NONLINEAR WAVEMIXING
IN LITHIUM NIOBATE NANOWIRES

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(Dr. sc. ETH Zurich)

presented by
ANTON SERGEYEV
M.Sc. Friedrich Schiller University Jena
born on 23 November 1986
citizen of Kazakhstan

accepted on the recommendation of
Prof. Dr. Rachel Grange
Prof. Dr. Thomas Pertsch
Dr. Maria-Pilar Bernal

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<td>AFM</td>
<td>atomic force microscope</td>
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<tr>
<td>AlN</td>
<td>aluminium nitride</td>
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<tr>
<td>CCD</td>
<td>charge-coupled device</td>
</tr>
<tr>
<td>CdS</td>
<td>cadmium sulfide</td>
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<tr>
<td>CW</td>
<td>continuous wave</td>
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<tr>
<td>DAPI</td>
<td>4′,6-diamidino-2-phenylindole</td>
</tr>
<tr>
<td>EMCCD</td>
<td>electron-multiplying charge-coupled device</td>
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<tr>
<td>FDTD</td>
<td>finite-difference time-domain</td>
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<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
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<td>FH</td>
<td>fundamental-harmonic</td>
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<td>FIB</td>
<td>focused ion beam</td>
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<tr>
<td>GaAs</td>
<td>gallium arsenide</td>
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<tr>
<td>GaP</td>
<td>gallium phosphide</td>
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<tr>
<td>IBEE</td>
<td>ion-beam enhanced etching</td>
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<tr>
<td>ICP-IRE</td>
<td>inductive coupled plasma reactive ion etching</td>
</tr>
<tr>
<td>ITO</td>
<td>indium tin oxide</td>
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<tr>
<td>KNbO\textsubscript{3}</td>
<td>potassium niobate</td>
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<td>LiNbO\textsubscript{3}</td>
<td>lithium niobate</td>
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<td>NA</td>
<td>numerical aperture</td>
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<td>NaNbO\textsubscript{3}</td>
<td>sodium niobate</td>
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<td>NIR</td>
<td>near-infrared</td>
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<td>PbI\textsubscript{2}</td>
<td>lead iodide</td>
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<td>RIE</td>
<td>reactive ion etching</td>
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<td>SEM</td>
<td>scanning electron microscope</td>
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<td>SF</td>
<td>sum-frequency</td>
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<td>SFG</td>
<td>sum-frequency generation</td>
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<td>SH</td>
<td>second-harmonic</td>
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<td>SHG</td>
<td>second-harmonic generation</td>
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<tr>
<td>Si</td>
<td>silicon</td>
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<td>SnO$_2$</td>
<td>tin dioxide</td>
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<td>SNOM</td>
<td>scanning near-field optical microscope</td>
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<tr>
<td>SNR</td>
<td>signal-to-noise ratio</td>
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<tr>
<td>SPA</td>
<td>single-photon absorption</td>
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<tr>
<td>TE</td>
<td>transverse electric</td>
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<tr>
<td>TM</td>
<td>transverse magnetic</td>
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<tr>
<td>TEM</td>
<td>transverse electro-magnetic</td>
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<tr>
<td>TPA</td>
<td>two-photon absorption</td>
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<td>ZnO</td>
<td>zinc oxide</td>
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Abstract

Currently, there is a tendency to miniaturize the modern devices as it may allow to increase their efficiency and cut the material costs. Using nanomaterials as building blocks could offer one of the potential solution. Furthermore, nanomaterials with advanced optical properties can serve for developing future devices and applications.

Nanowires are one of the promising types of nanomaterials. Thanks to the nanoscale confinement in two dimensions and a macroscopic third dimension, nanowires may connect the nanoscopic and the macroscopic worlds. Thus, their characteristic shape allows to confine light in two dimensions and guide it in the third dimension. Moreover, the waveguiding ability gives rise to numerous optical phenomena in nanowires such as lasing and standing waves. In addition, nanowires that are made of non-centrosymmetric crystals can provide nonlinear optical effects that may further expand their applications and be used for imaging and providing nonlinear light.

Currently, the research is mostly focused on semiconductor nanowires such as gallium arsenide, silicon and gallium phosphide. However, semiconductors show absorption in the visible spectrum and the size of the semiconductor structures is limited by the existing fabrication methods. As a consequence, the application range of the semiconductor nanowires is limited and new materials should be investigated. Lithium niobate (LiNbO$_3$), which is known for its electro-optic and ferroelectric properties, is transparent in a wide spectral range and possesses relatively strong nonlinearity. Furthermore, there are many elaborated top-down and bottom-up approaches to fabricate LiNbO$_3$ nanowires.

In this PhD project, we investigate nonlinear wavemixing in LiNbO$_3$ nanowires that are fabricated with an ion-beam enhanced etching method. The nanowires that are fabricated with this method have a usual cross-section size of $500 \times 500 \text{ nm}^2$ and can be easily detached off the substrate and placed onto another one.

First, we demonstrate generation and waveguiding of the second-harmonic and
Abstract

sum-frequency signals in the LiNbO$_3$ nanowires. Further, we experimentally and theoretically show strategies to enhance the guided nonlinear signals by either using modal phase-matching or by adjusting the nanowire length to increase the efficiency of the nanowires for future devices and applications. We also employ a polymerization technique, which allows to study the behaviour of the guided nonlinear signal in the nanowires without using near-field measuring techniques and may complement the adjustment of the nanowire length to obtain a stronger guided signal. After all, we demonstrate with the use of the sum-frequency generation effect that the phase-matching regime can be tuned and switched by varying the polarization of the incident laser beams. In the end, we show that the LiNbO$_3$ nanowires can be applied for localized imaging applications and offer spatial and spectral selection, which is needed for avoiding bleaching in long-term biological studies.

The demonstrated results prove that LiNbO$_3$ nanowires can be used for achieving efficient nonlinear optical waveguides or sources at sub-micron dimensions. Furthermore, based on the demonstrated results, one may further develop novel nanowire-based applications such as spectrometers, optical parametric oscillators and terahertz light sources.


Im Moment fokussiert sich die Wissenschaft insbesondere auf Halbleiter-Nanodrähte wie Galliumarsenid, Silizium und Galliumphosphid, obwohl diese im sichtbaren Spektralbereich stark absorbieren und ihre Größe durch die momentanen Herstellungsprozesse limitiert ist. Lithiumniobat, das für die elektro-optische und ferrelektro-optische Eigenschaften bekannt ist, ist transparent in einem breiten Spektralbereich und verfügt über eine relativ starke Nichtlinearität. Außerdem gibt es viele gut bekannte und nutzbare „top-down“ und „bottom-up“ Herstellungsverfahren, um Lithiumniobatnanodrähte herzustellen.

Im Rahmen dieser Dissertation forschten wir an nichtlinearer Wellenmischung in Lithiumniobatnanodrähten, die durch „ion-beam enhanced etching“ hergestellt wurden. Die Nanodrähte, die durch dieses Verfahren hergestellt wurden, haben einen durchschnittlichen Querschnitt von $500 \times 500 \text{ nm}^2$ und können leicht vom Substrat getrennt und auf ein Anderes gebracht werden.

Zuerst zeigten wir die Erzeugung und das Leiten des Frequenzverdopplungssignales und des Summenfrequenz-Signales in Lithiumniobatnanodrähten. Anschließend
Abstrakt


Die demonstrierten Ergebnisse zeigen, dass Lithiumniobatnanodrahnen für den Submikrometerbereich als effiziente nichtlineare Wellenleiter angewandt werden können. Außerdem können diese Ergebnisse dabei helfen neue Nanodrahntanwendungen, wie Spektrometer, optische parametrische Oszillatoren und Terahertzquellen zu entwickeln.
Chapter 1

Introduction

1.1 Motivation

In 1965, Gordon Moore predicted that the number of transistors in a processor should double each two years [1]. This prediction, that is usually referred as Moore’s law, proved to be accurate for more than 50 years [2]. Despite this fact, this law is expected to have limitations. Increasing the number of transistors requires a decrease of their size that recently reached 14 nm [3]. Consequently, once transistors reach the size of a single atom, their size cannot shrink any longer.

As a consequence, new approaches in transistor fabrication and computing have to be developed. A combination of nanomaterials and photonics may offer one of the potential solutions, since the speed of light significantly exceeds the speed of electrons and using nanomaterials as building blocks would allow to miniaturize devices [4, 5]. Furthermore, since the size of the nanomaterials is comparable with the wavelength of light, the light-matter interaction is modified and shows new physical effects. Based on these new effects, photonics and nanomaterials may help to miniaturize the existing devices and develop new ones not only in the information technology field [6, 7] but also in other fields such as imaging [8, 9], medicine [10, 11] and energy harvesting [12, 13].

One of the promising types of nanomaterials are nanowires. Due to the two-dimensional confinement and the third macroscopic dimension, nanowires differ from other types of nanomaterials and make possible waveguiding of light. Based on this guiding ability, nanowires can be applied for various applications. For example,
waveguiding process in semiconductor nanowires allows to use them as nanoscale lasers \([14, 15, 16]\), light-emitting diodes \([17, 18]\), interconnectors \([19]\) and detectors \([20, 21, 22]\). Furthermore, metallic nanowires guide light in terms of surface plasmon-polaritons \([23]\) and they can be used for optical signal processing \([24, 25]\) and interconnecting \([26]\).

However, many semiconductor materials and metals absorb light in the visible range \([27, 28]\). As a result, semiconductor and metallic nanowires show limitations and cannot guide electrical field over a large range. Consequently, one should look for other materials that would allow to overcome this limitation. Lithium niobate \((\text{LiNbO}_3)\) crystal could be one of the potential materials since it is transparent in a wide spectral range \((0.33 \mu m - 5.5 \mu m)\) \([29]\).

Furthermore, the \text{LiNbO}_3 crystal also shows a relatively strong nonlinear properties \([30]\) and can be used for nonlinear wavemixing such as second-harmonic generation (SHG) and sum-frequency generation (SFG), which could provide even more applications. For example, nanowires that generate and guide the second-harmonic (SH) signal can be used for localized excitation and imaging applications \([31]\). In turn, generation and waveguiding of the sum-frequency (SF) signal in nanowires, may allow to use them for all-optical switching \([32]\) and, thus, apply them in the role of logical elements. Furthermore, nonlinear nanowires can be also used in lab-on-chip applications to provide coherent light in the spectral range that usually cannot be obtained from the existing lasers. As a conclusion, nonlinear wavemixing effects can give a significant contribution to the development of the nanowire applications and miniaturization of the existing devices.

### 1.2 Challenges and goals

One of the disadvantages of the nonlinear wavemixing effects is the fact that they are volume-dependent effects and their efficiency scales down with volume of the material \([30]\). As a consequence, these effects are expected to be weak in nanostructures including nanowires. Thus, the nonlinear wavemixing effects in nanowires should
be studied and one should find approaches to enhance efficiency of the nonlinear wavemixing effects.

The fundamental goal of this work is to obtain generation and waveguiding of nonlinear wavemixing signals in LiNbO$_3$ nanowires. Besides, the nonlinear wavemixing effects should be investigated and ways of enhancing the nonlinear response of the nanowires should be proposed. Furthermore, we should demonstrate potential applications that the LiNbO$_3$ nanowires can be used for.

In this dissertation, we use LiNbO$_3$ nanowires that are fabricated through a top-down fabrication process called ion-beam enhanced etching (IBEE) [33]. Using individual LiNbO$_3$ nanowires$^1$, we demonstrate and study generation and waveguiding of the SH and SF signals. Further, we demonstrate phase-matching process and, thus, enhance the guided SH and SF signals. We also show optimization of the SHG signal by adjusting the nanowire length and study the behaviour of the SHG signal along the nanowire by photo-polymerization technique. After all, we show that the LiNbO$_3$ nanowires can be used for localized imaging by demonstrating excitation of the fluorescent material with the guided SH signal.

$^1$In general, the cross-section of the studied nanowires is around 500×500 nm$^2$ and their length is up to 50 µm. These dimensions do not fit the strict definition of nanomaterials, which requires a nanostructure to have at least one dimension below 100 nm [34]. Nevertheless, in literature, a term “nano” is used for sub-micron structures [31, 35, 36, 37, 38, 39]. That is why, we also call our structures nanowires in this dissertation.
Chapter 2

Theoretical background and state-of-the-art

2.1 Introduction

In this chapter, we provide theoretical background for waveguiding and nonlinear wavemixing processes. Furthermore, we review the state-of-the-art of these phenomena in nanowires and discuss ways of enhancing efficiency of the nonlinear wavemixing effects. After all, we review the existing methods of synthesizing and fabricating lithium niobate (LiNbO$_3$) nanowires.

2.2 Waveguiding

The waveguiding effect allows to confine light in medium and propagate it over a certain distance. To guide light, several conditions have to be fulfilled. The first condition requires that total internal reflection has to take place in order to trap a wave inside the guiding material (Figure 2.1). For this purpose, the incident light should fall onto the interface of two materials (with different refractive indices) with an angle that is below a critical angle. The critical angle $\theta_C$ is defined as follows:

$$\theta_C = \arcsin \left( \frac{n_2}{n_1} \right)$$ (2.1)

where $n_1$ and $n_2$ are refractive indices of the trapping medium and the surrounding medium, respectively.
2.2. Waveguiding

\textbf{Figure 2.1: Total internal reflection.} $\theta_C$ is the critical incidence angle, $\theta$ is the incidence angle, $n_1$ is the refractive index of the trapping media and $n_2$ is the refractive index of the surrounding media.

The second condition requires that the initial wave has to be reproduced after two reflections (Figure 2.2). Otherwise, destructive interference takes place and the light intensity goes down.

\textbf{Figure 2.2: The twice-reflected wave has to be in phase with the original wave, otherwise destructive interference takes place. Reproduced from Ref. [40]}

As a result, there is a set of discretized angles at which an incident wave is guided. Each angle from this set corresponds to a certain waveguide mode. Depending on the angle of incidence, each waveguide mode has a particular phase velocity and, consequently, a particular effective refractive index. Furthermore, each waveguide mode also has a specific pattern of the electromagnetic field, which is maintained while propagating in a waveguide.

Depending on the components of the electric and magnetic fields, waveguide
modes are classified into transverse electric (TE), transverse magnetic (TM) and transverse electromagnetic (TEM). Thus, in the propagation direction, TE modes do not have any electric field component, TM modes do not have any magnetic field component and TEM modes have both electric and magnetic components.

Furthermore, modes are also classified by orders $m$ and $n$. The orders show the number of lobes $m + 1$ and $n + 1$ that appear in the horizontal and vertical direction of a particular mode, respectively. Thus, transverse electric mode TE00 (Figure 2.3a), which is usually referred as fundamental mode, shows only one lobe in both directions, whereas electric mode TE10 shows two lobes in the horizontal direction and one lobe in the vertical direction (Figure 2.3b).

Figure 2.3: TE00 (a) and TE10 (b) modes calculated in a waveguide with width of 654 nm and height of 512 nm at the wavelength of 500 nm.

The waveguiding process is realized in waveguides of various structures and materials. This process is demonstrated in slot waveguides [41, 42, 43], ridge waveguides [44, 45, 46] and fibers [47, 48, 49]. Since waveguides confine light, it allows to enhance light-matter interaction. Thanks to this fact, waveguides and fibers are widely applied for filtering [50], sensing [43, 51, 52] and modulating [41, 53, 54] applications.

Furthermore, the waveguiding process is also maintained in subwavelength waveguides and nanowires [5, 55, 56]. Thus, waveguiding has been demonstrated in numerous semiconductor nanostructures such as silicon (Si) nanowaveguides [57, 58],
2.2. Waveguiding
gallium phosphide (GaP) nanopillars [35, 59, 60], lead iodide (PbI₂) nanowires [15],
cadmium sulfide (CdS) nanowires [32], zinc oxide (ZnO) nanowires [61, 62] and tin
dioxide (SnO₂) nanoribbons [19] and nanowires [63]. Besides, waveguiding is also
realized in nanowires of other types of materials such as potassium niobate (KNbO₃)
[31, 36], LiNbO₃ [36], sodium niobate (NaNbO₃) [36] and SU-8 polymer [64].

