MSc in Photonics

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Master in Photonics

MASTER THESIS WORK

Frequency doubling in SBN crystal affected by poling and thermal treatment

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Presented on date 9th September 2009

Registered at

Escola Tècnica Superior
d'Enginyeria de Telecomunicació de Barcelona

Frequency doubling in SBN crystal affected by poling and thermal treatment

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Abstract. The random anti-parallel micro-ferroelectric domains in SBN (Strontium-Barium Niobate, Sr0.61Ba0.39Nb2O3,) crystal can be used for efficient nonlinear optical processes at different frequencies. The ferroelectric domains in SBN crystal are easily influenced by temperature and electric field. By comparing different second harmonic generation (SHG) profiles and efficiencies of SBN crystal under electric field poling and thermal treatments at different temperatures, and observing the ferroelectric domain structures (sizes and directions) under the scanning electronic microscope (SEM), the mechanism of how the thermal treatment and poling affects the SBN crystal's inner structure, thus the frequency doubling process, is revealed. We found that for the poled SBN crystal, the SHG emission shows a speckle pattern; on the other hand, after a thermal treatment there is a clear maximum in the propagation direction of the fundamental light.

Keywords: second harmonic generation, SBN crystal, ferroelectric domains, poling, thermal treatment, speckle

1. Introduction

Quasi phase matching (QPM) has been widely used in nonlinear optical processes for efficient energy transfer from one wavelength to another. A general way to realize QPM is to periodically modulate the nonlinear property of the material. In ferroelectric materials, the simplest way is to fabricate a periodic anti-parallel structure with the consequent periodically reversed quadratic nonlinearity. Due to the refractive index dispersion, a fixed period can only modulate successfully the QPM process for one fixed wavelength. However, ferroelectric crystals with disordered structures can provide an almost infinite number of reciprocal space grating vectors [1], and thus generate light in an ultra broad frequency range. This has the tradeoff of losing some efficiency but still, the efficiency in such structures is much higher than in non phase-matched crystals.

SBN crystal has proved to be a crystal with high optical nonlinearity, and a special property of SBN crystal is that it has a great amount of randomly distributed anti-parallel ferroelectric domains [2]. Because these domains provide a large number of different grating vectors for phase matching, it has the potential to be used in nonlinear optical processes for generating different frequency waves with relatively high efficiency simultaneously. So far, SHG emission by unpoled and poled SBN crystals has been reported for many times [3]-[6]. We can distinguish two profiles on the emission of SHG depending on along which axis of the crystal the fundamental light propagates. If the fundamental light propagates along the polar c-axis of the SBN crystal, the SHG emission is cone-shaped [7], and when the fundamental light propagates perpendicular to the c-axis of the SBN crystal, there is SHG in the plane perpendicular to the c-axis.

In this master thesis, we concentrate on the plane SHG case, that is when the fundamental light is perpendicular to the c-axis of the SBN crystal. It is found that the efficiency of SHG in the SBN crystal along different directions could be changed by altering the ferroelectric domain structures of the crystal [8], which could be realized by electric field poling and thermal treatments at different temperatures. By measuring the SHG of the infrared light from an Nd:YAG laser in the SBN crystal, and observing the ferroelectric domain structures under the Scanning Electronic Microscope (SEM), we analyze how the poling and thermal treatment affect the ferroelectric domain structure, and consequently the SHG process of SBN. We studied the SHG emission by the poled SBN crystal, and found that the SHG emission shows a speckle pattern, which changes with the polishing of the two window surfaces through which the laser propagates. We think it is mainly coming from the random interferences by some not well poled domains, perhaps at the crystal surfaces. Although SHG emission by poled SBN crystal has been reported many times before, as far as we know, this speckle pattern of the SHG emission has not received attention. Understanding this phenomenon could help us to explain better the origin of the SHG in SBN crystals.

On the other hand, if we apply one thermal treatment by heating the crystal to 160℃ and cool it down naturally to room temperature, the profile of the SHG emission of this annealed SBN crystal changes, and one more obvious peak is observed in the direction of the laser propagation. What's more, the SHG emission of the poled SBN crystal after thermal treatment at several temperatures above the Curie temperature are compared, and it is found that the SHG emission of poled SBN after several thermal treatment is very similar to the SHG emission of an unpoled SBN crystal.

