Structure and dielectric properties of Na$_{0.5}$Bi$_{0.5}$TiO$_3$-CaTiO$_3$ solid solutions

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Despite wide studies of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ structure of this material and its connection with the observed physical properties still raise numerous questions due to mutually contradicting results obtained. Here, structure and dielectric properties of poled and unpoled Na$_{0.5}$Bi$_{0.5}$TiO$_3$-CaTiO$_3$ solid solutions are studied, projecting the obtained concentration dependence of structure and dielectric properties on pure Na$_{0.5}$Bi$_{0.5}$TiO$_3$ as the end member of this material group. X-ray diffraction patterns for Na$_{0.5}$Bi$_{0.5}$TiO$_3$-CaTiO$_3$ solid solutions reveal dominating of an orthorhombic Pnma phase, even for the compositions approaching the end composition (Na$_{0.5}$Bi$_{0.5}$TiO$_3$), whereas structure of pure Na$_{0.5}$Bi$_{0.5}$TiO$_3$ can be considered, assuming coexistence of rhombohedral and orthorhombic phases. This allows one to avoid appearance of a large difference of rhombohedral distortions between the unpoled and poled Na$_{0.5}$Bi$_{0.5}$TiO$_3$, if the rhombohedral distortion is calculated as for single R3c phase. Features of dielectric permittivity, corresponding to the observed structural phase transition, are identified. It is discussed that the rhombohedral R3c phase is responsible for appearance of the frequency-dependent shoulder of dielectric permittivity temperature dependence, characteristic for unpoled Na$_{0.5}$Bi$_{0.5}$TiO$_3$. © 2016 AIP Publishing LLC.

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I. INTRODUCTION

Structure of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ (NBT) is an object of long-lasting discussions. Description of it was very often based on assuming rhombohedral R3c symmetry group at room temperature, considered since discovery of NBT in 1962, with a wide temperature range of coexistence of rhombohedral R3c and tetragonal P4bm symmetries in a temperature range between 255 °C and 400 °C. However, lately it was realized that such an approach is not completely satisfying.

Studies of the superstructure, revealed in electron and neutron diffraction measurements and related to different tilt systems of oxygen octahedra, had an important role in further clarification of the symmetry. One of the first attempts to improve description of the structure was connected with transmission electron microscopy studies, which revealed a superstructure, compatible not with rhombohedral, but orthorhombic symmetry, above 200 °C.

Temperature-dependent streaks suggested that this orthorhombic phase can be represented by a thin sheet, separating regions of a rhombohedral symmetry, at lower temperatures, and only after approaching 300 °C it develops as a dominant phase.

Later, a careful study of x-ray diffraction patterns at room temperature revealed that the structure of NBT can be better described by a monoclinic symmetry instead of the rhombohedral symmetry. The Cc symmetry group was accepted since it is polar and can be responsible for the ferroelectric state of NBT. Confident results regarding pure rhombohedral structure of the poled NBT obtained lately, establish a logical consequence that the depoled state should be at least partly rhombohedral. Since a pure rhombohedral state cannot describe particular maxima of the diffraction pattern, coexistence with Cc was adopted. Still various combinations of coexisting phases, treated by the Rietveld analysis, do not allow us to extract the one, which would provide clearly the best coincidence. Therefore, other considerations are involved to make the choice.

In contrast to the structure of the unpoled NBT, which cannot be sufficiently described with a single symmetry group even at room temperature, the poled samples of this compound have a pure rhombohedral structure, which transfers to the structure characteristic for the unpoled samples only above the depolarization temperature $T_d$. This discovery was very important, since it shows the essential difference between structures of the poled and of the unpoled samples, while structure of unpoled samples is frequently considered together with physical properties (polarization, electromechanical properties) of poled samples in interpretation of phases of NBT and NBT-based solid solutions.

Since appearance of a Pnma orthorhombic structure is found in NBT, it becomes interesting how it develops in solid solutions with CaTiO$_3$ (CT), which represents a well-known pervoskite of the Pnma symmetry. Such studies, especially concerning superstructure, belonging to different tilt systems of the oxygen octahedra, revealed that (1-x)NBT-xCT compositions with CT concentration above x = 0.10 unambiguously have Pnma symmetry at room temperature, while coexistence with a rhombohedral symmetry is found in some CT concentration range including x = 0.10.

