

Investigation of thermal evolution of nanodomain structures in nonlinear barium sodium niobate crystals

S. V. Ivanova

P.N. Lebedev Physical Institute of RAS, Leninsky pr.53, Moscow 119991, Russia

Received September 30, 2007

By the 90° elastic light scattering investigation and far field observation in the range of 20 – 800 °C, the relation between behavior of light scattering anomalies and evolution of nanodomain structures in lattice of barium sodium niobate (Ba₂NaNb₅O₁₅, BSN) crystal was clarified. The correlation between anomalies on the temperature curves of the elastic light scattering intensity and temperature transformations of nanodomains was studied by X-ray and electron microscope methods. Phase transition near 500 °C and movement in field of scattering light could be explained by appearance of a new incommensurate phase.

OCIS codes: 190. 4400, 290. 5870.

The study of the fine-size effects in nonlinear systems has become very important because of their potential applications, especially as memory elements. Barium sodium niobate (Ba₂NaNb₅O₁₅, BSN) is a nonlinear material with a tetragonal tungsten bronze type of structure. The structure of this crystal was analyzed by Jamieson *et al.* using X-ray diffraction techniques^[1]. In addition, crystal which has excellent nonlinear optical properties and possesses an intricate sequence of phase transitions^[2,3], has attracted much attention. The characteristics of these phase transformations and their influence on a various physical properties have been investigated in detail, but a number of structural features are still the subjects of discussion. The phase transition at about 560 – 585 °C is the ferroelectric transition which is a function of the composition of the crystal. Another transition on cooling of crystal is about 300 °C (T_1). This is transition with symmetry change from tetragonal to orthorhombic structure $mm2$. By studying X-ray diffraction and neutron scattering, Schneck *et al.*^[2] have found two incommensurate (IC) phases in BSN below 300 °C: nearly commensurate stable up to 250 °C (T_2) and IC elongated up to 300 °C (T_1). The transition of about 300 °C at cooling one results in the appearance of the ferroelastic domains with orthorhombic symmetry. IC modulation lies along a_0 with the wave-vector

$$k = (a^* + b^*)(1 + \delta)/4 + c^*/2, \quad (1)$$

a^* , b^* , c^* are the parameters of the reciprocal lattice, δ is the misfit parameter which is the characteristic of the incommensurability. From room temperature to 250 °C, δ varies linearly and increases sharply at 250 °C. Phase transition at T_2 is discontinuous and at T_1 is continuous.

The existence of the discommensurations (DCs) in the IC phase of BSN crystal has been reported at ambient temperature^[3–6]. The geometry of the diffraction pattern has been constructed as plausible model of superstructure in the range of 300 – 330 °C^[3]. The hypothetical structure, in which all the sheared NbO₆-chains are parallel to c axis, would be commensurately modulated in “antiphase”. The locked-in commensurate superstructure consists of domain strips separated by antiphase

boundaries (or DC walls). In BSN the incommensurability is given by the ratio $\delta = R_0/D$, where R_0 is the projection of the displacement vector of the DC walls along the a_0 direction and D is their average separation. With increase of the specimen temperature, δ and the DCs density increase rapidly. Some of the DCs remain “frozen-in” on cooling back to room temperature causing the residual incommensurability. The DCs and the mobile point defects due to non-stoichiometry may be the cause of the observed large hysteresis of the transition reflected in the temperature dependence of a number of physical properties. In BSN, mobile defects are the Na ions.

In Refs. [3,4], dynamical effects associated with the nucleation and growth of DCs in BSN were examined in-situ by means of transmission electron microscopy. The DCs remain unchanged during up to 200 °C. Above 200 °C the density of DC increases rapidly as δ increasing. Pan *et al.*^[5] presented the evolution of the DCs pattern from room temperature to the normal phase.

Kiat *et al.*^[7] specified the phase diagram of BSN from 20 to 350 °C.

The main characteristics of the diagram are the coexistence of two IC phases in the vicinity of the normal-IC structure transition (300 °C): $2q$ tetragonal phase and $1q$ orthorhombic phase, and a progressive $2q/1q$ transformation in the temperature range where a large thermal hysteresis of the misfit parameter is observed. The IC parameter δ changes at the temperatures of $T_H = 190$ °C, $T_L = 260$ °C, and $T_1 = 300$ °C.