2. Theory

A common way to describe the light matter interaction is by using the relation between the electric field of light $\tilde{E}(t)$ and the polarization $\tilde{P}(t)$ of the material, which is the dipole moment per unit volume. In linear optics, the polarization induced in the material depends linearly on the electric field of light, and $\tilde{E}(t)$ and $\tilde{P}(t)$ has the linear relation:

$$\tilde{P}(t) = \chi^{(1)}\tilde{E}(t) \tag{1}$$

Where the constant $\chi^{(1)}$ is the linear susceptibility of the material.

In nonlinear optics, the optical response can be described by expanding $\tilde{P}(t)$ into a power series of $\tilde{E}(t)$ [9]:

$$\tilde{P}(t) = \chi^{(1)}\tilde{E}(t) + \chi^{(2)}\tilde{E}^2(t) + \chi^{(3)}\tilde{E}^3(t) + \ldots\ldots \equiv \tilde{P}^{(1)}(t) + \tilde{P}^{(2)}(t) + \tilde{P}^{(3)}(t) + \ldots\ldots \tag{2}$$

Where $\chi^{(2)}$ and $\chi^{(3)}$ are known as the second and the third order nonlinear susceptibilities of the material, and $\chi^{(2)}$ is a third-rank tensor, and $\chi^{(3)}$ is a fourth-rank tensor, and so on. Due to the fact that the nonlinear susceptibilities remain unchanged under symmetry operations of the medium, one important conclusion is that all the even-order susceptibilities such as $\chi^{(2)}$ and $\chi^{(4)}$ etc, are 0 for all the centro-symmetric crystals and isotropic materials. Ferroelectric crystals, however, are non centrosymmetric, and can produce effective even-order nonlinear effects.

SHG is the most common second-order nonlinear optical process, where the power of the incident field at frequency ω is partially transferred into an oscillation at double frequency 2ω. The polarization oscillating at 2ω acts as a source of electromagnetic dipole radiation that is not contained in the incident field. Due to the dispersion in the refractive index, the fundamental light travels at different velocity than the SHG light. Thus the generated second harmonic waves at different locations in the nonlinear material can interfere constructively or destructively.

Their sum increases due to their constructive interference up to the coherence length, at which distance the polarization and the generated second harmonic waves come out of phase, and the total SHG begins to decrease due to the destructive interference. In order to get constructive interference over longer distances, some kind of phase matching is required, which will maintain a fixed phase relation between the generated waves and the nonlinear polarization. This will allow more incident energy to be transferred to the SHG waves.

According to the phase matching condition which is required for momentum conservation during the SHG process, the grating vectors of the nonlinear material $\mathbf{k_g}$ should satisfy the vector equation $\mathbf{k_2=2k_1+k_g}$, where $\mathbf{k_2}$ is the wave vector of the SHG light, and $\mathbf{k_1}$ is the wave vector of the fundamental beam.

$$k_2=\frac{2\pi}{\lambda_2}n(\omega_2),\ k_1=\frac{2\pi}{\lambda_1}n(\omega_1),\ k_g=\frac{2\pi}{2D} \tag{3}$$

Where 2D is the periodicity of the domains.

In our case, the wavelengths of the fundamental beam and SHG signal are fixed, which means fixed values of $\mathbf{k_1}$ and $\mathbf{k_2}$. A scheme of the quasi phase matching condition is shown in figure 1. We could tell from Figure 1 that the bigger the angle between the fundamental beam and the SHG signal is, the larger $\mathbf{k_g}$ is needed for phase matching, and $\mathbf{k_g}$ should take values among [10]:

$$|k_2|-2|k_1|\leq|k_g|\leq|k_2|+2|k_1| \tag{4}$$

When our fundamental beam is 1064nm, and the SHG signal is 532nm, according to the refractive indices of SBN, we can calculate that the value range of k_g is:

$$1\mu m^{-1}\leq|k_g|\leq 50\mu m^{-1} \tag{5}$$

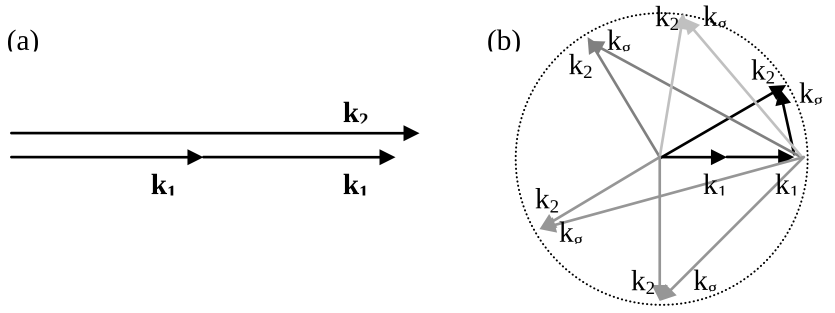

Figure 1. Scheme of the phase matching relation between $\mathbf{k_1}$, $\mathbf{k_2}$, and $\mathbf{k_g}$. (a) Collinear SHG. (b) Non-collinear SHG.

The ferroelectric domains of the unpoled SBN crystal have a columnar shape parallel to the c-axis and are randomly distributed with different sizes and orientations up or down in the crystal body [11]. Thus, the SHG can be approximately phase matched in the c-plane, so we expect weak SHG distributed in all directions in the c-plane.

The SHG of a poled SBN crystal is shown in figure 2 (b), and the SHG intensity is more in the forward direction and less at other orientations.

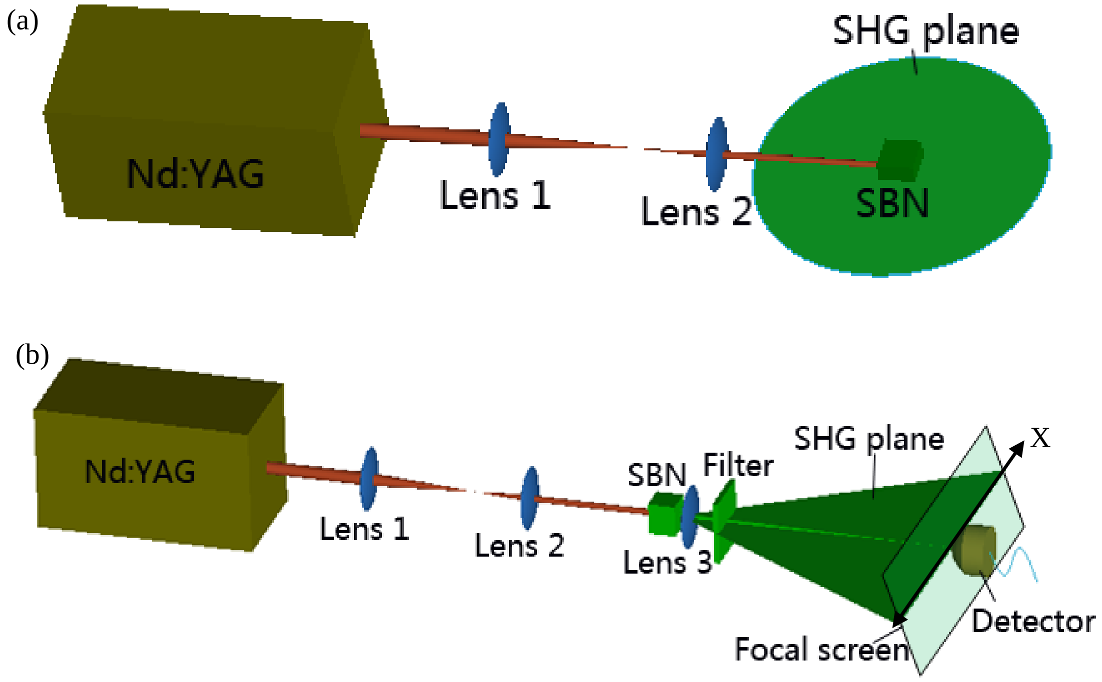

Figure 2. Scheme of the SHG generation of (a) an unpoled SBN crystal. (b) a poled SBN crystal.

