# Incommensurate phases in barium sodium niobate

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The x-ray-diffraction spectra of $Ba_2NaNb_5O_{15}$ have been investigated by means of a precession camera between room temperature and 500 °C, across the orthorhombic-tetragonal transition near $T_I = 300$ °C. Long exposures have revealed reflections, onsetting with the orthorhombic phase, which are incommensurate with respect to the periodicity of the basic crystal lattice. Referred to the pseudotetragonal lattice vectors, the modulation vector is $\vec{k} = (1+\delta)(\vec{a}^* + \vec{b}^*)/4 + c^*/2$ where $\delta$ increases, on heating, from a value of 0.01 at room temperature, up to 0.115 at $T_I$. Its variations exhibit an upward jump at $T_{II} = 275$ °C from 0.035 to 0.085. These results show for the first time, the existence of two incommensurate phases in barium sodium niobate. These incommensurate phases have the same modulation direction. They both have an average orthorhombic symmetry and are therefore ferroelastic on symmetry grounds. Above $T_I$, precursor effects are disclosed in the form of strong diffuse scattering rods which condense at $T_I$ into the satellite reflections. Birefringence and DTA (differential thermal analysis) measurements are consistent with the x-ray results.

## I. INTRODUCTION

In the large family of ferroelectrics having the tetragonal tungsten bronze structure,[1,2] barium sodium niobate, $Ba_2NaNb_5O_{15}$ (BSN), is the most studied compound both because of its high electro-optic,[3] piezoelectric,[4] and nonlinear-optical[5] efficiencies, and of its interesting features from the view point of phase transitions. An intricate pattern of transitions has been observed in it. In addition to a standard ferroelectric transition ($4/mmm \rightarrow 4mm$) at about 580 °C,[3] it undergoes two ferroelastic transformations at lower temperatures. The first one[6] nearby 300 °C corresponds to the symmetry change $4mm \rightarrow mm2$ on cooling. It is associated with the onset of a spontaneous shear strain $e_6$ in the $xy$ plane. The second one[7] at about (−160 °C) is unusual because it restores the initial $4mm$ point symmetry at low temperature. Finally, anomalies in the variations of the birefringence at (−100 °C),[7] of the dielectric constant at (−260 °C),[8] and the occurrence of a soft-optic mode[9] whose frequency decreases steadily down to −271 °C disclose the possibility of additional transitions whose existence however has not yet been confirmed.

Up to now, the 300 °C transition has been the subject of the most accurate investigations by a number of experimental techniques: DTA (differential thermal analysis),[10] optical birefringence,[11] Brillouin[12] and Raman[13] scattering, gamma-ray diffractometry, x-ray and standard dilatometry,[14] and x-ray rotating-crystal experiment.[15] The results of these various experiments were interpreted by assuming that BSN is a ferroelastic of the improper type,[16,17] i.e., that the spontaneous strain onsetting at the transition is the result of a nonlinear coupling to the order parameter. From examination of the available structural data[18] Tolédano[6] inferred that the mechanism of this transition should involve a doubling of the unit cell along the $c$ direction. X-ray rotating-crystal experiments along the $c$ axis actually brought a partial confirmation by showing that $c^*/2$ superlattice layer lines ($c^*$ being the reciprocal-lattice period along $c$), vanished above $T_I \approx 300$ °C.[15] However, the location of Bragg reflections in the superlattice planes were not investigated and it was taken for granted that they occurred, at the $Z$ point $(0, 0, c^*/2)$ of the Brillouin zone. On the other hand, it had been noted[11] that the orthorhombic phase did not appear at a sharp transition but rather at a diffused one[19] spread over 30 °C between 275 °C and 305 °C. The origin of this effect had been attributed to local compositional or structural variations in the crystal[11] on the basis of the well-known[20] ability of the tungsten bronze structure to allow a disorder among the cations.

Recent neutron scattering and x-ray measurements[21] have cast a doubt on some aspects of the former interpretations and, in particular, on the fact that the considered transition relates two crystalline phases. In the transition region, scattering has been detected, whose location in the superlattice planes was incommensurate. However, the occurrence of an

 

incommensurate phase could not be unequivocally asserted due to insufficient evidence for the static nature of these reflections.

In this paper, we present a detailed x-ray scattering study which has been undertaken to substantiate this inference. We show that below 300 °C the ferroelastic orthorhombic phase of BSN comprises two incommensurate phases one of which occupies the range of temperatures previously identified as the "diffused" transition region. The temperature dependences of the modulation wave vector and of the intensity of the satellites reflections have also been determined. These new results are discussed with respect to additional experimental data.

