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# Spatially-Controlled Second Harmonic Generation in Lithium Niobate Silicate and Borosilicate Glasses

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**Abstract:** This work investigates the role of B<sub>2</sub>O<sub>3</sub> addition into a silicate glass matrix on the orientational dependency of second harmonic generation (SHG), induced by LiNbO<sub>3</sub> crystals after femtosecond laser irradiation.

## 1. Introduction

Femtosecond (fs) laser direct writing (FLDW) is a powerful and versatile tool to enable a large variety of optical components to be fabricated in transparent materials such as glasses (e.g., Bragg gratings, waveguides, graded index lenses, birefringent optics) [1,2]. By controlling the fs-laser parameters (polarization, pulse energy, repetition rate, scanning speed) it becomes possible to induce controlled modifications inside the glass, hence local properties. As an example to this approach, LiNbO<sub>3</sub> crystals, having properties such as piezoelectricity and ferroelectricity, were induced in a 33%Li<sub>2</sub>O – 33%Nb<sub>2</sub>O<sub>5</sub> – 34%SiO<sub>2</sub> (molar percentage) glass matrix (LNS) [3]. It was shown that the orientation of the polar axis of the LiNbO<sub>3</sub> nanocrystals can be dictated by controlling the writing laser polarization. Because of axial symmetry, the second order susceptibility tensor ( $\chi^{(2)}$ ) of LiNbO<sub>3</sub> crystal is such that its nonlinear coefficient value along the polar axis ( $d_{33} = 34.4$  pm/V) is much greater than the nonlinear coefficients values along the axes perpendicular to it ( $d_{31} = 5.95$  pm/V,  $d_{22} = 3.07$  pm/V). Therefore, an angular modulation of  $\chi^{(2)}$  properties, such as second harmonic generation (SHG), occurs provided the crystals can be oriented in a non-random fashion.

In this context, the aforementioned work is extended and the role of the glass matrix on the crystal orientability is investigated herein. Furthermore, the partial substitution of SiO<sub>2</sub> with B<sub>2</sub>O<sub>3</sub> is of interest since introduction of B<sub>2</sub>O<sub>3</sub> lowers glass-making temperature. Consequently, addition of B<sub>2</sub>O<sub>3</sub> is expected to modify the kinetics of LiNbO<sub>3</sub> crystallization and the thresholds of the different regimes found for LNS glass. For this purpose, anisotropy of the SHG property is investigated in both static (writing speed = 0  $\mu\text{m/s}$ ) and scanning (writing speed  $\neq 0$   $\mu\text{m/s}$ ) fs-laser irradiation conditions.

## 2. Experimental procedure

Four glasses, with compositions given in Table 1, are fabricated using conventional melt-quenching technique, and are shaped into plates of ~1 mm thickness upon cooling. Both top and bottom surfaces of each sample are then polished until optical roughness is reached.

Table 1. Glass labels and batch compositions (molar percentage)

Label	Glass batch composition (molar percentage)
LNS34	33%Li <sub>2</sub> O – 33%Nb <sub>2</sub> O <sub>5</sub> – 34%SiO <sub>2</sub>
LNS27B7	33%Li <sub>2</sub> O – 33%Nb <sub>2</sub> O <sub>5</sub> – 27%SiO <sub>2</sub> – 7%B <sub>2</sub> O <sub>3</sub>
LNS20B14	33%Li <sub>2</sub> O – 33%Nb <sub>2</sub> O <sub>5</sub> – 20%SiO <sub>2</sub> – 14%B <sub>2</sub> O <sub>3</sub>
LNS13B21	33%Li <sub>2</sub> O – 33%Nb <sub>2</sub> O <sub>5</sub> – 13%SiO <sub>2</sub> – 21%B <sub>2</sub> O <sub>3</sub>

Each glass sample is thus irradiated using a femtosecond laser ( $\lambda = 1030$  nm, 300 fs, NA = 0.6) focused shifted by 350  $\mu\text{m}$  below the surface. A first set of experiments consists of static irradiations to investigate the incubation time until SHG is detected online, through the observation of an intense green light characteristic of SHG signal at  $\lambda_{\text{SHG}} = \lambda/2 = 515$  nm. In this experiment, laser parameters are varied, including pulse energy (from 0.25 to 2.5  $\mu\text{J}$ , step of 0.25  $\mu\text{J}$ ) and laser repetition rate (100 kHz, 200 kHz, 340 kHz, and 510 kHz). A second set of experiments is to write lines (fixed frequency of 200 kHz and writing speed of 1  $\mu\text{m/s}$ ) using different pulse energies (0.25  $\mu\text{J}$  to 2.0  $\mu\text{J}$ , step of 0.25  $\mu\text{J}$ ) and for three different laser polarization configurations: parallel (//), at 45°, and perpendicular ( $\perp$ ) to the laser writing direction. Following this experiment, the angular dependency (total of 180°) of the SHG intensity for each irradiated line is measured according to the azimuthal angle ( $\theta$ ) of the polarization of the probing beam.

