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OPTICAL PROPERTIES OF $Na_{0.5}Bi_{0.5}TiO_3$ CRYSTALS

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We report some peculiarities of behavior of domain structure and birefringence Δn of $Na_{0.5}Bi_{0.5}TiO_3$ crystals. Polarization-optical methods are used to study the domain structure and the birefringence Δn in temperature interval 25°C÷520°C and axial pressure interval 2.5÷60 bar. Single domain state is achieved by application of axial pressure along [100] and [110] directions at temperature near 500°C. Application of axial pressure ~50 bar along [100] direction leads to switching of the samples into anisotropic single domain state. While application of axial pressure ~0.5 bar along [110] direction results in exposition of visually isotropic state and the state is preserved during a cooling process in temperature interval ~500°C÷240°C. In both cases the anisotropic single domain state is observed at room temperature. It is shown that f axial pressure (2.5÷25 bar) application along [110] direction at room temperature leads to a significant increase of the birefringence. It is supposed that both the peculiarities of Δn behavior and the linear behavior of Δn = f(p) are associated with presence of the nanoregions with various orientations of optical indicatrices and their involvement into the orientation process under the action of axial pressure.

Keywords: $Na_{0.5}Bi_{0.5}TiO_3$, domain structure, birefringence, nanoregions.

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1. Introduction

$Na_{0.5}Bi_{0.5}TiO_3$ (NBT) is known as a material that belongs to the family of relaxor ferroelectrics. The extraordinary properties of the relaxors make them suitable for high tech electronic devices such as sensors, actuators, electro- or piezo-optical and photorefractive elements. The lead-free NBT has been considered as a good candidate for piezoelectric applications to replace widely used lead-based piezoelectric materials [1]. That is why most researches are aimed to study electrical and electromechanical properties of NBT and NBT-based ceramics. At the same time NBT crystals exhibit unusual optical properties which are associated with structure peculiarities. Really, the disordering of Na^+ and Bi^{3+} cations in the crystal lattice and formation of the polar nanoregions (PNR) with local Curie temperature lead to strong diffusion of the phase transitions and the peculiarities of NBT macroscopic properties. The studies and understanding of original optical properties of NBT crystals can be useful to obtain important information that promotes opening of new ways in practical application of this material.

In this paper we report some aspects of the effect of applied axial pressure on domain structure and birefringence in NBT crystals.

2. Experimental

The $Na_{0.5}Bi_{0.5}TiO_3$ crystals are grown by Czochralski method. Two types of samples in the form of 7×3×0.5 mm parallelepipeds are prepared for the investigations. The first (NBT1) – with (001) (100) and (010) main planes. The second (NBT2) – with (001) (110) and ($1\bar{1}0$) main planes.

The domain structure and the birefringence Δn behaviour are studied by polarization-optical method in temperature interval of 25°C÷520°C and in the axial pressure interval of 2.5÷60 bar. The optical transmission is measured at wavelength λ=632.8 nm. Polarized light is passed along the [001] direction. The sample is set between crossed Nicols and is adjusted to get maximum propagation of the light through the system. The axial pressure is applied to samples along [100] and [110] pseudo-cubic directions.

3. Results and discussion

Despite the significant number of studies, the discussions about the average and the local structure, the number and the nature of the phases in NBT continue. It is known that NBT undergoes the phase transformation from cubic paraphase to tetragonal ferroelastic phase at ~540°C÷520°C. The rhombohedral phase appears below 200°C where existence of the spontaneous polarization is detected [2]. In addition, work [3] reported coexisting of the cubic/tetragonal phases and the tetragonal/rhombohedral phases in temperature ranges 540°C÷500°C and 400°C÷255°C respectively. At the same time, temperature behavior of visually observed domain structure shows presence of two above mentioned phase transformations in NBT crystals. The (110)-type walls separating two domain states of tetragonal phase appear below ~520°C. The orientation of the domain walls is not changed in the temperature range of 520°C÷25°C during the cooling process. This is due to the possibility of existence of the same type walls in both the tetragonal and the rhombohedral phases. The peculiarity of the temperature behavior of the NBT optical properties is the presence of the "isotropization" point (at ~240°C÷250°C during cooling and ~280°C÷290°C during heating process) where the sample looks like optically isotropic in polarized light.

