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ACCURATE DETERMINATION OF IC MODULATION PARAMETER IN $Sr_xBa_{1-x}Nb_2O_6$ FROM SECOND-ORDER SATELLITES OF NEUTRON DIFFRACTION TOF SPECTRA

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1 Introduction

1.1 Modulation Properties of Tungsten Bronze Niobates

The incommensurate (IC) modulation structure of alkali alkaline earth niobates of tungsten bronze type was thoroughly studied by different methods, especially on barium sodium niobate (BSN). The features of modulation have been elucidated by means of the high-resolution TEM technique [1] and diffraction methods using X-rays [3], electrons [2] or neutrons [4]. Due to chemical composition barium strontium niobate mixed crystals $Sr_xBa_{1-x}Nb_2O_6$ (SBN-100x) are inherently disordered, and besides the IC modulation [5] the features of diffuse phase transitions occur [6].

Contrary to BSN which undergoes a lock-in phase transition (PT) into a (quasi-)commensurate phase, in the temperature range between room temperature (RT) and about 800K the IC modulation in SBN was found nearly independent on temperature [6]. The 2q-modulation is expressed by the modulation vectors

$$\mathbf{q}_{\delta\pm} = \pm(1+\delta)/4\ \mathbf{a}^* \pm (1+\delta)/4\ \mathbf{b}^* + 1/2\ \mathbf{c}^* \qquad (1)$$

($\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$ – basic vectors of reciprocal lattice)

At RT, the modulation parameter δ is only very weakly influenced by an external electric bias field [6]. It increases only slightly for the higher disordered compositions with higher Sr-content [7]. In the neutron diffraction pattern of SBN [6] besides the strong first-oder satellites the second-order and partly third-order peaks could be identified. The higher-order satellites are not easy to be seen by the other diffraction methods. However, there is no doubt that the new IC spots around (h+1/2 h+1/2 l) in the [110] zone, found in the electron diffraction at HREM studies of La-modifies SBN ceramics by Choo et al. [8], are only satellites of second order.

1.2 The Aim of Modulation Structure Studies

Many publications are concerned with the origin of the IC modulation in tungsten bronze niobates. Especially, the modulation features of the coexistence region of 1q- and 2q-modulation in BSN below the PT were investigated, and a simple relation between discommensuration density and modulation parameter δ was found [9].

The influence of imperfections (increased by doping or irradiation), as found in BSN [10], seems to exist in SBN, too. The HREM images of Choo [8] show the presence of {110} planar defects ({110} platelets of an unit cell spacing). These extended defects seem to induce a stabilization of the IC phase and enhance the nature of diffuse PT. Further electron diffraction measurements on SBN-50 [11] have shown that the IC modulation is changed at a PT.

For these reasons we are interested to measure also small induced changes of the δ-Parameter.

2 Accurate δ-Parameter Determination from Second-order Satellites

2.1 Methodical Aspects

The accuracy of the δ-parameter determination from the time-of-flight (TOF) data was limited by the facts that main peak and first-order satellite positions must be calculated from different scattering directions, recorded in different angular sections of the position sensitive detector. A change of δ is reflected by changes in time channels as well as in angular positions.

These disadvantages could be eleminated if we use the second-order satellite positions along the [110] direction for the determination of the IC modulation parameter.

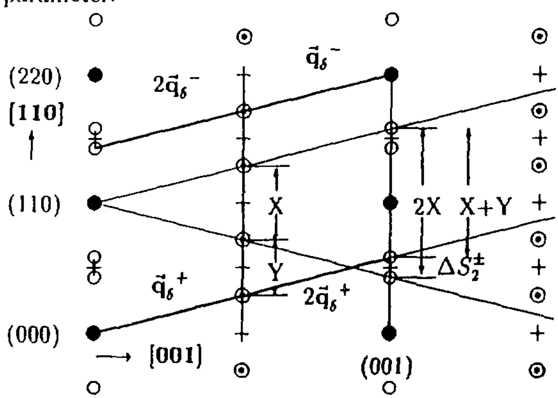

Figure 1: Localization of parent reflection (•), first-order (⊙), and second-order (o) satellites at the $(1\bar{1}0)$ reciprocal lattice plane