## 3. Results and discussion

Fig. 1a and 1b display the incubation time (in seconds), under static irradiation, to observe intense green light emission, characteristic of SHG. The comparison of the results for two glass samples, LNS34 and LNS20B14, illustrates well the fact that an addition of  $B_2O_3$  typically promotes fast crystallization, especially at low repetition rates. These data are consistent with differential scanning calorimetry (DSC) measurements, to be discussed at the conference, showing that borosilicate samples (LNSB), relative to the silicate (LNS) one, tend to crystallize at lower temperatures.

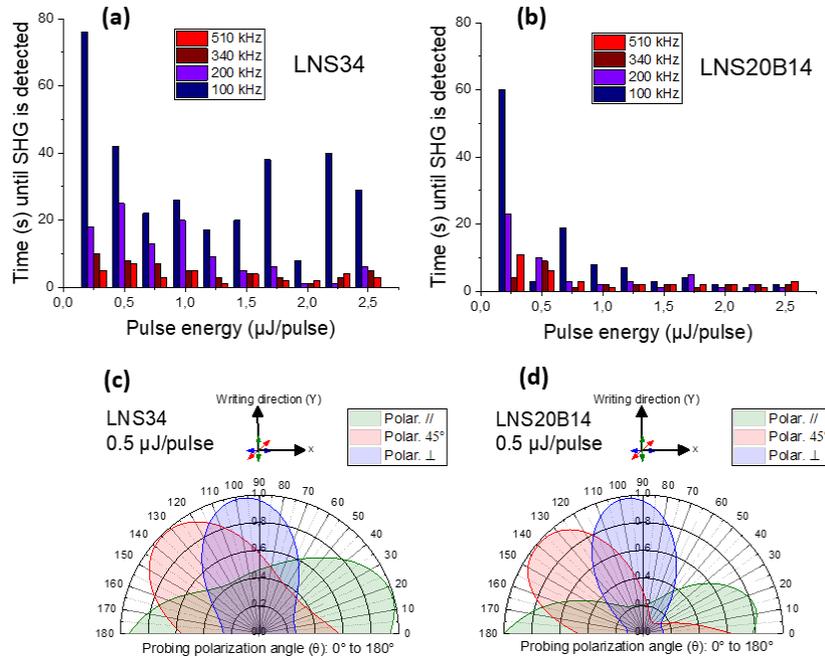


Fig. 1: (a) and (b): time (in seconds) until green light (indicative of SHG) is detected for LNS34 (a) and LNS20B14 (b) samples, using different pulse energies and repetition rates. (c) and (d): SHG intensity as a function of probing polarization angle (0 to 180 °) for LNS34 (c) and LNS20B14 (d) samples. Laser parameters and conditions for (c) and (d):  $\lambda_{\text{laser}} = 1030 \text{ nm}$  ( $\lambda_{\text{SHG}} = 515 \text{ nm}$ ),  $0.5 \mu\text{J/pulse}$ , repetition rate: 200 kHz, polarization //, at  $45^\circ$ , and  $\perp$  to the writing direction. Probing angle is in the YX plane.

In Fig. 1c and 1d are reported the normalized SHG intensity, measured for both LNS34 and LNS20B14 samples, in different writing configurations (i.e. //, at  $45^\circ$ , and  $\perp$ ) with respect to the writing direction (axis Y in Fig. 1c or 1d), at a fixed pulse energy value of  $0.5 \mu\text{J}$ . In both samples, the SHG intensity is strongly dependent on the probing polarization azimuthal angle ( $\theta$ ), and its maximum is found perpendicular to the writing polarization direction. This is consistent with findings in Refs. [3,4], where the polar axis (associated with maximum SHG intensity) is aligned perpendicular to the laser polarization (at low pulse energy). At higher pulse energies, the situation is more complex, and the maximum of SHG signal depends on both writing polarization conditions and glass matrix composition. These results will be discussed at the conference.

#### 4. Conclusions

Lithium niobate silicate and borosilicate glasses are fabricated, and are subsequently irradiated using a femtosecond laser to induce non-centrosymmetric nano-crystals. SHG measurements are performed in order to detect crystallization and the anisotropy in the SHG response reveals a crystal preferential orientation induced by the irradiation. It is shown that substitution of  $\text{SiO}_2$  with  $\text{B}_2\text{O}_3$  preserves tunability of SHG. The borosilicate glass family is advantageous due to its lower melting temperature. Details with respect to application possibilities will be discussed at the conference.

#### 5. References

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