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NEUTRON DIFFRACTION STUDIES OF THE INCOMMENSURATE MODULATION STRUCTURE IN $Sr_xBa_{1-x}Nb_2O_6$ SINGLE CRYSTALS OF VARIOUS COMPOSITIONS

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INTRODUCTION

Recently the features of the incommensurate (IC) modulation on niobates having a tungsten bronze (TB) structure were studied with increasing interest[1÷3]. A new interpretation of the modulation properties was brought out by high-resolution transmission electron microscopy (TEM) techniques. Especially the orthorhombic barium sodium niobate (BSN) but also some other TB's like potassium strontium niobate (KSN) and the disordered mixed system strontium barium niobate (SBN-x, $Sr_xBa_{1-x}Nb_2O_6$), were studied by this technique combined with electron diffraction.

In diffraction experiments the IC modulation is expressed in the pattern of the satellite structure around the Bragg reflections τ_{hkl} in the reciprocal space. On SBN the IC modulation is described by the modulation parameter δ of the modulation vector of the satellite structure

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

($\vec{a}^*, \vec{b}^*, \vec{c}^*$- reciprocal lattice parameter)[2].

The neutron diffraction measurements on SBN-x reported here are aimed to studying the dependence of δ on composition and at examining the influence of weak doping (with 0.2 w% Mn, 1.0 w% Nd) on it. Published data for the δ-parameter of SBN-x are given in Table 1. The values are determined from the satellite positions of first-rank satellite spots.

Table 1

Compilation of published data for the δ-parameter of SBN

Sr-content %	IC parameter δ	temp. K	measuring technique references
72	0.26±0.05	293	X-ray precision camera/2/
50	0.190(5)	203-423	electron diffraction /9/
	0.200(5)	93-198	
70	0.22±0.01	293	neutron diffraction /3/

EXPERIMENTAL PROCEDURE

The experiments were done on the DN-2 time-of-flight diffractometer at the pulsed reactor IBR-2 in Dubna employing temperature range between 100 K and 700 K. Using a position sensitive detector, Bragg and satellite peaks located in a sectorial area of the chosen reciprocal lattice plane were measured simultaneously. Czochralski-grown SBN-x samples of various composition ($0.46 \le x \le 0.75$) and of different origins were studied.

RESULTS

The IC modulation was studied on satellite reflections of first and second rank localized in the diffraction pattern at

$$\vec{\tau}^{\,\delta\pm}_{hklm} = \vec{\tau}_{hkl} + m\vec{q}_{\delta\pm} \qquad (h,k,l,m - \text{integer};\ m = 1,\ 2).$$

From peak positions of strong first-rank satellites (m=1) at many scans and for various samples the well-known modulation features were determined. As shown in Fig.1 the IC parameter δ varies only weakly with increasing Sr-content and obviously the modulation is not sensitive on such a doping, which significantly changes the dielectric and phase

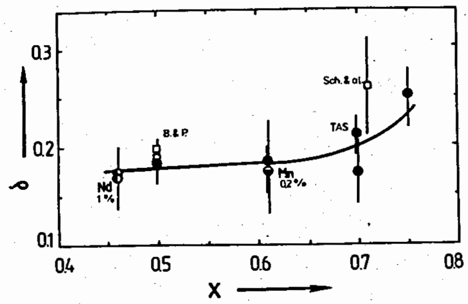

Fig.1 Dependence of the IC. modulation parameter δ on composition ((●), (○) - doped samples; □- from other methods /reference indicated/; TAS (●)- by triple-axis technique/3/.

transition (PT) properties/5/. The decrease in intensity of the modulation peaks with increasing temperature, and the observed thermal hysteresis in the intensity are shown in Fig.2 on the second-rank satellite $\tau^{\delta\pm}_{92\bar{1}2}$. Any change of δ, exceeding the error limit, was not found. The small step in δ at the low-lying PT, observed by electron diffraction on SBN-50 at about 198 K, is hardly detectable with the diffraction technique used here. Nevertheless, in the

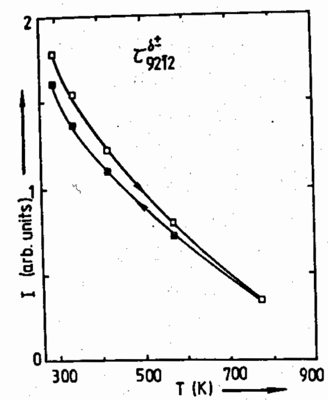

Fig.2 Temperature dependence of intensity of the second-rank satellite $\tau^{\delta\pm}_{92\bar{1}2}$ measured on SBN-70 at (001) plane.

investigated samples with x=0.70, 0.61 and 0,50 the PT is indicated in this temperature region by anomalies in the intensity of basic reflections as well as of modulation peaks.

DISCUSSION

Contrary to the behaviour expected for "true" IC modulated (ferroelectric) crystals, in SBN the modulation parameter was found to be very stable against a change of the temperature, which is the crucial external parameter. No lock-in transition into a commensurate state occurs on cooling, in contrast to BSN which shows a complicated change in the character of modulation at the transition from IC into a quasi-commensurate phase[6].

Previous measurements on SBN [3] have shown that δ does not depend on an external polarizing field. Only a small variation of δ with the Sr-content was found in this study, together with no significant influence of weak doping. From this it follows that the modulation is not strongly influenced by the change in distribution of the Sr and Ba ions over the different tunnels in the frame work of the oxygen octahedra. This is also supported by the fact that the δ-parameter of KSN ($K_2Sr_4Nb_{10}O_{30}$) $\delta=0.16\pm0.05$[2] lies near the value measured for SBN with the low x compositions. Only the weak increase of δ at the higher Sr-content seems to be connected with the increasing disorder.

These facts, and the results of the high-resolution TEM confirm that the niobates having the TB structure match the antiphase domain model[7] which is based on the (random) mixing of two different (commensurate) superstructures. These superstructures differ only in their antiphase domain structure, namely, in the periodicity of antiphase boundaries (in the aspect of modulation called discommensuration (DC) walls). The direct imaging of the antiphase boundaries and the their configurations within the slab structure of the octahedron chains, which was observed in BSN and KSN[4], confirms this interpretation. Further, the model is supported by the direct relationship between the δ- parameter of the IC modulation and the DC density [4] and the measured increase of both in irradiated BSN samples[6].

For tetragonal TB structure this model is not adequate because in SBN at a transition from the cubic high-temperature phase antiphase domains can not be generated. However, neutron diffraction studies of various SBN compositions show splitting of "tetragonal" reflections[8] indicating a symmetry lower than tetragonal. For SBN-50, an orthorhombic structure was postulated and confirmed by TEM images which show a ferroelectric as well as a ferroelastic domain structure[9]. Adapting such an antiphase domain model for SBN, the measured slow increase of modulation peak intensity at decreasing temperature could be understood by an expected gradual appearance of the modulated orthorhombic phase at a diffuse ferroelastic PT.

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