The role of the superstructure in determination of the symmetry of NBT and NBT-based solid solutions is relevant, but not always has a clear interpretation. One of the reasons could be intensity of the corresponding diffraction maxima,
which can be too weak to appear in particular measurements, especially if a coexistence of phases with complicated morphology has to be considered. Therefore, the absence of a diffraction maximum, responsible for some tilt system of oxygen octahedra, does not always allow one to exclude symmetry groups, which have such a tilt system, from consideration. Another problem in the interpretation is a coexistence of a superstructure with a pure cubic symmetry (so-called isotropization point), found in diffraction patterns close to 300°C, as well as its persistence far above the tetragonal-cubic phase transition, observed in NBT.7

The goal of our research is to study the structure and dielectric properties of poled and unpoled samples of NBT-CT compositions, trying to project the obtained concentration dependences on NBT as the end member of this solid solution system.

II. EXPERIMENTAL DETAILS

\((1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_{3} - x\text{CaTiO}_{3}\) ((1-x)NBT-xCT) ceramics with \(x = 0.0, x = 0.03, x = 0.05, x = 0.10, x = 0.20,\) and \(x = 0.40\) were prepared by the conventional solid state reaction method. Chemical-grade oxides and carbonates (purity > 99.5%), \(\text{Na}_2\text{CO}_3, \text{Bi}_2\text{O}_3, \text{CaCO}_3,\) and \(\text{TiO}_2\) were used as starting materials. The powders were weighed according to the formula, mixed with ethanol and milled in an agate ball mill for 24 h. The dried powders were calcined for the first time at 850–900°C for 2 h. Afterwards they were milled again in the same conditions for 24 h and calcined for the second time at 1000°C for 2 h. After milling in the same conditions for 24 h again, the powders were pressed uniaxially into disk-shaped pellets with diameter of \(\approx 17\) mm and height of \(\approx 10\) mm and then compacted under a pressure of 30 MPa using a hydraulic press. The disks were sintered at 1150–1200°C for 3–4 h depending on the composition. In order to prevent evaporation of Bi, calcination was carried out in covered platinum crucibles, whereas during the sintering, the disks were embedded in a powder of the same composition and placed under platinum crucibles on a platinum pallet.

Samples with thickness of 0.3–0.5 mm were cut, polished, and electrodes were made by firing of Au paste at 500°C for dielectric permittivity measurements. Weak-field dielectric properties in a temperature range from \(-150^\circ\)C to 300–450°C at various frequencies from 130 Hz to 1 MHz were obtained using an impedance analyzer HP precision LCR meter 4284A with a measuring electric field of 0.4 V/cm. The rate of the temperature change was \(\approx 2^\circ\)C/min.

The structure of the ceramics was examined using the x-ray diffractometer PANalytical X’Pert PRO. The studies were performed for crushed samples, as well as for bulk ceramics. The crushed ceramic samples were also checked for possible phase transition induced by mechanical impact, found in Ref. 6. A comparison of powdered unpoled samples just after crushing and after the following thermal annealing at 400–700°C did not reveal any differences of diffraction patterns between both cases.

Raman spectroscopy measurements were performed at room temperature for the bulk samples. Raman scattering spectra were excited by a 785 nm near-IR laser (cw, 10 mW) and measured in back-scattering geometry using a micro-Raman RxN1 spectrometer from Kaiser Optical Systems, Inc.

III. RESULTS AND DISCUSSION

Temperature dependences of the real part of dielectric permittivity for NBT-CT solid solutions are shown in Figure 1. Character of the real part of dielectric permittivity \((\varepsilon'(T,\omega))\) for the composition with \(x = 0.03\) resembles pure NBT due to the maximum at almost frequency-independent maximum temperature \(T_m\), the steep change of dielectric permittivity with thermal hysteresis in direction of lower temperatures (at the temperature \(T_c\)) and the frequency-dependent shoulder (Figure 2). The composition with \(x = 0.05\) also has a well-expressed dielectric permittivity anomaly, namely, a \(\varepsilon'(T)\) jump, at the temperature \(T_c\) with significant thermal hysteresis comparing heating and cooling (Figure 3(a)). We consider that the anomaly at \(T_c\) corresponds to the well-known steep change of \(\varepsilon'(T)\) in pure NBT, where it appears slightly below \(T_m\). In case of \(x = 0.05\), this steep change is more expressed (it also appears as a maximum in the temperature dependence of the imaginary part of dielectric permittivity \(\varepsilon''(T,\omega)\)—see Fig. 3(b)) and is not supplemented by a closely located additional maximum at \(T_m\). The frequency-independent maximum in this case seems to be shifted in direction of higher temperatures and appear as the change of slope above 400°C. In the composition with \(x = 0.10\) this jump (at \(T_c\)) and the corresponding thermal hysteresis is not so well expressed, while in the composition with \(x = 0.20\) it is transformed into \(\varepsilon'(T,\omega)\) dependence characteristic for relaxor ferroelectrics—with frequency-dependent temperature of dielectric permittivity maximum \(T_m(\omega)\) and nearly frequency-independent \(\varepsilon'(T)\) above \(T_m(\omega)\) in the frequency range \(\omega < \omega_t\), for any chosen measurement frequency \(\omega_t\).10

