Reinvestigation of Phase Transitions in $Na_{0.5}Bi_{0.5}TiO_3$ by TEM. Part II: Second Order Orthorhombic to Tetragonal Phase Transition

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NBT presents an orthorhombic to tetragonal second order phase transition that occurs near 320 °C. It corresponds to the so-called antiferroelectric−paraelectric phase transition. A model is presented in which the diffuse phase transition is achieved by the progressive canceling of the antiphase octahedra tilting prevailing within $a^-b^+a^-$ orthorhombic structure, whereas the in-phase tilting is maintained. This transformation gives finally rise to the $a^0a^0c^+$ octahedra tilting system of the tetragonal phase. Electron diffraction experiments show that a long-range ordering occurs within the tetragonal phase. It probably develops as $P4_2/mnm$ ordered nanoregions disseminated within a $P4/mbm$ disordered matrix. The order is still visible in the temperature domain of the cubic phase.

Introduction

$Na_{0.5}Bi_{0.5}TiO_3$ (NBT) is one of the rare perovskites with pseudocubic symmetry[1] built up by the stacking of corner sharing TiO_6 octahedra, forming a cuboctahedral cavity occupied by two different types of A cations. One main interesting point then relies on the possible, and maybe necessary, A site cationic ordering. An electrostatic order is indeed expected, owing to the contrasted valence between sodium (Na^+) and bismuth (Bi^{3+}). However, a brief review of the literature shows than upon the last 50 years, this idea has never been attested by any diffraction experiment whatever the temperature and the structural form of NBT.

At ambient temperature, this perovskite compound is rhombohedral. Based on X-rays diffraction experiments and cell parameter refinements, the polar $R3m$ space group was first proposed[2] in agreement with the ferroelectric behavior of NBT. Starting from the prototype cubic cell, the ambient form of NBT was first considered as a rhombohedral distortion without any octahedra tilting, the structure being consequently characterized by the $a^0a^0a^0$ tilt system.[3] However, octahedra tilt systems are relevant to the oxygen positions and are then better seen by neutrons experiments. Therefore, the first neutron diffraction experiments performed by Vakhrushev et al.[4,5] clearly evidence superlattice reflections inherent to a doubling of the cell parameters along the

$[111]_P$ direction of the pseudocubic cell, that is, the c direction of the hexagonal supercell. The structure was then refined with the $R3c$ space group with an $a^-a^-a^-$ tilt system. This conclusion was recently confirmed by Jones et al.[6] The ambient form has always been determined as a disordered structure[5,6] or considered as such.[7,8] However, since the beginning of the 1990s, few authors suggested, based on Raman or infrared (IR) spectrometry studies, that an ordering process arises within this compound.[9,10] In fact, compared to X-ray or neutron diffraction, it is well-known that Raman or IR spectrometry are highly sensitive to short-range ordering, down to the nanometer scale according to Reaney et al.[11] Recently Petzelt et al.[12] have clearly established that the spectroscopic data support the local Na−Bi ordering, even in the high temperature cubic phase. However, in parallel, the broad phonon spectra together with the frequency independent dielectric losses also speak for a strong lattice disorder. They finally concluded that the ordering process may only occur locally, in agreement with the structural studies for which no long-range ordering exist within NBT. Balagurov et al. took advantage of these results to interpret in situ neutron scattering experiment of the NBT single crystal.[13] According to these authors, the rhombohedral phase presents a one-dimensional incommensurate modulation linked to an A site ordering that took place within the high

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temperature tetragonal phase along the [001]$_T$ crystallographic direction.

The prime X-ray diffraction experiments suggested that the tetragonal phase was a polar phase with the *P4mm* space group and showing an a^{0}a^{0}a^0 tilt system.[2] However, in situ neutron scattering studies[4] revealed the occurrence of (*h* + 1/2, *k* + 1/2, *l*) reflections resulting from the soft mode condensation at the M point of the Brillouin zone, which corresponds to the rotation of the oxygen octahedra about one of the axes of the cubic lattice. In agreement with these results, further in situ neutron powder diffraction refinements concluded to a *P4bm* space group for the tetragonal phase.[6] This phase is disordered with an a^{0}a^{0}c$^+$ tilt system. Locally ordered regions may in this case present a *P4$_2$nm* space group.[12] These two space groups are noncentrosymmetric and also polar. The noncentrosymmetry of the tetragonal phase was ascertained using the second harmonic generation (SHG) powder technique.[6]

A disturbing problem however appears when comparing the results obtained from the structural refinements and the macroscopic physical properties measurements. It has been clearly shown by pyroelectric measurements that the polar character of NBT drastically decreases after 200 °C and could not be measured up to 230−250 °C.[14−16] In addition, above 450 °C[17] and maybe 400 °C,[18] the Curie−Weiss law is fulfilled attesting to the full paraelectric behavior of NBT above this temperature. Under this consideration, the space group of the high temperature tetragonal phase, stable in the 320−520 °C temperature range, could not be polar. Consequently, both *P4bm* and *P4$_2$nm*, which belong to the polar 4 mm point group (pyroelectric), could not be longer retained.

Thus, one of the aims of this paper is first to reconsider the possible space group of the high temperature tetragonal phase. In particular, it is of main interest to determine if, as suggested by previous spectroscopic studies, a long-range ordering of the A cations may exist or not. In the first part of that paper,[19] an orthorhombic intermediate phase was shown to develop at the expense of the rhombohedral one (see the section presenting the background on phase transitions arising in NBT), and consequently, the second goal of this article is to propose a structural model that accounts for such an orthorhombic to tetragonal phase transition. The phase transition between the tetragonal and the high temperature cubic form will be tackled.

