## Abstract

Ultrafast laser-oriented crystallization of glass materials is an emerging and promising research field. Glass is an ideal functionalization enabler material, and it permits the study of light-driven crystallization induced by ultrashort pulses. Femtosecond (fs, 1 fs = 10-15 s) laser direct writing (FLDW) is a tool that enables nano-structuring and multi-functionalization for the fabrication of new active photonic devices in 3D. It takes advantage of efficient nonlinear absorption processes triggered by high light power densities (typ. 1-100 TW/cm$^2$).

This Ph.D. work principally investigates the effect of laser irradiation conditions, through the control of four tunable laser parameters (pulse energy, repetition rate, polarization and scanning speed), on glass crystallization in 3D. The first part of this work relates on the synthesis of borate glasses by sol-gel technique, and silicate and borosilicate ones by the conventional melt-quenching one. Then, a second part is dedicated to femtosecond laser irradiation of the silicate and borosilicate samples to trigger, and control, localized and oriented crystallization of non-centrosymmetric nanocrystals of $LiNbO_3$. Patterns including dots and lines were written inside the glass samples, and laser-structural modification threshold energies were identified. A third part is related to the characterization of the laser-induced structures. Second harmonic generation (SHG), originating from $LiNbO_3$ nanocrystals, was investigated. The effect of laser polarization on the nanocrystal orientation was investigated through its angular dependency of SHG intensity. The study of nanocrystals orientation concerns the effect of $SiO_2$ substitution with $B_2O_3$ into the glass matrix. The nanocrystals orientation and laser track microstructure is further investigated through electron backscattering diffraction (EBSD).

Through laser writing, nanogratings, i.e., lamellar-like structures growing perpendicular to the laser polarization, were observed in both silicate and borosilicate glasses. These sub-wavelength structures induced a birefringent response taking its root from the local variation of refractive indices between glass and crystal phases. Additionally, it was found that $B_2O_3$-rich glasses promote fabrication of birefringent structures, precisely a larger and faster birefringent response (>150 nm at $\lambda$=550 nm) than $B_2O_3$-free glass as well as lower glass-making temperatures.

The effect of scanning speed on crystallization mechanisms is discussed through from the basis of Time Temperature Transformation (TTT) and Continuous Cooling Transformation (CCT) diagrams. For the ease to nucleate and grow crystals in $B_2O_3$-rich glasses (21% mol), the crystallization domain is wider relative to $B_2O_3$-free glasses glass. It is demonstrated that the progressive substitution of

$SiO_2$ with $B_2O_3$ (from 0% to 21% mol) leads to a progressively fast crystallization of $LiNbO_3$ nanocrystals induced by fs-laser irradiation.
As a final note, a suitable choice of laser parameters is critical to control both size and orientation of photo-precipitated nonlinear nanocrystals. A direct consequence is an enhanced tunability in optical properties essential for photonic applications.