In compositions with \(x \leq 0.05\), well-expressed rectangular polarization hysteresis loops \(P(E)\) were observed at room temperature, which clearly indicates presence of a ferroelectric state. Measurements of dielectric permittivity were performed also for the samples, poled at room temperature. In
In this case, the temperature of the phase transition from ferroelectric (rhombohedral) to relaxor state (T_r) was determined during heating measurements from anomalies of the real and the imaginary parts of dielectric permittivity—\( e''(T) \) and \( e''(T) \), respectively (Fig. 4(b)). \( e''(T) \) dispersion at a temperature range \( T > T_r \) becomes more expressed comparing with the unpoled (virgin) samples (Figure 4).

Concentration dependences of the characteristic temperatures are presented in Table 1. In general, increasing of \( T_m \) and decreasing of \( T_t \) is observed if concentration of Ca increases. The deviation of \( T_t(x) \) for the composition with \( x = 0.03 \) from this common trend could be related to a possibility that Ca ions partly occupy positions in the B-site of the perovskite structure \( \text{ABO}_3 \), which was observed earlier for \( \text{BaTiO}_3 \).\(^{11} \) However, evidence of such occupancy was not found in concentration dependence of the unit cell volume, as it will be shown below.

The Raman spectra of \((1 - x)\text{NBT}-x\text{CT}\) solid solutions (Figure 5) can be divided into four bands, as in other NBT-based compounds.\(^{12-14} \) The first Raman band located below 187 cm\(^{-1}\) (A-band) is due to A-O vibrations. Due to the large difference in the masses of Na and Bi ions, both occupying the A-site, the part of the A-band visible in the spectral range of 155–187 cm\(^{-1}\) is usually related to Na-O vibrations, whereas the contribution from Bi-O vibrations is expected at lower wavenumbers 109–134 cm\(^{-1}\).\(^{14} \) The second band between 187 cm\(^{-1}\) and 440 cm\(^{-1}\), denoted as B-band, is related to vibrations of TiO\(_6\) octahedra.\(^{14} \) The last two bands at 440–700 cm\(^{-1}\) (C-band) and 700–900 cm\(^{-1}\) (D-band) involve the oxygen atom vibrations.\(^{14} \)

FIG. 2. Temperature dependences of the real part of dielectric permittivity, measured at various frequencies for the unpoled samples of compositions \( \text{NBT} \) (a) and \( 0.97\text{NBT}-0.03\text{CT} \) (b), obtained on heating and cooling (temperature \( T_c \) on heating and on cooling is marked as \( T_c^{(h)} \) and \( T_c^{(c)} \) correspondingly).

FIG. 3. Temperature-frequency dependences of the real (a) and the imaginary (b) parts of dielectric permittivity, measured at various frequencies for the unpoled sample of composition \( 0.95\text{NBT}–0.05\text{CT} \), obtained on heating and cooling (temperature \( T_c \) on heating and on cooling is marked as \( T_c^{(h)} \) and \( T_c^{(c)} \) correspondingly).

FIG. 4. Temperature dependences of the real part of dielectric permittivity measured at various frequencies for the unpoled (a) and the poled (b) samples of \( 0.97\text{NBT}–0.03\text{CT} \) composition on heating. The corresponding temperature dependences of the imaginary part of dielectric permittivity are shown in the insets.
modes increases till 24. However, even in pure CT single crystal, the number of distinguishable modes is much smaller than the calculated value. Therefore, it is not reasonable to look for differences in the number of modes in Raman spectra obtained of ceramic NBT-CT solid solutions.

X-ray diffraction patterns confirm a single perovskite structure for all compositions. The diffraction pattern for the compositions with $x > 0.10$ can be well described by orthorhombic symmetry group Pnma at room temperature, which could be expected also from earlier studies. We have tried to describe the diffraction patterns with Pnma also at lower CT concentrations (Figure 6). (The indexing of the Bragg reflections in the figure and the following text is done with respect to a pseudocubic cell.)

