Mastery of nanoporosity and photo-induced birefringence by femtosecond laser in the silica-based glasses

Résumé: Irradiation of glasses based on silica by femtosecond laser leads to structural modifications of different kinds of changes in the order (fictive temperature change), phase change (crystallization, decomposition), chemical migration. These changes lead to changes in the physical properties (refractive index scalar or tensor, non-linear optical properties). Their spatial distribution is not always as obvious would suggest a simple energy deposition from the light pulse. The aim of the thesis is to understand one of the specific interaction to exploit: the formation of nanoporous networks formed by decomposition of the oxide glass and the form birefringence associated with the formation of these nanoarrays.

The method is to measure the index variation fields, birefringence, fictive temperature, relaxation of stress after irradiation; rationalize these data by dynamically simulated temperature field and stress using the finite element software COMSOL. We can deduce, then, the mastery of porous nanoarrays and origin of constraints, which allow us to produce prototypes of optical components in collaboration with ONERA Palaiseau Horiba Jobin and Yvon companies.

Scientific context, interdisciplinary challenges of technological innovations to the source of this argument, the expected impact.

The use of short pulses has a unique feature: the process of interaction of the laser with the material are strongly non-linear (for $10^{13\text{-}14}$W / cm^2 intensity) and thereby, a focused beam is naturally a very point allowing inscriptions in volume. It is the gateway to "write" 3D features such as polarizing features, functions integrated low cost by changing the refractive index, the oriented nanocrystal precipitation and even circular dichroism twist of the material. Because of the possibility to make these modifications in a large number of glasses, on one hand, to achieve the high-speed (cm/s), and secondly to the application (flexibility of the method), the impact at industrial level can be significant and should lead to a technological breakthrough in the field of functionalizing microstructuring transparent oxides, especially glasses.

Beyond simple energy deposition (long pulse lasers > 10ps), the femtosecond laser (<1 ps) leads to the creation of forces acting on the material combined with the already known effects, "print" in unkown nanostructures. Thus, the observed nanoarrays of (period of 200 nm) made of nanoporous oxide. The orientation of these nanoplans is connected to the writing polarization. This decomposition is initiated a fraction of ps and depends on the chemical composition of the glass irradiated (*e.g.* in SiO_2 is observed or borofloat33 but not in the BK7). Mastering nanoarrays and high birefringence associated (10^{-2} such as quartz) will exceed the current applications of lasers and open new opportunities in material sciences.

From a fundamental point of view, the aim of this thesis is to control the formation of these porous nanoarrays and residual stresses and based on laser parameters (ICMMO) and chemical composition (Institut of Physics of the Earth in Paris). For this, we must determine the spatial distribution of free deformation stresses and elastic response. We will then proceed to numerical simulation (finite element) measures to be carried out, on the one hand, the distribution of the refractive index tensor which depends on the distribution of the fictive temperature of the glass and the stress field. The problem is of thermo-mechanical type.

The mastering of nanoporosity produced by light in the oxide glasses (aim of the thesis) is at the crossroads of Materials Science laser, controlling properties of laser beams ultrashort pulses and interaction the wave associated with the material.

From the point of view of applications, our industrial partners (Thales R & T, Horiba Jobin-Yvon and ONERA) request to produce multilayer radiation and with low optical diffusion to obtain competitive specifications. Each irradiation produces a stress field. These multiple irradiations led by accumulated stress induced at times exceed the breaking limit and destroy the object at the end of treatment. Using the COMSOL tool, we reveal the origin of the stresses, we will be able to minimize them but also to control them (toward engineering stress birefringence). In the medium term, subject to the fundamental base, should lead to the creation of a start-up.

The most important applications are currently in the field of optics Vis-NIR (microscopy, spectroscopy, polarimetry, mid-IR imaging) with the development of any phase plates and suitable for all types of correction (wave front, Space aberration, polarization) including modifiable ocular implants in situ during the life of the individual. This is the refractive index of property that is changed by anisotropically, but we also work (other thesis funded by CSC for the period 2014 to 2017) on the functionalization of glasses precipitating optically nonlinear nanocrystals for the optical information processing.

Spatial control of precipitation allows structuring nonlinearities and should lead to the production of the original non-linear components such as parametric sources, wavelength converters. Control of the susceptibility of order 1 (index) and nonlinearities higher order indeed open a new field of freedom in the design of components. Knowledge of thermal fields and constraints may also allow us to control the orientation conditions optically nonlinear crystals in glass substrates.

