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Citation style: Kolesnikov Aleksandr, Grechishkin Rostislav, Malyshkina Olga, Malyshkin Yury, Dec Jan, Łukasiewicz Tadeusz, Ivanova Aleksandra. (2013). Conoscopic study of strontium-barium niobate single crystals. "IOP Conference Series: Materials Science and Engineering" (Vol. 49, iss. 1 (2013), art. no. 012010), doi 10.1088/1757-899X/49/1/012010

Conoscopic study of strontium-barium niobate single crystals

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Optically transparent single crystals of strontium-barium niobate, $Sr_xBa_{1-x}Nb_2O_6$, of different compositions (x = 0.26…0.7) were examined with the aid of conoscopic light interference figures. A regular change of the isochrome concentric ring number and diameters consistent with the temperature variation of the value of birefringence is demonstrated by direct observations of polar cuts of optically uniaxial samples. Anomalous violations of the conventional (uniaxial) interference patterns occur occasionaly in some samples being indicative of the existence of biaxial trait in their behaviour even though no voltage is applied. These features may depend on annealing treatments at elevated temperatures. The results of the study show that conoscopic images may serve as a sensitive indicator of the structural state of SBN crystals related to the effects of stress–induced change of optical anisotropy and temperature dependent birefringence parameters.

1. Introduction

Strontium barium niobate $Sr_xBa_{1-x}Nb_2O_6$ (SBN:x) lead-free environmentally friendly system represents a specific group of materials in which ferroelectric–relaxor behaviour depends on the x ratio Sr/(Ba+Sr) [1–7]. This system is characterized by a number of useful properties including piezoelectric, electro-optic and pyroelectric ones. Of special interest are large electro-optic coefficients (420×10^{-12} m/V) and high photorefractive sensitivity, which can be effectively used in optoelectronic devices [1]. One more advantage of SBN is the relatively low temperature where the structural phase transitions take place [7]

In spite of technological importance the understanding of SBN crystal properties is far from completeness, because, in addition to chemical composition, they strongly depend on the processing parameters, such as crystal growth method, heat treatment regimes and atmosphere, structure of dislocations and other defects, optical nonuniformity, etc.

In the present work we applied the method of conoscopic light interference pattern to the study optical properties of SBN single crystals with different concentrations of strontium. Conoscopic observations are known to be a powerful tool for characterization of the optic dielectric tensor of anisotropic media [8] including materials with phase transitions and internal stresses (see, e.g. [9, 10]).

2. Experimental

Single crystals of SBN were pulled along [001] crystallographic direction from a melt by the Czochralski method. Details of the growing procedure are described elsewhere [11]. After X-ray orientation and cutting into polar slices 5×5×1 mm the sample surface was carefully polished by diamond pastes. The conoscopic figures were observed in an optical polarizing microscope with Bertrand lens and narrow-band interference filters making use of objectives and condensers with a numerical aperture of 0.65 or higher. Following the suggestions of Steward [12] and to minimize the risk of damaging the microscope optics during heating the sample a very thin hot stage supplied with thin film thermocouple was constructed and installed on the microscope stage.

3. Results and Discussion

Figure 1 presents an excerpt from the videofilm illustrating the changes of the conoscopic figures of SBN70 polar cut as observed within the temperature range of 295...381 K. It is seen that at room temperature (RT) the interference pattern is presented by isochromes in the form of regular concentric rings having superimposed isogyres in the shape of a maltese cross. This pattern is typical of optically uniaxial crystals in a satisfactory agreement with the existing theoretical predictions [13, 14].

During heating above RT this pattern undergoes regular changes consisting firstly in an increase of the diameters of the isochromes which expand smoothly in radial directions. With this provision the external circles are one by one displaced from the field of view (FOV). As a result the total number of isochromes in the FOV reduces so that finally at T = 358 K one observes a uniform structureless dark background to be indicative of optical isotropy of the sample. Further heating above this particular isotropic point, however, results in a reappearance of the interference effects (Fig.1). This sequence of events is completely replicated in a reverse order with cooling back to the starting state.

Similar behaviour (radial expansion of isochromes – decreasing their number – transition to isotropy – reappearance of interference features with further heating – reversible return to the starting point) were observed in SBN35 samples (Fig.2), although the specific diameters of isochromes and their number are different.