3. Results and discussion

In order to investigate the SHG emission of the SBN crystal, we used a Nd:YAG laser system with a repetition rate of 10Hz, and the pulse duration at the wavelength of 1064nm is about 6 nanoseconds. Two lenses are used to generate a collimated fundamental beam directed perpendicular to the c-axis of the SBN crystal. The generated SHG signals from the crystal are focused by a lens placed right after the crystal, and are measured in the transverse direction perpendicular to the fundamental beam (the “X” direction shown in figure 2(b)), with a photodiode installed on a translation stage, which has a movement range of 500mm. The experimental set-up is shown in figure 2.

We compared the SHG emission of unpoled, poled, and thermal treated SBN crystal. The SHG pattern of the poled SBN crystal is studied, and the change of this SHG pattern by polishing the window surfaces of the poled SBN crystal is measured. The domains of the poled and annealed SBN crystal are observed under the SEM after chemically etching the crystal surfaces with HF aqueous solution at room temperature for 15 min [14]. Since the positive and negative polarized domains have different etching behaviors, imaging of the resulting topography after etching will represent the domain structure of SBN.

3.1 Comparison of the SHG emission of SBN crystal after poling and thermal treatments

A series of poling and thermal treatments are applied to the SBN crystal, and the measurements of the SHG emission are taken by the photodiode on the translation stage. The strength and the profile of the SHG emission are measured and compared.

3.1.1. SHG in unpoled SBN crystal

In a new SBN crystal as it is grown, neither poled nor heated, the SHG is relatively weak, and is emitted evenly in all the directions in the plane perpendicular to the c-axis. Thermal treatments at this stage don't seem to affect the SHG emission pattern.

3.1.2. SHG in poled SBN crystal

The poling of SBN crystal is achieved by applying a high electric field while it is being cooled down slowly from a temperature of 180 ℃ which is high above the Curie temperature of the crystal (between 80 and 100℃) [12]. We tried different electric fields such as 200 V/mm, 400 V/mm or 500 V/mm with similar results.

After the poling, the SBN crystal is supposed to be a mono-domain, where there are no longer anti-parallel domains satisfying the phase-matching condition in figure 1. Thus, the SHG emission is expected to obey the Maker fringe theory, which means there would be only one single SHG spot or no SHG emission in the laser propagation direction. However, after the poling of the SBN crystal, we can always observe SHG emission in a certain angular range in the forward direction (figure 2 (b)), which has also been observed by other researchers [13]. This necessarily means that the poling is not perfect and there are still a number of anti-parallel domains.