Background on Phase Transitions in NBT

Up to now, the phase transition between the rhombohedral low temperature form of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ to the tetragonal high temperature one is classically depicted by a progressive phase transition that spreads over a large temperature domain

covering more than 150 °C.[7] Until quite recently this idea of coexisting rhombohedral/tetragonal phases between 255 and 400 °C was proposed, based on Rietveld refinements of neutron diffraction patterns.[6] Within the broad range of the phase mix-up, the existence of polar regions was suggested[20,21] which are then interpreted as the occurrence of nuclei of the ferroelectric rhombohedral phase appearing and growing within the tetragonal phase during cooling.[20,15] More generally, many authors have explained the electric behavior of NBT and in particular the strongly diffuse phase transition[15,22] on the basis of such a phase mix-up. Nevertheless, this phase mix-up does not explain the ferroelectric−antiferroelectric phase transition earlier evidenced at 200 °C.[16,17] It is also worth noting that the peculiar temperature range of at least 140 °C required to achieve the R → T phase transition makes it a quite unique feature case of phase transitions. In summary and as previously noted by Geday et al.,[23] there is a considerable disagreement in the literature as to the structure of the different phases and the exact nature of their transition.

In view of the aforementioned information, a TEM study was undertaken by electron diffraction to reveal faint information on phase transition. This paper represents the second part of this study. As previously said in the introduction, the first part of this paper[19] has revealed the occurrence of an orthorhombic intermediate phase, with *Pnma* space group, which develops between the low temperature rhombohedral phase and the tetragonal one. The presence of such a orthorhombic phase is attested in Figure 1 by the appearance, at 200 °C, of new $^1/_2$(*oee*) superstructure spots (*o* and *e* meaning respectively *odd* and *even* Miller indices; see ref 24 for nomenclature) in the [001] selected area electron diffraction (SAED) patterns. Their intensity then gradually increases up to 300 °C. In the first part of the paper it is shown that the R → O phase transition is first order and proceeds via a modulated phase. At 280 °C, the modulated phase disappears (see Figure 1[19]), testifying the end of the R → O phase transition. The orthorhombic phase is then the only stable phase, and $^1/_2$(*oee*) superstructure reflections are still observed within SAED patterns.

Consequently, the R → O phase transition seems to be fully accomplished at 280 °C, and the present paper is then principally dedicated to a comprehensive study of the O ↔ T phase transition above that temperature.

Experimental Section

The compound Na$_{0.5}$Bi$_{0.5}$TiO$_3$ was prepared by classical solid state route. A detailed protocol of the synthesis as well as the experimental tools was presented in the first part of the paper.[19] The in situ temperature experiments by TEM were carried out at the ENSICAEN (France) at the CRISMAT laboratory. They were performed on a JEOL 2010 microscope equipped with a double tilt heating stage allowing experiments in the 20 °C−

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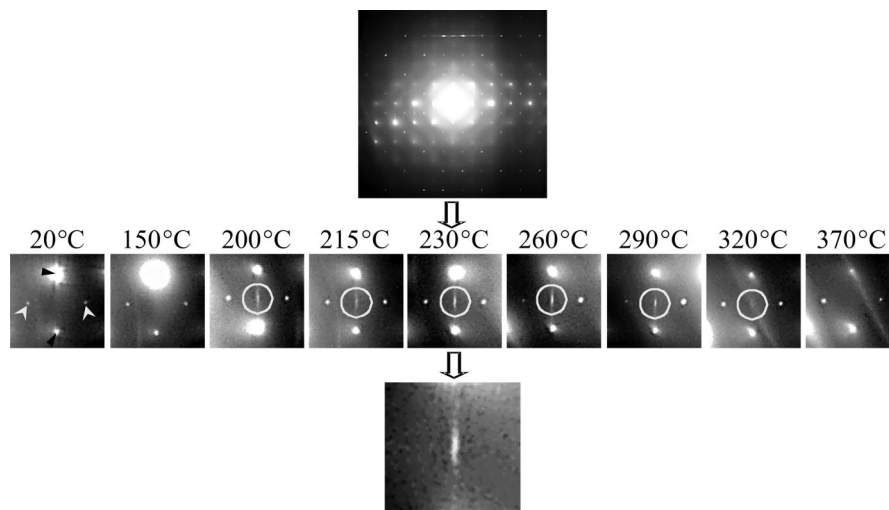(24) Woodward, D. I.; Reaney, I. M. *Acta Crystallogr.* **2005**, *B61*, 387–399.

Figure 1. Results obtained by an in situ electron diffraction study between 20 and 370 °C. Near the $[001]_P$ zone axis pattern direction, $^1/_2(oee)$ reflections characteristic of an orthorhombic phase appear. The temperature domain of stability of the orthorhombic phase is presented by a series of enlargements provided for the different investigated temperatures. On the first of them (at 20 °C) the black arrows indicate the cubic sublattice reflections while the white ones indicate the position of the $^1/_2(ooe)$ tetragonal reflections. Reprinted from ref 19.

700 °C temperature range. Samples for transmission electron microscopy were prepared by mechanical polishing followed by Ar-ion beam milling.

Results

As presented in the introduction, one of the main goals of the structural studies is to characterize the ordering tendency evidenced by spectrometry and so to check if a long-range order exists or not in NBT. The existence of a long-range ordering in this structure is however difficult to evidence, as the expected superstructure reflections due to the doubling of the cell along the three pseudocubic directions[12] will be of the type $^1/_2(ooo)$ and will then be superimposed with those of the rhombohedral surstructure. Therefore, the existence of a cationic order could not be unambiguously ascertained within the low temperature rhombohedral form of NBT. The question is then to know if such an ordering could be observed within the tetragonal phase at high temperature. For that, electron diffraction experiments were thus carried out in a temperature domain where the $a^-a^-a^-$ rhombohedral phase is clearly unstable.

In the first part of that paper,[19] we have shown that the $[013]_P$ zone axis pattern of the pseudocubic cell is well appropriated to observe both the $^1/_2(ooo)$ and $^1/_2(ooe)$ superstructure reflections. The evolution of their intensity with the temperature increasing has then been followed along this zone axis (Figures 2 and Figure 3).

