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GROWTH PECULIARITIES AND NON-LINEAR PROPERTIES OF PROFILED DOPED STRONTIUM-BARIUM NIOBATE CRYSTALS

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Growth peculiarities and non-linear properties of profiled doped strontium-barium niobate crystals

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Abstract

The nominally pure and doped with Ce, Cr, Co strontium-barium niobate crystals of SBN:61 were grown by modified Stepanov technique. The specific features of the technique were studied and growth conditions for obtaining the high homogeneous SBN crystals in bulk-profiled configuration were optimized. The photorefractive and non-linear properties of SBN pure and doped with Ce, Cr and Co were investigated. It was shown that SBN:Ce crystal is an excellent medium for high efficiency holographic information recording. SBN:Cr and SBN:Co crystals are promising photorefractive materials with short response time. The as-grown SBN crystals were also used to demonstrate the diffuse noncollinear second harmonic generation emitted by a random domain SBN structure and Stimulated Raman Scattering and two-photon absorption associated with cubic nonlinear susceptibility of the materials.

Introduction

The search of new non-linear materials and development of technologies for producing optically perfect crystals remains actual task up to now. Among solid-state materials an important role play ferroelectric crystals of strontium-barium niobate solid solutions $Sr_xBa_{1-x}Nb_2O_6$ (SBN:x), which belong to a class of active dielectric, exhibiting qualitatively new properties under influence of external factors [1-3]. SBN single crystals are characterized by the extremely large electro-optical coefficients and high nonlinear optical properties. Doping of the SBN solid solutions by rare-earth and transition metals allows to modify the properties of the crystals and to create new materials for different applications, particularly in the areas of pyroelectricity, piezoelectricity, electro-optics, photorefractive optics and non-linear optics [4-7].

The present investigation is directed on obtaining of high-homogeneous pure and doped with Ce, Cr, Co SBN:61 crystals and studying their photorefractive and non-linear properties.

Crystal growth

Choice of growth method was determined by the possibility to obtain from the melt the crystals of the required size and quality with reproducible characteristics. SBN:x is a solid solution with wide range of homogeneity ($0.25 \leq x \leq 0.8$). Introduction into the matrix doping ions of different type and concentration has a strong influence on crystal homogeneity. To obtain the crystals of given compositions and high optical quality the modified Stepanov technique with special die of capillary type was used (fig. 1).

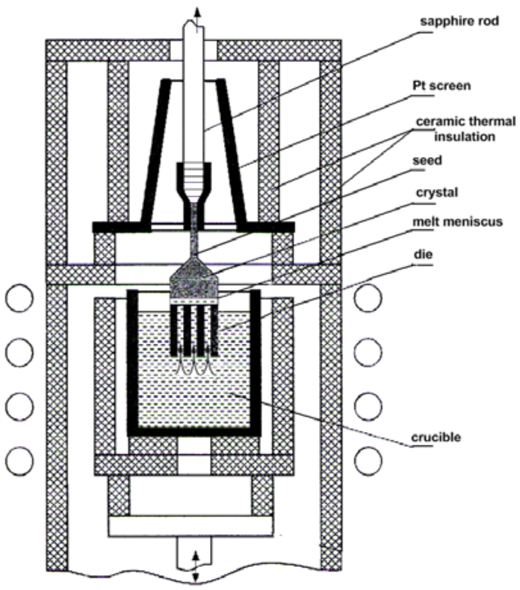


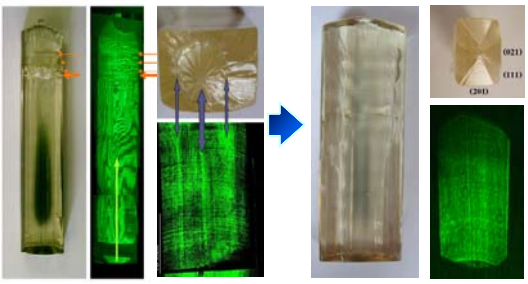
Fig. 1 Crystallization cell for growing SBN crystal