In Fig. 1 the positions of parent and satellite reflections (drawn up to the second-order) are given by

$$\vec{\tau}^{\delta\pm}_{hklm} = \vec{\tau}_{hkl} + m q_{\delta\pm} \quad (2)$$

(h,k,l,m - integers)
The $\vec{\tau}_{hkl}$ are the parent reflections (hkl) and $q_{\delta\pm}$ is the IC modulation vector, used as a fourth basis vector. From Fig. 1 it is easy to see that using the pair distance of second-order satellites the modulation parameter δ can be expressed by the following relations

$$\delta = \frac{X - Y}{X + Y} = \frac{\Delta(S_2^+, S_2^-)}{\Delta(\tau_h, \tau_{h+1})} = \frac{\Delta(S_2^+, S_2^-)}{\sqrt{2}a^*} \,, \quad (3)$$

with

$$\Delta(S_2^+, S_2^-) = |\vec{\tau}^{\delta}_{hh\ l-1\ 2} - \vec{\tau}^{\delta}_{h+1\ h+1\ l+1\ -2}| \quad (4)$$

$$\Delta(\tau_h, \tau_{h+1}) = |\vec{\tau}_{hhl} - \vec{\tau}_{h+1\ h+1\ l}| \,. \quad (5)$$

Using only a single second-order satellite position we get

$$\delta = 2\frac{|\Delta(S_2^\pm, \tau_{hkl}) - \frac{1}{2}(\Delta(\tau_h, \tau_{h+1})|}{\Delta(\tau_h, \tau_{h+1})} \quad (6)$$

with

$$\Delta(S_2^\pm, \tau_{hkl}) = |\vec{\tau}^{\delta}_{hh\ l-1\ 2} - \vec{\tau}_{h+1\ h+1\ l}| = |\vec{\tau}^{\delta}_{h+1\ h+1\ l+1\ -2} - \vec{\tau}_{hhl}| \,. \quad (7)$$

The here used advantage of this method comes from the fact that in SBN all these relevant peak positions may be determined from TOF scans along {110} zone directions alone.

In TOF technique at fixed scattering angle 2Θ , the lattice spacings d_{hklm} follow from the determination of the neutron wave length λ like this

$$\Delta(S_2^+, S_2^-) = |\frac{1}{d_{S_2^+}} - \frac{1}{d_{S_2^-}}| = |2\sin\Theta(\frac{1}{\lambda_{S_2^+}} - \frac{1}{\lambda_{S_2^-}})|, \quad (8)$$

$$\Delta(\tau_h, \tau_{h+1}) = |\frac{1}{d_{hhl}} - \frac{1}{d_{h+1\ h+1\ l}}| = |2\sin\Theta(\frac{1}{\lambda_{h+1\ h+1\ l}} - \frac{1}{\lambda_{hhl}})|. \quad (9)$$

The wave length λ is determined from the time-of-flight t and flight-path L by the relation

$$\lambda \propto \frac{t}{L} \,. \quad (10)$$

From a flight-time analyzer with a time channel width chw, started with a time shift t_{sh}, the time t is given by

$$t = chn\ chw - t_{sh} = chw(chn - del) \,. \quad (11)$$

For a fixed flight-path distance we have

$$\lambda \propto (chn - del) \tag{12}$$

and thus

$$\frac{1}{\lambda_1} - \frac{1}{\lambda_2} \propto \left(\frac{1}{chn_1 - del} - \frac{1}{chn_2 - del}\right) . \tag{13}$$

Introducing $chn^* = chn - del$ we get

$$\delta = \frac{\Delta(S_2^+, S_2^-)}{\Delta(\tau_h, \tau_{h+1})} = \left|\frac{\frac{1}{chn^*_{S_2^+}} - \frac{1}{chn^*_{S_2^-}}}{\frac{1}{chn^*_{hhl}} - \frac{1}{chn^*_{h+1\ h+1\ l}}}\right| = \left|\frac{chn^*_{S_2^+} - chn^*_{S_2^-}}{chn^*_{hhl} - chn^*_{h+1\ h+1\ l}}\right| F_K \tag{14}$$

with

$$F_K = \frac{chn^*_{hhl} chn^*_{h+1\ h+1\ l}}{chn^*_{S_2^+} chn^*_{S_2^-}} . \tag{15}$$

For the here used SBN data the factor $F_K \approx 1$, and we get

$$\delta \approx \frac{\Delta chn^*_{S_2^+, S_2^-}}{\Delta chn^*_{h,h+1}} . \tag{16}$$