Depending on the structure and material, nanowires can be used for various
applications. For example, semiconductor nanowires demonstrate lasing and can
be used as nanoscale sources of laser irradiation [14, 15, 62, 65]. Furthermore,
semiconductor nanowires also can be used for solar cells applications since the guided
light has a higher probability to be absorbed [13]. Besides, the guiding process in
a single semiconductor nanowire can be controlled and switched by external light
source [66]. Thus, nanowires can be used for developing optical logical elements [66].

**Figure 2.4:** Waveguide modes have its electric field in terms of evanescent field
outside the waveguide.

Moreover, nanowires that allow efficient waveguiding can be used for sensing
applications. Due to the nanoscale size of nanowires, large part of the guided modes
is located outside the nanowire in terms of evanescent field [61] as shown in Figure
2.4. Thus, nanowire can be used for analysis of chemical substances [5, 22] or
for localized imaging by exciting fluorescent material with evanescent field [39, 49,
67]. Since each guided mode has different fractions of evanescent field, the above-
discussed sensing application can be further optimized by switching guided modes
[61]. It is demonstrated that guided modes can be switched either by varying the
coup ling conditions [59, 61] or by structuring waveguides [37, 68].

Furthermore, localized imaging applications also can be realized by the guided signal at the nanowire output [63, 69]. Due to a large distribution angle [61, 62, 64], the guided light excites the fluorescent material only in the vicinity of the output facet of a nanowire. The position of the nanowire can be manipulated by a laser beam with optical tweezers and, thus, a sample can be scanned [31, 64, 70, 71]. Moreover, nanowire can be used not only for delivering light into a sample but also for collecting the signal from the sample and guiding it back for analysis [63].

As a conclusion, thanks to the waveguiding and linear optical effects, nanowires show a potential in developing a large range of applications and devices.

2.3 Nonlinear wavemixing

As mentioned in the introduction, for further development of nanowire applications, nonlinear wavemixing effects such as second-harmonic generation (SHG), sum-frequency generation (SFG) and difference-frequency generation (DFG) can be applied [55, 72].

![Figure 2.5: Localized imaging with a nanowire. The NIR laser beam manipulates a nanowire and couples some light into it. The guided NIR light generates the SH signal, which locally excites fluorescent material at the nanowire output.](image)

For example, by using the SHG process, one may expand the localized imaging
2.3. Nonlinear wavemixing

applications [31, 73] as demonstrated in Figure 2.5. In this case, the guided second-harmonic (SH) light can be used for exciting the fluorescent material and a near-infrared (NIR) laser can be used to manipulate the nanowire position. As a result, the fluorescent material will be neither excited, nor bleached by the laser beam but is only excited by the guided SH light. Similarly, the SHG process can be used for nanowire microscopy applications [31]. In this application, the sample is scanned by an optically-trapped nanowire and by controlling the transmitted SH light, one can deduce information about the sample topography. Furthermore, based on DFG [32] and SFG [74] effects, nanowires can be used as nonlinear light sources and be further applied for lab-on-chip applications.

Nonlinear wavemixing is a nonlinear optical effect at which several photons interact and photons with different frequencies are generated. Nonlinear wavemixing effects are classified according to the order of the involved in the process susceptibility tensor $\chi$.

For example, the second-order nonlinear effects comprise SHG, SFG and DFG and the third-order nonlinear effects comprise third-harmonic generation and four-wave mixing.

![Energy diagrams of the second-harmonic generation (a) and the sum-frequency generation (b) processes.](image)

In this PhD project, the study is focused on the SHG and the SFG effects. The SHG effect converts two photons of the same frequency $\omega$ (usually referred as fundamental-harmonic (FH)) into a single photon with the doubled frequency $2\omega$
(Figure 2.6a). In turn, the SFG effect converts two photons with different frequencies $\omega_1$ and $\omega_2$ into a single photon with the frequency that is the sum of frequencies of the incoming photons $\omega_1 + \omega_2$ (Figure 2.6b).

Both effects show dependence on the incident electric field. The polarization density of the SHG response $\vec{P}(2\omega)$ depends quadratically on the incident electric field (Equation 2.2), whereas the polarization density of the SFG response $\vec{P}(\omega_1 + \omega_2)$ depends linearly on the intensities of the incident electric fields (Equation 2.3).

$$\vec{P}(2\omega) = \epsilon_0 \cdot \chi^{(2)}(2\omega, \omega) \cdot \vec{E}^2(\omega) \quad \text{(2.2)}$$

$$\vec{P}(\omega_1 + \omega_2) = \epsilon_0 \cdot \chi^{(2)}(\omega_1 + \omega_2, \omega_1, \omega_2) \cdot \vec{E}(\omega_1) \cdot \vec{E}(\omega_2), \quad \text{(2.3)}$$

where $\vec{P}(2\omega)$ is the polarization density at the SH frequency, $\vec{P}(\omega_1 + \omega_2)$ is the polarization density at the SFG frequency, $\epsilon_0$ is the vacuum permittivity, $\vec{E}(\omega)$ is the incident electric field at frequency $\omega$, $\chi^{(2)}$ is the second-order susceptibility tensor.

The components of the susceptibility tensor $\chi^{(2)}$ show contribution of the $x$-, $y$-, $z$-components of the pump electric field to the $x$-, $y$-, $z$-components of the generated electric field. Generally, the susceptibility tensor $\chi^{(2)}$ has 27 components, but their number can be reduced if any crystal symmetry is applied. Thus, applying Kleinmann symmetry, which assumes lossless medium, the number of the susceptibility tensor can be reduced down to 18 components and the contracted susceptibility tensor $\chi^{(2)}$ is usually denoted as $d$ [30]. In this case, Equation 2.2 for the SHG process is modified as follows:

$$\begin{pmatrix} P_x(2\omega) \\ P_y(2\omega) \\ P_z(2\omega) \end{pmatrix} = 2\epsilon_0 \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix} \begin{pmatrix} E_x^2(\omega) \\ E_y^2(\omega) \\ E_z^2(\omega) \\ 2E_x(\omega) \cdot E_y(\omega) \\ 2E_x(\omega) \cdot E_z(\omega) \\ 2E_y(\omega) \cdot E_z(\omega) \end{pmatrix}. \quad \text{(2.4)}$$
For the second-order nonlinear optical effects to take place, the crystal structure of the material has to be non-centrosymmetric. As a result, the second-order nonlinear effects SHG and SFG can only be observed in bulk in a limited number of materials or at a break of symmetry of the crystal structure [30, 75].

In Table 2.1, we show several properties (bandgap wavelength, second-order susceptibility tensor, bio-compatibility) of materials that are used for waveguiding. Silicon is a widely used material in optics but has a centrosymmetric crystal structure. As a consequence, bulk silicon structures cannot be used for generating second-harmonic or sum-frequency signals and are usually applied for higher order nonlinear effects as third-harmonic generation [76] and four-wave mixing [38, 58, 77, 78]. Numerous semiconductor materials including gallium arsenide (GaAs), ZnO, CdS and GaP are non-centrosymmetric and show strong nonlinearity. As a result, SHG and SFG studies have been performed in various semiconductor structures, such as nanoneedles [79], nanowires [32, 74, 80, 81] and nanopillars [35, 59, 60]. However, many semiconductor materials absorb in the visible spectral range and, consequently, nanowires made of these materials cannot be used for efficient generation and waveguiding of the nonlinear signals. According to our knowledge, up to now, generation and waveguiding of the SH signal in semiconductor nanostructures was only demonstrated in GaP nanopillars [35, 59, 60], aluminium nitride (AlN) nanowaveguides [82] and CdS nanowires [32]. Furthermore, free-standing semiconductor nanostructures are limited in size due to the fabrication process [83, 84, 85] and they show biotoxicity and, thus, cannot be applied for biological applications [86]. Consequently, the application range of the semiconductor nanostructures is limited.

Metal-oxide materials such as LiNbO$_3$, KNbO$_3$ and NaNbO$_3$ can be a good alternative to the semiconductor materials. Even though oxide materials show weaker nonlinear properties than some semiconductor materials, they are transparent in a broader spectral range covering visible and infrared spectra. As a consequence, generation and waveguiding of the SH signal has already been shown in LiNbO$_3$ micrometer-scale waveguides [90, 91]. In addition, LiNbO$_3$ nanoparticles are proved to be non-toxic [86] and, thus, they can be used for biological applications. Further-
Chapter 2. Theoretical background and state-of-the-art

Table 2.1: Properties of several semiconductor and oxide materials that are used for generating and waveguiding of the SH signal.

<table>
<thead>
<tr>
<th>Material</th>
<th>Bandgap wavelength, nm</th>
<th>The largest component of the second-order susceptibility tensor, pm/V</th>
<th>Biocompatibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>1107.1</td>
<td>0</td>
<td>Unknown</td>
</tr>
<tr>
<td>GaAs</td>
<td>870.79</td>
<td>370 [30]</td>
<td>No [86]</td>
</tr>
<tr>
<td>ZnO</td>
<td>375.76</td>
<td>5.5 [87]</td>
<td>No [86]</td>
</tr>
<tr>
<td>GaP</td>
<td>548.67</td>
<td>159 [88]</td>
<td>Unknown</td>
</tr>
<tr>
<td>CdS</td>
<td>512.4</td>
<td>78 [30]</td>
<td>Unknown</td>
</tr>
<tr>
<td>KNbO₃</td>
<td>376.76</td>
<td>22.3 [88]</td>
<td>Yes [86]</td>
</tr>
<tr>
<td>LiNbO₃</td>
<td>310</td>
<td>-34.4 [89]</td>
<td>Yes [86]</td>
</tr>
</tbody>
</table>

more, generation and waveguiding of the SH signal has also been demonstrated in chemically synthesized LiNbO₃, KNbO₃ and NaNbO₃ nanowires [31, 36]. However, the existing chemical synthesis methods do not give full control over such parameters of nanowires as cross-section size and crystal structure, which are crucial for the nonlinear response of nanowires [36, 73, 92, 93, 94]. As a result, there is a need in developing top-down fabricated nanowaveguides and nanowires that can be used for nonlinear wavemixing.

2.4 Phase-matching

Efficiency of the nonlinear wavemixing effects quadratically scales down with the volume of the crystalline material [30]. As a result, the generated power of the SH and SF signals is initially low in nanoscale structures and one should find strategies to enhance the efficiency of these processes.
To enhance the nonlinear signal, one can use metallic structures, which locally enhance the electric field with plasmonic resonances [95, 96, 97]. Furthermore, one can also enhance coupling efficiency of the laser light into nanowires by using plasmonic antennas [98] or shaping the input facet [32, 99].

Another way to enhance the efficiency of a nonlinear wavemixing process is to take into account the phase-matching process. Phase-matching is an important aspect of nonlinear wavemixing and influences its overall efficiency. Because of the material dispersion, refractive indices vary with frequency. As a result, interacting waves propagate with different phase-velocities and the waves that are generated along the propagation direction in a crystal may interfere destructively. As a consequence, overall nonlinear wavemixing response may be weak at the output of the material. This effect is called phase-mismatching and is characterized by a wavevector mismatch $\Delta k$. The wavevector mismatches for the SHG and SFG processes are defined as:

$$\Delta k_{\text{SHG}} = 2 \cdot k(\omega) - k(2\omega)$$  \hspace{1cm} (2.5)

$$\Delta k_{\text{SFG}} = k(\omega_1) + k(\omega_2) - k(\omega_{\text{SFG}})$$  \hspace{1cm} (2.6)

where $\Delta k_{\text{SHG}}$ is the wavevector mismatch for the SHG process, $\Delta k_{\text{SFG}}$ is the wavevector mismatch for the SFG process, $k(\omega)$ is the wavevector of an interacting wave with frequency $\omega$.

To demonstrate influence of the wavevector mismatch, we plot the behaviour of the SH power in the cases of phase-matching ($\Delta k = 0$, blue solid line) and phase-mismatching ($\Delta k \neq 0$, red dashed line) in Figure 2.7. In the case of phase-matching, the SH power constantly grows, whereas, in the case of phase-mismatching, the SH power oscillates periodically along the propagation direction [30]. The oscillation period is equal to the coherence length $L_{\text{COH}}$ that is found as follows:

$$L_{\text{COH}} = \frac{2\pi}{\Delta k}.$$  \hspace{1cm} (2.7)
Figure 2.7: The calculated SH power as a function of the propagation distance in the cases of phase-matching (blue solid line) and phase-mismatching (red dashed line).

The overall intensity of the SHG and SFG signals are defined as follows:

\[ I(2\omega) = \eta \cdot I^2(\omega) \cdot L^2 \cdot \text{sinc}^2\left(\frac{\Delta k \cdot L}{2}\right) \]  

(2.8)

\[ I(\omega_1 + \omega_2) = \eta \cdot I(\omega_1) \cdot I(\omega_2) \cdot L^2 \cdot \text{sinc}^2\left(\frac{\Delta k \cdot L}{2}\right), \]  

(2.9)

where \( \eta \) is the conversion efficiency, \( I(\omega) \) is intensity at frequency \( \omega \) and \( L \) is the length of the crystal.

In Figure 2.8, we plot the SH intensity versus the pump wavelength around the phase-matching wavelength. The behaviour follows the shape of a sinc-function with the center at the phase-matching wavelength of 846 nm.

To achieve phase-matching, there have been several techniques developed such as angle tuning [100], temperature heating [101] and periodic poling of crystals [102, 103, 104].

Angle tuning is applied in birefringent crystals whose refractive index depends on the propagation direction [30]. Thus, this method allows to find the propagation direction in the crystal at which the pump waves and the to-be-generated waves
2.4. Phase-matching

The behavior follows the shape of a sinc-function with the center at the phase-matching wavelength of 846 nm.

Temperature tuning can be applied in a crystal whose refractive index strongly depends on temperature [30]. By heating such crystal, its refractive indices may be shifted and the wavevectors of the interactive waves may be equalized. Thus, the crystal should be heated to different temperatures to obtain phase-matched signal at different frequencies.

Periodic poling of a crystal means periodic structuring of a crystal with the period equal to a half of the coherence length $L_{\text{COH}}/2$ along the propagating direction [30]. Within the first half of the coherence length, the generated signal interferes constructively and the periodic poling shifts the phase-mismatch vector and prevents destructive interference. As a result, the generated signal constantly grows as shown in Figure 2.9. This method is referred as quasi-phase-matching [105, 106, 107].

In waveguides, one may also obtain modal phase-matching [108, 109, 110]. Modal phase-matching is made possible by the fact that light in waveguides propagates...
in terms of modes. Each guided mode has a distinctive effective refractive index, which also varies with wavelength \[111\]. As a result, the wavevector mismatch $\Delta k$ of the modes at the interacting wavelengths may be equal to zero and, consequently, phase-matching may be achieved. Besides the wavevector mismatch, efficiency of the nonlinear wave mixing effects depends on the overlap integral of the interacting modes. Thus, for an efficient process, one should phase-match the modes that provide the largest overlap integral \[112\].

Modal phase-matching of the SH signal was previously demonstrated in LiNbO$_3$ micrometer-scale waveguides \[90, 113\]. Phase-matching of the nonlinear wave mixing processes in submicrometer nanowires is still to be achieved. Moreover, since the single-mode regime in LiNbO$_3$ nanowires is expected to start only in cross-sections below $200 \times 200 \text{ nm}^2$ (at the wavelength of 800 nm), submicrometer waveguides provide a multi-mode regime. As a consequence, multiple phase-matching effects with different modes are expected to be obtained.
2.5 Chemical synthesis and top-down fabrication of LiNbO$_3$ nanowires

The LiNbO$_3$ nanowires can be obtained through either bottom-up or top-down processes. Below, we give an overview over the possible synthesis and fabrication methods.

2.5.1 Bottom-up chemical synthesis methods

Unlike the synthesis of the semiconductor nanowires [83, 114, 115], there are only two bottom-up techniques for synthesizing LiNbO$_3$ nanowires in literature. The LiNbO$_3$ nanowires can be fabricated either through the molten sol-gel method [36, 92, 94] or hydrothermal method [36, 73, 93].