Application of axial pressure to the NBT samples near 500°C results in obtaining a stable single domain state. Application of axial pressure ~50 bar along [100] direction for the NBT1 samples leads to switching into anisotropic single domain state (Fig.1 a). At the

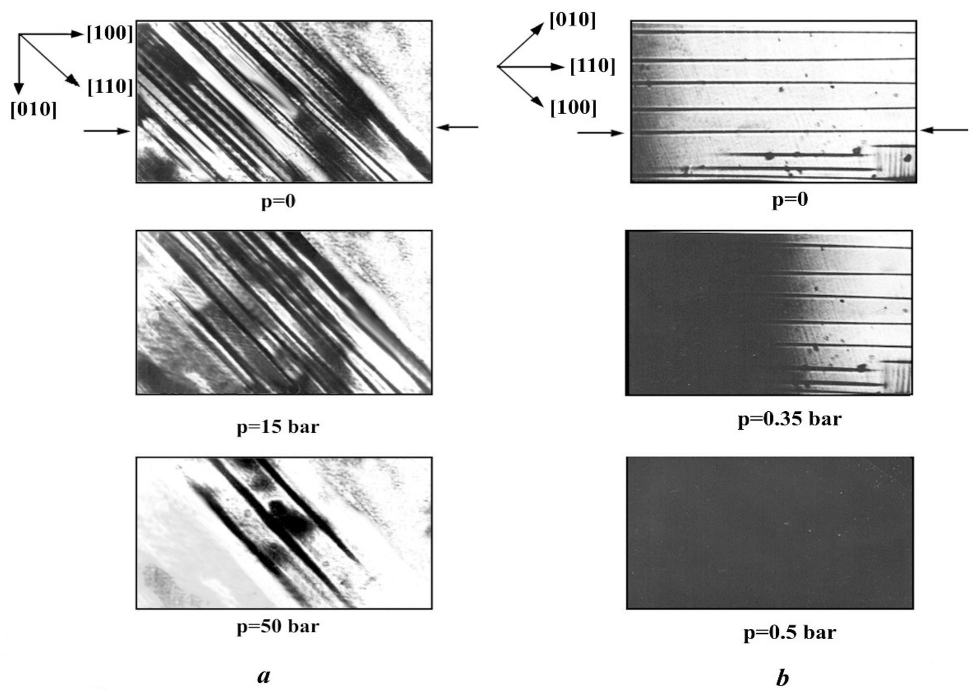

Fig. 1. Formation of single-domain state of NBT crystals: (a) application of axial pressure along [100] direction and (b) along [110] direction near 500°C.

same time the visually isotropic state in the NBT2 samples appears after axial pressure ~0.5 bar application along [110] direction (Fig.1 b). The macroscopic single domain state is preserved during cooling process (to room temperature) of both the «stressed» and the «free» samples that corresponds to results in [4]. However, at room temperature the NBT1 samples show appearance of regions with strong mechanical stresses. While the NBT2 samples become anisotropic below ~240°C at cooling process and do not show visible mechanical stresses. Heating of the NBT2 samples leads to exhibition of isotropic state above the "isotropization" point (~290°C). Then, the single domain samples NBT1 and NBT2 are used to study spontaneous birefringence Δn and how application of axial pressure affects Δn. The temperature behavior of spontaneous birefringence Δn=f(T) in the NBT1 sample is associated with the presence of the "isotropization" point at ~290°C during heating, where the sign of the birefringence changes, with temperature hysteresis in range ~220°C÷300°C and the tetragonal/cubic phase transition at ~520°C. Such Δn=f(T) behavior is in correspondence with the results of temperature behavior of spontaneous birefringence Δn presented in [5]. Axial pressure (6÷20 bar) application along [100] direction at room temperature leads to insignificant change of absolute values of the birefringence in temperature range 25°C÷520°C.

