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Detection of randomized nonlinear photonic crystal structure in a non-ferroelectric crystal

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Abstract
A spontaneously grown randomized nonlinear photonic crystal structure formed by 180° domains has been detected in strontium tetraborate via nonlinear diffraction. Domains have the form of sheets lying in the *bc* crystallographic plane with the domain walls oriented perpendicularly to the *a* crystallographic axis. The effective thickness of domains contributing to the nonlinear diffraction is determined from the Fourier spectrum of inverse superlattice vectors, and it falls within the range 180 nm to 6 μm. Nonlinear diffraction at the third harmonic frequency was observed in the same crystal sample.

Keywords: nonlinear generation, nonlinear diffraction, nonlinear photonic crystal, domains

1. Introduction

Quasi-phase matching (QPM) is widely studied in nonlinear optics, mainly as the means for enhancement of nonlinear conversion efficiency in crystalline waveguides [1]. Berger [2] suggested that these structures be classified as nonlinear photonic crystals. QPM requires the existence of domains with alternating oppositely poled static polarization, which leads to a periodic change of the sign of the second-order nonlinear susceptibility. Periodic reversal of the sign of nonlinear susceptibility in the neighbouring domains partially compensates for the absence of phase matching in the chosen direction compared to a single-domain crystal. Periodically poled domains are exclusively created in ferroelectric crystals, because artificial domain structures can be produced in them whether by the ion exchange method or by simply applying a static electric field of appropriate strength. Potassium titanyl phosphate (KTP) is the most suitable crystal for this method of phase matching. A number of efficient nonlinear conversion schemes utilizing domain-reversed structures were implemented in this crystal due to its high nonlinearity. QPM enables one to employ the highest nonlinear coefficient, d_{33}, of this crystal, which does not contribute to the effective nonlinear coefficient in the case of using the nonlinear conversion in the direction of perfect angular phase matching. The transparency region of KTP in the ultraviolet (UV) range is limited to 350 nm. Another advanced material for periodical poling is lithium niobate; however, its transparency range is limited to 330 nm. This hindrance has stimulated the search for nonlinear crystals with a shorter wavelength transparency limit. Such crystals as barium borate (BBO), lithium triborate (LBO) and a number of other borates are often used for nonlinear conversion into the UV; however, they have some limitations, too. For instance, phase-matched direct second harmonic generation in BBO can be obtained at wavelengths up to 210 nm with the effective nonlinearity approaching zero, while the transparency limit is about 190 nm for this crystal. The search for domains with a nonlinear susceptibility reversal in borates or in any other materials transparent in the region below 0.33 nm has not been successful to date. The only exception is ferroelectric $BaMgF_4$, but its nonlinear susceptibility is very low.

Strontium tetraborate was investigated as a nonlinear crystal by Oseledchik *et al* [3]. They suspected a rather high nonlinear susceptibility; however, it was established that there was no angular phase matching through equality of refractive indices in the entire range of wavelengths studied for this crystal. Later studies of SBO admitted these conclusions [4]. Phase-mismatched generation of 125 nm radiation has recently

been obtained in SBO by means of non-collinear interaction of femtosecond laser beams for the purpose of ultrafast diagnostics [5]. SBO is not a ferroelectric crystal, and a possibility of QPM is not considered for this crystal, like for other borates. However, as any non-centrosymmetric crystal, SBO may possess domains of some other nature. Its symmetry allows for the presence of 180° domains that can be suitable for QPM.

In the present communication, we report on the detection of a spontaneously grown domain structure in SBO. To observe this structure, we employed nonlinear diffraction. The phenomenon of nonlinear diffraction was discovered in 1968 for NH_4Cl crystal [6]. Later, the second harmonic scattering on domain structures was studied in ferroelectric triglycine sulfate (see [7] and references therein). Further studies of ferroelectric domains by means of nonlinear processes involved parametric scattering, which provided more information obtained from spectral measurements [8].