## II. EXPERIMENTAL

Monochromatic x-ray measurements have been performed using a Buerger precession camera. Such a setup provides an undistorted image of reciprocal planes. In order to avoid contamination of the photographs by harmonics of the radiation used, the voltage applied to the tube was occasionally below the excitation potential for $\frac{1}{2}\lambda$. Observation of reciprocal planes perpendicular to $c^*$ was achieved by using a thin plate (150 $\mu$m) of BSN perpendicular to the $c$ axis. The crystal had the same origin as the ones used in a number of previous experiments.[7–13]

Exposure times for the main Bragg reflections of the $(hk0)$ or $(hk1)$ type was 2 h. Times as long as 60 h were sometimes used for these planes in order to detect additional weak reflections. In the superlattice planes, usual exposure time was 40 h for a full rotation with a precession angle of 10°. In the final stage of the investigation, when a closer sampling of the temperature was operated, a reduced area of the reciprocal plane was explored by making oscillations of 100°. In that case the exposure time was reduced to 15 h.

The location of the reflections in the reciprocal space and their intensity have been evaluated through microdensitometer reading of the photographs.

Heating of the crystal was achieved using a stream of dried nitrogen blown through a Dewar pipe containing a heating coil. The crystal was mounted on an alumina pin in order to isolate it thermally from the goniometer head. To ensure the temperature stability, the gaseous stream was arranged to follow the motion of the crystal. Turbulences were prevented by surrounding the crystal with a cylinder of Lindemann glass enclosing the Dewar pipe. Probing the temperature was achieved with two copper-constantan thermocouples. The first one was at the end of the Dewar pipe, the second one was in the Lindemann glass cylinder at about 5 mm behind the x-ray beam. The long-term stability of the temperature was found to be ± 1 °C. However, in spite of the former precautions, a static gradient as large as 65 °C has been noted between the two thermocouples in the relevant temperature range, the temperature of the crystal being intermediate. Replacing the crystal by a thermocouple we were able to reduce this uncertainty and estimate the crystal's absolute temperature within (± 10 °C). Finally, we have relied on these temperature indications to provide us mainly with a relative temperature scale. More accurate absolute values of the characteristic temperatures have been reached through additional measurements of the same sample by birefringence techniques and differential thermal analysis using experimental setups previously described[10,11] and in which the absolute temperatures are reliably known.

## III. RESULTS AND DISCUSSION

In the high-temperature phase the photographs of the $(hk0)$ and $(hk1)$ reciprocal planes at about 500 °C show Bragg spots forming a simple tetragonal lattice ($P$) corresponding to $a = b \approx 12$ Å and $c \approx 4$ Å in agreement with previous reports.[6] In the planes considered, the main reflections appear consistent with the $P4bm$ space group usually assigned to the tetragonal polar phase of the tungsten bronze.[1] However some very weak reflections of the $(0(k = n)0)$ type have been detected which would rather denote a $P4mm$ symmetry. No superlattice reflections exist in this phase. On cooling the crystal in the 300 °C transition region, photographs reveal the progressive onset of new reflections in the $(hk\frac{1}{2})$ and $(hk\frac{3}{2})$ planes. These reflections (see Fig. 1) corre-

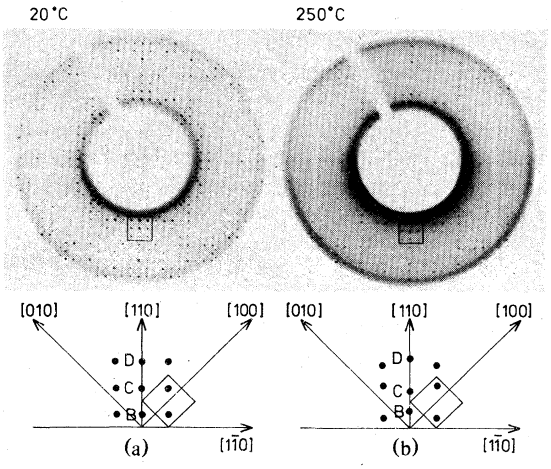


FIG. 1. Precession photographs and schematic representation of the $(hk\frac{1}{2})$ reciprocal plane showing the arrangement of the satellite reflections in this plane. The Brillouin zone of the high-temperature phase is represented by a square on the schematic representation; (a) 20 °C photograph, (b) 250 °C photograph.