From Equ. (6) follows analogously

$$\delta = \left|\frac{2chn^*_h \ \Delta chn^*_{h+1, S_2^+}}{chn^*_{S_2^+} \ \Delta chn^*_{h,h+1}} - 1\right| = \left|\frac{2chn^*_{h+1} \ \Delta chn^*_{h, S_2^-}}{chn^*_{S_2^-} \ \Delta chn^*_{h,h+1}} - 1\right| . \tag{17}$$

The Equ. (14) shows that (at fixed channel width) *the accuracy of the determination of the channel numbers* in the spectra determines the experimental error. In particular, this method is now sensitive enough for *measuring of very small changes* of the IC modulation parameter which occur in SBN under influence of external parameters (temperature, electric field) and at relaxation processes.

The main problem of this method is the low intensity of the second-order satellites. An enlarged measuring time is required to get reasonable peak fit data. However, because from the fitting only the peak position is needed a relatively low fit quality could be accepted, too.

If only one of the two S_2 satellites are detectable a determination of δ is possible by using Equ. (17).

Table 1: Field dependence of the modulation parameter δ of SBN-70 at room temperature

Reflections: $(hh0),(h+1\ h+1\ 0)$	F_K − Faktor
(1 1 0), (2 2 0)	1.0356 ± 0.5%

$E \parallel \vec{c}$ /$kVcm^{-1}$	$\Delta chn^*_{S_2^+,S_2^-}$ /channels	$\Delta chn^*_{S_2^+,S_2^-}$ /channels	$\Delta chn^*_{h,h+1}$ /channels	δ	δ
	Peak − Fit©	UPEAK		Peak − Fit©	UPEAK
−1.0	40.65±3%	40.57±4.2%	198.18±0.03%	0.2124±3.5%	0.2120±4.5%
±0.0	39.85±2%	40.48±3.8%	198.22±0.03%	0.2082±2.5%	0.2115±4.3%
+0.2	40.56±2%	40.81±3.1%	198.24±0.03%	0.2124±2.5%	0.2132±3.6%
+0.5	40.43±2%	40.35±4.2%	198.21±0.03%	0.2112±2.5%	0.2082±4.7%
+1.0	39.10±3%	38.99±4.8%	198.32±0.03%	0.2042±3.5%	0.2036±5.3%

Reflections: $(hh0),(h+1\ h+1\ 0)$	F_K − Faktor
(2 2 0), (3 3 0)	1.0152 ± 0.5%

$E \parallel \vec{c}$ /$kVcm^{-1}$	$\Delta chn^*_{S_2^+,S_2^-}$ /channels	$\Delta chn^*_{S_2^+,S_2^-}$ /channels	$\Delta chn^*_{h,h+1}$ /channels	δ	δ
	Peak − Fit©	UPEAK		Peak − Fit©	UPEAK
−1.0	18.79±4%	18.84±4.7%	98.87±0.04%	0.1929±4.5%	0.1934±5.2%
±0.0	19.10±4%	18.86±4.8%	98.97±0.04%	0.1959±4.5%	0.1935±5.3%
+0.2	20.15±5%	19.55±5.7%	98.94±0.04%	0.2068±5.5%	0.2006±6.2%
+0.5	18.94±5%	18.95±5.4%	98.93±0.04%	0.1944±5.5%	0.1945±5.9%
+1.0	18.52±4%	18.50±4.7%	98.89±0.04%	0.1901±4.5%	0.1900±4.2%

3 Results

3.1 Influence of an electric field on IC parameter δ

For comparison the fitting of the peaks was done using the program systems *PeakFit*©[1] and *UPEAK*[2]. The results for peak positions, which are only relevant here , are given in Table 1.

It is obtained that the error of δ-parameter is dominated by the error value of $\Delta chn^*_{S_2^+,S_2^-}$. The amount of the other errors does not exceed 1%. Two typical pictures of fitting the low-intensity second-order satellites are