Using transmission electron microscope method on single crystals Mori *et al.*^[8] presented schematic description of the ferroelastic domain structure at temperatures of 260, 270 °C, and room temperature. Ferroelastic domain structure is constituted of complicated array of two types of $1q$ ferroelastic microdomains with a size of about 20 nm at 270 and 260 °C. When the temperature is lowered to around 230 °C, domain structure abruptly changes into a large scaled domain structure with the orthorhombic symmetry. The size of the domains is estimated to be about 1 μ m on average. In each ferroelastic domain, modulation occurs only along the a_0 direction, as in the case of microdomains. These experimental results in-

dicates that the domain structure drastically changes at around 230 °C, although the continuous change in the domain structure takes place between 300 and 230 °C.

Using high resolution X-ray diffraction and transmission electron microscope methods in single crystals Kiat *et al.*^[7] and Mori *et al.*^[8] showed that the structure had a tetragonal symmetry in the range from 300 to 270 °C and consists of the complicated array of two types of ferroelastic microdomains with the size of about 20 nm with orthorhombic symmetry. Using transmission electron microscopy method, Pan *et al.*^[4] proposed that the IC modulation of BSN extended far into the tetragonal phase and disappeared only at about 600 °C near the ferroelectric to paraelectric phase transition point.

We have studied optical and ferroelectric properties of the BSN crystals by means of light scattering method in the range of 20–800 °C and have reported two 2nd-order phase transitions at about 200 and 500 °C and self focusing of laser beam near ferroelectric phase transition^[9,10].

In this paper thermal and temporal changes of the light scattering have been observed in the range of 20–800 °C under steady illumination of BSN crystals by incident laser beam (628.8 nm). The crystals were grown in M. V. Lomonosov State University by Czochralskiy pulling procedure. The focused beam ($F = 150$ mm) propagated through the oriented sample and registered on the screen in far field about 250 cm from the sample. The sample ($3 \times 4 \times 5$ (mm)) oriented along the crystallographic axes was mounted inside an oven. The 90° elastic scattering of light was registered by means of DFS-12 spectrometer. The directions of the laser beam were perpendicular or parallel to the optical c axis of crystal.

In this paper the temperature dependent on the elastic light scattering intensity and the patterns of light scattering on the screen in far field are studied. The experimental setup is shown in Fig. 1. At the excitation of the BSN crystal by He-Ne laser ($\lambda = 628.8$ nm) at 530 °C the laser beam splits into two beams, as shown in Fig. 1.

The angle distance between two laser scattering spots in far field increases to T_c and above the temperature ferroelectric phase transition ($T_c = 560$ °C) shrinks rapidly. In this temperature range the movement was observed in light field in the direction about 45° to the c axis where the split of spot on the screen was observed. On cooling of crystal the direction of movement in illumination field is opposite to the direction on heating one. Arrows in Fig. 2 represent the direction of movement on heating of crystal. Above ferroelectric phase transition one spot of scattering light and the movement absence were observed.

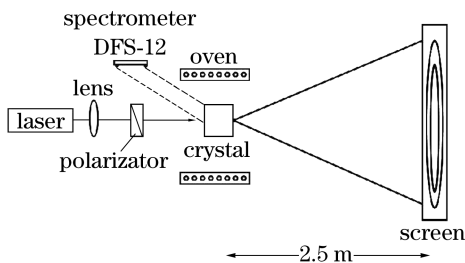


Fig. 1. Experimental setup.

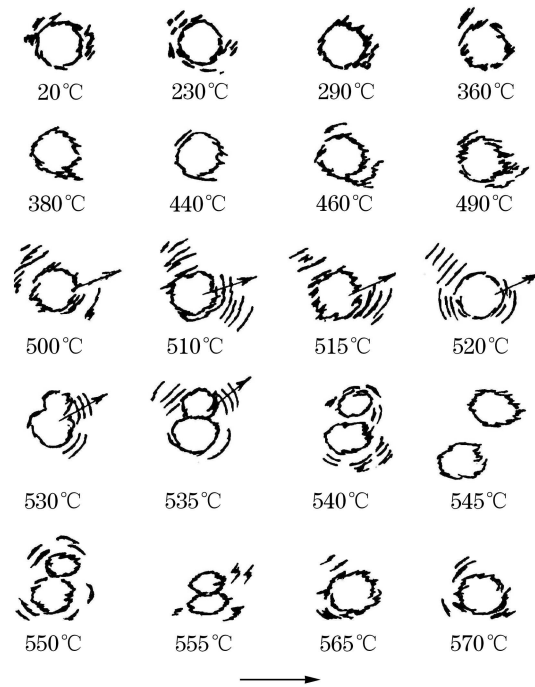


Fig. 2. Far field transmitted beam patterns from nanodomain BSN crystal, the beam splits in the range of 500 °C, $\lambda = 628.8$ nm; beam direction is perpendicular to the c axis. Arrows represent the direction of movement in the illuminated field.