spond to the superlattice layers which were previously detected in rotating-crystal experiments around the $c$ axis.[15,22] However the location of these reflections in the plane is not associated with a simple multiplication of the unit cell. The extra spots are actually situated at positions $\pm([h+(1+\delta)/4]\,[k+(1+\delta)/4]\,\frac{1}{2})$. Though $\delta$ is small, their incommensurate location with respect to the basic tetragonal lattice is doubtless. Qualitatively, the fact that $\delta \neq 0$ is obviously shown on the pictures obtained [Fig. 1(b)] by the fact that the succession of these reflections form zig-zag lines in the superlattice plane, while they would be lined up if $\delta = 0$. This is quantitatively confirmed by the microdensitometer measurements. In addition, $\delta$ has a pronounced temperature dependence which is described below. Consequently, in this temperature range, the diffraction pattern corresponds to a modulated crystal in which the reflections cannot be indexed in the usual way using three independent vectors ($\vec{a}^*$, $\vec{b}^*$, $\vec{c}^*$). A fourth vector[23] is needed, the modulation wave vector

$$\vec{k}^* = [(1+\delta)/4]\vec{a}^* + [(1+\delta)/4]\vec{b}^* + \vec{c}^*/2 \ ,$$

which is not expressed by simple fractions of the three others. Then each reflection in the reciprocal space can be generated by $\vec{u} = n_1\vec{a}^* + n_2\vec{b}^* + n_3\vec{c}^* + m\vec{k}^*$ ($n_1, n_2, n_3, m$ integers).

A remarkable feature of the incommensurate reflection ("satellites") is their situation on only one of the two bisector directions of the tetragonal cell, i.e., the [110] direction (Fig. 1). As a consequence, their onset necessarily breaks the tetragonal symmetry of the crystal because [110] and [1$\bar{1}$0] become unequivalent. This is consistent with the orthorhombic point symmetry $mm2$ which is established from macroscopic observations below 300 °C. Actually the x-ray pictures also show incommensurate reflections along the other bisector [1$\bar{1}$0] at

$$\pm([h+(1+\delta)/4]\,[k-(1+\delta)/4]\,\tfrac{1}{2}) \ .$$

A detailed examination reveals, however, that the intensity of these spots is not the same as that of the [110] ones (Fig. 1) and that it varies considerably with the number of domains in the investigated region of the sample. In particular, the extra spots are not observed when care is taken to explore a single domain region (these regions are easily selected by an optical observation in polarized light[11]). Hence, the incommensurate phase detected below 300 °C, does not retain an "average" crystalline symmetry identical to that of the high-temperature tetragonal phase. This symmetry is orthorhombic with two possible orientations constituting domains in the sample. The two domains possess the same period of modulation but modulation directions perpendicular to each other.

The temperature dependence of $\delta$ has been deduced from the relative location of three consecutive satellites $B$, $C$, and $D$ (Fig. 1). As shown in Fig. 2, four important features can be noticed.

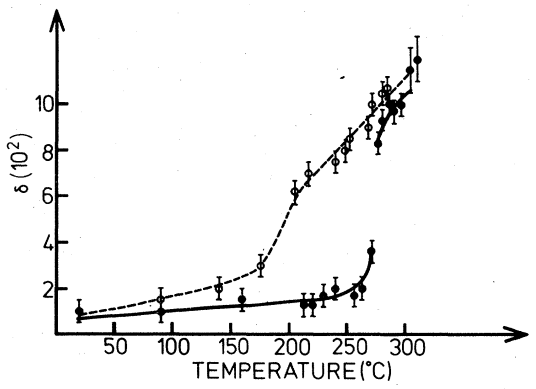


FIG. 2. Temperature dependence of $\delta$: full line (on heating); broken line (on cooling).

(i) $\delta$ has a large temperature variation. It increases from $0.01 \pm 0.005$ to $0.115 \pm 0.005$ at $T_I$.

(ii) The room-temperature phase appears to retain a weak incommensurability. The value of $\delta \approx 0.01$ is close to the limit of experimental accuracy, but the measurements of the distance $BC$ and $CD$ undertaken on a large series of three consecutive spots gives systematically $BC < CD$ and confirms the nonzero value of $\delta$ at room temperature [Fig. 1(a)].

(iii) An apparently discontinuous change in the values of $\delta$ from $0.035 \pm 0.005$ to $0.085 \pm 0.005$ is disclosed on heating at $T_{II} \approx 275$ °C.

(iv) The variations of $\delta$ on cooling disclose a very large thermal hysteresis and are somewhat blurred compared to those observed in the heating process.