[1]Jandel Scientific 1991

[2]written by Zlokazov, JINR Dubna

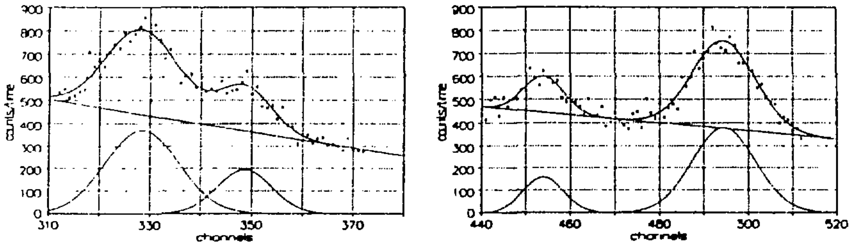

Figure 2: Examples for the fitting of separated and overlapping weak peaks of second-order satellites of SBN-70

shown in Fig. 2. The dependence δ on the external field $\vec{E} \parallel \mathbf{c}^*$ is shown in Fig. 3. As found earlier [6], for these field strengths the measured small changes do not exceed the experimental error limits. From Table 1 and Fig. 3 it is obvious that the values of the δ-parameter obtained from the $S_2^{\pm}$-pair between (220) and (330) are systemtatically lower than those from the pair between (110) and (220). The difference values are comparable with the full amount of the experimental error . However, more extended methodical studies would be necessary to find out the cause of these differences.

3.2 Temperature dependence of IC parameter δ

At cooling from RT down to 10 K, the temperature dependence of δ was determined by Equs. (14) and (17). The results for SBN-70 are given in Fig. 4 .The data are received from the second-order satellite pair between (110) and (220) reflections . The higher error level of about 7% comes from the lower satellite peak intensity due to the shorter chosen measuring time.

4 Discussion

The method described above possesses an improved accuracy which allows to study very small changes of the IC modulation parameter δ in SBN. On

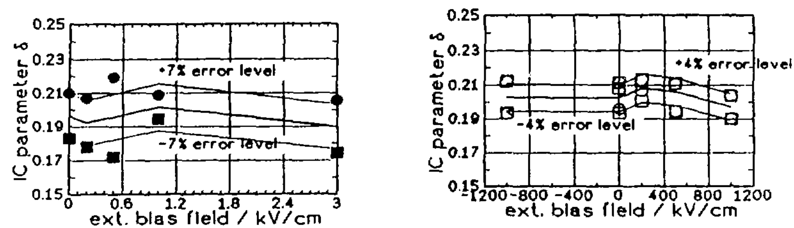

Figure 3: Dependence of IC modulation parameter δ on external field at RT for SBN-70 and SBN-75 (error levels related to mean values (boldface lines); (□) and (○) - *results from* UPEAK *and* ***PeakFit***© ; upper values (•) | lower values (■) from $S_2^{\pm}$ between (110) and (220)| (220) and (330))

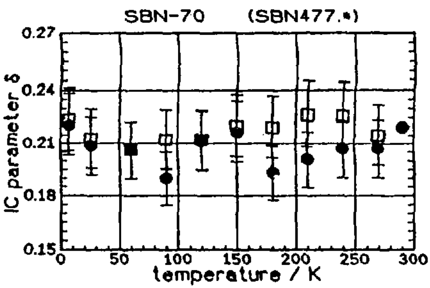

Figure 4: Temperature dependence of IC modulation parameter of SBN-70 at cooling ((□) - using $S_2^{\pm}$ pairs; (•) - single S_2 satellites)

SBN-70 and SBN-75 the influence of an electric field $\vec{E} \parallel \mathbf{c}^*$ on δ was studied and, in agreement with our older results [6], only small changes were found for both compositions. Small deviations occur in the 'critical' field region after switching, in which anomalies in Bragg and satellite intensities were also observed.

At cooling from room temperature down to 20 K, SBN undergoes several structural phase transitions [12]. In [6] was inferred that the modulation seems not to be directly coupled with the ferroelectric properties. Nevertheless, small changes of δ-parameter could give additional informations for the understanding and characterization of the the structural changes at the different PT's .

Within the error limit, our data of the temperature dependence of δ show small anomalies in two extended regions around the known PT's at about 200 K and 60 K, respectively. If we assume that the IC modulation express the discommensuration (or anti-phase domain boundary) density [11], it follows that at these transitions the order relation of the two intergrowing orthorhombic structures is changed. These conclusions are supported by the agreement of our data with the electron diffraction data [11]. On SBN-50 after the PT at 198 K, a significant change of the δ-parameter was found, too. The values increase sharply from 0.190 above to 0.200 below the PT. The more diffuse changes of the δ, observed in SBN-70, could be caused by the the higher structural disorder of this material, which also shows the features of a diffuse ferroelectric PT.

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