As shown below, the domain structures in SBO, which can be obtained in our crystal growth experiments, are not regular, but they have random domain thickness. This refers us to another interesting area of studies in modern nonlinear optics, namely to nonlinear optical processes in randomly structured media. Both theoretical and experimental studies [9–11] have shown that nonlinear conversion exhibits a phenomenon known as 'random quasi-phase matching' in the media with no angular phase matching but with polycrystals or domain structures with randomized domain sizes. Our results suggest that domain structures in SBO might be a new object for studies of these phenomena.

2. Crystal growth procedure

A strontium tetraborate single crystal was grown by the Chochralski method on an oriented seed. The starting temperature on the melt surface was 1000 °C. The seed-rotation rate was 10 rpm, and the pulling rate was 2.4 mm/day. The crystal was grown to a diameter of approximately 20 mm at a cooling rate of 1 °C/day. After 5 days, a transparent, colorless SBO single crystal was obtained with an approximate size of 20 mm × 20 mm × 15 mm. As-grown crystals had regions with some inclusions, but most of their volume was transparent and free from macroscopic defects. X-ray investigations of the crystal powder obtained from the single crystal were carried out with a Bruker D8 Advance diffractometer using Cu Kα radiation. The crystal parameters were found to be close to those reported in [3]: $a = 4.4255$ Å, $b = 10.709$ Å, $c = 4.423\,41$ Å. SBO is a biaxial crystal belonging to the orthorhombic symmetry class $mm2$. We will follow the classification of [3, 5] who define the spatial symmetry group as $Pnm2_1$. Static polarization of the unit cell in SBO is directed along the polar axis c.

3. Measurement of nonlinear coefficients of SBO

Three independent nonlinear coefficients of SBO, d_{31}, d_{32} and d_{33}, were measured in [5] using 800 nm fundamental radiation and 50 fs pulses. The other two nonzero nonlinear coefficients, d_{15} and d_{24}, were not measured, since they were assumed to be equal to d_{31} and d_{32}, respectively, as Kleinman symmetry requires. However, measurements in other crystals often do not give definite evidence to support this assumption, as is the case for instance with KTP, belonging to the same symmetry class $mm2$ as SBO. The latest research [12] proved the equality of d_{xxz} and d_{zxx} within measurement error, but leaves unresolved the question about the equality of d_{yyz} and d_{zyy}. We recently reported the measurement of all nonlinear coefficients of SBO using nanosecond pulses [14], which will be briefly reviewed below.

Table 1. Nonlinear coefficients of strontium tetraborate (SBO).

	Nonlinear coefficient value (pm V^{-1})	
Nonlinear coefficient	Petrov *et al* (800 nm, 50 fs) [4]	Our work (1.064 μm, 15 ns)
d_{caa} (d_{31})	0.8	1.7
d_{ccc} (d_{33})	1.5	3.5
d_{aac} (d_{15})		0.9
d_{bbc} (d_{24})		0.7
d_{cbb} (d_{32})	1.1	2.0

We measured all five nonzero nonlinear coefficients of SBO using a Q-switched Nd:YAG laser (several mJ per pulse, 15 ns duration). The measurements were performed on oriented plates having a thickness of the order of the coherence length. The nonlinear coefficient d_{15} of a KTP crystal [12] was used as the reference value. The reference KTP sample was cut in the Y direction and had the thickness 51 μm. This thickness is slightly larger than the coherence length for the conversion process $xz \rightarrow x$ $l_c = \pi/\Delta k = \pi/(k_{2x} - k_{1x} - k_{1z})$, $\Delta k = (4\pi/\lambda)(n_{2x} - (n_{1x} + n_{1z})/2)$. The calculated coherence length is 45 μm ($n_{1x} = 1.7379$, $n_{1z} = 1.8297$, $n_{2x} = 1.7779$ [13]). The fundamental radiation was polarized at 45° to the X and Z axes. The second harmonic signal polarized along the X axis was selected with the help of a Glan–Thomson prism, so that only d_{15} contributed to the signal from the reference crystal. Nonlinear coefficients d_{aac}, d_{caa} and d_{ccc} of SBO were measured on a 44 μm thick plate perpendicular to the b axis direction, the plate thickness being three times the coherence length for the process $aa \rightarrow c$ ($n_{1a} = 1.721$, $n_{2c} = 1.741$). Nonlinear coefficients d_{bbc} and d_{cbb} were measured on a plate perpendicular to the a axis direction of the same thickness, 44 μm. The measured values of the second harmonic signals were corrected for mismatch of the coherence lengths in different conversion schemes using the factor $F(\Delta k, t) = \sin^2(\Delta k t/2)/(\Delta k t/2)^2$, where t is the plate thickness. The results obtained are presented in table 1.