In the molten sol-gel method, the oxides of the LiNbO$_3$ constituents are used. The mixture of the oxides is mixed and heated up above the melting temperature. After the oxides are melted and further mixed, LiNbO$_3$ starts nucleating and nanowires can grow. The molten sol-gel method is also used for synthesizing other perovskite nanowires such as KNbO$_3$ and NaNbO$_3$ nanowires [36].

In the hydrothermal method, temperature and pressure are used to synthesize nanowires. For this goal, powders of lithium hydroxide and niobium pentoxide are mixed in distilled water. When heating up the mixture and applying pressure, LiNbO$_3$ starts to crystallize and precipitate. This process allows to synthesize nanoparticles of various shapes including nanowires, nanoparticles and nanocubes [36]. The obtained structures depend on the concentration, fill-factor, time, oven temperature and applied pressure [36, 73].

The molten sol-gel method and the hydrothermal methods are used to synthesize LiNbO$_3$ nanowires with an aspect ratio up to 10 and 14, respectively [73, 93]. Furthermore, the synthesized LiNbO$_3$ nanowires are shown to generate [73, 93] and guide the SH [36].

Nevertheless, the described synthesis methods do not give full control over such
parameters of the nanowires as cross-section size and crystal structure, which are crucial for the nonlinear response of the nanowires.

2.5.2 Top-down fabrication methods

A wider range of top-down methods have been developed for fabricating LiNbO$_3$ waveguides and nanowires. There are several fabrication methods that allow submillimeter buried and ridge waveguides. Buried waveguides are obtained by titanium indiffusion [116], proton exchange [117, 118] and laser writing [101, 119]. Ridge waveguides are obtained by fluorine-containing gases plasma etching [120] and mechanical milling [121, 122]. To fabricate micro- and nanowaveguides, one can find in literature such methods as focused ion beam (FIB) milling [123], inductive coupled plasma reactive ion etching (ICP-IRE) [91] and ion-beam enhanced etching (IBEE) [33, 113].

The FIB milling is a maskless fabrication method [123]. Instead of masks, it only uses a focused beam of highly energetic ions, which removes the material off the substrate. This method offers high precision and is used to fabricate nanowires with the width down to 700 nm [123]. However, this method has several limits. It produces nanowires with inclined walls and damages the crystal structure of the waveguides [123]. In addition, this method is relatively slow and, as a result, can only be used for fabricating only individual nanowires.

To fabricate multiple nanowires simultaneously, ICP-RIE [91] and IBEE [33, 113] methods are preferred. Both methods use protective masks, which are fabricated on the surface of a LiNbO$_3$ membrane and define widths and positions of the to-be-fabricated waveguides. In the ICP-RIE method, argon-ion plasma is used to etch the open areas. In the IBEE method, argon-ion beam irradiation is used to amorphize open areas, which lose their chemical resistivity and are removed with wet etching in hydrofluoric acid. In both methods, the mask-protected areas of the LiNbO$_3$ stay undamaged and form waveguides. The thickness of the membrane defines the height of the nanowires.
2.5. Chemical synthesis and top-down fabrication of LiNbO$_3$ nanowires

All the above discussed top-down fabrication methods use a thin film of a LiNbO$_3$ crystal on an insulator substrate because these methods damage the LiNbO$_3$ only at surface. In addition, the IBEE method allows using pure LiNbO$_3$ wafers for fabrication if it is complemented with helium-ion beam irradiation. Since the helium ions have lighter mass, they penetrate into the LiNbO$_3$ wafer and damage it at a certain depth, thus forming a buried layer [124, 125, 126]. The penetration depth depends on the energy of the ions and defines the height of the waveguides [33]. In this PhD project, we used nanowires fabricated with this method and we describe this method in more details in Chapter 3.

The ICP-IRE method was used to fabricate waveguides with the cross-section down to 700 nm $\times$ 4 $\mu$m [127]. In turn, the IBEE method was used to fabricate nanowires with the cross-section down to $50 \times 50$ nm$^2$ [33]. However, the thinnest nanowire that was fabricated by the IBEE method and optically tested had the cross-section of $265 \times 287$ nm$^2$ [33].
Chapter 3

Fabrication of the LiNbO$_3$ nanowires and sample preparation

3.1 Introduction

In this chapter, we discuss sample preparation for the nonlinear wavemixing measurements. First, we describe the fabrication flow of the studied lithium niobate (LiNbO$_3$) nanowires. Second, we explain the elaborated techniques for bringing the nanowires onto glass substrates for optical and scanning electron microscope (SEM) studies.

3.2 Fabrication process of the LiNbO$_3$ nanowires

The LiNbO$_3$ nanowires, that are studied in this PhD project, are fabricated with a top-down fabrication method that is called Ion Beam Enhanced Etching (IBEE) in Friedrich Schiller University in Jena, Germany [33]. This method uses ion irradiation to damage the LiNbO$_3$ crystal structure and increase its etching speed. The regions to be irradiated are defined by a mask. In Figure 3.1, we show the main steps of the fabrication flow.
3.2. Fabrication process of the LiNbO$_3$ nanowires

**Figure 3.1:** Fabrication flow of the LiNbO$_3$ nanowires: (a) LiNbO$_3$ wafer, (b) deposition of silica, chromium, and electron-beam resist, (c) electron-beam lithography (d) reactive ion etching of chromium and silica, (e) argon-ion irradiation, (f) helium-ion irradiation and (g) LiNbO$_3$ membrane with nanowires after wet etching. See also the detailed description in the text.
Chapter 3. Fabrication of the LiNbO$_3$ nanowires and sample preparation

Initially, an x-cut LiNbO$_3$ wafer (Figure 3.1a) is covered with layers of fused silica (1000 nm), chromium (80 nm) and electron-beam resist (300 nm, ZEP520A) (Figure 3.1b). These layers are used for fabricating a mask. First, the mask is written into the electron-beam resist with electron-beam lithography (Figure 3.1c). Further, the mask is transferred into the chromium and silica layers with reactive ion etching (Figure 3.1d). The mask defines width, length and position of the to-be-fabricated nanowires.

After the mask is prepared, the LiNbO$_3$ wafer is treated with a series of argon-ion irradiation (Figure 3.1e). The argon-ion irradiation amorphizes the unmasked regions of the wafer at surface and in depth.

After the mask is removed, the wafer is further irradiated with helium ions (Figure 3.1f). Due to a small weight of the helium ions, they penetrate into the crystal, damage the wafer only at certain depth and, thus, create a buried layer of the amorphized LiNbO$_3$ crystal [124]. It is designed the way that the amorphized buried layer connects with the regions damaged by the argon-ion irradiation.

The penetration depth of the argon and helium ions depends on the kinetic energy. A series of argon-ion irradiations are performed at the following energies: 600 keV with the fluence of $7.2 \cdot 10^{14}$ cm$^{-2}$ and 350, 150, 60 keV with the fluence of $1.38 \cdot 10^{14}$ cm$^{-2}$. The helium ion irradiation is performed at the kinetic energy of 285 keV and the fluence of $5 \cdot 10^{16}$ cm$^{-2}$ [33].

At last, the LiNbO$_3$ wafer is chemically etched in hydrofluoric acid. The LiNbO$_3$ crystal has a strong chemical resistivity. However, the amorphized regions lose this resistivity and their chemical etching is accelerated. Thus, wet etching removes the amorphized regions and the LiNbO$_3$ nanowires are formed (Figure 3.1g). The nanowires are fabricated to be free-standing on the substrate and they are only attached at their ends to the wafer. In Figure 3.2, we show an SEM picture of a LiNbO$_3$ wafer with fabricated nanowires.

The studied nanowires usually have a typical length of 50 $\mu$m and the cross-section of around $500 \times 500$ nm$^2$. However, this method has been reported to fabricate nanowire with the width down to 50 nm [33]. Depending on the crystal
3.2. Fabrication process of the LiNbO$_3$ nanowires

structure of the wafer, nanowires with different crystal structure can be obtained. The nanowires that were studied in this project have the $y$-axis of the crystal structure along the nanowire length and the $x$- and $z$-axes in the nanowire cross-section. Thus, depending on the way nanowires are deposited onto the experimental substrate, the nanowire may have two different crystal orientations as shown in Figure 3.3.

![Figure 3.2: The fabricated LiNbO$_3$ nanowires on a wafer. The SEM image is taken by Reinhard Geiss at the Institute of Applied Physics Jena, Germany.](image)

*Figure 3.3: Two possible crystal orientations of the fabricated LiNbO$_3$ nanowires.*
3.3 Processing of the LiNbO$_3$ nanowires

To perform characterization of the nanowires, they are placed on a glass substrate. Several techniques are elaborated to detach singles nanowires off the wafer and move them onto a glass slide for further optical and SEM studies.

- The first method involves sonication of the wafer with the nanowires in ethanol for several seconds. The nanowires break off the wafer and, as a result, a solution of the nanowires and ethanol is obtained. Afterwards, several droplets of the solution are deposited onto the glass slide. After ethanol evaporates, nanowires stay attached to the glass surface with Van der Waals forces.

- The second method is based on a micromanipulator. The micromanipulator is used to transport a nanowire off the wafer onto the glass slide in an SEM (Figure 3.4) or an optical microscope. The main advantages of this technique is a precise and controlled positioning of the nanowires. Furthermore, this technique also allows to transfer a nanowire to an edge of the glass slide.
  
  - In an SEM, a nanowire is glued to a metallic micromanipulator by depositing platinum (Figure 3.4a). After the nanowire is placed onto the glass substrate, the nanowire is cut off the micromanipulator with a focused ion beam (Figure 3.4b).
  
  - In an optical microscope, a nanowire gets attached through electro-static forces to a tapered silica tube that is controlled by a micromanipulator (Figure 3.5a). The nanowire mechanically gets detached when it is deposited onto a glass slide (Figure 3.5b).

For the measurements, we use glass slides that are initially covered with an indium tin oxide (ITO) coating and patterned with microstructures and coordinates. Since the ITO-coating is conductive and also transparent in the visible spectral range, it allowed to perform both SEM and optical measurements of the nanowires. In turn, the pattern with coordinates facilitates to locate the nanowires on the glass substrates.
3.3. Processing of the LiNbO$_3$ nanowires

![SEM images](image)

**Figure 3.4:** SEM images of a nanowire when it is attached to a micromanipulator (a) and after it was deposited onto a glass substrate (b). The images are taken by Detlef Schelle at the Institute of Applied Physics Jena.
Chapter 3. Fabrication of the LiNbO$_3$ nanowires and sample preparation

Figure 3.5: Light microscope images of a nanowire attached to a silica tube (a) and nanowires deposited on a glass slide (b). The images are taken by Marc Reig at ETH Zürich.
Chapter 4

Simulation of the waveguiding and generation of the second-harmonic and sum-frequency signals in LiNbO$_3$ nanowires

4.1 Introduction

During the PhD project, we developed a code to simulate generation and waveguiding of the second-harmonic (SH) and sum-frequency (SF) signals in a nanowire. The simulation results were used to verify the obtained experimental results with the theoretical expectations. In this chapter, we describe in detail the flow and the realization of this simulation code.

4.2 Description of the model

To develop the code, we applied a semi-analytical model, which was initially developed to describe the second-harmonic generation (SHG) process in photonic crystals [128] and was further adapted for nanowaveguides [112].

Figure 4.1 shows a schematic of the simulation flow, which is written in MATLAB software and consists of three main parts.
Chapter 4. Simulation of the waveguiding and generation of the second-harmonic and sum-frequency signals in LiNbO$_3$ nanowires

Figure 4.1: The schematic of the simulation flow. The schematic is based on the SHG process. In the first part, we use COMSOL to calculate the guided modes and their effective refractive indices for a waveguide with a particular height, width, and crystal structure at a particular wavelength. In the second part, we use MATLAB to calculate the conversion efficiency and wavevector mismatches of all possible groups of modes at the interacting wavelengths. In the third part, we use MATLAB to calculate the behaviour of the generated signal as a function of the pump wavelengths and nanowire length.
4.2. Description of the model

In the first part, MATLAB code uses COMSOL functions to calculate all modes and their effective refractive indices that can exist in a waveguide with particular crystal structure, width and height and at a certain wavelength. For the SHG process, we calculate modes at the wavelengths of the fundamental-harmonic (FH) and second-harmonic (SH). For the sum-frequency generation (SFG) process, we calculate modes at both pump wavelengths and at the to-be-generated SF wavelength. In the calculation, we take into account the wavelength-dependent refractive index tensor of the lithium niobate (LiNbO$_3$) crystal at the temperature of 23 °C from Ref. [129] and wavelength-dependent refractive index of fused silica from Ref. [130]. In order to find all existing waveguide modes at each wavelength, we set COMSOL to find a higher number of modes than there exist in a particular cross-section and at a particular wavelength. After the modes are calculated, we check them and use only the existing ones for further calculation. As a result, we make sure that the simulation takes into account all guided modes.

In the second part, we use the calculated modes and their effective refractive indices to calculate conversion efficiencies and wavevector mismatches for each group of modes at the interacting wavelengths with the use of the MATLAB code. For the SHG process, we calculate conversion efficiency of each FH mode with each SH modes. For the SFG process, we calculate conversion efficiency of each mode at the first pump wavelength with each mode at the second pump wavelength and each mode at the SFG wavelength. For the calculation, we use the second-order susceptibility tensor of the LiNbO$_3$ crystal from Ref. [89]. A more detailed description of the calculation process is provided in §4.3.

In the third part, we use the calculated values of the wavevector mismatches and conversion efficiencies to estimate the overall behaviour of the guided SH and SF signals in the considered nanowire. A more detailed description is provided in §4.4.
Chapter 4. Simulation of the waveguiding and generation of the second-harmonic and sum-frequency signals in LiNbO$_3$ nanowires

4.3 Calculation of the conversion efficiency

The conversion efficiency is a parameter that defines how much power of a particular mode at the pump wavelength contributes to a particular mode at the to-be-generated wavelength. The equations for conversion efficiency are derived in [112, 128] with the use of undepleted pump approximation and slowly varying amplitude approximation [30]. In the SHG process, there are two interacting modes: an FH mode and an SH mode. Whereas, in the SFG process, there are three interacting modes: a mode at the first pump wavelength, a mode at the second pump wavelength and a mode at the SFG wavelength. Consequently, equations for the SHG and SFG processes slightly vary and their discussion will be split in two subsections. In the first subsection (§4.3.1), we describe calculation of the conversion efficiency for the SHG process and, in the second subsection (§4.3.2), we describe calculation of the conversion efficiency for the SFG process.

4.3.1 Calculation of the conversion efficiency for the SHG process

It is found that the conversion efficiency $\eta_{ij}$ of the $i$-th SH mode and the $j$-th FH mode depends on the second-order susceptibility tensor $d_{ls}$, which defines the coupling strength of the electric field components of the FH mode ($E_x(\omega)$, $E_y(\omega)$, $E_z(\omega)$) with the electric field components of the SH mode ($E_x(2\omega)$, $E_y(2\omega)$, $E_z(2\omega)$).

Table 4.1: The coupling strength of the $x$-, $y$- and $z$-components of the fundamental and second-harmonic fields through the second-order susceptibility tensor of the LiNbO$_3$ crystal [88].