At room temperature (Figure 2a), these two types of reflections are present. At that temperature, the strong $^1/_2(ooo)$ superstructure reflections are induced by the $a^-a^-a^-$ tilt system of the rhombohedral phase, while the tiny $^1/_2(ooe)$ surstructure reflections are due to the $a^0a^0c^+$ in-phase tilting of a residual tetragonal phase trapped within the rhombohedral matrix.[25] At room temperature (Figure 2a), these $^1/_2(ooe)$ reflections are typically elongated along $[100]^*_P$ as a consequence of the restricted thickness of the tetragonal

domains which are in fact platelets of only a few cells thick. In addition, this experimental pattern also presents characteristic diffuse streak lines parallel to $[100]^*_P$.

When the SAED patterns are obtained in the stability domain of the tetragonal phase, the $^1/_2(ooo)$ superstructure reflections must then not be observed. If present, they ought to be due to the expected long-range ordering, the rhombohedral phase being no longer present at that temperature (upper limit at 280 °C). At 480 °C, NBT is in any cases tetragonal for the two following reasons.

(1) The broad maximum of the dielectric constant around 320 °C corresponds to the antiferroelectric−paraelectric phase transition so often mentioned in the literature.[16–18,22,26] This transition takes place between 320 and 400 °C, the temperature above which the Curie−Weiss law is fulfilled,[17,18,27] attesting to the pure paraelectric behavior classically attributed to such a tetragonal phase. These data from the literature are in fair agreement with the results obtained from the in situ electron diffraction study proposed in Figure 1. Indeed, the $^1/_2(oee)$ superstructure reflections characteristic of the orthorhombic phase vanishes at 320 °C and have completely disappeared at 370 °C, whereas the $^1/_2(ooe)$ surstructure reflections of the tetragonal phase are the only ones present. Therefore, the lower limit of the stability domain of the tetragonal phase is below 370 °C.

(2) The upper limit of the stability domain of the tetragonal phase is defined by the last phase transition giving rise to the cubic form near 520 °C.[2,4,6,23,28,29]

At this temperature of 480 °C the $^1/_2(ooo)$ reflections are still clearly observed (Figure 2b). The evolution of the intensity of the superstructure reflections is more precisely shown in Figure 3. It presents line profiles performed along one of the reciprocal rows of the $[013]_P$ zone axis pattern

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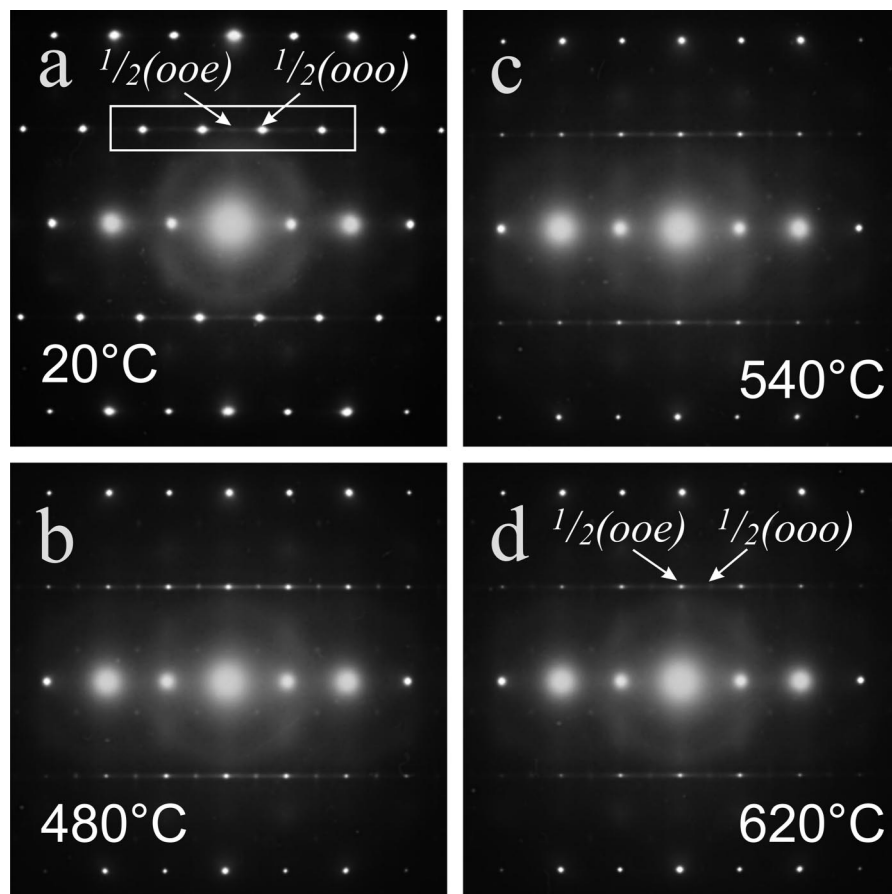
Figure 2. Evolution of the [013]$_P$ SAED pattern with the temperature increasing during the in situ experiment. The respective temperatures are (a) 20 °C, (b) 480 °C, (c) 540 °C, and (d) 620 °C.

along which $^1/_2(ooo)$ and $^1/_2(ooe)$ reflections alternate. The location of the enlargement of the SAED patterns is shown by the rectangular area in Figure 2a. Figures 2 and 3 show that, as the temperature rises, (1) the intensity of the $^1/_2(ooo)$ reflections progressively decreases while that of the $^1/_2(ooe)$ increases until 480 °C; (2) above 540 °C, the intensity of the $^1/_2(ooe)$ reflections seems to decrease (Figure 3); (3) the two types of superstructure reflections, $^1/_2(ooo)$ and $^1/_2(ooe)$, are still observed within the pattern obtained at 620 °C, which is in contradiction with the cubic symmetry expected above 520 °C; and (4) finally, it is worth noting that the diffuse streak lines parallel to [100]$_P^*$ at the ambient are still observed, all along the experiment. A maximum of intensity is observed between 400−480 °C.