On the other hand, Fig. 3 shows that the intensity of the satellites decreases when the temperature is raised. Above $T_I$ the sharp Bragg spots are replaced by diffused scattering. This scattering has the shape of rods linking consecutive satellites positions along

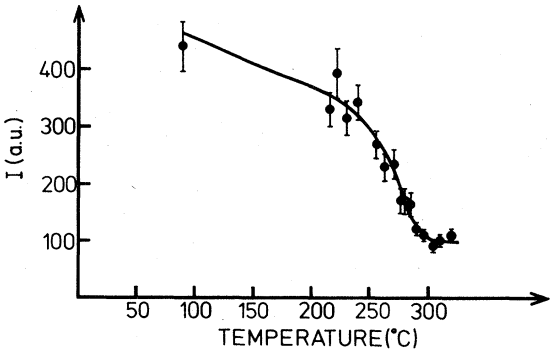


FIG. 3. Temperature dependence of the intensity of the satellite reflections.

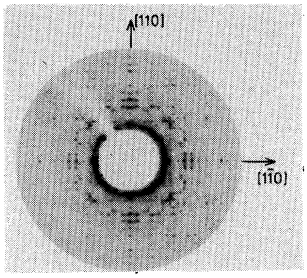


FIG. 4. Precession photograph of the $(hk\,\frac{1}{2})$ reciprocal plane taken about 10 °C above $T_I$ showing the diffuse rods linking consecutive satellites positions.

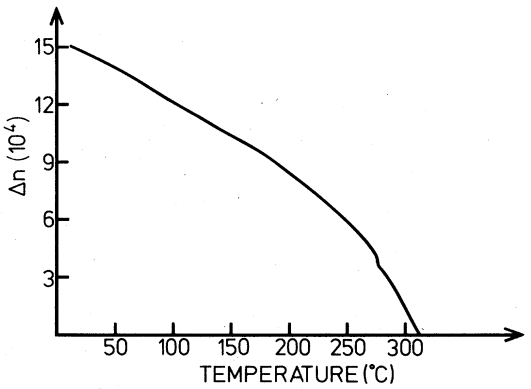


FIG. 5. Temperature dependence of the birefringence $\Delta n$ in the (001) plane.

[1$\bar{1}$0] (Fig. 4). Far above $T_I$, the intensity of these rods are uniform. On cooling towards $T_I$, the intensity condenses at the position of appearance of the satellite reflections. Outside the latter positions, the intensity of the diffuse scattering peaks approximately at $T_I$. It is hardly observable below 290 °C.

It is well known that an incommensurate modulation sometimes gives rise to satellite reflections corresponding to harmonics of the basic period. For the considered modulation the satellites of even rank should appear in the $(hkl)$-type plane while those of odd rank should be found in the $(hk\,(l+\frac{1}{2}))$-type plane. Actually, long exposure (60 h) of the $(hk0)$ plane at room temperature disclosed weak reflections centered at $((h+\frac{1}{2})(h+\frac{1}{2})0)$. Due to the weakness of $\delta$ at these temperatures these reflections could correspond to second harmonics of the modulation. Their intrinsic nature (i.e., not spurious effects due to the lack of monochromaticity of the beam) was carefully checked by cutting $\frac{1}{2}\lambda$ in the beam. However these reflections could not be observed in the temperature region where the larger value of $\delta$ would make their incommensurate location, and their splitting easier to detect, because their intensity decreased very rapidly on heating.

An additional characterization of the two phase transitions has been performed by birefringence and DTA measurements. As stressed above, the onset of the modulated structure below $T_I$ involves the breaking of the tetragonal symmetry into an average orthorhombic symmetry. It is expected to give rise to a birefringence $\Delta n$ in the (001) plane. Besides, this quantity should also provide us with an accurate location of $T_I$ and $T_{II}$. On the other hand, the detection of DTA signals would precise the orders of the two transitions. Such measurements are already available on BSN[10,11] but it is well known that variations of compositions occur in this material.[24] These variations could influence significantly the temperature of occurrence of the expected anomalies. Consequently the measurements were repeated on the same sample used in the x-ray experiment. The birefringence behavior is reproduced on Fig. 5. This quantity vanishes continuously at 305 ± 2 °C a temperature which should therefore be identified with $T_I$. Below this temperature, the variations display two types of behavior, separated by a sharp inflection at 275 ± 2 °C which should be identified with $T_{II}$. On the other hand, the heating DTA run discloses a small thermal peak at 275 ± 2 °C and none at 305 °C. On cooling the thermal peak is somewhat blurred and is detected at 255 ± 5 °C.

Up to now, the temperature region between $T_I$ and $T_{II}$ had been interpreted as corresponding to a broadening of the transition caused by local compositional and structural variations in the crystal.[11] The experimental results described above contradict this interpretation and show that $T_I$ and $T_{II}$ correspond to two distinct phase transitions.