Our values are higher than those obtained in [4]. This discrepancy can be explained by the influence of the group velocity dispersion, which is negligible in nanosecond pulses. Note that d_{ccc} is the maximum coefficient (the same as for KTP), and the measured values of d_{aac} and d_{bbc} are lower than the values of d_{caa} and d_{cbb}.

4. Observation of nonlinear diffraction in SBO

The sample under study had the following dimensions: 6 mm in the direction of the a axis, 8 mm in the direction of the b axis and 4.6 mm in the direction of the c axis. Linear optical homogeneity of the crystal was verified with the help

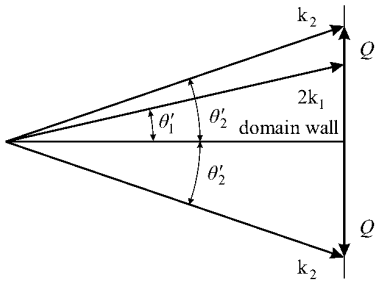

Figure 1. Phase-matching diagram for nonlinear diffraction of the second harmonic.

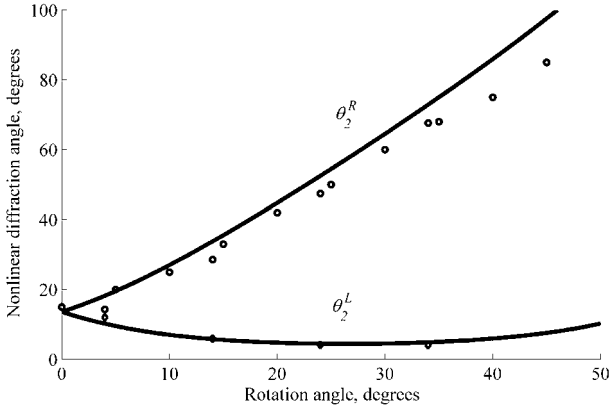

Figure 2. Dependence of nonlinear diffraction angles upon crystal rotation angle. Solid lines are calculations, circles and diamonds are the experimental data obtained for the right-hand beam and for the left-hand beam, respectively.

of a He–Ne laser at 633 nm. No sign of diffraction of this radiation due to inhomogeneity of the refractive index was observed. Q-switched Nd:YAG laser radiation (several mJ per pulse, 15 ns duration) was used for nonlinear optical studies. This radiation was focused into the crystal by a 10 cm focal length lens. The input facet of the crystal was perpendicular to the crystallographic b axis. The fundamental beam contained polarizations along both crystallographic axes a and c. A non-phase-matched second harmonic beam collinear to the fundamental beam was observed behind the crystal. However, additional second harmonic beams brighter than the non-phase-matched second harmonic beam were observed at certain positions of the fundamental beam on the input facet. Under normal incidence of the fundamental, two groups of beams at equal angles were observed on the left and on the right of the fundamental beam. Each beam group consisted of three beams: two of them had polarization along the vertical axis (corresponding to the c axis of the crystal), and the third beam was horizontally polarized (along the a axis of the crystal). In view of the linear homogeneity of the crystal, the observed beams must be attributed to the nonlinear diffraction due to inhomogeneity of the second-order nonlinear susceptibility of the crystal. This leads us to believe that the crystal contains domains with identical linear optical properties but with different nonlinear optical properties. The absence of beams diffracted outside the horizontal plane suggests that the domains have the form of sheets perpendicular to the a axis. However, in the case of periodic inhomogeneity, nonlinear diffraction must be observable in a narrow range of angles between the selected direction inside the crystal and the direction of the fundamental beam.

In contrast, rotation of the crystal around the c axis does not lead to disappearance of the diffracted beams but causes their angular displacement. If the crystal is rotated clockwise when viewed from above, then left group of beams (when viewed in the direction of propagation of the laser beam) slowly approaches the position of the fundamental beam, while the right group of beams rotates clockwise at a faster rate approaching 90° when crystal is rotated by 45°. The intensity of the beams during rotation varies less than would be expected for nonlinear diffraction on a periodic structure.