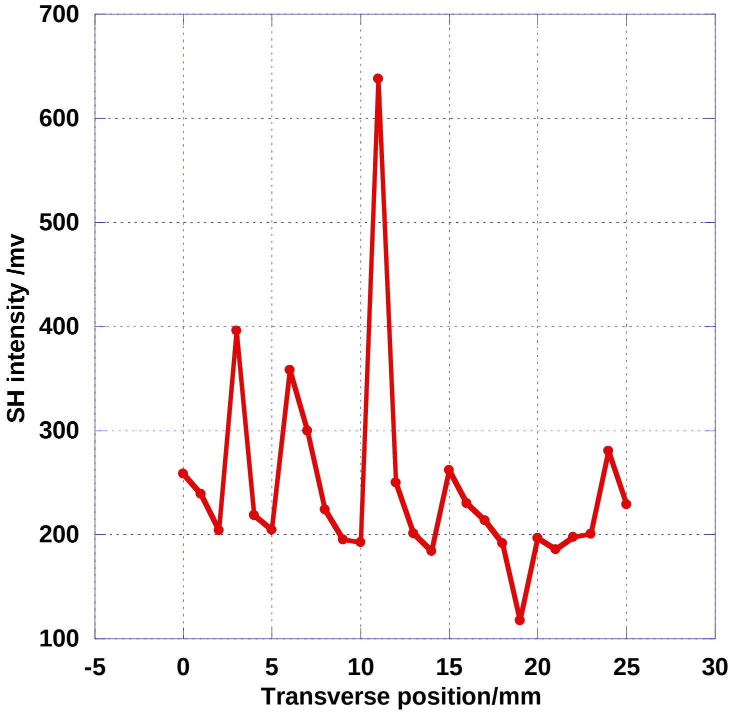

Figure 3. SHG of the poled SBN crystal

3.1.3. SHG in poled SBN crystal after a thermal treatment

To investigate how the temperature affects the SHG emission of the SBN crystal, we heat the poled SBN crystal to a lower temperature around 373K, which is still above the Curie Point, and then cool the crystal down to room temperature again. When we put the SBN crystal under the infrared light, we could find a much wider spreading and weaker SHG line along the transverse X direction but with an obvious peak in the direction of the fundamental beam (figure 4). After the thermal treatment, the domain polarization decreases, and there can be more grating vectors provided by the crystal to meet the phase-matching condition, which leads to SHG in a much wider angle range as shown in figure 1.

An explanation of this effect could be that after the thermal treatment to the SBN crystal, the ferroelectric domains in the crystal have increased in number, which means smaller domain period, leading to bigger $\mathbf{k_g}$. On the other hand, SHG emission in the propagation direction of the fundamental light becomes more obvious than that in other directions. This could be verified by an increased ratio between the peak SHI (second harmonic intensity) in the laser propagation direction and SHI at other positions (at other angles from the laser propagation direction) after the thermal treatment. We think that this could be related to a bigger size of the domains as we will see in section 3.3.

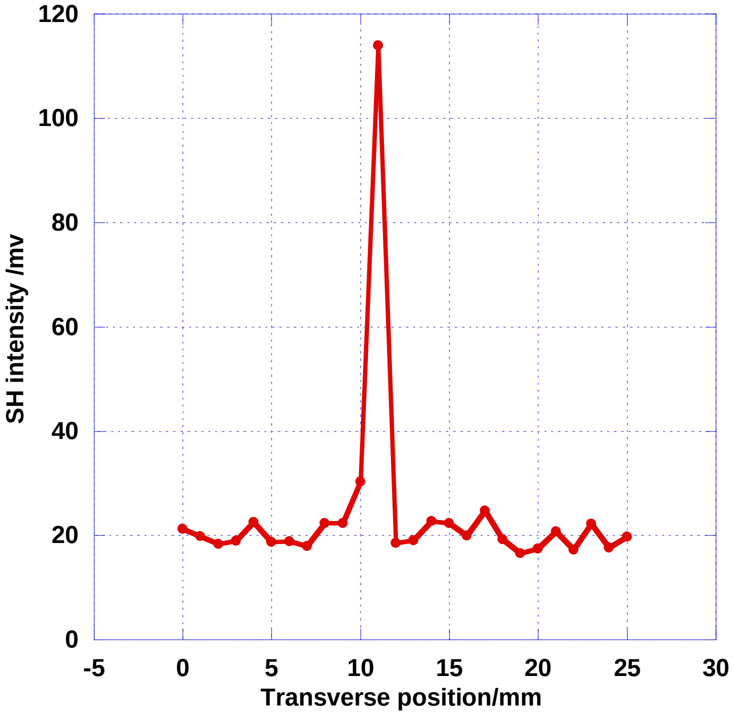

Figure 4. SHG of the poled SBN crystal after an additional thermal treatment

3.1.4. SHG in SBN crystal after several additional thermal treatments at different temperatures

Additionally, we do a series of thermal treatments to the SBN crystal, with different temperatures separately at 373K, 393K, 413K, and 433K, and then cool it to the room temperature. It is found that each time we do an additional thermal treatment at a higher temperature, the peak of the SHG that we got will become much weaker. When we heat the SBN crystal to the temperature at 433K, at which temperature we arrived while we did the poling, and cool it down, the SHG will become as weak as the original unpoled state before the poling treatment (figure 5).