The first transition at $T_I \approx 305$ °C corresponds to the onset of the incommensurate orthorhombic structure. It gives rise to satellite reflections and to a spontaneous birefringence in the (001) plane. As shown by previous experiments it is also characterized by the onset of a ferroelastic shear strain in the $xy$ plane. The continuous vanishing of the birefringence and of the strain at $T_I$ as well as the absence of a DTA signal suggest that this transition is second order. This would be consistent with the observation of marked precursor effects detected by the strong diffuse x-ray scattering. One drawback of this assignment is that it does not explain the thermal hysteresis, which is found to start at $T_I$ in all the measured properties of BSN.[10–12]

The second transition at $T_{II} \approx 275$ °C appears as a first order one through the jump recorded in the $\delta$ values and in the detection of a latent heat[10] in the DTA experiment. This discontinuity is less apparent in the birefringence data which rather display an inflexion. Usually such a discontinuity in the temperature-dependent behavior of the modulation vector occurs at a lock-in transition as in $K_2SeO_4$ (Ref.

25) or in a transformation to an incommensurate structure having a new direction of modulation as in the case in TTF-TCNQ.[26] In BSN it only corresponds to a change in the period of modulation. Such a situation does not seem to have been observed before. As the values of $\delta$(0.01 to 0.035) below this transition are small, we cannot exclude the possibility that we observe an "incomplete" lock-in transition due to an internal strain of the sample or effects of a disorder. Actually, the variations of $\delta$ near 275 °C resemble to the variations of the order parameter at a first-order transition under application of a conjugate force.

Another peculiarity of the incommensurate phase properties in BSN is their combination with ferroelastic properties. This combination appears at the origin of the incommensurate domains, and at the breaking of the average point symmetry discussed above. Up to now, insulating materials with an incommensurate phase were mostly related to the onset of ferroelectric properties below the lock-in transition. This is the case for instance of thiourea,[27] $K_2SeO_4$ (Ref. 25), or $NaNO_2$.[28] For these materials the average point symmetry of the incommensurate phase is the same as that of the high-symmetry phase. The coincidence of incommensurate and ferroelastic properties as pointed in BSN have not been claimed in other materials up to now. However, we can note that the occurrence of domains in a sample can be confused with the existence of a simultaneous modulation, with the same period, along several directions. In this respect, available results[29,30] show that such a problem is not unambiguously solved for the incommensurate phase of $BaMnF_4$. This material could possibly provide a breaking of the average point symmetry thus providing a situation similar to that of BSN.

The microscopic nature and the dynamics of the described transitions cannot be inferred on the basis of the former x-ray experiment. A detailed neutron scattering investigation[31] to be reported later on indicates however that the modulation discovered in BSN is probably partially of a displacive type since it is observed to be associated to a soft mode.

On the other hand, preliminary results of x-ray measurements still in progress performed on several members of the tungsten-bronze family (i.e., barium strontium niobate, potassium strontium niobate, strontium sodium niobate) show that incommensurate phases exist in all these materials and that the features described in BSN are actually realized in a similar way in many members of this important structural family.

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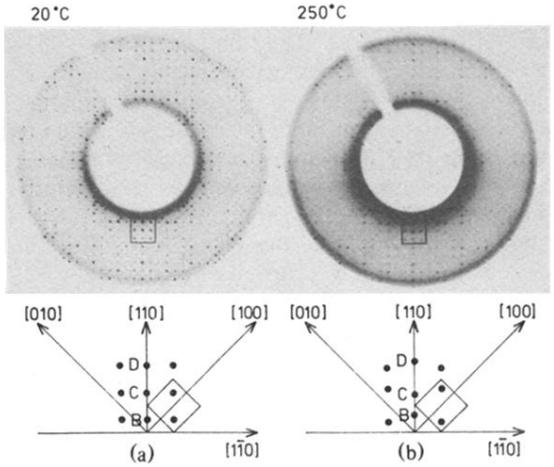


FIG. 1. Precession photographs and schematic representation of the $(hk\,\frac{1}{2})$ reciprocal plane showing the arrangement of the satellite reflections in this plane. The Brillouin zone of the high-temperature phase is represented by a square on the schematic representation; (a) 20 °C photograph, (b) 250 °C photograph.

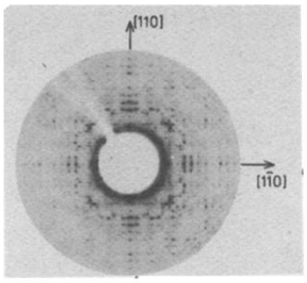


FIG. 4. Precession photograph of the $(hk\ \frac{1}{2})$ reciprocal plane taken about 10 °C above $T_I$ showing the diffuse rods linking consecutive satellites positions.