The expected angular behavior of the diffracted beams can be easily calculated from the vector condition of the phase matching for nonlinear diffraction:

$$\vec{k}_2 = 2\vec{k}_1 + \vec{Q} \qquad (1)$$

Table 2. Calculated and measured nonlinear diffraction angles.

Conversion scheme and nonlinear coefficient	aac, d_{15}	ccc, d_{33}	caa, d_{31}
Calculated nonlinear diffraction angle	13.4°	14.5°	15.3°
Measured nonlinear diffraction angle	13.4°	14.2°	15.4°

where $\vec{k}_2$ and $\vec{k}_1$ are the wavevectors of the diffracted second harmonic and of the fundamental, respectively, and $\vec{Q}$ is the wavevector describing the domain structure, or the inverse vector of the domain superlattice. In the case of a rectangular dependence of the nonlinear susceptibility on the coordinate with oppositely poled domains of equal thickness, $d|\vec{Q}| = \frac{\pi}{d}a, a = 1, 3\ldots$, and the vector $\vec{Q}$ is directed perpendicularly to the domain walls. Consider the fundamental beam propagating inside the crystal at the angle θ_1' to the domain wall (figure 1). The angles of propagation of the beams diffracted on the right and on the left of the fundamental beam, $\theta_2^{\mathrm{R,L}}$, measured outside the crystal, must be

$$\theta_2^{\mathrm{R,L}} = \arcsin\sqrt{n_2^2 - n_1^2 + \sin^2\theta_1} \pm \theta_1, \qquad (2)$$

where θ_1 is the angle of the fundamental beam incidence to the crystal facet measured outside the crystal, and $n_{1,2}$ are the refractive indices of the fundamental and the harmonic. If the fundamental wave contains different polarizations, then the vector $2\vec{k}_1$ must be substituted by $\vec{k}_{1i} + \vec{k}_{1j}$, where i and j denote different polarizations, and n_1 must be substituted by $(n_{1i} + n_{1j})/2$. Generally, a total of six diffracted beams must exist on each side of the fundamental beam, corresponding to the conversion schemes aaa, aac, acc, caa, cac, and ccc. Due to the symmetry of the crystal studied, some nonlinear coefficients are zero (namely, aaa, acc and cac), and the number of beams is reduced to three on each side of the fundamental beam. The angles of nonlinear diffraction calculated for $\theta_1 = 0$ using refractive indices from [1], and measured experimentally, are presented in table 2, and they demonstrate a good agreement.

The dependence of the diffraction angle on the angle of incidence of the fundamental is shown in figure 2. The

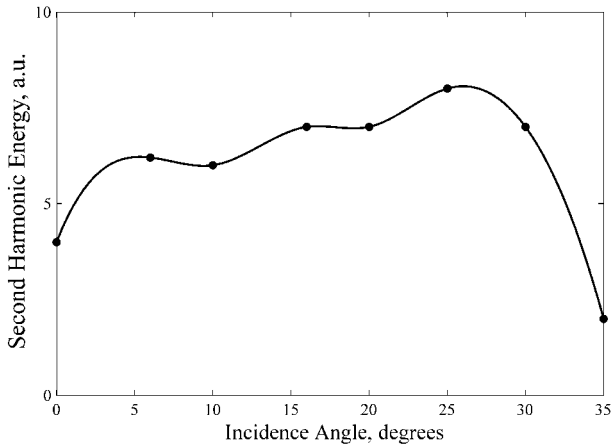

Figure 3. Dependence of diffracted second harmonic energy upon incidence angle. $\theta_1 = 0$ corresponds to $Q^{\mathrm{L,R}} = \pi\ \mu\mathrm{m}^{-1}$, and $\theta_1 = 35°$ corresponds to $Q^{\mathrm{R}} = \pi/0.22\ \mu\mathrm{m}^{-1}$.

