only above 780 K [5].

We assume that the Na displacements in the clusters include small orthogonal components disordered over 6 [100]$_P$ directions in addition to the cooperative shift along the polar [111]$_P$ axis. If this displacement of Na from the three-fold symmetry axis is small, the approximation by an axially symmetric tensor is valid. At low temperatures, when reorientation of the electric dipole moments is frozen [4], the orthogonal components inside the cluster are ordered along one of the six [100]$_P$ directions. Thus, the polar clusters are of the monoclinic symmetry, while the average structure of the crystal maintains the trigonal symmetry.

Above 500 K, the narrowing of the ^{23}Na NMR lines belonging to the clusters (see Table) reveals the positional exchange in the multi-welled potential. It should be noted that reorientations of the orthogonal components are correlated within the cluster volume. It is clearly seen that the motional averaging results again in the trigonal structure, maintaining it at high temperatures. The motional averaging, however, cannot cause a sharp q_{trig} decrease observed between 540 K and 580 K at heating (Table). The spontaneous decrease of Na/Bi displacements in the polar clusters along the [111]$_P$ directions is unexpected. Nevertheless, a sharp decrease of the second optical harmonics generation level was revealed at similar temperatures [3].

Table show that above 500 K, the relative volume of the tetragonal phase, X_{tetr}, increases mainly at the expense of the volume occupied by the polar clusters. The [111]$_P$ displacement becomes very small at approaching T_{C2}. Thus, the clusters in this temperature region may act as the tetragonal phase nucleation centers, since they include the "tetragonal" displacements along [100]$_P$. The monoclinic polar clusters and the tetragonal phase nuclei are of nearly

equal energy in the region between 580 K and T_{C2} (610 K). This makes possible the appearance of heterophase fluctuations. A rather wide (~30 K) temperature interval where close in energy but different in structure regions coexist, suggests a competition between tetragonal and monoclinic ordering. At further temperature increase, fast growth of the tetragonal nuclei results in the transition to the long-range *P4bm* structure. Such transition type does not require complete reorganization of the local cluster structure as it would take place at the change of symmetry $P4bm, Z = 2 \rightarrow R3c, Z = 6$.

An anomalous dielectric relaxation and broad ε' maximum are observed just in the region about 30 K below T_{C2} [8] where, according to the above data, fast reorientation of the local polarization and heterophase fluctuations occur in the NBT structure. Low potential barriers which prevent the local polarization hopping are certainly caused by a very small displacement of Na along $[111]_P$ in the polar clusters at the temperatures between 580 K and T_{C2}. Piezoelectric properties of NBT are most probably connected with the monoclinic symmetry of the polar clusters as it takes place in $PbZr_{0.5}Ti_{0.5}O_3$ (PZT); $PbMg_{0.3}Nb_{1-x}Ti_xO_3 x\sim0.35$ (PNM/PT) [9, 10].

References

1. G.A.Smolensky, V.A.Isupov, A.I.Agranovskaya, N.N.Kraynik, *Fiz. Tverd. Tela*, **11**, 2982 (1960).
2. S.B.Vakhrushev, B.E.Kvyatkovsky, R.S.Malysheva et al., *Kristallografiya*, **34**, 154 (1989).
3. G.O.Jones, P.A.Thomas, *Acta Crystallogr.*, **B 58**, 168 (2002).
4. I.P.Aleksandrova, Yu.N.Ivanov, A.A.Sukhovsky, S.B.Vakhrushev, *Fiz. Tverd. Tela*, **48**, 1055 (2006).
5. I.P.Aleksandrova, Yu.N.Ivanov, A.A.Sukhovsky et al., *Fiz. Tverd. Tela*, **50**, 479 (2008).
6. A.Abragam, The Principles of Nuclear Magnetism, Oxford University Press, Oxford (1961).
7. S.B.Vakhrushev, B.E.Kvyatkovsky, N.M.Okuneva et al., *Pis'ma Zh. Eksp. Teor. Fiz.*, **35**, 111 (1982).
8. J.A.Zvirgzds, P.P.Kapostins, *Ferroelectrics*, **40**, 75 (1982).
9. B.Noheda, J.A.Gonzalo, L.E.Cross et al., *Phys. Rev. B*, **61**, 8687 (1999).
10. B.Dkhil, J.M.Kiat, G.Calvarin et al., *Phys. Rev. B*, **65**, 024104 (2002).

Локальний полярний порядок у сегнетоелектрику-релаксорі $Na_{1/2}Bi_{1/2}TiO_3$ за дослідженням ЯМР ^{23}Na

Ю.Є.Яблонська, І.П.Александрова, А.А.Суховський, Ю.М.Іванов

Проведено вимірювання спектрів ЯМР ^{23}Na у дуже слабкому магнітному полі при температурах між 293 К та 729 К. Досягнене розрішення є достатнім для тестування різних моделей ближнього порядку у структурі $Na_{1/2}Bi_{1/2}TiO_3$ (NBT) при використанні комп'ютерної симуляції форми спектральної лінії. Найкращого узгодження між експериментальними та розрахунковими спектрами досягнуто для неоднорідної структури, де полярні наноділянки зі зміщеннями Na вздовж псевдокубічних напрямів $[111]_P$, включення тетрагональної фази зі зміщеннями Na вздовж напрямів $[100]_P$ та "матриця", що має дуже незначні відхилення від кубічної структури, співіснують у температурному інтервалі 293 К–580 К.