This growing technique provides: high optical quality of single crystals, free of growth striations, inclusions and other inhomogeneities of chemical composition; definite cross-section and sizes of growing of single crystalline rods [1, 2]. The specific feature of the Stepanov technique is that the melt is transported via a feed capillary to the meniscus on the top plane of a die. It is assumed that there is no convective mixing of the melt in the capillary- no convective striations in as-grown crystal. Profiled crystals were grown without rotation – no rotation striations in as-grown crystals. The form and size of the bulk -profiled crystals were defined by the character of the top plane of a die. Nominally pure single SBN crystals of different composition ($x = 0.61; 0.75$) have been grown as well as ones doped with Ce, Cr or Co ions (fig. 2). Doping ions were introduced into the matrix (congruently melting SBN:61) in the form of oxides. The crystals (14x24mm) in cross-section and up to 80 mm in length were grown.

Fig.2 SBN crystals grown by modified Stepanov technique

Crystal growth parameters such as temperature gradients in thermal cell, bulk crystallization rate, time and temperature of annealing processes were optimized for crystals of different chemical composition.

The control of optical quality of the crystals was performed by optical and polarization-optical methods, laser radiation scattering technique. The method of dynamic holography, developed in our laboratory, was used for investigation of real structure of as-grown crystals [3]. The method allows to carry out the high-speed monitoring of the presence or absence of phase inhomogeneities in the bulk of large single crystals with minimum mechanical treatment of crystal surfaces. Figure 3a illustrate typical defects of the SBN crystal real structure – growth striations(→) and under seed part (→), which formed in non-optimal growth conditions. Optimization of crystallization process provides the highly-homogeneous crystal growth (fig. 3b).



a b

Fig.3 The typical growth defects in SBN crystals

Photorefractive properties

Bulk-profiled SBN crystals have a high optical quality and reproducible photorefractive characteristics. The photorefractive properties of pure SBN and SBN crystals doped with Ce, Cr and Co were studied in two-wave mixing scheme (fig. 4). A continuous single-mode He-Ne laser as a source of coherent radiation for the grating recording was used. The gain coefficients and response times were measured. The photorefractive properties of the doped materials are summarized in table 1 [4-7].

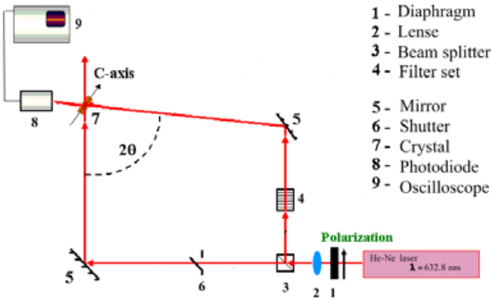


Fig. 4 Two-wave mixing scheme for grating recording

The values of the half-wave voltage were measured depending on type and concentration of doping ion. The electrooptical coefficients were calculated for all doped crystals.

The value of half-wave voltage for pure SBN:75 crystals is 80 V, that corresponds to the electrooptical coefficient of 750 pm/V. This value is almost three times higher than for nominally pure SBN:61. $U_{\lambda/2}$ for SBN:61 doped with Ce, Co and Cr at low concentrations is practically the same as for nominally pure SBN:61 – 240-250V. Dark conductivity and product of the mobility and the recombination time of charge carriers increase with increasing of dopant concentrations. Introduction of Ce, Co or Cr into the matrix strongly decrease the ratio of electron and hole conductivities.

Maximal value of two-wave gain coefficient was measured for heavy doped Ce:SBN –45cm^{-1}. For Cr and Co doped materials this value varies from 15 to 33cm^{-1} depending on dopant concentration. It was shown that SBN crystal doped with Ce is an excellent medium for high efficiency holographic information recording. SBN crystal doped with Ce is an excellent for high efficiency holographic information recording. SBN crystals doped with Cr, Co are interesting media for holographic recording where short response time is required.