Fig.2 (a) shows Δn=f(T) behavior for the NBT2 sample. The birefringence absence above ~290°C is the result of macroscopically isotropic state of the NBT2 sample. The

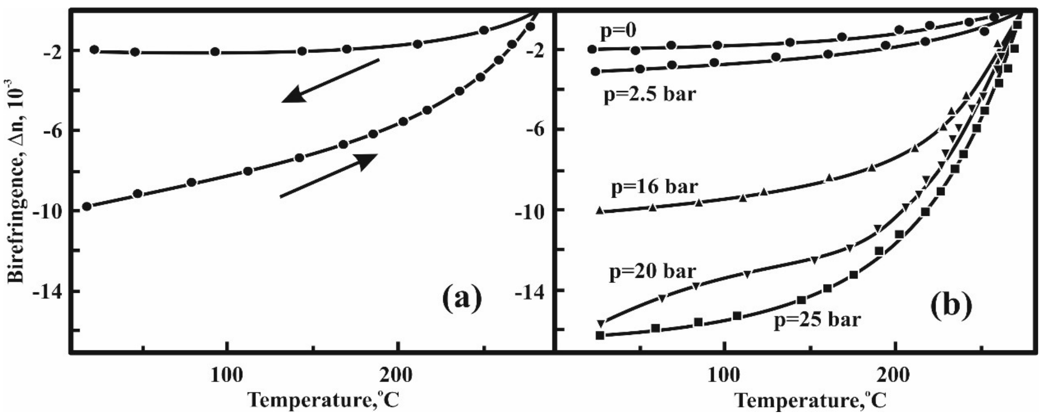

Fig.2. The temperature dependence (a) spontaneous birefringence Δn, (b) birefringence at different values of the axial pressure applied along [110] direction of NBT2 samples at heating process.

possibility of existence of the nanoregions with various orientations of optical indicatrices can be one of the reasons for the visual macroscopic isotropy. Really the investigations in [6] show presence of the polar nanoregions (PNR) in the rhombohedral ferroelectric phase. It is reported that the nanoregions are not well organized, however, there is some tendency for organization along the [110] direction. Thus, it can be assumed that the process of switching the NBT2 samples into macroscopic single domain state stimulates the preferred orientation of the PNR along [110]. It leads to significant increase of spontaneous birefringence (Fig.2 a) at room temperature. During a cooling process, the organization of the polar nanoregions is destroyed and Δn decreases. Further application of axial pressure (2.5÷25 bar) along [110] direction at room temperature leads to significant increases of the birefringence with an increase of axial pressure (Fig.2 b). The decrease of Δn with increase of temperature can be explained as follows. In accordance with [3], a coexistence of the tetragonal and the rhombohedral phases is observed in temperature range 255°C÷400°C. Probably, tetragonal phase nanoregions with various orientations of optical indicatrices appear above ~200°C and the axial pressure has no such significant orienting effect on them. With temperature increase, the number of tetragonal phase nanoregions increases and the number of the PNRs of the rhombohedral phase decreases, and thus Δn decreases.

It should be noted that the birefringence in the NBT crystals linearly depends on applied axial pressure (Fig.3). The slope of the Δn=f(p) straight lines is determined by the temperature. That is typical for such relaxor ferroelectrics as $Pb_3MgNb_2O_9$ and $Pb_3ZnNb_2O_9$ and is explained by the orientation of the polar nanoregions that contribute to Δn under the action of axial pressure.

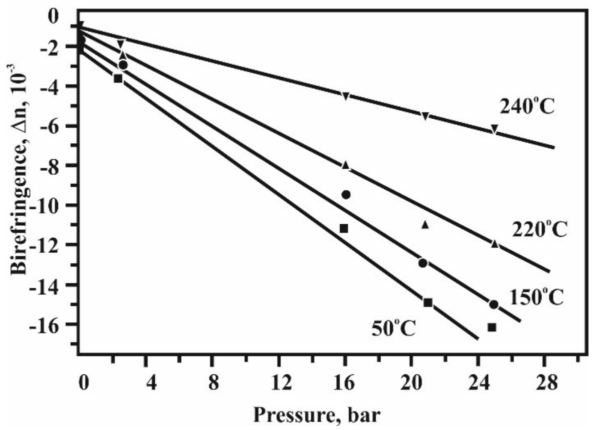

Fig. 3. The effect of the axial pressure applied along [110] direction on birefringence of NBT2 samples.

4. Conclusions

In the work single domain NBT crystals are obtained with application of axial pressure near the point of the tetragonal/cubic phase transition. It is shown that not less than 50÷60 bar of axial pressure should be applied to the samples along [100] pseudocubic direction to switch them into the single domain state. Axial pressure application along [110] direction switches the samples into the single domain state at significantly lower values of the stress. It is determined that axial pressure application along [110] direction is most favorable for inducing birefringence in the samples. It is assumed that the orientation processes make a significant contribution to the temperature behavior of birefringence under the action of axial pressure.

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