<table>
<thead>
<tr>
<th>$E_x(2\omega)$</th>
<th>$E_y(2\omega)$</th>
<th>$E_z(2\omega)$</th>
<th>$2E_x(\omega) \cdot E_y(\omega)$</th>
<th>$2E_x(\omega) \cdot E_z(\omega)$</th>
<th>$2E_y(\omega) \cdot E_y(\omega)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_x(2\omega)$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$d_{15}$</td>
<td>$-d_{16}$</td>
</tr>
<tr>
<td>$E_y(2\omega)$</td>
<td>$-d_{16}$</td>
<td>$d_{15}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$E_z(2\omega)$</td>
<td>$d_{15}$</td>
<td>$d_{15}$</td>
<td>$d_{33}$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
4.3. Calculation of the conversion efficiency

For the LiNbO$_3$ crystal, the components of the second-order susceptibility tensor vary as shown in Table 4.1. As a result, in order to find the conversion efficiency $\eta_{ij}$ of the $i$-th mode SH and the $j$-th FH mode, one has to find first the conversion efficiency of their components $(E_x, E_y, E_z) \eta_{ijlm}$:

$$\eta_{ijlm} = \frac{\omega_{SHG}^2 \cdot d_{lm}^2 \cdot n_{g,SH}^2 \cdot n_{g,FH}^2 \cdot \epsilon_0 \cdot c^3 \cdot A_{ijlm}}{2 \cdot n_{SH}^2 \cdot n_{FH}^4}, \quad (4.1)$$

where $\omega_{SHG}$ is the SHG angular frequency, $d_{lm}$ is a component of the second-order nonlinear susceptibility tensor, $n_{g,SH}$ is the group refractive index of the $i$-th SH mode, $n_{g,FH}$ is the group refractive index of the $j$-th FH mode, $\epsilon_0$ is the vacuum permittivity ($\epsilon_0 = 8.85 \cdot 10^{-12}$ F/m), $c$ is the speed of light in vacuum ($c = 3 \cdot 10^8$ m/s), $A_{ijlm}$ is the normalized overlap integral of the $l$-th component of the $i$-th SH mode, $m$-th component of the $j$-th FH mode and $p$-th component of the $j$-th FH mode, $l$, $m$ and $p$ denote electric field components $(E_x, E_y, E_z)$ of the interacting modes and define the involved component of the second-order susceptibility tensor.

The index $s$ of the susceptibility tensor component is defined as:

$$s = \begin{cases} 
  m, & \text{if } m = p \\
  9 - m - p, & \text{otherwise} 
\end{cases} \quad (4.2)$$

The normalized overlap integral $A_{ijlm}$ is found as follows:

$$A_{ijlm} = \frac{\left( \int E_{FH}^2 \cdot dx \cdot dz \right) \cdot \left( \int E_{SH}^2 \cdot dx \cdot dz \right)}{\left| \int_{NL} E_{SH_l}(x,z) \cdot E_{FH_m}(x,z) \cdot E_{FH_p}(x,z) \cdot dx \cdot dz \right|^2}, \quad (4.3)$$

where $E_{SH_l}$ is the $i$-th SH mode, $E_{FH_m}$ is the $j$-th FH mode, $E_{SH_{il}}$ is the $l$-th electric field component of the $i$-th SH mode, $E_{FH_{jm}}$ is the $m$-th electric field component of the $j$-th FH mode.

Conversion efficiency of the $i$-th SH mode and the $j$-th FH mode $\eta_{ij}$ can be found by summing up the conversion efficiencies of the electric field components $(E_x, E_y, E_z)$ of the corresponding FH and SH modes:

$$\eta_{ij} = \sum_{l=x,y,z} \left( \sum_{m=x,y,z} \sum_{p=x,y,z} \eta_{ijlm} \right), \quad (4.4)$$
where $L$ is the length of the waveguide, $\Delta k_{ij}$ is the wavevector mismatch of the $i$-th SH mode and the $j$-th FH mode.

Overall contribution of the $j$-th FH mode to the SH field can be found by summing up the conversion efficiencies of the $j$-th FH mode with all considered SH modes and by taking into account the corresponding wavevector mismatch $\Delta k$:

$$\eta_j = \sum_{i=\text{all SH modes}} \left( \eta_{ij} \cdot L^2 \cdot \text{sinc}^2 \left( \frac{\Delta k_{ij} \cdot L}{2} \right) \right), \quad (4.5)$$

The wavevector mismatch $\Delta k_{ij}$ of the $i$-th SH mode and the $j$-th FH mode can be found as [30]:

$$\Delta k_{ij} = \left| n_{\text{SH},i} - n_{\text{FH},j} \right| \cdot \frac{4\pi}{\lambda_{\text{FH}}}, \quad (4.6)$$

where $n_{\text{SH},i}$ is the effective refractive index of the $i$-th SH mode, $n_{\text{FH},j}$ is the effective refractive index of the $j$-th FH mode, $\lambda_{\text{FH}}$ is the FH wavelength in free space.

### 4.3.2 Calculation of the conversion efficiency for the SFG process

Since there are three waves interacting in the SFG process (two pump waves and one to-be-generated SF wave), we need to consider three modes (one mode at each wavelength). Furthermore, in order to find the conversion efficiency $\eta_{ijk}$ of the $i$-th mode at the to-be-generated wavelength, the $j$-th mode at the first pump wavelength and the $k$-th mode at the second pump wavelength, one has to calculate first the conversion efficiencies of the electric field components ($E_x$, $E_y$, $E_z$) of the interacting modes $\eta_{ijk_{\text{imp}}}$ [112]:

$$\eta_{ijk_{\text{imp}}} = \omega_{\text{SFG}}^2 \cdot d_{\text{imp}}^2 \cdot \frac{2 \cdot n_{g,\text{SFG},i} \cdot n_{g,\text{Pump1},j} \cdot n_{g,\text{Pump2},k} \cdot \epsilon_0 \cdot c^3 \cdot A_{ijk_{\text{imp}}}}{n_{\text{SFG},i}^2 \cdot n_{\text{Pump1},j}^2 \cdot n_{\text{Pump2},k}^2}, \quad (4.7)$$

where $\omega_{\text{SFG}}$ is the SFG angular frequency, $d_{\text{imp}}$ is a components of the second-order nonlinear susceptibility tensor, $n_{g,\text{SFG},i}$ is the group refractive index of the $i$-th mode at the SFG wavelength, $n_{g,\text{Pump1},j}$ is the group refractive index of the $j$-th mode at the first pump wavelength, $n_{g,\text{Pump2},k}$ is the group refractive index of the $k$-th mode at the second pump wavelength.
4.3. Calculation of the conversion efficiency

at the second pump wavelength, $\epsilon_0$ is the vacuum permittivity ($\epsilon_0 = 8.85 \cdot 10^{-12}$ F/m), $c$ is the speed of light in vacuum ($c = 3 \cdot 10^8$ m/s), $A_{ijk_{imp}}$ is the normalized overlap integral of the $l$-th component of the $i$-th SFG mode, the $m$-th component of the $j$-th mode at the first pump wavelength and the $p$-th component of the $k$-th mode at the second pump wavelength, $l$, $m$ and $p$ denote electric field components ($E_x$, $E_y$, $E_z$) of the interacting modes and define the involved components of the second-order susceptibility tensor.

The index $s$ of the susceptibility tensor component is defined as:

$$s = \begin{cases} 
m, & \text{if } m = p \\
9 - m - p, & \text{otherwise} 
\end{cases} \quad (4.8)$$

The normalized overlap integral of the components of the interacting modes $A_{ijk_{imp}}$ is found as follows [112]:

$$A_{ijk_{imp}} = \frac{\int E_{SFG,i}^2 \, dx \, dz \cdot \int E_{Pump1,j}^2 \, dx \, dz \cdot \int E_{Pump2,k}^2 \, dx \, dz}{|\int N L E_{SFG,i,l}(x,z) \cdot E_{Pump1,j,m}(x,z) \cdot E_{Pump2,k,p}(x,z) \, dx \, dz|^2}, \quad (4.9)$$

where $E_{SFG,i}$ is the $i$-th SFG mode, $E_{Pump1,j}$ is the $j$-th mode at the first pump wavelength, $E_{Pump2,k}$ is the $k$-th mode at the second pump wavelength, $E_{SFG,i,l}$ is the $l$-th electric field component of the $i$-th SFG mode, $E_{Pump1,j,m}$ is the $m$-th electric field component of the $j$-th mode at the first pump wavelength and $E_{Pump2,k,p}$ is the $p$-th electric field component of the $k$-th mode at the second pump wavelength.

The conversion efficiency of the $i$-th SFG mode, the $j$-th mode at the first pump wavelength and the $k$-th mode at the second pump wavelength can be found by summing up the conversion efficiencies of the electric field components ($E_x$, $E_y$ and $E_z$) of the corresponding modes:

$$\eta_{ijk} = \sum_{l=x,y,z} \left( \sum_{m=x,y,z} \left( \sum_{p=x,y,z} \eta_{ijk_{imp}} \right) \right). \quad (4.10)$$

The overall contribution of the $j$-th mode at the first pump wavelength and the $k$-th mode at the second pump wavelength to the generated SF field $\eta_{jk}$ can be found
Chapter 4. Simulation of the waveguiding and generation of the second-harmonic and sum-frequency signals in LiNbO$_3$ nanowires

by summing up conversion efficiencies of the $j$-th mode at the first pump mode and the $k$-th mode at the second pump wavelength with all SFG modes and by taking into account the corresponding wavevector mismatch $\Delta k$:

$$
\eta_{jk} = \sum_{i \text{= all SFG modes}} \left( \eta_{ijk} \cdot L^2 \cdot \text{sinc}^2 \left( \frac{\Delta k_{ijk} \cdot L}{2} \right) \right), \quad (4.11)
$$

The wavevector mismatch $\Delta k_{ijk}$ of the $i$-th SFG mode, the $j$-th mode at the first pump wavelength and the $k$-th mode at the second pump wavelength can be found as follows:

$$
\Delta k_{ijk} = \left| \frac{2\pi}{\lambda_{\text{SFG}_i}} n_{\text{SFG}_i} - \frac{2\pi}{\lambda_{\text{Pump}_1}} n_{\text{Pump}_1j} - \frac{2\pi}{\lambda_{\text{Pump}_2}} n_{\text{Pump}_2k} \right|, \quad (4.12)
$$

where $n_{\text{SFG}_i}$ is the effective refractive index of the $i$-th SFG mode, $n_{\text{Pump}_1j}$ is the effective refractive index of the $j$-th mode at the first pump wavelength, $n_{\text{Pump}_2k}$ is the effective refractive index of the $k$-th mode at the second pump wavelength, $\lambda_{\text{SFG}}$ is the SFG wavelength in free space, $\lambda_{\text{Pump}_1}$ is the first pump wavelength in free space and $\lambda_{\text{Pump}_2}$ is the second pump wavelength in free space.

4.4 Calculation of the behaviour of the generated and guided field

Having calculated the conversion efficiency of particular pump modes to the generated field and the power of the pump modes, one can find the power of the field that is generated by the considered pump modes. Thus, the guided SH power $V_j$ that is generated by the $j$-th FH mode can be found using the following equation:

$$
V_j = \eta_j \cdot U_j^2, \quad (4.13)
$$

where $U_j$ is the power of the $j$-th FH mode, $\eta_j$ is the overall conversion efficiency of this mode to the SH field.
4.4. Calculation of the behaviour of the generated and guided field

In turn, the guided SFG power $V_{jk}$ that is generated by the $j$-th mode at the first pump wavelength and the $k$-th mode at the second pump wavelength can be found by using the following equation:

$$V_{jk} = \eta_{jk} \cdot U_j \cdot U_k,$$  \hspace{1cm} (4.14)

where $U_j$ is the power of the $j$-th mode at the first pump wavelength, $U_k$ is the power of the $k$-th mode at the second pump wavelength, $\eta_{jk}$ is the overall conversion efficiency of the $j$-th mode at the first pump wavelength and the $k$-th mode at the second pump wavelength to the guided SFG field.

Since the LiNbO$_3$ nanowires that we study support a multimode regime in the visible range, it is not possible to control the distribution of the coupled laser power into the guided pump modes and, as a consequence, it is not possible to quantify the power of the nonlinear field that is generated by a particular pump mode. Nevertheless, this model might be convenient to qualitatively evaluate the wavemixing ability of the nanowires.

Furthermore, using the conversion efficiency values, one can estimate the behaviour of the generated field at the varied pump wavelength and along the nanowire length.

To estimate the behaviour of the guided nonlinear field that is generated by a particular pump mode at the varied pump wavelength, one should plot conversion efficiency as a function of the pump wavelength as shown in Figure 4.2.

In turn, the behaviour of the guided SH nonlinear field that is generated by a particular FH mode along the nanowire length can be analysed by plotting the overall conversion efficiency of the $j$-th FH mode to the generated SH field as a function of length. As an example, we show behaviour of the calculated conversion efficiencies of the 3rd FH mode with thirty SH modes at the FH wavelengths of 806 nm (Figure 4.3a) and 846 nm (Figure 4.3c) in logarithmic scale as a function of the nanowire length and the calculated overall conversion efficiency of the 3rd FH mode to the SH field at the wavelengths of 806 nm (Figure 4.3b) and 846 nm (Figure...
Chapter 4. Simulation of the waveguiding and generation of the second-harmonic and sum-frequency signals in LiNbO$_3$ nanowires

Figure 4.2: Calculated conversion efficiency of the 3rd FH mode and the 23rd SH mode as a function of the FH wavelength.

4.3d) as a function of the nanowire length. The overall conversion efficiency of the $j$-th FH mode to the generated SH field as a function of length can be calculated as follows:

$$\eta_j(l) = \sum_{i=\text{all SH modes}} \left( \eta_{ij} \cdot l^2 \cdot \text{sinc}^2 \left( \frac{\Delta k_{ij} \cdot l}{2} \right) \right). \quad (4.15)$$

where $l$ is the length of the waveguide, $\eta_{ij}$ is the conversion efficiency of the $j$-th FH mode and the $i$-th SH mode and $\Delta k_{ij}$ is the wavevector mismatch of the $j$-th FH mode and the $i$-th SH mode.

In case of the SFG process, the behaviour of the SFG field that is generated by the $j$-th mode at the first pump wavelength and the $k$-th mode at the second pump wavelength along the nanowire length can be found by calculating the overall conversion efficiency of the $j$-th mode at the first pump wavelength and the $k$-th mode at the second pump wavelength to the generated SH field as a function of the nanowire length:

$$\eta_{jk} = \sum_{i=\text{all SF modes}} \left( \eta_{ijk} \cdot l^2 \cdot \text{sinc}^2 \left( \frac{\Delta k_{ijk} \cdot l}{2} \right) \right). \quad (4.16)$$

where $l$ is the length of the waveguide, $\eta_{ijk}$ is the conversion efficiency of the
4.4. Calculation of the behaviour of the generated and guided field

\[ i \]-th SFG mode, the \( j \)-th mode at the first pump wavelength and the \( k \)-th mode at the second pump wavelength and \( \Delta k_{ijk} \) is the wavevector mismatch of the \( i \)-th SFG mode, the \( j \)-th mode at the first pump wavelength and \( k \)-th component at the second pump wavelength.

\[ \text{(a)} \]

\[ \text{(b)} \]

\[ \text{(c)} \]

\[ \text{(d)} \]

**Figure 4.3**: Calculated conversion efficiencies of the 3rd FH mode and thirty SH modes as a function of the nanowire length at the FH wavelengths of 806 nm (a) and 846 (c) in logarithmic scale and the calculated overall conversion efficiency of the 3rd FH mode to the SH field at the wavelengths of 806 nm (b) and 846 nm (d) as a function of the nanowire length. In the simulation, a nanowire with width of 778 nm and height of 560 nm was considered.
Chapter 5

Second-harmonic generation in LiNbO$_3$ nanowires

5.1 Introduction

In this chapter, the results on the second-harmonic generation (SHG) in lithium niobate (LiNbO$_3$) nanowires are presented. First, we demonstrate waveguiding and generation of the second-harmonic (SH) signal. Second, we show strategies to enhance the waveguided second-harmonic signal.

5.2 Experimental setup for the second-harmonic generation measurements

Figure 5.1 shows the schematic of the experimental setup for the SHG measurements. We use a femtosecond laser (Spectra-Physics MaiTai HP) as a pump source. The pulse repetition rate of the laser is 80 MHz and the laser wavelength can be tuned in the range of 690-1040 nm. The pulse duration of the laser varies in the range of 200-300 fs depending on the wavelength.

At the input of the setup, the laser beam passes through a half-wave plate, which is used to rotate the polarization, and, thus, maximize the SHG response. After passing through the half-wave plate, the laser beam is focused with a 10x objective (RMS10X with working distance of 10.6 mm and NA of 0.25) onto the sample down...
5.2. Experimental setup for the second-harmonic generation measurements

Figure 5.1: The schematic of the experimental setup for SHG measurements. See details in the text.

to a beamspot of 1.6 \( \mu \text{m} \) \((1/e)\). A 100x objective (Zeiss Epiplan LD with working distance of 4 mm and NA of 0.75) is used to collect the sample response and image it onto an electron-multiplying charge-coupled device (EMCCD) camera (ANDOR Ixon3 885). At the input of the EMCCD camera, a bandpass filter (BG39) is placed to filter out the laser light and detect only the SH signal.