Table 1: Photorefractive properties of SBN crystals

Crystal	SBN :75	SBN :61	SBN:61:CeO_2			SBN:61: Cr_2O_3		SBN:61:Co_3O_4			
Dopant concentration, wt.%	Pure	Pure	0.002	0.01	0.1	0.002	0.01	0.002	0.01	0.05 light	0.05 dark
K_{eff}	-	-	1	-	-	0.9	-	0.3	-	-	-
α, cm^{-1} 488nm	-	0.1	0.3	0.9	7.5	0.5	1.6	0.8	1.8	7	12
T_{max}°C 1kHz	56	82			76				75		
$U_{λ/2}$,B 633 nm	80	250	250	250	240	240	240	240	240	240	240
r_{33}, pm/V	750	245	255	255	255	255	255	255	255	255	255
Γ, cm^{-1}	15	14	30	40	45	15	20	10	14	25	33
Ls, μm	-	2.1			0.43	1.16	1.02	1.49	1.25	0.94	0.67
τ, ms, 476.5nm	-	-	235			70		174			
N_{eff}, 10^{17} cm^{-3}	-	0.12			2.5	0.37	0.48	0.22	0.31	0.55	1.07
σn/σp	-	10.8			3.6	2.9	3.2	2.9	3.2	6	6.6
σd, 10^{-12} $Ω^{-1}$ cm^{-1}	-	9			0.2	25.6	44.7	1.4	4.5	5.1	1
τμr, 10^{-10} cm^2/V	-	0.9			0.03	0.22	1.06	1.35	0.57	0.15	0.04

K_{eff} – effective segregation coefficient; $U_{λ/2}$ - half-wave voltage; r_{33} – electrooptical coefficient; Γ – two-wave mixing gain; τ – response time; α – absorption coefficient; T_{max} – Curie temperature; L_s – Debye screening length; N_{eff} – effective concentration of carrier traps; $σ_n/σ_p$ – ratio of electron and hole conductivities; $σ_d$ – dark conductivity;$μτ_r$ – product of the mobility and the recombination time of charge carriers.

Non-linear properties

The specific features of the material include the presence of domain structure – set of domains with different polarization vector orientation. The unit microdomains and regular 1D- (linear) and 2D- (planar) domain arrays are interesting objects for investigation due to practical application in optical-frequency conversion and waveguiding structures. Nanoscale domain structures in SBN crystals have been studied using an atomic force microscopy (AFM) by means of applying low (within 10 V) DC voltages [8]. SBN crystals are presented an attractive object for experimental research ferroelectric processes at micro- and nanolevels and for "domain architectures" in the field of AFM probe [8, 9]. The pictures 4 and 5 illustrate the possibility to create linear and planar microdomain structures, respectively. The domain structures recorded by means of a point-to-point tip displacement, with distances between points 29nm for line and 50nm for squares. The exposure conditions were UDC=10 V, tp=10ms at any point of the images.

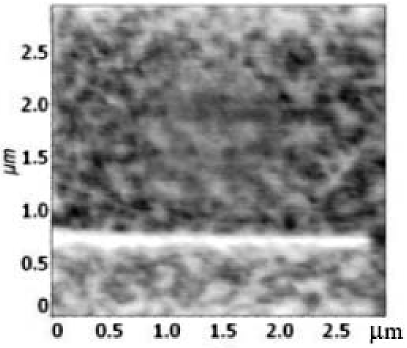


Fig. 4 The domain lines recorded by means of a point-to-point tip displacement in a chosen direction

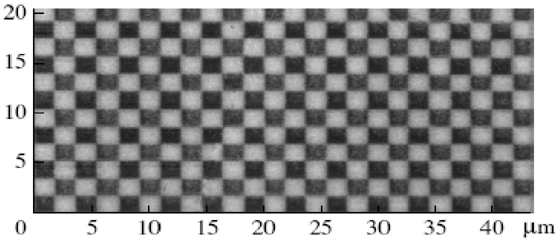


Fig. 5 The domain chessboard consisting of opposite signs domains

The method of force microscopy of the piezoelectric response was used to visualize the domain structure. The figure 6 shows AFM images of regular domain structure with the spatial period 3.6μm in SBN:61 crystal in 5 min after recording and after 3 month. It was estimated that the structure is stable to aging.