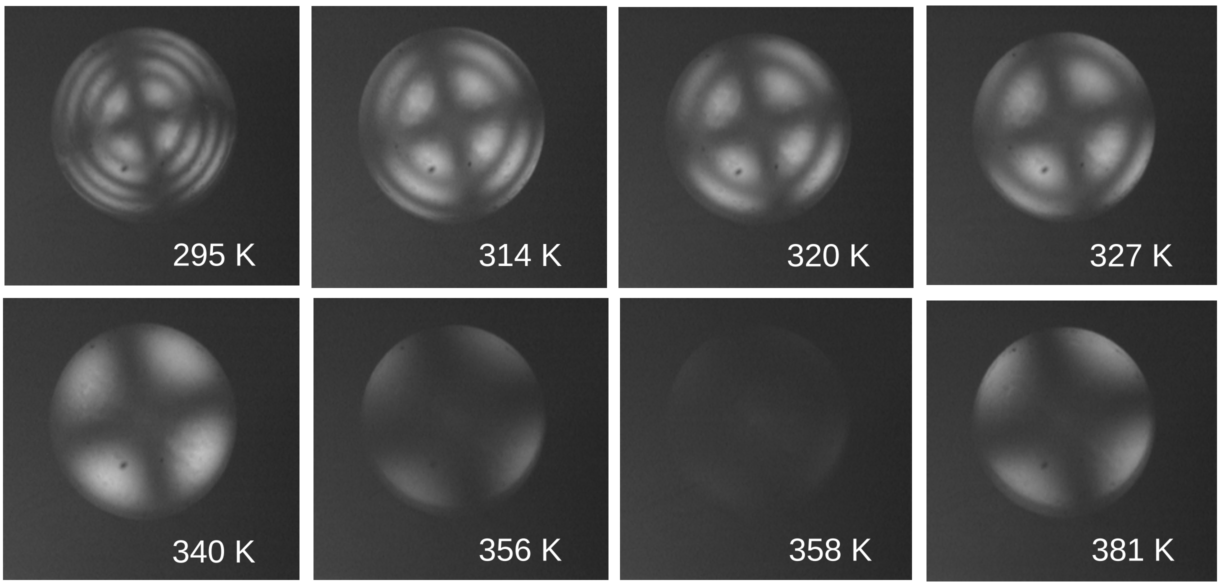

Figure 1. Effect of temperature on the conoscopic figures of SBN70 polar cut. Before observations the sample was annealed at 580 K for 2 hours.

The observed radial expansion of isochrome rings typical of uniaxial crystals and decrease of their number with temperature in SBN crystals may be understood as follows. The refractive indices n_0 of SBN are known to increase slightly with temperature [15]. At room temperature the refractive indices n_e are smaller than n_o. However, n_e increases with temperature much faster than n_o, so the difference $\Delta n = n_o - n_e$ decreases with heating giving rise to the isochrome diameters. At some point Δn becomes zero (crystal becomes isotropic); further heating changes the optical sign of the crystal as demonstrated by the experiment (Fig. 1).

However, detailed examination of SBN samples has shown that the uniaxial type of conoscopic patterns is often violated by the appearance of interference effects peculiar to optically biaxial materials. Some examples of such patterns are shown in Figure 3,*a*-*c* for SBN26, SBN61 and SBN70 samples. For the sake of comparison Figure 3,*d* shows the conoscopic figure of gadolinium molybdate (GMO) single crystal, which is a well known typical representative of the biaxial medium. It is seen that the given examples of the SBN samples bear the peculiarities of both uniaxial and biaxial behaviour, although the latter are not as distinct as in purely biaxial crystals. It should be added that in some cases these anomalies may be removed by annealing. For example, the distorted conoscopic figure of SBN70 shown in Figure 3,*c* was transformed to a normal uniaxial appearance shown in Figure 1 by heat treatment at 580 K for 2 hours.