agreement between the calculations and the experiment is fairly satisfactory again. This proves that the observed phenomenon has a nonlinear diffraction nature and that nonlinear optically active domain orientations do exist in the crystal under study. However, the diffracted beams observed in a wide range of the angles indicate that the values of $\vec{Q}$ form a much richer spectrum than in the case of a regular domain structure with a constant domain thickness. It is clear that domains have random thickness, so the Fourier spectrum of the dependence of the second-order nonlinear susceptibility $\chi^{(2)}$ on the coordinate in the direction perpendicular to the domain walls is a continuum of values rather than discrete harmonics. The boundaries of the spectrum of $Q^{\mathrm{L,R}}$ can be estimated from the smallest and largest observed angular positions of the left and the right diffracted beams using the formulae

$$Q^{\mathrm{L,R}} = \left[n_2 \left(1 - \frac{n_1^2}{n_2^2} + \frac{\sin^2\theta_1}{n_2^2} \right) \mp n_1 \left(\frac{\sin\theta_1}{n_1} \right) \right] = \frac{4\pi}{\lambda} \left[\sqrt{n_2^2 - n_1^2 + \sin^2\theta_1} \mp \sin\theta_1 \right]. \quad (3)$$

These values are found to be equal to approximately $\pi/6$ and $\pi/0.2\ \mu\mathrm{m}^{-1}$ respectively, i.e. the effective domain width ranges from 200 nm to 6 μm. The space occupied by domains does not cover the entire volume of the studied sample. Its thickness in the direction of the a axis is nearly two millimetres.

Based on the measured dependence of the diffraction angles on the angle of incidence, one can expect that the average thickness of domains in the studied sample would be of order of several microns. According to reference [11], the regime of interest for the study of quasi-phase matching in randomized structures is expected to be found when average size domain thickness is larger than the coherence length. The typical values of coherence length for second harmonic generation in SBO are above 10 μm for the fundamental wavelengths above 1 μm, but they become shorter than 3 μm for fundamental wavelengths less than 0.6 μm.

The dependence of the diffracted second harmonic intensity on the rotation angle is shown in figure 3. This dependence reflects the behavior of the function $\chi^{(2)}(Q)$, being the Fourier transform of the $\chi^{(2)}(x)$ function. This dependence slowly varies in the region from zero to 30°, after which it begins to drop noticeably. The presence of the wide spectrum of Q indicates that nonlinear diffraction at frequencies other than the second harmonic can also be observed. Indeed, when the horizontally polarized fundamental and the vertically polarized second harmonic beams were focused into the crystal, the nonlinearly diffracted third harmonic beam was observed. For $\theta_1 = 0$, the experimental diffraction angle equals 16°. The expected value for this angle can be calculated using the relation

$$\theta_2^{\mathrm{R,L}} = \arcsin \sqrt{n_3^2 - \left[\frac{\sqrt{n_1^2 - \sin^2\theta_1} + 2\sqrt{n_2^2 - \sin^2\theta_1}}{3} \right]^2} \mp \theta_1, \quad (4)$$

and it equals 16.5°. Obviously, this result causes us to suggest that randomized QPM structures can be more tolerable to the wavelength tuning than strictly periodic structures, not only in respect of the nonlinear diffraction but also in the case of an ordinary nonlinear conversion.

5. Conclusion

Nonlinear diffraction was observed in the non-ferroelectric strontium tetraborate crystal at the frequencies of the second and third harmonics of Nd:YAG laser. This diffraction reveals the presence of partially ordered alternate oppositely poled domains suitable for use in nonlinear optics. The shape and orientation of domains are found to be the same as in the ferroelectric KTP crystal belonging to the same symmetry class $mm2$, i.e. the domains have the form of sheets with the domain walls perpendicular to the a axis. The thickness of domains is a random quantity; the spatial Fourier spectrum of the nonlinear susceptibility ranges from $\pi/6$ to $\pi/0.2\ \mu\mathrm{m}^{-1}$. Our results indicate that SBO crystal exhibits a tendency to form domains with the orientation in the bc plane. These domains, however, cannot be as easily controlled as in the case of KTP. A further investigation of the mechanism governing the domain structure formation and the search for methods to control it are necessary before the results reported in the current communication can be used in practical nonlinear optics.

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