Upon decreasing of CT concentration (moving towards pure NBT), the Rietveld analysis indicates slight increasing of the reliability factor $R_{wp}(O)$, which characterizes compatibility of the calculations, assuming pure Pnma, with the experimental data (Table I). However, even for the composition with $x = 0.03$ and $x = 0.00$, contrary to Refs. 8 and 9, description by pure Pnma leads to a better compatibility with the observed diffraction pattern than by pure R3c. This is indicated by $R_{wp}(O) < R_{wp}(R)$ at a concrete CT concentration, as it is seen in Table I (here, $R_{wp}(R)$ corresponds to the description by a single R3c symmetry, and lack of $R_{wp}(R)$ for $x > 0.10$ indicates that this description was not applicable for the corresponding compositions).

The increasing of $R_{wp}(O)$ in direction of low CT concentrations can be considered as a result of appearance of the phase coexistence with another phase, namely, R3c. However only in pure NBT the shape of diffraction maxima

<table>
<thead>
<tr>
<th>(1-x)NBT-xCaT composition</th>
<th>$T_m$ (°C) at 1 kHz on heating</th>
<th>$T_c$ (°C) on cooling</th>
<th>$T_t$ (°C) on heating</th>
<th>$R_{wp}(O)$</th>
<th>$R_{wp}(R)$</th>
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<tr>
<td>x = 0.00</td>
<td>336</td>
<td>266</td>
<td>310</td>
<td>180</td>
<td>2.70</td>
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<tr>
<td>x = 0.03</td>
<td>370</td>
<td>210</td>
<td>300</td>
<td>94</td>
<td>1.97</td>
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<tr>
<td>x = 0.05</td>
<td>465</td>
<td>201</td>
<td>246</td>
<td>103</td>
<td>1.96</td>
</tr>
<tr>
<td>x = 0.10</td>
<td>...</td>
<td>71</td>
<td>83</td>
<td>...</td>
<td>1.91</td>
</tr>
<tr>
<td>x = 0.20</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>1.62</td>
</tr>
<tr>
<td>x = 0.40</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>1.64</td>
</tr>
</tbody>
</table>

FIG. 5. Raman spectra for (1-x)NBT-xCT solid solutions at room temperature.

FIG. 6. Experimentally obtained profiles of x-ray diffraction maxima (111)$_{pc}$ and (202)$_{pc}$ at room temperature and corresponding profiles, calculated by the Rietveld method assuming pure Pnma symmetry for (1-x)NBT-xCT compositions with $x = 0.00$ (a), $x = 0.05$ (b), and $x = 0.10$ (c) (crushed samples). (Black solid line—observed, red dashed line—calculated, and blue line below—difference.)
(Figure 6), calculated for pure Pnma, clearly deviated from the measured pattern. Indeed, calculations, considering coexisting Pnma and R3c, remarkably improve correspondence between the measured and the calculated shapes of the diffraction maxima (Figure 7). Since coexistence of phases with R3c and Pnma symmetry is well documented in NBT in a temperature region above 200 °C, extension of such a coexistence in direction of lower temperatures, including room temperature, at least reduces the number of phases involved in construction of phase diagram of NBT, comparing with Ref. 6. Introducing of the phase coexistence allows one also to avoid appearance of the large difference of rhombohedral distortions between the unpoled and poled NBT, if the rhombohedral distortion is calculated as for single R3c phase for the unpoled sample. A comparison of splitting of diffraction maxima (101)pc, (111)pc, and (202)pc, calculated for R3c symmetry for both cases, can be seen in Figure 7. Unfortunately, addition of the R3c symmetry in the calculations does not improve reliability of the diffraction pattern calculated by the Rietveld analysis, which was observed also earlier with this, as well as with other combinations of coexisting phases.

If a pure orthorhombic phase is assumed for all studied solid solutions, unit cell parameters decrease upon increasing of Ca concentration (Figure 8), while orthorhombic distortions c/a and b/a slightly increase. The unit cell volume also continuously decreases, if CT concentration is increased, which corresponds to the thermal hysteresis of the observed $\varepsilon'(T)$ jump (Figure 3) pretty well. This correspondence strongly supports earlier suggestions that the steep change of $\varepsilon'(T)$ at a temperature close to $T_m$ in NBT is connected with a phase transition, especially taking into account the same thermal hysteresis. Moreover, taking into account the dominating role of the phase with Pbmn symmetry in the composition with $x = 0.05$, as well as in pure NBT below $T_c$, the observed $\varepsilon'(T)$ jump at $T_c$ can be related to a structural first order phase transition between phases of Pnma and P4bm structures. Since this phase transition is not ferroelectric, only a jump of $\varepsilon'(T)$ is observed between the values of dielectric permittivity, characteristic for each of the phases.