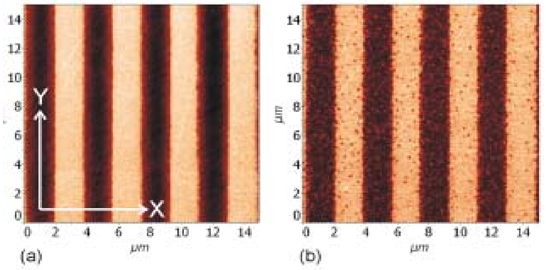


Fig. 6 The record of regular domain structures in SBN:61 crystal in the field of atomic force microscope. AFM images: a - 5 min after recording, b - 3 month after recording. The light and dark lines correspond to positive and negative domains

To illustrate the elasticity of the material arbitrary domain image (see Fig. 7) was recorded in the strontium–barium niobate crystal with the use of the corresponding graphic pattern for the voltage exposure with the parameters Ut=±10V and tp=10ms [9]. The image was obtained in the piezoelectric response regime; the light and dark elements of the image correspond to antiparallel domains recorded with Ut with an opposite sign. The image relaxation time is about several days. The possibility of creating domain microstructures of arbitrary configurations is attractive for applications.

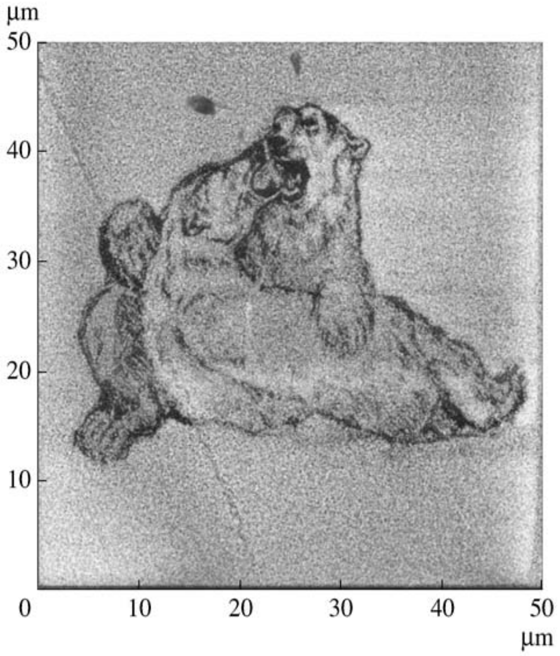


Fig. 7 The AFM record of arbitrary microdamain picture in polydomain SBN:61 crystal [10]

Nonlinear processes can occur in SBN crystal under irradiation with high laser intensity. Stimulated Raman Scattering (SRS) [11] and two-photon absorption (TPA) [12] as physical phenomena associated with cubic nonlinear susceptibility of the materials were observed in as-grown SBN crystals in our experiments for the first time.

The SRS in the strontium barium niobate crystal was investigated under laser pumping at 1064 nm with 18 ps pulse duration. Figure 8 shows spectra of light transmitted through the crystal under different pump energies. The crystal optical axis was oriented parallel to polarization of the pump radiation. There is no stimulated Raman scattering at pump pulse energy of W p = 0.6 mJ (solid red line). The first Stokes component was observed at Wp=1.2 mJ (blue line). At W p = 1.5 mJ the first and second Stokes components (green line) can be defined. The Raman gain coefficient was calculated 0.42cm/GW at 1064 nm

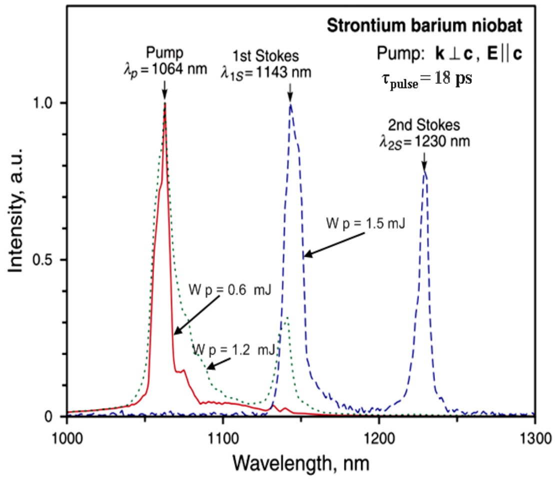


Fig. 8 The SRS radiation spectra in the SBN:61 crystal at the various pump pulse energy