A second set of data was obtained according to the [110]$_P$ zone axis pattern (Figure 4). These SAED patterns are characterized by alternating strong (s) and faint (f) reciprocal rows. The strong reflections are due to the pseudocubic sublattice while the faint ones are characteristic of $^1/_2(ooo)$ superstructure reflections. The $^1/_2(ooo)$ reflections are still observed at 540 °C (Figure 4c) and 620 °C (Figure 4d), in the temperature domain of both tetragonal (upper limit) and cubic phase, confirming the results previously obtained on the [013]$_P$ zone axis pattern.

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Discussion

Four main points will be developed. The first one will be devoted to the analysis of a possible ordering process, taking place or not in NBT. In the second part of the discussion, a structural model explaining the orthorhombic to tetragonal phase transition, will be presented. Then, the orthorhombic to tetragonal phase transition will be discussed in connection with the macroscopic electrical properties mentioned in the literature. Finally, the high temperature phase transition through the cubic phase will be tackled.

1. Long-Range Ordering of the A Cations in NBT. As presented in the Introduction, the question of a local order within NBT remains a crucial point as the latter was indeed never directly evidenced by structure refinements, either by X-rays or neutron experiments, but only by IR or Raman spectrometry.[9,10,12]

Above 370 °C, the rhombohedral phase is not stable (c.f. supra), and the presence of the $^1/_2(ooo)$ reflections in the SAED patterns must be reconsidered. Figure 5 reports the [013]$_P$ experimental SAED pattern obtained at 400 °C, and its simulations for the two possible space groups, *P4bm*[6] and *P4$_2$nm*,[12] mentioned in the literature. It is shown that the persistence of the $^1/_2(ooo)$ reflections above 400 °C (see also Figure 2b) could not be justified by the *P4bm* space group classically adopted. These $^1/_2(ooo)$ reflections were still observed by Woodward et al.[24] during in situ electron
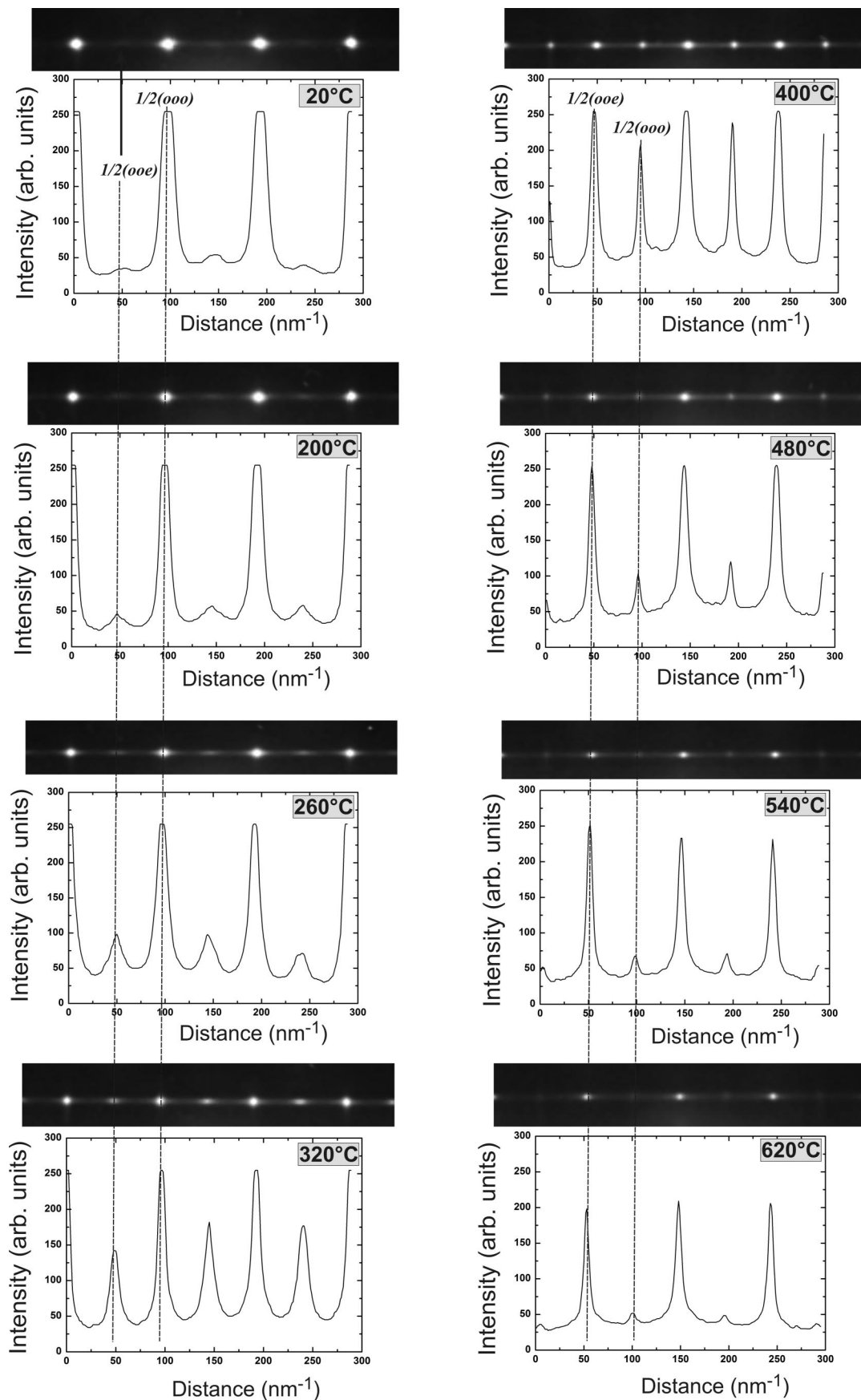
Figure 3. Line profiles showing the evolution of the intensity distribution along a reciprocal row in which $^1/_2(ooo)$ and $^1/_2(ooe)$ reflections alternate. These profiles are extracted from $[013]_P$ SAED patterns obtained at different temperatures. The area of interest is localized by the rectangular area in Figure 1a. An enlargement of each pattern is provided above the profile. The R → O phase transition takes place from 20 to 260 °C while the O → T transition temperature range is 260−400 °C. At 480 °C the final T → C transition is in progress.
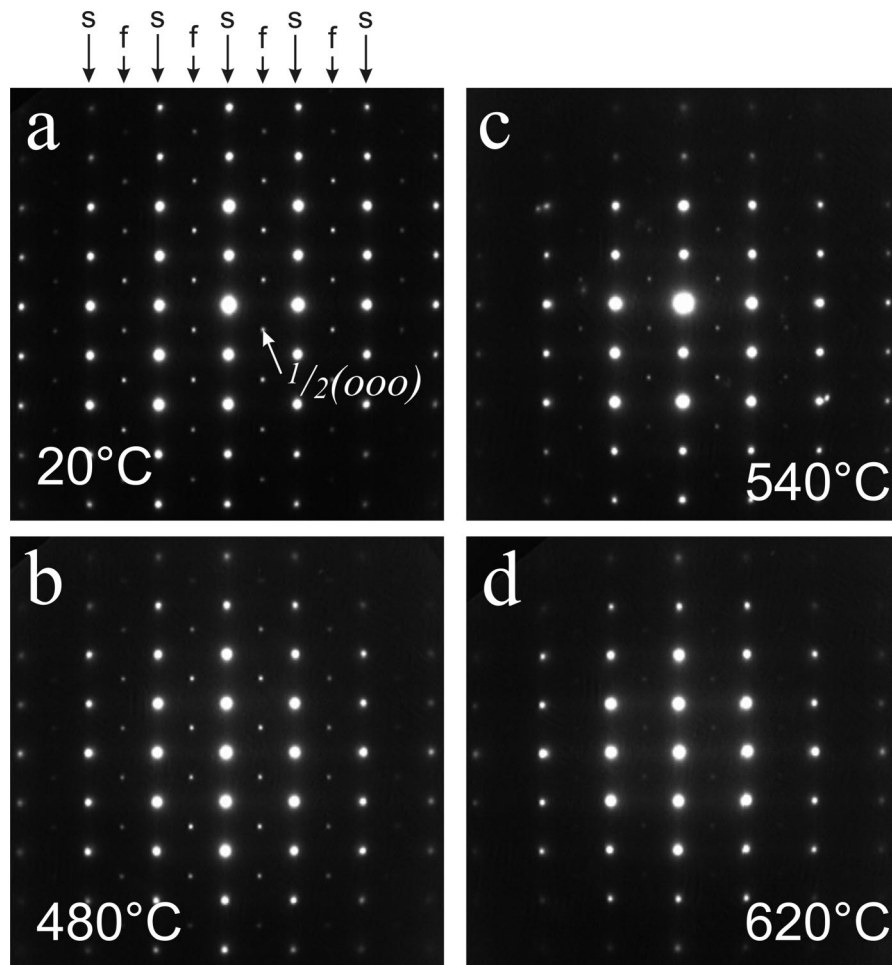
Figure 4. Evolution of the $[011]_P$ SAED pattern with the temperature increasing during the in situ experiment. The respective temperatures are (a) 20 °C, (b) 480 °C, (c) 540 °C, and (d) 620 °C.