The proposed research program, methods to be used,

The proposed method to achieve the goal of the thesis is to measure index variations of fields, birefringence of fictive temperature, after breaking stress relaxation, post-mortem way to streamline these data by dynamically simulating fields of temperature and stress. Next put the ingredients to simulate observations, we can deduce, then, the origin of constraints. The main expected result is the mastery of nanoarrays porous (pore size, volume fraction) and the associated form birefringence (magnitude and orientation of the neutral axis). In the third part of this thesis, it is expected to produce prototypes of birefringent components with minimal optical scattering and low residual stresses.

The program is based on three pillars:

1) Characterization of structural changes and photoinduced properties depending on the parameters of the laser. At this stage, the material will be analyzed structurally in its nanoscale (SEM, TEM) and optical properties at the microscopic scale (variation index, birefringence, dichroism, optical diffusion ...). At the end of this step, the boundaries of the relevant parameters of the laser beam (polarization, pulse repetition frequency, pulse duration, energy) are determined for the silica glasses studied (alumino-borosilicate high in SiO2 but also, if time permits, in germanate for applications in the mid-IR).

2) Understanding the interaction mechanisms (origins of the stress field), which leads to structural changes in the silica-based glasses. Understanding the limitations of laser parameters and link with glass composition (alumino-borosilicate high in SiO_2).

3) Applications: integrated optical devices of Prototypes 3D such as optical low-cost and space-saving for shaping a beam phase, amplitude and/or polarization (waveplate to compensate for aberrations, networks microlenses achromatic or birefringent micro-patterned blades for microscopy or polarimetry) will be fabricated and characterized in collaboration with Thales RT and Jobin-Yvon but with ONERA in the field of IR imaging.

The expected results in terms of future developments in research and applications:

1) Progress on the laser interaction processes with femtosecond transparent oxides:
In the case of femtosecond lasers, originality based on the formation of a plasma. Electronic and thermal relaxation ensuing then lead to permanent changes in the irradiated glass as the occurrence of stresses, the high-speed decomposition of the oxide (and migration of O_2) at the origin of the birefringence that we seek

to exploit. Collaborations have been established within the Saclay plateau between ICMMO/UPSud, the LSI/CEA/Ecole Polytechnique (S. Guizard) but also with other labs around Paris and especially the IPGP (D. Neuville). This is a dynamic deformation problem of a solid in an electromagnetic field. Understanding will allow us to control the porosity and birefringence associated while minimizing the problems associated with the accumulation of stresses and Rayleigh scattering losses.

2) Control of the writing process in glassy materials
The aim is to develop the fundamental knowledge to master the writing process (determination of stress fields induced by light, nanoarrays atomic density variation in refractive index, nanocrystals precipitation, chemical migration). In particular, a major challenge of this project is to increase our knowledge about the originality of the interaction of femtosecond laser with silicate glasses: the creation of porous nanostructures that are the source of a strong birefringence format which is possible to control the orientation. These discoveries which we have largely contributed, we rank first to consider applications.

3) The creation of new optical devices
Technological barriers in this area are clearly identified:

1 / On the one hand, the transition to 3D remains a real challenge for the future. Indeed, optical devices integrated 3D (and low cost) have become of key importance for future optical communication systems, imaging, lasers, biophotonics or optical memories for permanent storage. The conventional production method is the combination of lithography and dry etching. This method is difficult to use, in addition, it requires a lot of expensive steps.

2 / In addition, current methods for the laser light-entry of passive optical components are limited to a few types of photosensitive silica glass with UV such as doped germanium or silver phosphate.

3 / Most photonic components have larger sizes in mm incompatible with the degree of integration of their counterparts in microelectronics or in the context of applications in the field of biophotonics.

Micro and nano-structured materials by direct writing using a femtosecond laser are excellent candidates to blow these technological obstacles. Currently it is already possible to make some devices, including networks and waveguides, but the goals of our project go further and plan to produce new structures and thus new 3D optical devices such as optical microstructures linear birefringent also circular (what is innovative!). These studies are related manufacturers such as Thales R & T, Horiba Jobin-Yvon, ONERA.

Understanding these permanent effects allow us to develop the exploitation of the potential of this new method and maximum use of the qualities and characteristics of the interaction. Because of the possibility to make these modifications in most glasses (but also crystals and polymers) on the one hand, and to realize the high-speed (up to cm/s), on the other hand. The impact at the industrial level is recognized to be important, which may lead to a technological breakthrough in the field of structuring linear optical properties of transparent and non-linear materials.

Proposals have to be sent before the 30 April 2015 to :

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