We found that in the visible range the TPA nonlinear process dominates over the SRS in SBN crystals. The TPA in SBN:61 and SBN:75 crystals were studied under exitation by trains of 523.5 nm laser pulses with 20 ps pulse duration. Figure 9 shows the synchronized oscillograms of pulse trains the input I_0 (a) and the output I (b) of SBN:75 crystal.

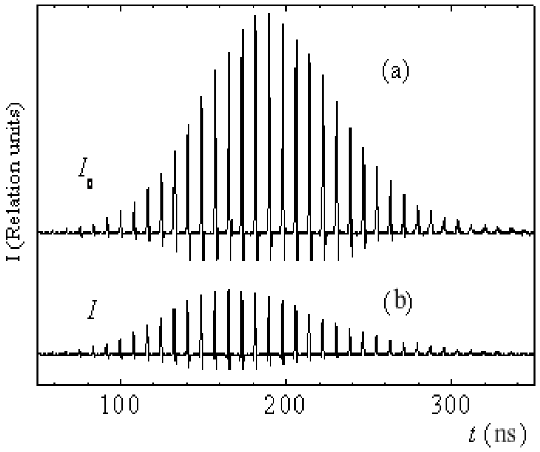


Fig. 9 Oscillograms of picoseconds pulse trains at the input I_0 (a) and the output I (b) of SBN:75 crystal

One can see that shape of the envelope is changed and maximum of the output radiation shifts to the beginning of the pulse train. This is explained by a decrease in the pulse intensity due to TPA, as well as by induced one-photon absorption (OPA). The dependences of the output radiation intensity on the incident radiation intensity for SBN:75 are given in fig. 10. The experimental dependence gradually deviates from the liner law due to the TPA process. The hysteresis behavior was attributed to the induced OPA.

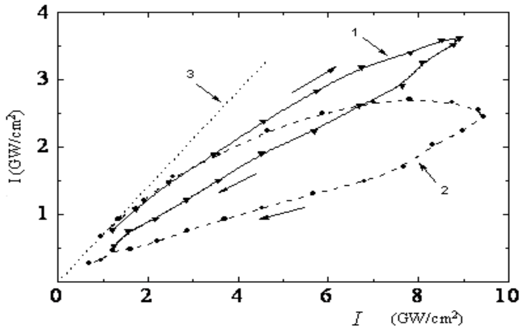


Fig. 10 Dependences of the intensity I of the output radiation on the input radiation intensity Io in SBN:75 (length 11mm with E⊥C4 (curve 1) и E||C4 (curve 2), and the estimated linear relationship taking into account the Fresnel losses (curve 3)

The two-photon absorption coefficients were determined as 0.17 – 0.31cm/GW depending on laser beam polarization (table 2). SBN:75 has maximal TPA coefficient 0.31 cm/GW in the optical axis direction.

Table 2: The values of TPA coefficients β (λ=523.5nm), measured for two polarizations of pump radiation

Crystal	β, cm/GW	
	E⊥C4	E||C4
SBN:61	0.23	0.27
SBN:75	0.18	0.31

The relatively low values of TPA coefficients and steady-state Raman gain coefficient (0.42 cm/GW at 1064 nm) result from low cubic nonlinear susceptibility of SBN crystals.

Conclusions

SBN crystals of high optical homogeneity, pure and doped with Ce, Cr, Co, suitable for various nonlinear-optical experiments, were grown by modified Stepanov technique. The photorefractive parameters of the materials were investigated depending on type and concentration of doping ions. The regular domain structures were recorded in SBN matrix using AFM technique. Stimulated Raman Scattering in SBN crystals was observed for the fist time. Two-photon absorption coefficients were determined depending on laser beam polarization and crystal composition.

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