Figure 5.2 depicts a schematic of the laser coupling into a nanowire and signal collection from a nanowire. The optical axes of the focusing and collecting objectives are perpendicular to the sample surface. As a result, the laser beam is focused perpendicularly onto the nanowire facet and only a small fraction of the laser power is coupled into the nanowire. Similarly, the collection objective collects only a fraction of the guided signal that is scattered towards it.

Figure 5.2: The coupling configuration of the laser light into a nanowire. See details in the text.
5.3 Demonstration of the guided second-harmonic signal in LiNbO$_3$ nanowires

Figure 5.3a depicts a bright field microscope image of one of the studied nanowires. The dashed circle indicates the focused laser beamspot. To generate and guide the SH signal, the laser light is first coupled into the nanowire. For this purpose, the input facet of the nanowire is brought into the laser beamspot. Further, the position of the nanowire is adjusted to optimize the coupling, which is very low. For example, when 36 mW of the laser light are focused onto the input facet of one of the nanowires, only several microwatts of the guided laser power are detected at the output. Moreover, coupling efficiency varies for each nanowire and depends on several factors such as input facet [32] and polarization of the incident laser beam [59].

![Laser beam spot](image1)

(a)

![Second harmonic at input](image2)

(b)

**Figure 5.3:** (a) The bright-field microscope image of the studied nanowire. (b) The SH response from the nanowire. Both images are taken with the setup shown in Figure 5.2.

In Figure 5.3b, we depict an image obtained from the EMCCD camera with the SHG response of the nanowire. Figure 5.3b demonstrates the SH signal at both the nanowire input and output. The SH signal at the input is generated by the
5.3. Demonstration of the guided second-harmonic signal in LiNbO$_3$ nanowires

incident laser beam. Whereas the SH signal at the output cannot be generated by
the incident laser beam and, thus, indicates a waveguiding process.

![Guided SH power as a function of the incident laser beam power (blue dots) and a quadratic fit (red solid line).](image)

To confirm that the detected signal at the nanowire output is, indeed, the SH and
not the fundamental-harmonic (FH), we measure the power of the guided signal as a
function of the incident laser power whereas a quadratic dependence is expected. The
power values are found by taking a picture of the guided signal with an EMCCD
camera, integrating the levels of the pixels in the image and back-converting the
integrated value into watt by taking into account the quantum efficiency of the
camera, acquisition parameters and transmission of the experimental setup. Figure
5.4 plots the measured power of the guided signal as a function of the laser power
(blue dots). Besides, Figure 5.4 also plots the quadratic fit (red solid line), which
matches the measured data with the goodness of fit ($R^2$) being 0.9916.
5.4 Enhancement of the guided second-harmonic signal

The SHG effect quadratically depends on the volume of the crystalline material [9, 30]. As a result, the SHG efficiency in nanowires is expected to be low and ways of enhancing the SHG efficiency should be found. In this section, we discuss two methods of increasing the SHG efficiency. First, we show that the LiNbO$_3$ nanowires support modal phase-matching and, thus, provide a possibility to enhance the guided SHG signal. Second, we demonstrate that the phase-mismatched guided SH signal can be optimized by adjusting the nanowire length.

5.4.1 Phase-matching of the guided second-harmonic signal

Modal phase-matching takes place when effective refractive indices of a mode at the FH and of a mode at the SH are equalized as discussed in §2.4. Since the effective refractive index varies for each wavelength and each mode, modal phase-matching can be achieved by tuning the laser wavelength.

Figure 5.5 shows a scanning electron microscope (SEM) image of one of the studied nanowires. According to the SEM measurement, the studied LiNbO$_3$ nanowire has the width of 778±38 nm, the height of 541±27 nm and the length of 52±2 µm. The inset shows the crystal structure of the nanowire with the $y$-axis along the nanowire length, the $x$-axis along the nanowire height and $z$-axis along the nanowire width.

![Figure 5.5: The SEM image of the studied nanowire. Inset: Crystal structure of the nanowire.](image)
5.4. Enhancement of the guided second-harmonic signal

To demonstrate modal phase-matching in the nanowire, we sweep the laser wavelength in the range of 780-920 nm with a step of 5 nm and measure the guided SH signal at each wavelength. The result of the measurements is plotted in Figure 5.6 (dashed line with squared markers). As one can see, the SH power strongly depends on the incident laser wavelength. Furthermore, the curve in Figure 5.6 reveals peaks at the pump laser wavelengths of 800 nm, 855 nm and 900 nm, which are referred to the modal phase-matching effect, which is discussed in §2.4. Thanks to these peaks, the SH can be significantly enhanced. For example, in the observed experiment, the guided SH is increased by a factor of 48, when the laser wavelength is tuned from 830 to 855 nm.

![Figure 5.6: The experiment and simulation results of the guided SH power versus incident laser wavelength.](image)

To confirm theoretically the phase-matching process in the studied nanowire, we simulate waveguiding and generation of the SH in a nanowire. The flow of the simulation is described in detail in Chapter 4. In the simulation, first three FH and thirty SH guided modes are considered. The simulation is performed for all cross-sections within the uncertainty range of the SEM measurement. The best match between the simulation and the experiment curves is obtained at the width of 778
nm and the height of 560 nm. In Figure 5.6, we plot the calculated curve of the guided SH power versus the laser wavelength (blue solid line). Since the fractions of the laser power that are coupled into each FH mode are unknown, contributions of each FH mode are adjusted to fit the heights of the peaks in the theoretical and experimental curves. Nevertheless, there is still a slight lateral discrepancy between the experiment and the simulation curves. This discrepancy can be explained by a high order of the guided modes, which are sensitive to slight variations of the nanowire cross-sections [59, 62]. Indeed, according to the simulations, the peak at 800 nm is created by the 1st FH mode and 17th SH mode, the peak at 855 nm is created by the 3rd FH mode and the 23rd SH mode and the peak at 900 nm is created by the 2nd FH mode and 17th SH modes. The intensity profiles of the mode profiles are shown in Figure 5.7.

![Figure 5.7: The intensity profiles of the 1st mode at 802 nm (a), the 3rd mode at 846 nm (b), the 2nd mode at 900 nm (c), the 17th mode at 401 nm (d), the 23rd mode at 423 nm (e) and the 17th mode at 450 nm (f).](image)

Besides matching effective refractive indices, the interacting FH and SH modes should also have a large overlap to assure high conversion efficiency. If a pair of the interacting FH and SH modes have a small overlap (and as a consequence low con-
5.4. Enhancement of the guided second-harmonic signal

version efficiency), this mode pair may not give any strong contribution to the total guided SH signal. Thus, in order to get an efficient SHG process, one should phase-match the pairs of the FH and SH modes that show a high conversion efficiency. It can be achieved by a careful design of the nanowire cross-section.

5.4.2 Adjustment of the nanowire length for optimizing the phase-mismatched guided second-harmonic signal

As shown in Figure 5.6, nanowires provide phase-matching possibilities only at a limited number of wavelengths. Thus, the SH signal may not be enhanced by the phase-matching effect at any desired wavelength in a particular nanowire. Nevertheless, nanowires may still provide pairs of the FH and SH modes that have a high conversion efficiency due to a large overlap area. As a result, the power of the guided phase-mismatched SH can be also optimized by adjusting the nanowire length, since it oscillates along the propagation distance [30] as discussed in §2.4. To demonstrate it, we calculate the behaviour of the guided SH power generated by the 1st FH mode at the pump wavelength of 820 nm in a nanowire with the height of 510 nm and the width of 728 nm. In the calculation, we take into account the first thirty guided SH modes. The result of the calculation is shown in Figure 5.8.

The calculated result in Figure 5.8, indeed, indicates a variation of the guided SH, which oscillates along the nanowire length. Moreover, after analysing the obtained curve in Figure 5.8, we conclude that the guided SH power mostly propagates in terms of three guided modes that are the 4th, the 16th and the 17th SH modes. These modes have the highest conversion efficiency with the 1st FH mode and, thus, give the highest contribution to the calculated guided SH power that is shown in Figure 5.8. Interaction behaviour of the discussed SH modes with the 1st FH mode are plotted in Figure 5.9. The intensity profiles of the modes are shown in Figure 5.10.

Since the discussed SH modes are not phase-matched with the 1st FH mode, the conversion efficiency curves show oscillations. The periods of the oscillations
Chapter 5. Second-harmonic generation in LiNbO$_3$ nanowires

Figure 5.8: The calculated guided SH power generated by the 1st FH mode as function of the nanowire length at the pump wavelength of 820 nm in a nanowire with the height of 510 nm and the width of 728 nm.

![Figure 5.8](image1.png)

Figure 5.9: The calculated conversion efficiency of the 1st FH mode with the 4th (blue dash-dotted line), 16th (red dashed line) and 17th (green dotted line) SH modes.

![Figure 5.9](image2.png)

correspond to the coherence lengths. Thus, the coherence lengths for the interaction of the 1st FH mode with the 4th, 16th and 17th FH modes are 1 µm, 7.5 µm and 6.5 µm, respectively. Since the coherence length depends on the wavevector mismatch of the interacting FH and SH modes, it increases in the vicinity of the phase-matching
5.4. Enhancement of the guided second-harmonic signal

![Intensity profiles](image)

*Figure 5.10: The intensity profiles of the 1st mode at 820 nm (a), 4th mode at 410 nm (b), 16th mode at 410 nm (c) and 17th mode at 410 nm (d).*

Due to the multiple number of guided SH modes, the behaviour of the guided SH power gets more complicated and shows local minima and maxima. As a result, the length of the nanowires has to be carefully adjusted to maximize the guided phase-mismatched SH power.

To demonstrate it experimentally, we perform a series of experiments with a nanowire that has the height of $728 \pm 36$ nm, the width of $510 \pm 26$ nm and the initial length of $34.8 \pm 0.5 \mu m$. In each series, we shorten the nanowire with a focused ion beam (FIB) milling [131] and measure the guided SH power after each milling procedure. The pump laser has the wavelength of 820 nm, power of 10 mW and polarization of $154^\circ$ with respect to the nanowire. Since the period of the phase-mismatched SH oscillation is unknown for this nanowire, the cutting steps are chosen arbitrarily and vary from $0.61 \mu m$ and $6 \mu m$ in this experiment. In Figure 5.11, we plot the obtained guided SH power at various lengths of the nanowire. The result demonstrates that the guided SH power strongly depends on the nanowire length. Moreover, by cutting the nanowire, the guided SH power is increased by a factor of 47.
The obtained experimental results confirm that the power of the guided phase-mismatched SH signal can be optimized by adjusting the nanowire length. However, to know the required length of the nanowire, one has to define the coherence length and position of the peaks of the phase-mismatched SH field. This information can be obtained by measuring the behaviour of the near-field of the guided modes along the nanowire with a scanning near-field optical microscope [87, 132, 133]. In Chapter 6, we show an alternative method, which is based on cross-linking a photosensitive polymer and allows to estimate the coherence length of the guided phase-mismatched SH field.

5.5 Conclusion

In the chapter, we showed the results of the study on generation and waveguiding of the SH signal in LiNbO$_3$. First, we demonstrated generation and waveguiding of the SH. Further, we demonstrated that phase-matching effect could be achieved in LiNbO$_3$ nanowires and, thus, enhance the guided SH signal. After all, we also showed
that the phase-mismatched guided SH signal can be also optimized by adjusting the nanowire length.
Chapter 6

Mapping the guided second-harmonic light with a photosensitive polymer

6.1 Introduction

As discussed in §2.4 and §5.4.2, the power of the guided phase-mismatched second-harmonic (SH) signal oscillates along the propagation direction as shown in Figure 6.1. Thus, it can be optimized by adjusting the nanowire length. For this purpose, one should know the behaviour of the guided SH signal including the oscillation period and the precise positioning of the maxima.

This information can be obtained with a scanning near-field optical microscope (SNOM), which senses the evanescent field of the guided light [132, 134]. However, this technique is time-consuming and noise-sensitive and it also requires complex equipment.

We propose to use an alternative technique, which is based on a photosensitive polymer that gets cross-linked by being irradiated with light. This technique was previously applied to study light-matter interaction in nanoparticles [135, 136, 137, 138, 139, 140]. By being cross-linked by the evanescent field at the surface of the nanoparticles, this technique allows to image and analyse the behaviour of the light-matter interaction.

In this work, we apply this technique to study the guided SH light in LiNbO$_3$ nanowires. We show that it allows to study the guided SH light along the propagation inside the nanowire and distribution of the guided light at the nanowire.
6.2 Absorption properties of the SU-8 polymer

For the cross-linking experiments, we use an SU-8-2000.5 polymer from MicroChem. In Figure 6.2, we show normalized absorbance spectra of the SU-8 polymer. This spectrum indicates that the SU-8 polymer shows a direct absorption in the spectral range below 400 nm and a negligible absorption in the near-infrared range [141]. As a result, in the spectral range of the used laser (690-1040 nm), SU-8 absorbs light only through a two-photon absorption (TPA) process (Figure 6.3a), which is weak and requires high laser intensities [142]. Thus, the polymer can be cross-linked by the SH light from a LiNbO$_3$ nanowire when it is illuminated with the laser light below 800 nm through a single-photon absorption (SPA) process (Figure 6.3b).

The TPA properties of the polymer are usually used for fabricating optofluidic devices [143], three-dimensional printing of microstructures [64] and creating photoresist masks [144, 145]. Recently, it was also applied for mapping plasmon...
resonances in metallic nanoparticles [136, 137, 138, 139] when they were embedded in the polymer and irradiated by an infrared laser.

The previously demonstrated works show that SU-8 can be cross-linked by evanescent field and, thus, map its intensity variation [135, 136, 137, 138, 139]. As a result, this technique can be applied for visualizing and analysing the behaviour of the light-matter interaction.

Figure 6.2: The normalized absorbance of post-exposure baked SU-8 polymer as a function of wavelength. Source: [141].

![Normalized absorbance of SU-8 polymer](image)

Figure 6.3: The energy diagrams of the two-photon absorption (a) and single-photon absorption (b) processes.
6.3 Experimental setup

In Figure 6.4, we show a schematic of the experimental setup that is used for the cross-linking experiments. The experimental setup is coupled with a tunable femtosecond Ti:Sapphire laser (the spectral range can be varied from 690 to 1040 nm, the pulse repetition rate is 80 MHz and the pulse duration is around 295 fs at the sample position at the wavelength of 760 nm). First, the laser passes through a half-wave plate to rotate the laser polarization and optimize the guided SH power at the nanowire output. Further, we send the laser beam perpendicularly to the glass slide and focus it with a 10x objective down to a beamspot with the radius being 1.6 $\mu$m ($1/e$). We collect the SH response with a 100x objective and image it onto an electron multiplying charge-coupled device (EMCCD) camera. At the EMCCD camera, we place a band-pass filter to block the laser light and to detect only the SH signal.

![Figure 6.4: The schematic of the experimental setup. See details in the text.](image)

To couple the laser beam into a nanowire, we focus it onto the input facet of the nanowire as shown in Figure 6.5. The optical axes of the focusing and collection objective is perpendicular to the sample surface. As a result, the laser beam is focused perpendicularly onto the nanowire facet and only a small fraction of the laser power is coupled into the nanowire.
Figure 6.5: The coupling configuration of the laser light into a nanowire. See details in the text.

6.4 Polymerization procedure

The main steps of the sample preparation and flow of the experiments are shown in Figure 6.6.

First, we dropcast nanowires onto a glass substrate (Figure 6.6a) using the methods described in §3.3. For the cross-linking experiment, we cover the glass slide with a polymer layer (Figure 6.6b). The polymer is spin-coated onto the glass slide with nanowires at 1000 rpm for 1 minute and further baked at 95°C for 1 minute.