diffraction experiments. Two possibilities can then be suggested to account for their presence.

(1) The tilt system of the tetragonal phase is not $a^0a^0c^+$. In this case, a supplementary antiphase rotation is expected to generate these $^1/_2(ooo)$ reflections.

(2) The doubling of the c parameter of the tetragonal cell involved by the existence of an order may also explain the occurrence of these $^1/_2(ooo)$ reflections.

The first hypothesis must however be precluded as the combination of a supplementary antiphase tilting together with the in-phase rotation and will invariably induce the existence of $^1/_2(oee)$ reflections within the SAED patterns. This is in contradiction with our observations (Figure 1) which demonstrate that if such reflections appeared near 200 °C, they disappeared below 370 °C. They are in any case absent at 400 °C. It is then concluded that these $^1/_2(ooo)$ reflections are unambiguously linked to the existence of an order within NBT. From a structural point of view, two kinds of structural order may be invoked: an order in the cationic displacements (A cations or B cations or both) or, more simply, an order of occupancy in the A site of the perovskite. The first possibility, also named antiferroelectric order, may not be retained as NBT is paraelectric above 400 °C.[17,18,27] We then concluded that above 400 °C the $^1/_2(ooo)$ super-structure reflections are characteristic of a Na−Bi ordering.

The order is here due to an electrostatic equilibrium as these two cations display contrasted valences (+1 for Na against +3 for Bi).

The $^1/_2(ooo)$ reflections, which lead to the doubling of the c parameter, are generated by a Na−Bi order along the $[111]_P$ direction. The $(111)_P$ planes are then successively occupied by Na^+ and Bi^{3+} which alternate along the three main axes of the pseudocubic cell. Such an ordering has still been proposed by Petzelt et al.[12] and may lead to the $P4_2nm$ space group (with a doubled parameter along c, compared to $P4bm$ [6]). Figure 5 shows that this $P4_2nm$ space group accounts for the diffraction patterns obtained at 400 °C in the stability domain of the tetragonal phase. However, as presented in the introduction, the $P4_2nm$ space group as well as $P4bm$ belong to the polar $4mm$ point group, which is not compatible with the paraelectric behavior of NBT above 400 °C.[17,18,27] Consequently, the tetragonal phase must necessarily present a nonpolar space group.