This could be explained by the fact that the polarization decreases faster when increasing temperature in poled SBN than in non-poled SBN [12]. After each thermal treatment, the polarization in the poled SBN attenuates [15], and many domains get back closer to the state before the poling, that is the random anti-parallel state with a big number of small size domains. The higher the temperature of the thermal treatment is, the more the polarization in the poled SBN decreases, until the domains totally returns to the original unpoled state, thus the poled SBN crystal after several thermal treatments generates SHG similar to one unpoled SBN crystal.

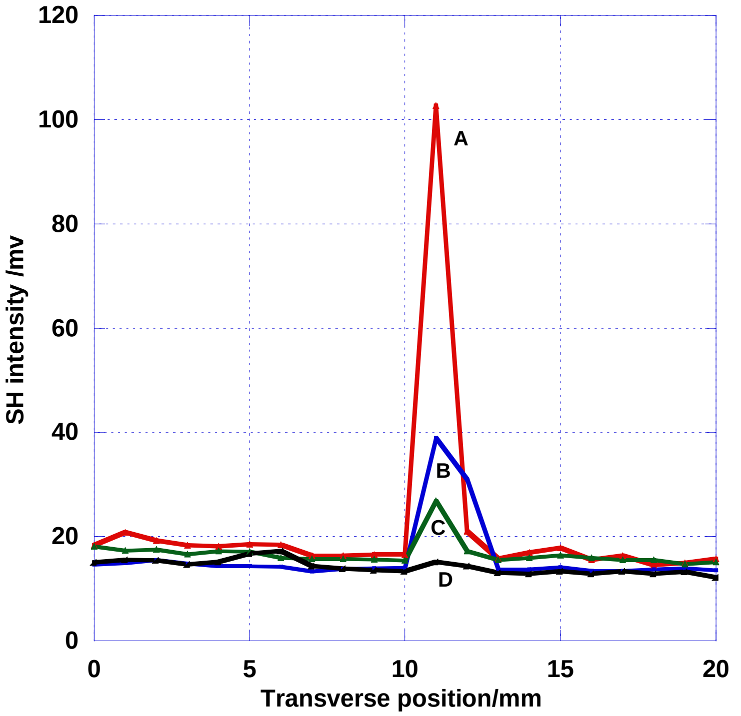

Figure 5. SHG in SBN crystal after several thermal treatments at different temperatures. (A) Thermal treatment at 373K. (B) 393K. (C) 413K. (D) 433K.

3.2. The speckle pattern of SHG emission in poled SBN crystal

We observed that the SHG emission in poled SBN crystal shows a speckle pattern, which means that apart from a SHG peak in the direction of the fundamental beam, there are also a great number of weaker peaks along the SHG line, the intersection of the SHG plane with the focal plane as shown in figure 2(b) (along the transverse X direction). This SHG speckle pattern might come from the random intensity interferences from the domains in the bulk of the SBN crystal or at the surfaces of the SBN crystal.

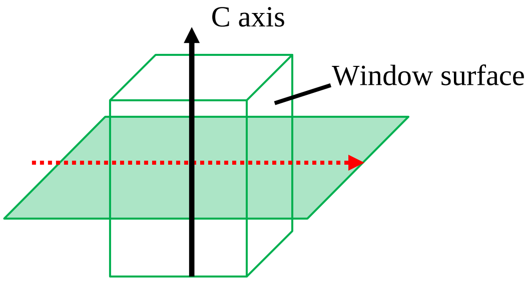

Figure 6. A schematic of the SBN crystal and its window surfaces.

As we polish the two window surfaces of SBN (figure 6), the SHG pattern changes, however, the intensity does not go down. Furthermore, during the polishing of the SBN crystal, due to the limitation of the polishing equipment at present, it is unavoidable to stick the SBN crystal to the polishing set with wax heated to a certain temperature around the Curie Point of the crystal. This heating could also influence the domain polarization in the SBN. Thus it is still not clear whether the SHG comes from domains at the surfaces or in the bulk. More experiments are under way to resolve this question.