The cross-linking experiment is performed for 60 minutes (Figure 6.6c). In the experiment, the laser beam is coupled into a nanowire and guided. To couple the laser light, we bring the input facet of the nanowire into the focused laser beam spot. In all experiments, we set the laser wavelength to 760 nm, keep the incident laser power at 20 mW and adjust the laser linear polarization to maximize the guided SH signal at the nanowire output.

After the cross-linking experiment is performed, we develop the sample by first baking it at 95°C for 1 minute, then rinsing it with a developing solution (Mr-dev 600, MicroChem) for 1 minute and with isopropanol for 20 seconds. As a result, the polymer is removed and only the cross-linked polymer stays on the sample (Figure 6.6d).
6.5 Mapping the guided phase-mismatched second-harmonic with the SU-8 polymer

Figures 6.7a and 6.7b show scanning electron microscope (SEM) images of two nanowires with cross-linked polymer. These images reveal three main polymer structures: at input and output facets of the nanowires and also along the nanowires. In Figures 6.8a and 6.8b, we show zoomed-in SEM images of the polymer structure at the nanowire input, which have a circular shape. A similar structure is also obtained when a laser beam irradiated a polymer film and a nanowire was out of the laser beam spot (See Figure 6.8c). Thus, we conclude that the polymer structure at the nanowire input is cross-linked by the incident laser beam through the TPA.
Chapter 6. Mapping the guided second-harmonic light with a photosensitive polymer

Figure 6.7: SEM images of two nanowires with cross-linked SU-8 polymer. Dashed rectangles indicate the parts of the nanowires whose zoomed-in images are shown in Figures 6.10a and 6.10c.

The polymer structures at the nanowire output and along the nanowire are of more interest. Since these parts of the nanowires were not illuminated by the incident laser beam, the polymer structure at the nanowire output facet and along the nanowire can only be created by the guided light. Thus, a thorough study of
6.5. Mapping the guided phase-mismatched second-harmonic with the SU-8 polymer

these structures will provide information about the behaviour of the guided light.

Figure 6.9: (a) SEM image of the polymer structure at the output facet of the nanowire shown in Figure 6.7a; (b) SEM image of the polymer structure at the output facet of the nanowire shown in Figure 6.7b.

In Figures 6.9a and 6.9b, we show polymer structures at the nanowire output. According to the shape of the structures, one can conclude that these structures map the distribution of the guided light after it is irradiated from the output facet. Consequently, this technique allows to study the distribution of the guided light, which is crucial for such applications as localized imaging [63, 146] and nanowire microscopy [31].

The polymer structure at the nanowire output can be cross-linked by both the guided fundamental-harmonic (FH) through the TPA process or the guided SH light through the SPA process, since both harmonics are detected at the nanowire output. However, according to our estimation, the threshold intensity to cross-link the polymer through the SPA process is at least $10^5$ weaker than the threshold intensity to cross-link the polymer though the TPA process in our experimental conditions. Since the guided SH signal is usually $10^3 - 10^5$ times weaker than the guided FH signal, we expect that polymer at the nanowire output to be mostly cross-linked by the guided SH through the SPA process.

In Figures 6.10a and 6.10c, we show zoomed-in SEM images of the afore-shown
Chapter 6. Mapping the guided second-harmonic light with a photosensitive polymer

nanowires, which indicate periodical oscillation of the polymer thickness along the nanowire. Since the guided light is confined inside the nanowire, the polymer structure along the nanowire can only be cross-linked by the evanescent field of the guided light. Thus, this structure reveals the behaviour of the light while it is guided inside the nanowire.

To quantitatively characterize the thickness of the oscillations, the structures are measured in an atomic force microscope (AFM). Figures 6.10b and 6.10d plot the obtained profiles of the polymer structures as a function of length. From the profiles, the oscillation period for the first and the second nanowires are found to be 2.1±0.1 µm (Figure 6.10b) and 2.4±0.3 µm (Figure 6.10d), respectively.

The oscillations of the polymer thickness indicate an intensity oscillation of the guided light (either FH or SH) along the nanowire. This intensity oscillation can be caused by either a standing wave inside the nanowire [147, 148] or by intensity oscillation of the phase-mismatched SH light [149]. In case of the phase-mismatching, the intensity oscillates with the period equal to the coherence length $L_{COH}$ as discussed in §2.4. In case of the standing wave, the intensity oscillates with a period $\Delta$ that can be found as:

$$\Delta = \frac{\lambda}{2 \cdot n},$$

where $\lambda$ is the wavelength of light and $n$ is the refractive index.

Standing waves of the coupled laser light were previously measured in waveguides with SNOM [147, 148]. However, the period of the standing wave cannot exceed half the wavelength of the guided light. Taking into account that the wavelengths of the FH and SH are 760 nm and 380 nm, respectively, the period of the intensity variation created by a standing wave can be at most 380 nm. Whereas, the polymer structures observed in Figure 6.10 have periods above 1 µm and, thus, cannot be created by any standing wave.

On the contrary, the intensity oscillation period of the phase-mismatched guided SH signal covers a large range, which also includes the measured periods of the
6.5. Mapping the guided phase-mismatched second-harmonic with the SU-8 polymer

Figure 6.10: (a) and (b) zoomed-in SEM image and measured AFM profile of the nanowire from Figure 6.7a; (c) and (d) zoomed-in SEM image and measured AFM profile of the nanowire from Figure 6.7b. Arrows indicate positions of the maximum polymer height.
Chapter 6. Mapping the guided second-harmonic light with a photosensitive polymer structures. The oscillation period of the phase-mismatched guided SH signal is defined by the wavevector mismatch $\Delta k$ of the coupled FH mode and the generated SH modes.

The wavevector mismatch $\Delta k$ of the coupled FH mode and a particular SH mode defines the coherence length $L_{COH}$ and, as a consequence, the oscillation period of the guided phase-mismatched SH signal of the considered SH mode as discussed in §2.4 and §4.3:

$$L_{COH} = \frac{2\pi}{\Delta k}.$$  \hspace{1cm} (6.2)

Thus, in case the wavevector mismatch $\Delta k$ is large, the coherence length and, consequently, the oscillation period are small. When the wavevector mismatch goes down, the oscillation period gets bigger and in case of phase-matching (wavevector mismatch is zero), the oscillation period becomes infinite.

As a result, we conclude that the periodical polymer structure can be only cross-linked by the guided phase-mismatched SH light. This photo-polymerization technique can be used for studying the electric field of the generated and guided phase-mismatched guided SH field. Furthermore, knowing the behaviour of the guided SH field, one can adjust the nanowire length to optimize the guided SH power as discussed in §5.4.2.

### 6.6 Conclusion

In conclusion, we have applied the photo-polymerization technique for studying the behaviour of the SH light that is generated and guided in individual LiNbO$_3$ nanowires. Using this method, we have mapped the intensity oscillation of the guided phase-mismatched SH light in the LiNbO$_3$ nanowires.

Besides, using the photo-polymerization technique, we have visualized the light distribution that is irradiated from the nanowire output. However, at the moment, it is not clear, if the polymer structure at the nanowire output images irradiation of
the guided FH or SH light. This question and, as well as, a thorough study of the light distribution of the irradiated light are left for future investigations.

The shown results can contribute to the development of the nanowire applications that involve nonlinear wavemixing. Moreover, the demonstrated polymerization technique can be further applied for studying scattering [150, 151] and cavity [80, 152, 153] resonances in nonlinear optical nanostructures.
Chapter 7

Sum-frequency generation in LiNbO$_3$ nanowires

7.1 Introduction

Besides the second-harmonic generation (SHG), sum-frequency generation (SFG) is also an interesting effect since it gives an access to a broader wavelength range. Moreover, this effect in nanowires can be used as a source of nonlinear light [32] or for all-optical switching [32, 66]. In this chapter, we review results on generation and waveguiding of the SFG signal. First, we demonstrate generation and waveguiding of the SF signal. Further, we show phase-matching of the guided SF light. In the end, we demonstrate tuning of the phase-matching peaks and, thus, changing the spectral response of the nanowires.

7.2 Experimental setup for the sum-frequency generation measurements

In Figure 7.1, we demonstrate a schematic of the experimental setup for the SFG measurements. The experimental setup is coupled with two lasers: a tunable pulsed Ti:Sapphire laser and a CW laser. The pulsed laser has the pulse repetition rate of 79.5 MHz and the wavelength in the range of 690-1040 nm. The pulse duration of the laser varies for each wavelength and is around 100 fs. The CW laser emits
7.2. Experimental setup for the sum-frequency generation measurements

irradiation at the fixed wavelength of 1550 nm. The laser beams are combined at
the input of the setup with a non-polarizing beamsplitter and focused onto the sam-
ple with a focusing lens (focal distance is 13.86 mm and the numerical aperture is
0.18). The radii \(1/e\) of the beamspots of the pulsed and the CW lasers at the
sample position are 3.3 \(\mu m\) (at 790 nm) and 6.3 \(\mu m\), respectively. A 100x objec-
tive (Olympus LMPFLN100x, focal distance is 3.4 mm and the numerical aperture
is 0.8) collects the sample response and the sample response is sent either to an
electron-multiplying charge-coupled device (EMCCD) camera (Rolera EM-C2) or to
a spectrometer (Acton SP-2356). The EMCCD camera is used for alignment pur-
poses and the spectrometer is used for quantitative measurements. We use a fiber
to collect the sample response and deliver it to the spectrometer. Due to a limited
numerical aperture of the fiber, the signal is collected from an area within a radius
of 9.8 \(\mu m\). As a result, the signal from different parts of a nanowire (input facet,
output facet and the nanowire profile) are studied separately.

In each laser beam path before the beamsplitter, we use a half-wave plate to
rotate the polarizations of the lasers. We also use a telescope in the beam path of
the CW laser. By shifting one of the telescope lenses, we overlap the focal points of
the pulsed and CW laser beams.

*Figure 7.1: The schematic of the experimental setup for the SFG measurement.*

*See description in the text.*
7.3 Generation and waveguiding of the sum-frequency signal in LiNbO$_3$ nanowires

Figures 7.2a and 7.2b depict scanning electron microscope (SEM) images of one of the used nanowires for the SFG studies. As shown in Figure 7.2a, the nanowire is attached to the substrate only with one end and is located at an angle of approximately 15° with respect to the substrate. The nanowire has a length of 34.05±0.5 µm, a height of 517±50 nm and a width of 654±50 nm. The deviation is caused by the combination of the fabrication procedure and the contrast limits of the SEM image. The inset in Figure 7.2a shows the crystal structure of the nanowire with the $y$-axis along the nanowire length, the $x$-axis along the nanowire height and $z$-axis along the nanowire width. The angle between the nanowire and the glass substrate was obtained arbitrarily and had no purpose. However, we expect that the angle between the nanowire and the substrate may influence efficiencies of the coupling process and collection of the guided light.

![Figure 7.2: The SEM images of the studied nanowire (a) and its output facet (b). The inset in (a) demonstrates the crystal structure of the studied nanowire.](image)

To generate and guide the sum-frequency signal in the nanowire, both laser beams are coupled by focusing them onto the input facet of the nanowire. We achieve the highest laser coupling into the nanowires by improving the overlap of the laser beam spots and adjusting the position of the nanowires within the beam spots of the incident lasers. The intensity of the collected guided signal is quantified by the...
7.3. Generation and waveguiding of the sum-frequency signal in LiNbO$_3$ nanowires

spectrometer and, as a result, it allows to achieve the highest coupling of the laser beams into the nanowire. Figure 7.3 displays the spectrum of the signal collected at the nanowire output facet when the pulsed laser wavelength is set to 790 nm. The shown spectrum in Figure 7.3 reveals a signal with the central wavelength at 522.3 nm whereas the SFG signal is expected at 523 nm:

\[
\lambda_{SFG} = \frac{\lambda_{CW} \cdot \lambda_{Pulsed}}{\lambda_{CW} + \lambda_{Pulsed}}
\]

(7.1)

where \(\lambda_{SFG}\) is the SFG wavelength, \(\lambda_{CW} = 1550\) nm is the wavelength of the CW laser and \(\lambda_{Pulsed} = 790\) nm is the wavelength of the pulsed laser.

**Figure 7.3**: The spectrum of the signal collected at the nanowire output and measured with the spectrometer. The signal at 522.3 nm is the SFG signal, the peak at 790 nm corresponds to the pulsed laser wavelength and the signal at 395 nm corresponds to the SH of the pulsed laser.

The spectrum in Figure 7.3 also reveals the guided pulsed laser irradiation (790 nm) and the SH (395 nm) that is generated by the pulsed laser. In Figure 7.3, the spectra of the CW laser beam (1550 nm) and its SH signal (775 nm) are not observed because the CW laser wavelength (1550 nm) is out of the sensitivity range of the spectrometer and the SH signal of the CW laser beam (775 nm) is too weak to be detected. In the experiment, the polarizations of the pulsed and CW laser were set to 74° and 32° with respect to the long axis of the nanowire and the power of the pulsed and CW lasers were 36 mW and 168 mW at the sample position.
To confirm that the observed signal is generated through the SFG effect, we perform power and spectral measurements of the signal, whereas linear dependencies on the power and wavelength of the incident lasers are expected. First, we show linear dependence of the intensity of the observed signal on the incident power of the lasers. Figures 7.4a and 7.4b display the obtained dependencies. In the measurements, we kept the power of one of the lasers, while we changed the power of the other laser. In Figures 7.4a and 7.4b, we also show linear fits (red solid lines) that perfectly match the measured data with the goodness of fit (R²) being 0.9982 and 0.9938, respectively.

Second, we measured the dependence of the studied signal on the pulsed laser wavelength. For this purpose, we swept the wavelength of the pulsed laser in the range of 700-850 nm with a 5 nm step and recorded the studied signal at each wavelength with constant acquisition parameters. In Figure 7.5, we plot the central wavelengths of the measured signal versus the pulsed laser wavelength (blue circles). Using Eq. 7.1, we calculated the expected SFG wavelengths in the used spectral range of the pulsed laser beam and the obtained values are also shown in Figure 7.5 (red solid line). The measured and the calculated values show a good agreement with the goodness of fit (R²) being 0.9997.

Since the studied signal depends linearly on the incident laser power (Figures 7.4a and 7.4b) and is spectrally in agreement with the theoretical values (Figure 7.5), we conclude that the observed signal is, indeed, the guided SFG signal.

As expected, the SFG signal is also detected at the nanowire input where it is generated by the incident laser beams. Furthermore, we also detect a weak SFG signal along the nanowire. We refer this signal to scattering of the guided SFG light at the roughness of the nanowire. Similar scattering was also observed in the SHG measurements of the nanowires (See Chapter 5).
7.3. Generation and waveguiding of the sum-frequency signal in LiNbO$_3$ nanowires

Figure 7.4: (a) The intensity of the guided SFG signal versus the incident power of the pulsed laser (the CW laser power was kept at 168 mW). (b) The intensity of the guided SFG signal versus the incident power of the CW laser (the pulsed laser power was kept at 36 mW).

7.3.1 Enhancement of the guided sum-frequency signal

By observing the guided SFG signal in the nanowires, the next logical step is to verify that the phase-matching of the SFG signal is possible. For this purpose, we measure the SFG intensity over a broad wavelength spectrum of the pulsed laser. In
Chapter 7. Sum-frequency generation in LiNbO$_3$ nanowires

Figure 7.5: SFG wavelength versus the pulsed laser wavelength (the wavelength of the CW laser is 1550 nm).

Figure 7.6, we plot the measured SFG intensity versus the pulsed laser wavelength (blue dots). The curve in Figure 7.6 reveals two peaks (at 755 nm and 780 nm) and a significant amplitude variation of the guided SFG signal with the change of the pulsed laser wavelength. Thus, by shifting the pulsed laser wavelength from 835 nm down to 755 nm, the SFG signal has been increased by a factor of 17.9. The observed change of intensity is referred to modal phase-matching that was already observed for the guided SHG signal (See §5.4.1).