The reasons given to account for the polar space group are in fact not so clear. It is possible that the choice of a polar space group during the structure refinement may rely on an artifact. The choice may have been forced and influenced by the purity of the sample. Indeed, during the synthesis experiments performed during the present study
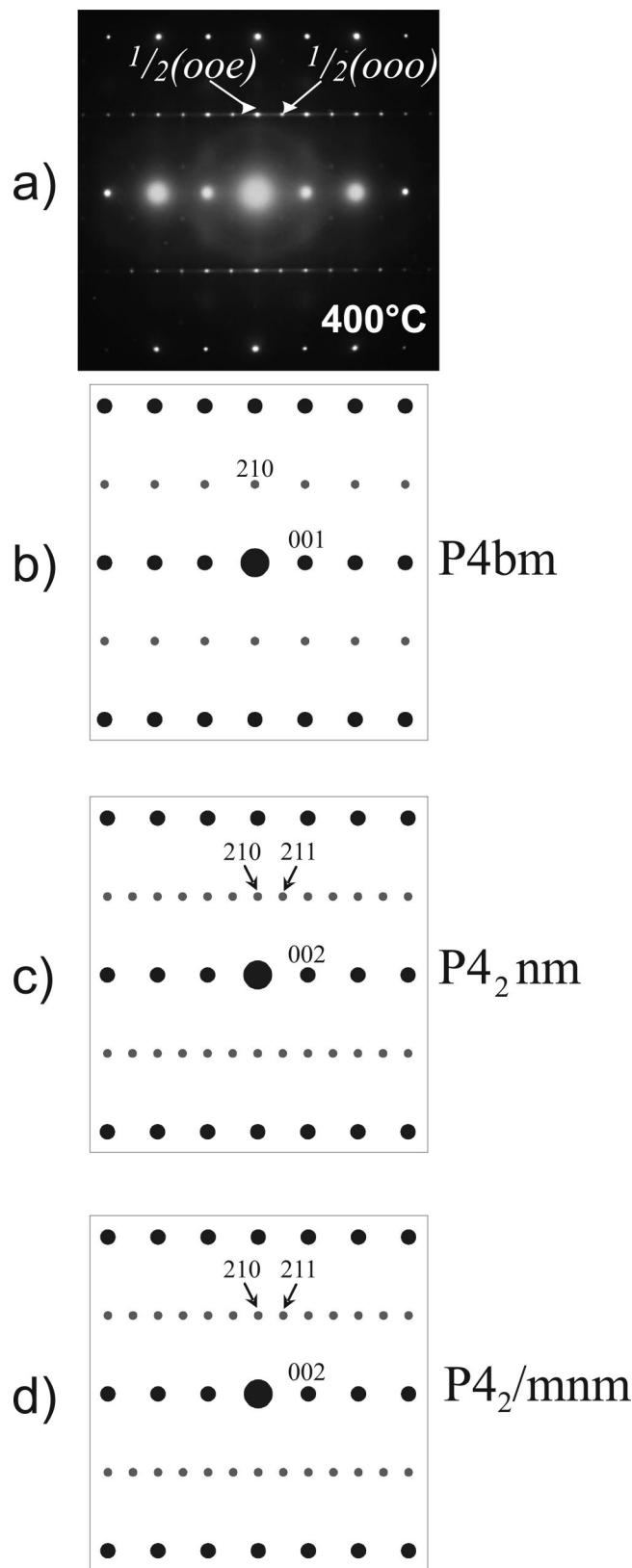
Table 1. Atomic Coordinates within the $P4_2/mnm$ Tetragonal Phase of NBT[a]

	NBT with $P4_2/mnm$ space group		
cell parameters	$a = a_p\sqrt{2}$	$b = a_p\sqrt{2}$	$c = 2a_p$
Wyckoff position	x	y	z
Na 2b	0	0	0.5
Bi 2a	0	0	0
Ti 4d	0	0.5	0.25
O(1) 4c	0	0.5	0
O(2) 8j	$0.25 - d$	$0.25 - d$	0.25

[a] The "d" value reported for the atomic position of oxygen depends on the value of the octahedra tilting angle.

on samples issued from the prime tries of synthesis of NBT were characterized by the two anomalies commonly observed (at 230 and 320 °C) and a third supplementary one at higher temperature (near 400–450 °C), related to a peculiar superparaelectric behavior of the compound.[30] The improvement of the synthesis conditions allows obtaining better samples for which the paraelectric behavior is in fact obtained since 320 °C and for which the third anomaly is then absent. This third anomaly has been observed by Zvirgzds et al.[2] on samples used to establish the *P4mm* polar space group of NBT. The presence of impurity and/or defects within samples is then probably the reason why Zvirgzds et al.[2] and later on Jones et al.[6] could not manage refining the structure of NBT with a non polar space group.

Consequently, in order to propose a new possible space group for the tetragonal phase, one must consider the structural origin of the polar character invoked in this compound. For both *P4bm* and *P4₂nm* space groups, the polar character is due to the displacements of cations along the 4-fold axis. Then, starting from the ordered *P4₂nm* space group proposed by Petzelt et al.[12] and after having canceled these cationic displacements, the centrosymmetric $P4_2/mnm$ space group was obtained. The characteristics of the corresponding unit cell are reported in Table 1. The structure is presented in Figure 6. The latter allows observing the Na–Bi order on the A site. As seen in Figure 5d, the proposed space group is well suited to index the experimental SAED pattern (Figure 5a). The $\frac{1}{2}(ooo)$ reflections arising from the order are quite spotty, attesting of the establishment of a long-range ordering of the A cations. Nevertheless, compared to the intensity of the sublattice reflections, their intensity remains quite weak. On the other hand, if we also consider that such structural Na–Bi ordering was never observed by X-ray or neutron diffraction, we finally concluded that the ordering arises only locally, within nanometer sized domains. Therefore, we suggest that, in NBT, nanometer sized ordered domains are present within a disordered matrix. The space group of such a disordered paraelectric phase will then be *P4/mbm*. The A-type cation order seems to vanish progressively as the temperature increases, but in agreement with Petzelt et al.,[12] signs of order are still present within the stability domain of the cubic phase, as shown by the occurrence of very weak $\frac{1}{2}(ooo)$ reflections in the SAED pattern observed at 620 °C (Figure 2d).