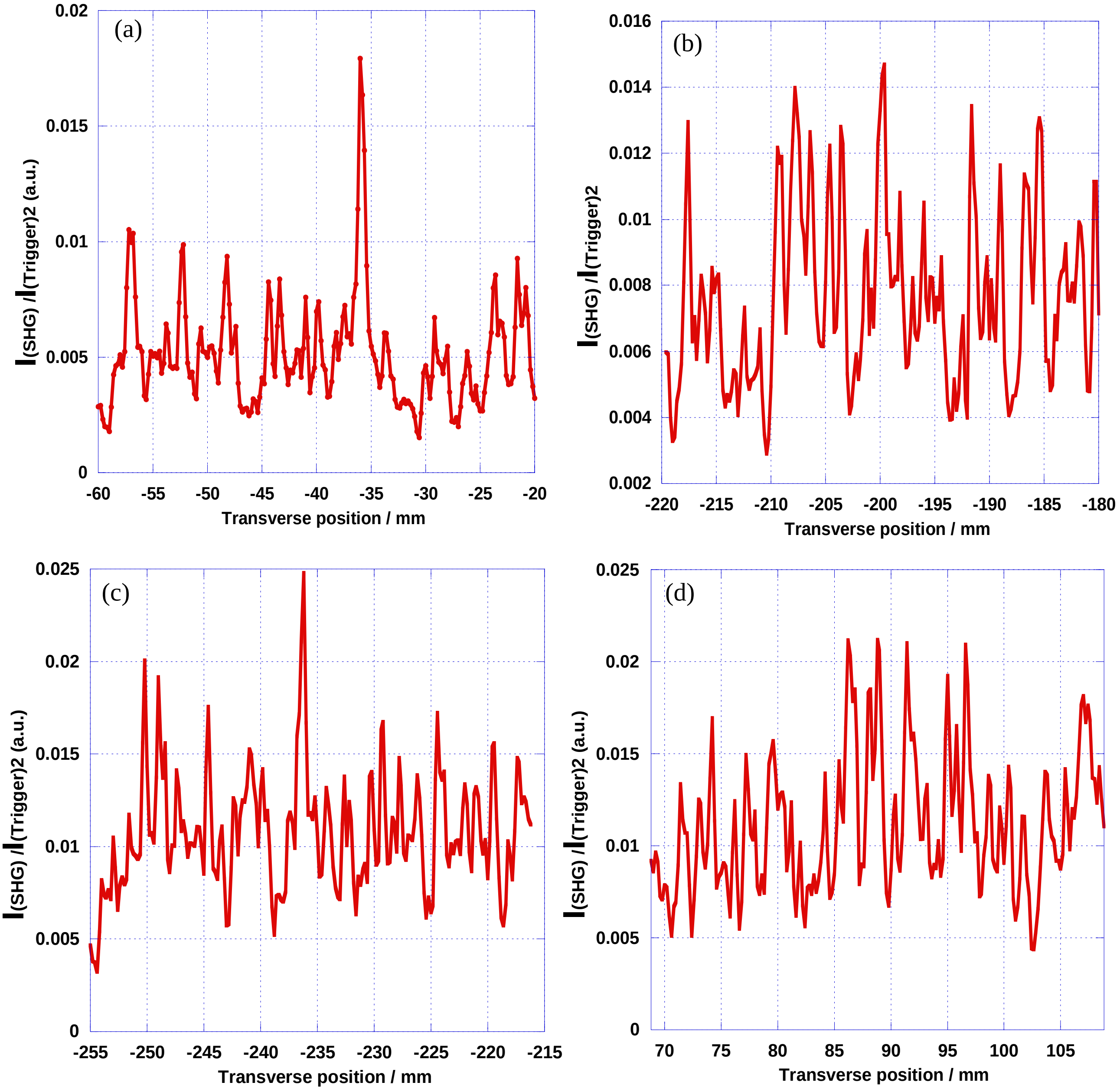

Figure 7. The SHG emission pattern of SBN crystal. (a) A poled SBN crystal. (b) A poled SBN crystal with two window surfaces polished. (c) A poled SBN crystal with two window surfaces polished for the second time. (d) A poled SBN crystal with two window surfaces polished for the third time.