To theoretically show that modal phase-matching can take place in the considered nanowire, we simulate generation and waveguiding of the sum-frequency signal. In the simulation, we consider a nanowire with a cross-section within the deviation range of the SEM measurement. For each cross-section, we calculate two modes at 1550 nm, up to ten modes at each pulsed laser wavelength and up to thirty modes at each corresponding SFG wavelength. In the considered cross-sections, there exist less guided modes at particular wavelengths of the pulsed laser and the SFG signal than we try to calculate. As a result, we make sure that we take into account all existing guided modes in our simulation. Further, we find conversion efficiencies and wavevector mismatches $\Delta k$ of all possible groups of modes (one at
7.3. Generation and waveguiding of the sum-frequency signal in LiNbO$_3$ nanowires

Figure 7.6: The intensity of the guided SFG signal versus the wavelength of the pulsed laser. The measurements at each wavelength are performed with constant acquisition parameters.

1550 nm, one at the pulsed laser wavelength and one at the corresponding SFG wavelength). In the calculation, we consider the second-order susceptibility tensor [89] and wavelength-dependent refractive index [129] of the LiNbO$_3$ crystal and crystal structure of the nanowire that is shown in the inset of Figure 7.2a. Based on the calculated conversion efficiencies and wavevector mismatches $\Delta k$, we find overall contributions to the SFG signal for each possible pair of modes at the CW laser wavelength (1550 nm) and at each pulsed laser wavelength.

Having found contributions of each pair of modes at the CW laser wavelength (1550 nm) and at each pulsed laser wavelength to the SFG signal, we determine that the best match of the experiment and the simulation is obtained for the nanowire width of 654 nm and height of 512 nm. At this cross-section, two groups of modes could contribute to the SFG signal and create two observed phase-matching peaks. According to the simulation, the peak at 755 nm is created by the 2nd mode at 1550 nm and the 9th mode mode at 755 nm and the peak at 780 nm is created by the 2nd mode at 1550 nm and the 10th mode at 780 nm. The profiles of the
considered modes are demonstrated in Figure 7.7. The summed-up contributions of these two pairs of modes are plotted in Figure 7.6 in a red solid line. Since the coupled power of the laser light into the considered modes is unknown, the strength of both contributions are adjusted to fit the heights of the peaks in the experimental and theoretical curves. In Figure 7.6, one can also notice a lateral mismatch between the experimental and simulation curves. This mismatch is referred to variation of the nanowire cross-section (in shape and size) along the nanowire length due to the fabrication procedure.

![Mode profiles](image)

**Figure 7.7: Mode profiles of the 9th mode at 755 nm (a), the 10th mode at 780 nm (b) and the 2nd mode at 1550 nm (c).**

Based on the aforementioned results, we conclude that phase-matching of the guided SFG is possible in LiNbO$_3$ nanowires and this effect can be used for enhancing the SFG effect, as previously shown for the SHG effect in §5.4.1.

### 7.3.2 Tuning of the guided sum-frequency signal

In nanowires, one can use several parameters to tune the phase-matching effect and control the enhancement of the converted signal in a wide spectral range. For example, the nanowire cross-section influences the phase-matching process, since it determines the shape of the waveguide modes and their effective refractive indices. Consequently, for different nanowire cross-sections, the phase-matched wavelengths and the conversion efficiency are different for a particular set of the pump and SFG waveguide modes. To experimentally demonstrate the influence of the cross-section
7.3. Generation and waveguiding of the sum-frequency signal in LiNbO$_3$ nanowires

on the phase-matching process, we measure the SFG response in a second nanowire with a different cross-section. The inset in Figure 7.8a shows the SEM picture of the output facet of the nanowire. The SEM image indicates that the nanowire has a non-rectangular cross-section with the width of $511 \pm 30$ nm and the height varying from $439 \pm 30$ nm up to $797 \pm 30$ nm. In the measurement, the power of the pulsed and CW lasers were 36 mW and 168 mW and the polarizations of the pulsed and CW laser were set to $2^\circ$ and $54^\circ$ with respect to the long axis of the nanowire. In Figure 7.8a, we show the measured guided SFG intensity versus the pulsed laser wavelength. The obtained SFG responses of the first (Figure 7.6) and the second nanowires (Figure 7.8a) are completely different. The SFG curve of the nanowire shows phase-matching peaks at 755 nm and 780 nm, whereas the second nanowire shows only phase-matching peaks at 730 nm and 785 nm. Thus, the obtained results confirm that nanowires with different cross-sections provide different phase-matching responses. As a result, it is possible to obtain phase-matching and, thus, enhance the SFG response in the desired spectral range by a careful choice of the nanowire cross-section.

Besides the nanowire cross-section, the incident laser polarizations can also be used to control the phase-matching response. The laser polarization determines to which modes the laser light is coupled [59]. In turn, a different phase-matching response is obtained for each waveguide mode. To experimentally demonstrate the impact of the laser polarization on the guided SFG signal, we measure the SFG response of the second nanowire when the polarization of the pulsed laser was set to $32^\circ$ and $58^\circ$ with respect to the long axis of the nanowire whereas the polarization of the CW laser stayed at $54^\circ$ with respect to the long axis of the nanowire. We plot the obtained SFG responses in Figure 7.8 (b).

The curves in Figures 7.8a and 7.8b reveal three pronounced phase-matching peaks at 725 nm, 785 nm and 810 nm. The heights of the peaks strongly vary with the laser polarization and each peak reaches its maxima at a different polarization of the pulsed laser. Thus, the peak at 810 nm is maximized at the pulsed laser polarization of $32^\circ$ with respect to the long axis of the nanowire, whereas strong
Figure 7.8: Intensity of the guided SFG signal versus the wavelength of the pulsed laser when the polarization of the pulsed laser is 2° (a), 32° (red squares in (b)) and 58° (blue circles in (b)) with respect to the long axis of the nanowire. In all three measurements, the polarization of the CW laser was set to 54° with respect to the long axis of the nanowire. The measurements at each wavelength are performed with constant acquisition parameters. In the inset of (a), we show the output facet and the crystal structure of the nanowire.
peaks at 725 nm and 785 nm are obtained at the pulsed laser polarization of $2^\circ$ with respect to the long axis of the nanowire. Moreover, the peaks can be eliminated by choosing a proper laser polarization. Thus, when the laser polarization is rotated to $2^\circ$, $32^\circ$ and $58^\circ$, one diminishes the peaks at 810 nm, 785 nm and 725 nm, respectively.

As a result, one can control the phase-matching response of the SFG signal by rotating the incident polarization of the pump beams. Moreover, changing the laser polarization makes it possible to switch the phase-matching peaks so that LiNbO$_3$ nanowires could be used for applications such as all-optical switching [66].

7.4 Conclusion

In this chapter, we reviewed the results on the SFG in LiNbO$_3$ nanowires. First, we demonstrated generation and waveguiding of the SF signal in the LiNbO$_3$ nanowires. Further, we showed the possibility of modal phase-matching to achieve an enhancement of the SFG signal. After all, we demonstrated tunability of the phase-matching response by either using a nanowire with a different cross-section or by varying polarization of the incident laser beams.

The demonstrated results prove that the LiNbO$_3$ nanowires could serve in the future as building blocks for miniaturized optical devices. For example, they can be applied for pulse characterization [74] and logical gating [32]. In addition, LiNbO$_3$ nanowires can serve as nonlinear light sources and can be used for further development of nanowire-based optical parametric oscillators and terahertz radiation sources.
Chapter 8

Localized dye excitation with the guided second-harmonic light

8.1 Introduction

As discussed in §2.3, nanowires can be used for localized imaging of tiny objects such as living cells [63, 64]. Moreover, the ability of a nanowire to generate and guide second-harmonic (SH) light allows to further develop this application. A powerful laser beam can be used for manipulating a nanowire in liquid [70] and generating guided SH that excites the fluorescent material at the nanowire output. Since the laser light and the SH are spectrally separated, one can use such a laser wavelength $\lambda$ so that the fluorescent material is not excited by the laser beam but only by the generated SH at $\lambda/2$.

In this chapter, we demonstrate that the lithium niobate (LiNbO$_3$) nanowires generate and guide enough SH power for efficient excitation of fluorescent material. Further, we estimate the threshold power of the guided SH for efficient dye excitation. Finally, we calculate the smallest cross-section at which nanowire provides enough guided SH power for dye excitation.

8.2 Sample preparation and experimental setup

For the dye excitation experiments, we use a 4′,6-diamidino-2-phenylindole (DAPI) dye since it is widely applied in biological applications for staining nuclei of cells.
8.2. Sample preparation and experimental setup

The DAPI dye absorbs light below 500 nm with the absorption peak at 359 nm through the single-photon absorption process (SPA) (Figure 8.2a). As a result, a near-infrared (NIR) laser can only excite this dye through a two-photon absorption process (TPA) (Figure 8.2b), which is highly inefficient and requires high laser intensity [156]. Consequently, an NIR laser can be applied to generate the SH for the fluorescence excitation. Moreover, since the emission spectrum has a maximum at 456 nm, the SH and the fluorescence signals are easily differentiated by using appropriate bandpass filters in front of the camera.

Figure 8.1: The absorption and fluorescence spectra of DAPI dye. Source:[157].

Figure 8.2: The energy diagrams of the single-photon (a) and two-photon (b) absorption and fluorescence processes.
Chapter 8. Localized dye excitation with the guided second-harmonic light

The dye solution is prepared by mixing water and DAPI dye in different concentrations. In Figure 8.3, we depict the procedure of the sample preparation. We dropcast nanowires onto a glass slide (Figure 8.3a) and add 10 µl of the dye solution (Figure 8.3b). To prevent evaporation of the solution, the sample is sealed with a cover slip (Figure 8.3c). In all experiments, we use only freshly prepared samples, in order to prevent agglomeration of the dye.

We performed the dye excitation experiments in the setup that is described in detail in §5.2. We used a BG39 bandpass filter to detect the SH response and an FGL400 longpass filter to detect the excited fluorescence signal.

8.3 Observation of the fluorescent dye excitation with the guided signal

For the dye excitation experiment, a laser beam with the wavelength of 760 nm and with the average power of 85 mW is used to generate and guide the SH light at 380 nm. Figures 8.4a and 8.4b show obtained fluorescent signal that is excited by two different nanowires, which are embedded in solution with dye concentrations of 1 µg/ml and 50 ng/ml, respectively.

Figures 8.4a and 8.4b reveal an excited fluorescence signal both at the input and at the output of the nanowires. At the input, the fluorescence signal is most probably

![Figure 8.3: The procedure of the dye sample preparation: (a) dropcasting nanowires onto the glass substrate; (b) adding 10 µl of the dye solution; (c) sealing the dye solution with a cover slip.](image)
8.4. Contribution of the FH and the SH signals to dye excitation

Figure 8.4: The images of the fluorescence signal in DAPI dye solution with concentrations of 1 µg/ml (a) and 50 ng/ml (b). The dashed and the dotted circles indicate the illumination area of the incident beamspot and the fluorescence signal at the nanowire output, respectively. The dash-dotted line indicates the position of the nanowire.

excited by both the incoming laser beam through the TPA process and by the generated SH signal through the SPA process. At the output, the fluorescence signal is excited by a guided signal. It is worth mentioning that the typical concentration for biological applications varies in a range 50 ng/ml - 1.5 µg/ml [158, 159]. Thus, the LiNbO$_3$ nanowires can be used for biological applications.

8.4 Contribution of the FH and the SH signals to dye excitation

Since the nanowires guide the fundamental-harmonic (FH) and SH signals, both signals may contribute to the dye excitation. The FH can excite the fluorescence through the TPA process, whereas the SH can excite the fluorescence through the SPA process. To differentiate contributions of both signals to the dye excitation,
we theoretically estimate the fluorescence power that can be excited by the guided laser and guided SH light.

For this purpose, we first measure the power values of the guided FH and SH signals for one of the tested nanowires when they were embedded in water. We find the power values by taking a picture of the guided signal with an electron-multiplying charge-coupled device (EMCCD) camera, integrating the levels of the pixels in the image and back-converting the integrated value into watts. Having done all the steps, we find the guided laser light and SH power to be 441±44 nW and 2.57±0.26 nW, respectively.

Further, using the rate equations for the SPA and TPA processes [160], we calculate the fluorescence power values excited by 441 nW of the FH power and 2.57 nW of the SH power in a 1 µg/ml DAPI dye solution. In Table 8.1, we show the used rate equations and estimated contributions of the FH and SH signal to the fluorescence signal. In the calculation, we take into account the quantum efficiency $q = 1.7\%$ [161], the SPA cross-section $\sigma_A = 64.6 \cdot 10^{18} \text{cm}^{-2}$ [162] and the two-photon emission (TPE) cross-section $\beta_E = 0.16 \cdot 10^{-50} \text{cm}^{-4} \cdot \text{s/photon}$ of the DAPI dye [163]. The constant $c$ stands for the dye molecule concentration and $\beta_A$ denotes TPA cross-section. The initial intensity values $I_0$ are calculated by assuming the nanowire cross-section to be 500×500 nm and that the propagated FH signal keeps the pulse duration of the incident laser beam. The layer thickness of the DAPI dye solution $x = 20 \mu\text{m}$ is estimated by dividing the used volume of the dye solution by the area of the cover slip.

According to the calculation, 441 nW of the guided FH do not excite any fluorescence, whereas 2.57 nW of the guided SH should excite 1.028 pW [146]. Thus, we conclude that the fluorescence signal at the nanowire output is excited by the guided SH signal.
8.5 Threshold values of the SH power and nanowire cross-section for dye excitation

Table 8.1: Rate equations for the SPA and TPA processes and their contribution to fluorescence excitation. See the detailed description of the constants in the main text.

<table>
<thead>
<tr>
<th></th>
<th>Single-photon process</th>
<th>Two-photon process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption law</td>
<td>( \frac{dI}{dx} = -\sigma A \cdot c \cdot I )</td>
<td>( \frac{dI}{dx} = -\beta A \cdot c \cdot I^2 )</td>
</tr>
<tr>
<td>Fluorescence</td>
<td>( \eta_{\text{SPE}} = q \cdot [1 - \exp(-\sigma A \cdot c \cdot x)] )</td>
<td>( \eta_{\text{TPE}} \approx \beta E \cdot c \cdot x \cdot I_0 )</td>
</tr>
<tr>
<td>Calculated results</td>
<td>( \eta_{\text{SPE}} = 0.0004% )</td>
<td>( \eta_{\text{TPE}} \rightarrow 0 )</td>
</tr>
</tbody>
</table>

8.5 Threshold values of the SH power and nanowire cross-section for dye excitation

For the localized imaging application of biological samples, the imaging resolution is expected to depend on the nanowire cross-section. However, the SHG process quadratically depends on the volume of the crystalline material [9, 30]. As a result, the generated SH signal gets weaker in thinner nanowires. The generated SH signal can be always increased by using a stronger pump power. However, the pump power is limited by the damage threshold power of the biological samples that are to be studied. Thus, the used nanowire should not have a cross-section below a certain limit for successful performance of localized imaging. In this section, we theoretically estimate the smallest cross-section of a nanowire that can be used for efficient dye excitation in biological samples.

For this purpose, we calculate the maximum guided SH power that is generated with the laser beam in a nanowire with varied cross-sections. For the calculation, we first theoretically estimate the threshold power of an NIR laser beam for damaging a cell and the smallest guided SH power for efficient dye excitation.

To set the threshold power of the NIR laser light, we assume that the full laser
power is coupled into a nanowire and the power of the guided laser beam is limited by the damage threshold power of a living cell. The damage threshold average power is estimated to be around 18.5 mW at the wavelength of 760 nm [164]. For the estimation, we assume a nanowire cross-section of 500×500 nm and a pulse duration of 200 fs.

To estimate the smallest guided SH power for efficient fluorescence excitation, we perform two measurements with the same nanowire. In the first measurement, the studied nanowire is embedded in pure water and we quantify power values of the guided FH and SH light. In the second measurement, the nanowire is embedded in a dye solution with the DAPI concentration of 1 μg/ml, we quantify the power of the excited fluorescent and we find the signal-to-noise-ratio (SNR) for the excited fluorescence signal. Figure 8.5a plots the calculated fluorescence power and the guided SH power versus the incident beam power. In Figure 8.5b, we plot the SNR of the excited fluorescence signal versus the guided SH power. To define the SHG threshold power, we use the Rose criterion [165]. According to the Rose criterion, the image features can be unambiguously identified only for the images with the SNR above 5. Thus, we set the threshold of the SNR to 5 and estimate the threshold SHG power to be 63±6 pW.