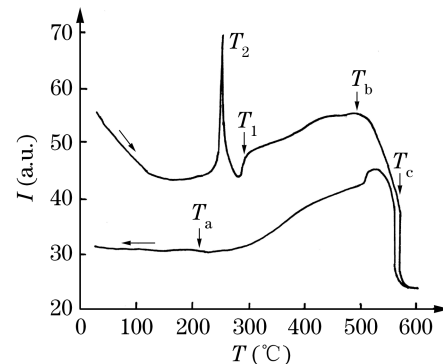


Fig. 3. Dependence of elastic light scattering intensity by BSN crystal on temperature. Laser beam is perpendicular to the c axis; polarization is parallel to this one. Arrows along the curves represent the direction of the change of temperature.

This reversible nonlinear response of BSN crystal near the phase transition of 500 °C may be declared by structural IC transformation near the ferroelectric phase transition. It is consistent with the result in Ref. [4]. The movement in far field can be explained by Na mobile ions which remove toward the microdomain boundaries. The temperature dependence of elastic light scattering intensity are shown in Figs. 3,4, where the sharp peaks appear at temperature of about 240 °C (T_2), anomalies at about 200 °C (T_a), 300 °C (T_1), and near 500 °C (T_b).

The large thermal hysteresis was observed in behavior of light scattering intensity which is correlated with misfit parameter δ ^[7]. In Fig. 3, anomalies near T_a , T_2 , and T_1 , are corresponded with transformations of nanostructure at T_H , T_L , and T_1 ^[7] and near ferroelectric phase transition^[4,5]. The anomaly near 200 °C (T_a) is

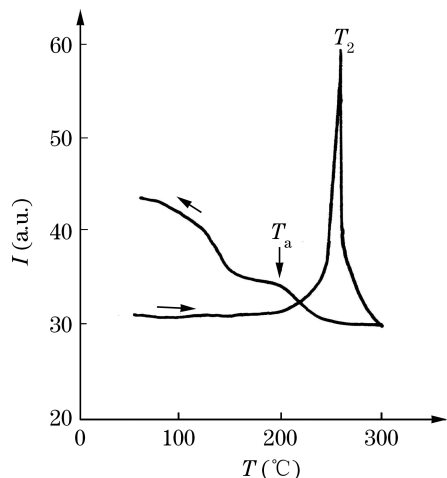


Fig. 4. Dependence of elastic light scattering intensity by BSN crystal on temperature. Laser beam is perpendicular to the c -axis; polarization is parallel to this one. Arrows represent the direction of the change of temperature.

correlated with the appearance of discommensurations on cooling process^[3–6] as shown in Fig. 4.

Nano-particles undergoing transformation between structural phases with different optical properties are the key components to clear the origin of nonlinear properties

of crystal.

Author thanks to A. D. Kudryavceva for the support. S. V. Ivanova's e-mail address is ivanova@sci.lebedev.ru.

References

1. P. B. Jamieson, S. C. Abrahams, and J. L. Bernstein, *J. Chem. Phys.* **48**, 5048 (1968).
2. J. Schneck, J. C. Toledano, C. Joffrin, J. Aubree, B. Joukoff, and A. Gabelotaud, *Phys. Rev. B* **23**, 1766 (1982).
3. Van Tendeloo, S. Amelinckx, C. Manolikas, and S. Wen, *Phys. Stat. Sol. A* **91**, 483 (1982).
4. X. Pan, M. Hu, M. Yao, and D. Feng, *Phys. Stat. Sol. A* **91**, 57 (1985).
5. X. Pan and D. Feng, *Phys. Stat. Sol. A* **106**, K117 (1988).
6. S. Barre, H. Mutka, and C. Roucau, *Phys. Rev. B* **38**, 9113 (1988).
7. J. M. Kiat, G. Calvarin, and J. Schneck, *Phys. Rev. B* **49**, 776 (1994).
8. S. Mori, N. Yamamoto, Y. Koyama, and Y. Uesu, *Phys. Rev. B* **52**, 6158 (1995).
9. S. V. Ivanova and T. T. Sultanov, *Optics* **64**, 100 (1997).
10. S. V. Ivanova, *Int. J. Nanoscience* **3815**, (2004).