3.3 The SEM imaging of the domains of the SBN crystal

The ferroelectric domains of the SBN crystal are observed under SEM (figure 8). It is found that after poling, most part of the SBN crystal is oriented in one direction, but there are still some anti-parallel domains with sizes around 0.5μm, which are left not well polarized due to the imperfect poling of the crystal. Because these anti-parallel domains are distributed randomly in the SBN crystal but at relatively big distances, we could expect a large number of small grating vectors for the phase matching condition in the c-plane.

Thus the SHG will be concentrated in the forward direction, according to the phase matching condition described in section 2. This explains the SHG pattern observed after the poling.

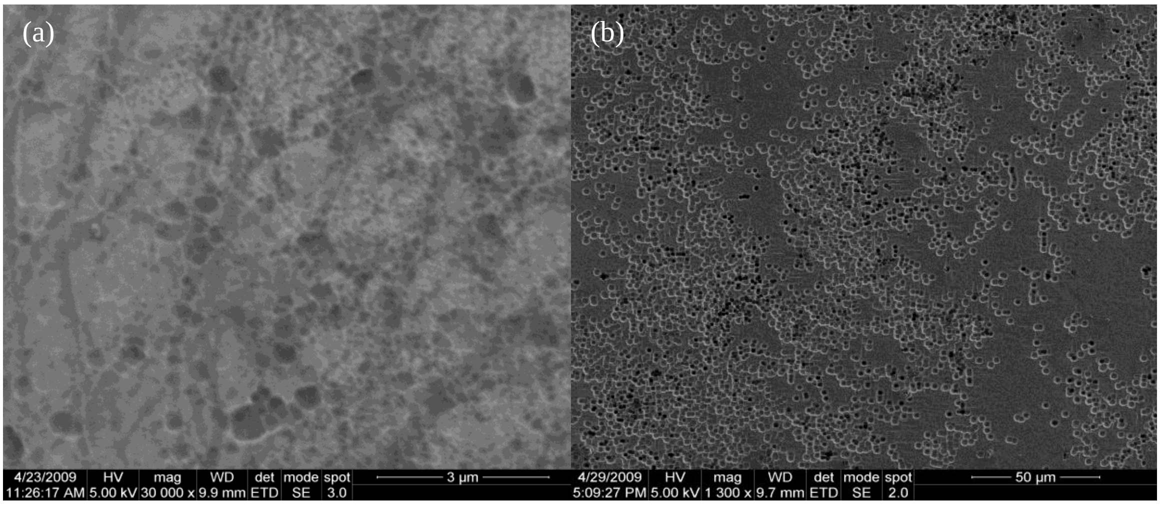

Figure 8. SBN structures observed under the SEM. (a) Poled sample, domain size is around 0.5µm. (b) Poled and annealed sample, domain size is around 5µm.

After a thermal treatment (annealing) to the poled sample, we could see that anti-parallel domains with much larger sizes around 5µm are distributed in the SBN crystal. If we consider the SHG from domains that are of dimensions similar or bigger than the coherent length in the crystal, the emission is directed largely in the propagation direction of the fundamental beam. A sum of the contributions from these randomly distributed domains will still give a stronger signal in the propagation direction of the fundamental beam. That could explain the stronger peak found after a poling and a thermal treatment shown in figure 4.

4. Conclusion

In conclusion, we investigated the SHG emission of unpoled, poled and thermal treated SBN crystals, and how the poling and thermal treatments affect the SHG emission of the crystal. A peak in SHG is observed in the direction of the fundamental beam. A SEM imaging of the random ferroelectric domains in the SBN crystal is shown to help to explain the frequency doubling phenomenon under those different treatments. Moreover, the speckle pattern of the SHG emission from a poled SBN crystal is studied.

Acknowledgements

I am indebted to ICFO- the institute of photonic science for the financial and environmental support of my master project. I am greatly thankful for the support and inspiration from my co-director Doctor Francisco Rodriguez and my director Professor Jordi Martorell all through my work for this master thesis. I am also thankful to all my group members for their encouragement and help during my work processes. The poling equipment from Professor Valerio Pruneri is also gratefully acknowledged. Finally, I would like to mention Mr. HuangXingxing who gives me suggestions about my presentations during the master courses and his considerate attending during my master period.

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