Having estimated the damage threshold power of the NIR laser and the threshold SH power for efficient dye excitation, we simulate generation and waveguiding of the SH signal. The simulation flow is described in Chapter 4. In the simulation, we vary the width and height of a nanowire from 30 up to 100 nm with steps of 10 nm and perform it for six possible crystal structures varying the crystal axes parallel to the nanowire width, height and length. We use the estimated laser power to find the maximum excited SH signal and to compare with the estimated SH threshold power. As an example, in Figure 8.6, we show calculated power of the guided SH signal at various heights and widths of a nanowire that has an x-axis parallel to the height and z-axis parallel to the width.

Having performed the simulations for each crystal structure, we find the smallest cross-section at which the nanowires provides enough SH signal for detectable dye
8.5. Threshold values of the SH power and nanowire cross-section for dye excitation

Figure 8.5: (a) The guided SH and excited fluorescence signal versus the incident laser beam power. The squares correspond to the guided SH and the circles correspond to the fluorescence signal. (b) SNR of the fluorescence signal versus the average power of the guided SH. The dashed line shows the limit value of the SNR equal to 5 at which the features of the image can be unambiguously identified according to the Rose criterion [165].

excitation. For this goal, we compare the simulation results with the above-defined threshold of the SH average power for detectable dye excitation ($63 \pm 6 \text{ pW}$). The simulations show that only nanowires possessing three out of the six studied crys-
Chapter 8. Localized dye excitation with the guided second-harmonic light

Figure 8.6: (a) Calculated power of the guided SH signal at various nanowire height and width. (b) The graph indicates the cross-sections of the nanowire at which SH power above 63 pW is obtained. The calculation is performed for a nanowire that has an x-axis parallel to the nanowire height and z-axis parallel to the nanowire width.

Table structures are potentially able to provide an average power of the propagated SH signal above the set threshold value for the nanowire cross-section size below $100 \times 100$ nm$^2$. For the nanowires with these three crystal structures, we summarize the simulation results of the limiting cross-section size and the corresponding predicted average power of the propagated SH signal in Table 8.2.

Table 8.2: The smallest nanowire height and width for various nanowire crystal structures at which the nanowires provide a propagated SH average power above $63 \pm 6$ pW and the predicted average power of the SH signal.

<table>
<thead>
<tr>
<th>The crystal axis parallel to the nanowire height</th>
<th>The crystal axis parallel to the nanowire width</th>
<th>Nanowire cross-section, nm$^2$</th>
<th>Calculated guided SH power, pW</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x$</td>
<td>$z$</td>
<td>$40 \times 60$</td>
<td>106.2</td>
</tr>
<tr>
<td>$x$</td>
<td>$y$</td>
<td>$40 \times 60$</td>
<td>96.4</td>
</tr>
<tr>
<td>$z$</td>
<td>$y$</td>
<td>$60 \times 60$</td>
<td>113.9</td>
</tr>
</tbody>
</table>
According to the results in Table 8.2, the smallest cross-section at which efficient dye excitation is possible is $40 \times 60 \text{ nm}^2$. Taking into account that the existing fabrication methods allow to fabricate nanowires down to $50 \times 50 \text{ nm}^2$ [33], LiNbO$_3$ nanowires have a great potential in localized delivery of light.

8.6 Conclusion

In this section, we showed that the LiNbO$_3$ nanowires generate and guide enough SH signal to efficiently excite fluorescent dye. Further, we defined the range of the SH power required for achieving detectable dye fluorescence signal. Knowing this range and modelling generation and waveguiding of the SH light in a nanowire, we estimated the smallest nanowire cross-section, at which a nanowire is potentially able to provide enough SH light for detectable dye excitation. Thus, LiNbO$_3$ nanowires with the cross-section down to $40 \times 60 \text{ nm}^2$ have a potential to provide enough SH power for detectable dye excitation. Furthermore, the existing fabrication methods allow to fabricate LiNbO$_3$ nanowires down to a cross-section of $50 \times 50 \text{ nm}^2$.

However, ways of increasing the coupling efficiency and the amount of the guided SH signal are still to be explored. For example, one can increase the amount of the propagated FH light by optimizing the coupling efficiency. Alternatively, one can also synthesize a gold nanoshell around the nanowire surfaces to achieve enhancement of the SH signal by means of plasmon resonances [96, 97]. As a result, we showed that the LiNbO$_3$ nanowires have great potential in localized delivery of light. In addition, the nanowires can be applied not only for bringing light at a certain location but also for collecting it [63]. Thus, the LiNbO$_3$ nanowires are very promising types of nanomaterials in various future applications for both biological and non-biological purposes.
Chapter 9

Summary and perspectives

9.1 Summary

During this PhD project, we studied nonlinear wavemixing in individual lithium niobate (LiNbO$_3$) nanowires that are fabricated with the ion-beam enhanced etching method [33]. Namely, we studied generation and waveguiding of the second-harmonic (SH) and sum-frequency (SF) signals. Both the second-harmonic generation and sum-frequency generation are the second-order nonlinear optical effects and require less pump laser power than any other higher-order nonlinear optical effect.

In the first part of the dissertation, we focused our study on the second-harmonic generation (SHG) process in the LiNbO$_3$ nanowires.

- We demonstrated generation and waveguiding of the SH signal in the nanowires. To demonstrate waveguiding, we coupled an incident laser beam into a nanowire and recorded the guided signal from the nanowire output by an electron-multiplying charge-coupled device camera. Further, we showed that the guided signal is, indeed, the SH signal by confirming the quadratic dependence of the guided signal on the incident laser power.

- We showed strategies for enhancing the guided SH signal, which is relevant for nonlinear wavemixing in nanostructures since the nonlinear wavemixing effects quadratically depend on the volume of the crystalline material and the guided SH power in nanowires is expected to be weak.
We demonstrated modal phase-matching in the LiNbO$_3$ nanowires, which allows to significantly enhance the guided SH signal. Furthermore, the used nanowires allow multimode regime in the visible range and, consequently, multiple phase-matching peaks can be obtained from the same nanowire in different spectral ranges.

We also showed that the phase-mismatched guided SH signal can be also optimized. Since the phase-mismatched guided SH oscillates along the propagation direction, the power of the guided SH signal can be optimized by adjusting the nanowire length. It was demonstrated by performing a series of experiments by shortening the same nanowire with a focused ion beam milling and measuring the guided SH after each milling procedure.

- We demonstrated that a photo-polymerization technique can be used to study the behaviour of the guided signal in LiNbO$_3$ nanowires.

We showed that this technique allows to image oscillations of the phase-mismatched guided SH signal along the nanowire length. Analysing the polymer structures allows to precisely define the coherence length and positions of the maximum guided SH power in the phase-mismatching regime. Thus, the photo-polymerization technique can be applied for adjusting the nanowire length to optimize the guided phase-mismatched guided SH power and it can serve as a powerful alternative to scanning near-field optical microscopy.

We also showed that, using this technique, one can image the distribution of the guided SH signal after it is coupled from the nanowire. As a consequence, this technique can be applied for studying light distribution and facet design to obtain the required light distribution, which is relevant for such nanowire application as nanowire microscopy and localized imaging.

In the second part of the dissertation, we focused our study on the sum-frequency generation (SFG) process in the LiNbO$_3$ nanowires.

- We demonstrated generation and waveguiding of the SF signal in the nanowires.
For this purpose, we performed spectral and power measurements of the guided signal collected from the nanowire output. By varying the wavelength of one of the incident laser, we detected the wavelength change of the guided signal, which was in agreement with the theoretical prediction. Further, we demonstrated that the power of the studied guided signal linearly reacts on the power of the incident lasers.

- We obtained modal phase-matching of the guided SF signal, which also allowed to enhance the guided SF signal.

- We demonstrated control of the phase-matching peaks and switched them by changing the polarization of the incident laser beams. Thus, SFG-emitting nanowires can be further applied for all-optical switching [32].

**In the third part** of the dissertation, we discussed applicability of the LiNbO$_3$ nanowires for the localized imaging.

- We demonstrated that the LiNbO$_3$ nanowires provide enough guided SH power to locally excite fluorescent material.

- We experimentally estimated the threshold power of the guided SH signal that is required for an efficient dye excitation.

- Using the estimated threshold power and theoretical simulation, we found that the LiNbO$_3$ nanowires can provide enough guided SH power for efficient dye excitation at the nanowire cross-section being down to $40 \times 60 \text{ nm}^2$.

The demonstrated results prove that the LiNbO$_3$ nanowires have a potential for being exploited as building blocks for the future devices and applications. Thanks to the ability of the LiNbO$_3$ nanowires to generate and guide nonlinear signal, the nanowires can serve as sources of nonlinear light in lab-on-chip applications. Furthermore, they can be also used for even more sophisticated applications. Thus, the SH-generating nanowires can be used for localized imaging, nanowire microscopy and chemical analysis and the SF-generating nanowires can be applied for all-optical
9.2 Perspectives

In order to develop nanowire-based applications, further research should be performed on nanowires. After all, ways of increasing the coupling efficiency should be found. It will allow to use smaller nanowires and, thus, complement further miniaturization of the future devices. We expect that the coupling efficiency can be increased by shaping the input facet of the nanowires. Thus, one should study how the shape of the input facet influences the coupling efficiency of light into nanowires. Besides, we expect that the shape of the input facet defines the excited waveguide modes. Thus, by engineering the shape of the input facet, one may excite a mode that gives the largest contribution to the generated field. Furthermore, the coupling efficiency can be increased by changing the coupling configuration. The coupling configuration (Figure 9.1a) that was used in our experiments is not optimal. A higher coupling efficiency can be achieved by changing the configuration and focusing the laser beam directly onto the nanowire facet as shown in Figure 9.1b. However, nanowires are usually short and the second configuration would not work. Thus, one should either fabricate millimeter long nanowires or elaborate an effective method for bringing nanowires to the edge of the substrates.

Further, one should investigate light distribution of the guided light after it is outcoupled from the nanowires. This study may help to precisely quantify the guided generated signal. Furthermore, the light distribution of the guided light is relevant for the nanowire-based applications such as localized imaging and nanowire microscopy. Thus, a thorough study may define the factors that influence the light distribution and suggest ways to manipulate it.

After all, other properties of the LiNbO$_3$ crystal may also be applied. For ex-
Chapter 9. Summary and perspectives

Figure 9.1: (a) The coupling configuration that is used in our measurements. (b) An alternative coupling configuration that should provide higher coupling efficiency.

ample, the phase-matching regime can be also tuned by applying electric field [54] or heating [101]. Furthermore, since the LiNbO$_3$ is a ferroelectric material, LiNbO$_3$ nanowires may charge when exposed to light and, thus, be used for photovoltaic and sensing applications [166, 167]. Finally, nanowires can also be used for modulating and filtering the guided signal, as it is demonstrated in LiNbO$_3$ millimeter-size waveguides [50, 168].

Finally, further applications of the LiNbO$_3$ nanowires should be demonstrated. For example, such nonlinear optical effects as optical parametric amplification and oscillation may make LiNbO$_3$ nanowires an invaluable component in lab-on-chip applications [169]. Furthermore, one may use LiNbO$_3$ nanowires as sources of terahertz irradiation using difference-frequency generation [102, 170]. Finally, LiNbO$_3$ nanowires can be also applied for other applications such as nanowire spectrometers, which is based on a standing wave-pattern [171].
Bibliography


Bibliography


Bibliography


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This PhD project lasted for almost 4.5 years and it was influenced and supported by a large number of people who shared their experience, ideas and suggestions with me.

Here, I would like to acknowledge contributions of these people and list their names. However, I would like to apologize to those whose names I may have un-deliberately forgotten to mention here. This PhD project was such a long journey that it is sometimes difficult to recall its each step.

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Reinhard Geiss
Waltraut Gräf

**Rachel Grange**
Nicholas Hendricks
Norik Janunts
Roman Kiselev
Angela Klein
Marc Lehner
Bayarjargal Narantsatsralt
Dragomir Neshev

Thomas Pertsch
Marc Reig
Jörg Reinhold
Giacomo Scalari
Detlef Schelle
Natali Sergeev
Frank Setzpfandt
Dmitry Sivun
Alexander Solntsev
Andrea Steinbrück
Flavia Timpu
Michal Wojdyr
Anton SERGEYEV

**PERSONAL DATA**

**DATE OF BIRTH:** 23 November 1986  
**ADDRESS:** Schwamendingenstrasse 81, 8050 Zürich, Switzerland  
**NATIONALITY:** Kazakhstan, Residence permit type B  
**EMAIL:** AntonASergeyev@gmail.com  
**PHONE:** +49 15 78 26 96 147

**EXPERIENCE**

| Jan 2015 - Today | Research assistant, **Institute for Quantum Electronics, ETH Zürich**  
| | - Experiment and simulation study of nonlinear wavemixing effects in lithium niobate nanowires  
| | - Generation and waveguiding of the sum-frequency signal  
| | - Enhancement and tuning of the guided sum-frequency signal  
| | - Mapping the guided second-harmonic signal with the use of a photosensitive polymer  
| | - Scientific writing and presenting at scientific conferences  
| | - Teaching assistance in multiple courses  

| May 2012 - Dec 2014 | Research assistant, **Institute for Applied Physics, Friedrich Schiller University Jena**  
| | - Experiment and simulation study of nonlinear wavemixing effects in lithium niobate nanowires  
| | - Generation and waveguiding of the second-harmonic signal  
| | - Enhancement of the guided second-harmonic signal  
| | - Localized dye excitation with the guided second-harmonic signal  
| | - Scientific writing and presenting at scientific conferences  
| | - Supervision of two Master student research projects  

| Oct 2010 - Feb 2011 | Teaching Assistant, **Friedrich Schiller University Jena**  
| | Correction of weekly submitted assignments for the course “Fundamentals of Modern Optics”  

| Mar 2010 - Apr 2010 | Tutor, **Friedrich Schiller University Jena**  
| | Support of students in exam preparation for the course “Fundamentals of Modern Optics”  

**EDUCATION**

| May 2012 - Today | PhD Candidate in Physics, **ETH Zürich**, Switzerland  
| | Institute for Quantum Electronics, ETH Zürich, Switzerland (Jan 2015 - today)  
| | Institute for Applied Physics, Friedrich Schiller University Jena, Germany (May 2012 - Dec 2014)  
| | Dissertation: “Nonlinear wavemixing in lithium niobate nanowires”  

| Oct 2009 - Jun 2012 | Master of Science in Photonics, **Friedrich Schiller University Jena**, Germany  
| | GPA: 1.6/4.0 (best possible grade: 1.0)  
| | Thesis: “Second-harmonic waveguiding and resonance modes in oxide and semiconductor nanowires”  

| Sep 2005 - Jun 2009 | Bachelor of Science in Photonics and Optoinformatics, **Tomsk State University of Control System and Radioelectronics**, Russia  
| | GPA: 4.76/5.00 (best possible grade: 5.0)  

| Sep 1994 - Jun 2005 | High school education, **Rudny Gymnasium**, Kazakhstan  
| | GPA: 4.89/5.00 (best possible grade: 5.0)
Skills

• Experiment and simulation skills
• Design and construction of complex optical setups
• Sample characterization in scanning electron microscope (SEM)
• Sample processing and milling with focused ion beam (FIB)
• Automatization of data analysis by coding in Matlab
• Automatization of experiments and device integration by coding in Labview

Languages

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Computer Skills

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Interests and Activities

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Scholarships

• Scholarship for Master studies at Friedrich Schiller University Jena
• Scholarship for Bachelor studies at Tomsk State University of Control Systems and Radioelectronics
List of publications

Publications


List of publications


List of attended conferences

Conferences


• Sergeyev A., Grange R., “Nonlinear wavemixing in lithium niobate nanowaveguides”, *EMN Meeting on Nanowires*, Amsterdam, 2016. **Invited talk.**