X-ray diffraction patterns for the poled samples (with $x \leq 0.05$) reveal a pure R3c symmetry (Figure 10(a)), like it was observed earlier in pure NBT. Temperature dependence of x-ray diffraction patterns reveals that this phase is destroyed at the depolarization temperature $T_d$, which is revealing a temperature hysteresis, which corresponds to the thermal hysteresis of the observed $\varepsilon'(T)$ jump (Figure 3) pretty well. This correspondence strongly supports earlier suggestions that the steep change of $\varepsilon'(T)$ at a temperature close to $T_m$ in NBT is connected with a phase transition, especially taking into account the same thermal hysteresis. Moreover, taking into account the dominating role of the phase with Pbmn symmetry in the composition with $x = 0.05$, as well as in pure NBT below $T_c$, the observed $\varepsilon'(T)$ jump at $T_c$ can be related to a structural first order phase transition between phases of Pnma and P4bm structures. Since this phase transition is not ferroelectric, only a jump of $\varepsilon'(T)$ is observed between the values of dielectric permittivity, characteristic for each of the phases.

FIG. 7. Profiles of experimentally obtained x-ray diffraction maxima (101)pc, (111)pc, and (202)pc at room temperature and calculated profiles assuming pure R3c symmetry (a) and coexistence of R3c with Pnma symmetries (b) for pure crushed NBT sample. (Black solid line—observed, red dashed line—calculated, magenta solid line—Pnma component in the calculations (42%), dark cyan solid line—R3c component in the calculations (58%), and blue line below—difference).

FIG. 8. Concentration dependences of unit cell parameters, corresponding to Pnma symmetry, determined at room temperature for the (1-x)NBT-xCT solid solutions (crushed samples).
close to the phase transition temperature from ferroelectric to relaxor phase \((T_d)\), observed in \(\varepsilon'(T)\) measurements (Figure 4). Since R3c phase is responsible for ferroelectric properties, it is reasonable to assume that polar nanoregions of this phase are responsible also for relaxor properties in the unpoled (virgin) state. The frequency-dependent \(\varepsilon'(T,\omega)\) shoulder, observed in the unpoled samples of the solid solutions with \(x \leq 0.05\), allows us assume that these solid solutions also contain some amount of the R3c phase, even if we were not able to detect it clearly in the diffraction patterns.

The more expressed dielectric dispersion above \(T_d\) (and, respectively, above \(T_t\), Figure 4), observed also in Mn-doped NBT on heating a poled sample,\(^{19}\) could be related to a higher residual concentration of the R3c phase just after heating the poled samples above \(T_d\). This state, obtained by heating the poled sample just above \(T_d\), will be denoted as “depoled” to stress the difference from the state obtained after heat treatment above 300°C, which is assumed to be the same as the unpoled (virgin) state.\(^{6}\) Indeed, differences in shape of x-ray diffraction maxima between the depoled and the unpoled samples are observed, although these differences do not give a clear answer about concentration of the R3c phase comparing both cases. Particularly, for the depoled bulk samples diffraction patterns do not reveal presence of R3c at 200°C and higher temperatures (Figure 10(c)), whereas in the crushed depoled samples at 200°C, the R3c phase is dominating (Figure 10(b)). However, it is possible that in the crushed state depolarization takes place at a higher temperature.

**IV. CONCLUSIONS**

Coexistence of R3c and Pnma phases can be chosen to characterize \((1-x)\)NBT-\(x\)CT solid solutions with \(x \leq 0.05\), including pure NBT \((x = 0.00)\). This is motivated by existence of the pure R3c phase in the poled samples and persistence of the Pnma phase in the unpoled samples even at low concentrations of CT. The characteristic jump of \(\varepsilon'(T)\), observed in NBT and NBT-based solid solutions, corresponds to the first order structural phase transition between orthorhombic and tetragonal phases. The remarkably more expressed dielectric dispersion in the depoled state comparing with the unpoled state of \((1-x)\)NBT-\(x\)CT with \(x \leq 0.05\) can be explained by a larger concentration of the R3c phase in the first case.

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