In fact, there is no reason that the order disappears as the temperature decreases and such order may be present within

Figure 5. [013]$_P$ SAED pattern and its geometrical simulations corresponding to different possible space groups. (a) Experimental pattern obtained at 480 °C. (b) Simulation performed with the *P4bm* space group. (c) Simulation performed with the *P4₂nm* space group. (d) Simulation performed with the $P4_2/mnm$ space group.

to elaborate our samples, we noticed that the evolution of the permittivity versus temperature is typically controlled by the synthesis conditions. The permittivity curves obtained

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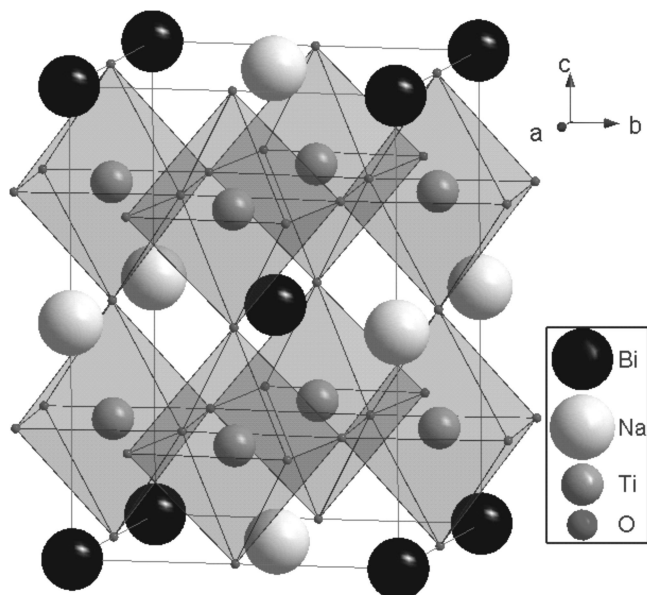
Figure 6. Representation of the ordered form of the $P4_2/mnm$ phase of NBT (with $d = 0.02$: see Table 1).

Figure 7. Structural representations showing the progressive decrease of the rotation amplitude along O$_x$ and O$_z$ of the antiphase octahedra tilting system. (a) Original *Pnma* structure in which the amplitude of the antiphase octahedra tilting around O$_x$ and O$_z$ is close to that observed for the in-phase rotation around O$_y$. (b) Intermediate step of the orthorhombic form in which the amplitude of the octahedra rotation around O$_x$ and O$_z$ is less than the in-phase rotation around O$_y$. (c) Final tetragonal structure in which the amplitude of the antiphase octahedra tilting around O$_x$ and O$_z$ is zero while the in-phase octahedra tilting along O$_y$ is maintained.

the low temperature rhombohedral phase. If there is no doubt that above 400 °C, that is, when the Curie–Weiss law is perfectly fulfilled,[27] the ordered domains are not polar, below 400 °C they may be polar. Indeed, as suggested by Burton et al.[31] in other relaxors like Pb(Sc$_{1/2}$Ta$_{1/2}$)O$_3$ (PST) the polar regions and the chemically ordered ones may be related. However, this assumption is not mandatory to explain the relaxor property of NBT. Indeed, as suggested in the first part of this paper, it is possible that NBT does not behave as a classical relaxor such as Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN) or PST [see ref 19].

The last point will deals with the origin of the diffusion observed within NBT. In the previous paper devoted to the study of NBT at room temperature,[25] the presence of the diffuse lines observed parallel to the [100]$_P^*$ direction in the SAED patterns (see also Figure 2a) was related to an aperiodic distribution of the tetragonal platelets within the $R3c$ matrix. In the present study, we also show that such diffuse lines are always present from the room temperature up to 620 °C (Figure 3), that is, well above the temperature at which the tetragonal phase is stable. Therefore, the tetragonal platelets are not the unique cause of the diffusion arising within NBT. At high temperature the diffuse lines pass through the $^1/_2(ooo)$ superstructure reflections that account for the ordering process and are then consequently linked to the establishment of such local order.

2. Second Order Orthorhombic to Tetragonal Phase Transition. The $^1/_2(oee)$ superstructure spots due to the orthorhombic phase have definitely disappeared at 370 °C (Figure 1). At that temperature the O → T phase transition is then achieved. Above that temperature, within SAED patterns all the observed reflections are those of the tetragonal phase. Owing to the group to subgroup relationship existing between the $P4/mbm$ tetragonal phase and the *Pnma* orthorhombic one, the phase transition is possibly of second order.
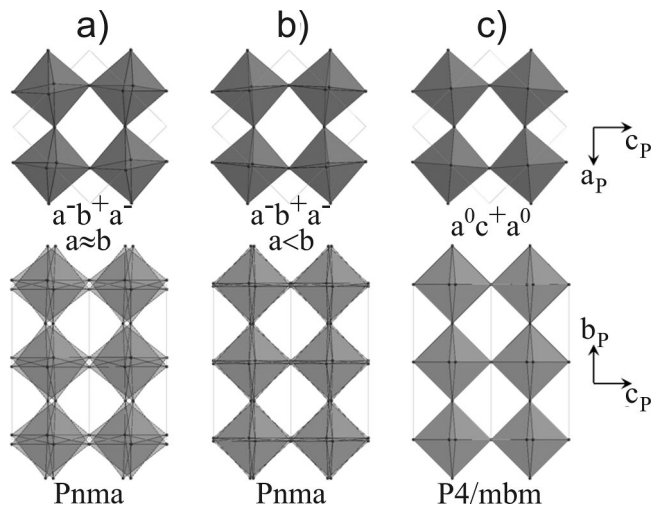
(31) Burton, B. P.; Cockayne, E.; Waghmare, U. V. *Phys. Rev. B* **2005**, 72, 064113.