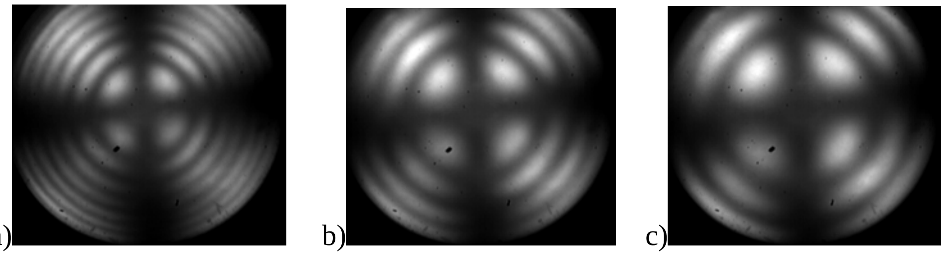

Figure 2. The conoscopic figures of SBN35. 320 K (*a*); 340 K (*b*); 350 K (*c*)

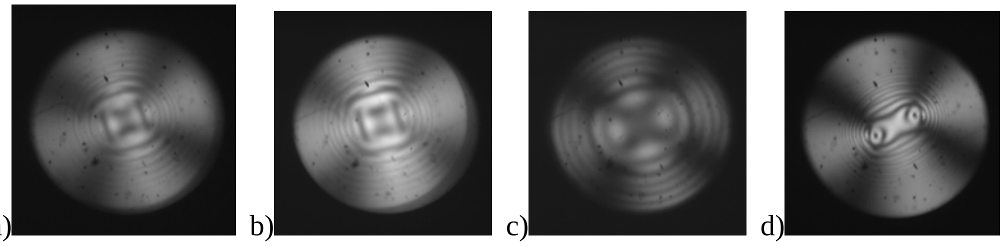

Figure 3. The conoscopic figures of SBN26 (*a*), SBN61 (*b*), SBN70 (*c*) and GMO (*d*)

The effect of anomalous biaxiality in uniaxial crystals may be understood in the following way. In general the biaxiality may be induced by electrooptic and piezooptic effects or induced by internal mechanical stresses [16]. Since the samples under study possess piezoelectric properties, the respective piezomodule d_{31} as determined at room temperature by the resonance–antiresonance method are given in Table 1.

Table 1. Piezoelectric modulus values of the SBN crystals.

Composition	SBN35	SBN50	SBN61
d_{31}, 10^{-12} C/N	–10	–17	–20

The existence of the piezoeffect permits us to estimate the mechanical stresses using the relation for the angle between optical axes (2*V*) [13]:

$$\tan V = \frac{\sqrt[4]{\left[\left(\pi_{1\mu}-\pi_{2\mu}\right)\sigma_{\mu}\right]^{2}+\left(2\pi_{6\mu}\sigma_{\mu}\right)^{2}}}{\sqrt{n_o^{-2}-n_e^{-2}}},$$

where n_o and n_e are the ordinary and extraordinary indices of refraction, $\pi_{i\mu}$ is the matrix of piezooptic coefficients, σ_{μ} are the mechanical stresses. The data for the piezooptic coefficients and refractive indices for SBN70 were taken from the references [1, 15, 17], while the value of tan*V* was obtained with the aid of a calibrating sample of gadolinium molybdate crystal as schematically shown in Figure 4. It follows that

$$V_{\mathrm{SBN}} = V_{\mathrm{GMO}} \frac{n_{\mathrm{GMO}}}{n_{\mathrm{SBN}}} \frac{L_{\mathrm{SBN}}}{L_{\mathrm{GMO}}} .$$

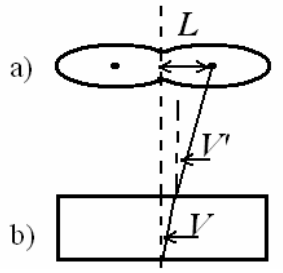

Figure 4. Diagram for determining the optical angle. (*a*) anomalous isochromes as observed from the top view, (*b*) transmission of the light through the sample

As a result we obtain an estimate of the order of reasonable mechanical stresses $2\cdot 10^7\ N/C < \sigma < 3\cdot 10^7\ N/C$ which may account for the observed anomalies in SBN70.

4. Conclusion

The performed study shows that the conoscopic method provides useful information on the characterization of SBN crystals. Experimental data on the effect of temperature on the conoscopic figures were presented for the first time and explained by the known temperature behaviour of SBN refractive indices. Specific biaxial optical anomalies in (uniaxial) SBN crystals not reported earlier were detected, thus demonstrating usefulness of the conoscopy technique in the studies of complex structure transformation in SBN system.

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