The fact that this transformation is not associated to any thermal anomaly supports this hypothesis.[28]

In the following we then develop a crystallographic model explaining this progressive and continuous transformation. The orthorhombic and tetragonal phases only differ by their octahedra tilting conditions, a$^-$b$^+$a$^-$ and a^{0}a^{0}c$^+$, respectively. These two tilt systems have in common their in-phase rotation that respectively takes place along O$_y$ and O$_z$ in the orthorhombic and tetragonal phases. If the common in-phase rotation is chosen along the same O$_y$ crystallographic direction, then the tilt system of the tetragonal phase becomes a^{0}c$^+$a^0 (O$_y$ and O$_z$ directions are permutated within the tetragonal phase). In this new reference frame, the O → T transformation can then be depicted by a progressive evolution from a$^-$b$^+$a$^-$ to a^{0}c$^+$a^0 by a progressive decrease of the antiphase tilt angle along O$_x$ and O$_z$ until cancelation. Such an evolution is shown in Figure 7. Starting from the a$^-$b$^+$a$^-$ tilt system (with a ≈ b, Figure 7a) characteristic of the orthorhombic phase stable at 280 °C,[19] the phase transition toward the tetragonal phase begins by a progressive evolution of the orthorhombic structure. The amplitude of rotation of the octahedra, initially important along O$_x$ and O$_z$ (Figure 7a), reduces progressively along these two directions. For a given intermediate state (Figure 7b), the amplitude of rotation becomes lower along O$_x$ and O$_z$ than along O$_y$, along which the in-phase tilting is roughly maintained. Thus, the tilt system is still a$^-$b$^+$a$^-$ but with a < b. As the temperature increases, the amplitude of the antiphase rotation becomes zero along O$_x$ and O$_z$ (Figure 7c). The tetragonal phase is achieved in the 320–370 °C temperature range (Figure 1) when the $^1/_2(oee)$ spots disappeared (Figure 1).

3. Relationship between the Structural Evolution and the Macroscopic Electrical Properties. The temperature of the O → T phase transition (∼320 °C) perfectly corresponds to that of the main dielectric anomaly evidenced on the

permittivity curves.[1,16,17,26] This maximum of permittivity attests to a change in the electrical properties of NBT, which is associated to this structural phase transition. In fact, this anomaly corresponds to the antiferroelectric–paraelectric phase transition.[16,19] On one side, the orthorhombic phase being antiferroelectric, it presents a centrosymmetric nonpolar space group (*Pnma*) with antipolar cationic displacements of the A cations and no B cation displacements.[32,33] On the other side, the tetragonal phase (*P4/mbm*) being paraelectric, all the cations are localized in the center of their cubocta-hedral or octahedral cavities. This phase transition is then possibly associated with the canceling of the A cations displacements prevailing in the orthorhombic phase. Such cationic displacements are then concomitant to the change in the octahedral tilting system described above. The A cations may progressively move toward the center of their cavities as the antiphase tilting angle of the octahedra decreases, in order to cancel the dipolar moments responsible of the antiferroelectric character of the orthorhombic phase. Consequently, the antiferroelectric–paraelectric transition seems to be controlled by A cation displacements.

4. Toward the Tetragonal to Cubic Phase Transition. With regard to Figures 2 and 3, it should be noticed that both $^1/_2(ooe)$ and $^1/_2(ooo)$ reflections are still visible at 620 °C, which theoretically means that both $a^0a^0c^+$ octahedra tilting and cationic ordering are maintained at that temperature. This observation is however in contradiction with the previous results obtained by DSC measurements which have clearly shown that a T → C first order phase transition occurs near 520 °C.[28] If the occurrence of the $^1/_2(ooo)$ reflections may indicate that the local cationic order, evidenced in the tetragonal phase, is preserved in the cubic phase, the presence of the $^1/_2(ooe)$ reflections above 520 °C is questionable, as the whole octahedra tilting ought to be canceled in the cubic phase. We suggest that a small amount of $a^0a^0c^+$ tetragonal domains remain trapped in the cubic phase and only disappear slowly as the temperature raises, explaining the progressive decrease of the $^1/_2(ooe)$ reflections intensities.

Conclusion

All results derived from the part I[19] and part II (this article) of this paper are summarized in Figure 8. The study of the O → T phase transition by electron diffraction allows proposing the following results.

(32) Kay, H. F.; Bailey, P. C. *Acta Crystallogr.* **1957**, *10*, 219–226.
(33) Ali, R.; M. Yashima, J. *J. Solid State Chem.* **2005**, *178*, 2867–2872.
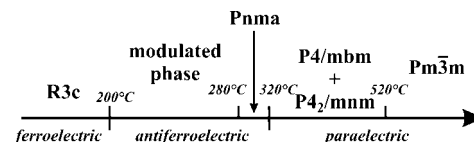

Figure 8. Schematic representation summarizing structural results obtained from the first and second parts of this work (part I, ref 19, and part II, this paper). It shows the stable phases in the different domains of temperature together with their macroscopic electric properties.

(1) The phase transition from the orthorhombic phase (*Pnma*) to the tetragonal one (*P4/mbm*) occurs near 320 °C. It corresponds to the antiferroelectric to paraelectric phase transition so often invoked in the literature.

(2) Based on the results from the literature and on the group to subgroup relation occurring between *Pnma* and *P4/mbm*, it is suggested that this transformation is a second order phase transition.

(3) A structural model explaining how such a phase transition arises is proposed. On one hand the antiphase tilting of the octahedra along O_x and O_z in *Pnma* ($a^-b^+a^-$) progressively decreases until being zero, while on the other hand, the in-phase tilting of the octahedra along O_y is roughly maintained ($a^-b^+a^- \leftrightarrow a^0b^+a^0$). It then corresponds to the usual $a^0a^0c^+$ tilt system characteristic of the tetragonal phase.

(4) The paraelectric tetragonal phase presents a globally disordered structure (*P4/mbm* space group) but locally ordered on the A site. The ordered domains are at least organized at the nanometre scale as diffraction spots are observed. At high temperature (above 400 °C), the $P4_2/mnm$ space group is suggested for these nanodomains, in agreement with the centrosymmetric and nonpolar properties required from the literature.

(5) The long-range ordering decreases progressively as the temperature increases but is always persistent at high temperature within the cubic phase.

(6) The tetragonal phase may be present as relics within the cubic phase.