Vilnius University
Faculty of Physics
Laser Research Center

Laboratory assignement No. MNFT-4

MODIFICATION OF REFRACTIVE INDEX OF GLASS EMPLOYING ULTRASHORT PULSED IRRADIATION

For students of Laser Physics and Optical Technologies and Laser Technology programmes

Vilnius 2017

1 The goal

The goal of this laboratory assignment is to familiarise yourself with modification of refractive index in glass (I and II type modifications) employing femtosecond laser source.

2 Lab exercises

1. Using direct laser writing system fabricate phase gratings in calcium nitrate silicate glass (soda-lime glass) with varied gratings period and exposure intensity.
2. Using optical microscope evaluate what type modifications were produced with different exposure parameters.
3. Using optical characterization setup (HeNe laser and screen) compare diffraction efficiency of produced gratings. Measure distance between zero and first-order difraction maximums. Calculate periods of the gratings and compare with the values which were set in the programm code during fabrication.

3 Pre-lab questions

1. Modifications in transparent materials and their types.
2. Parameters of the laser irradiation required to induce modifications.
3. Applications of the modifications in transparent materials.

4 Materials and equipment

During laboratory assignement you will use laser direct writing (DLW) system (Fig. 1), optical microscope and optical characterization setup with HeNe laser. Modifications will be formed in nitrate silicate glass. The main component of the system is femtosecond solid state laser "Pharos" (Light Conversion, Lithuania): an activemedium is Yb:KGW crystal, central wavelength of the fundamental irradiation is λ=1030nm. The laser generates pulses of τ<300 fs duration. Repetition rate can be adjusted in order of 1-200 kHz.

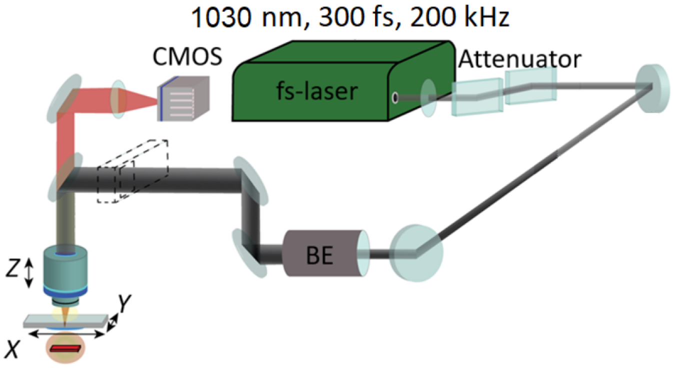

Fig. 1 Schematic of the DLW system.

5 Workflow

Before the laboratory assignment, remember laser safety requirements. In this work youwill use 4th class laser, which means that scattered light can cause eye or skin injuries if safety requirements are not fulfilled.

1. Under supervision of lecturer, check if the laser system is ready to use.
2. Fabrication of 3D structures in glass.
   (a) Turn on „wxPropView“ program for Live observation of fabrication and active it by pressing buttons Use and Live
   (b) Turn on 3DPoli 6.12 Compiler and 3DPoli 6.12 Fabrication programs. The first one is used to prepare and edit code, which defines the fabrication, the second one controls DLW system
   (c) Before starting fabrication process, it is necessary to find a focus position. To implement this, you need to lower the objective changing its position via „3DPoli Fabrication“ program. In the program you can define the step of the stages movements

in µm. The objective is lowered (by movements every 100µm) till you can clearly see the surface of the glass substrate . Glass substrate thickness is 1 mm, working distance of the objective is 0.55 mm, thus the objective can be moved additional 0.2-0.3 mm to the glass. In the program „wxPropView“ appears bright dot. It shows the focus position. Now the fabrication code can be executed. After the fabrication process is done, the objective must be moved away from the glass cover slip around 10-20 mm, then you can remove the sample fromthe stages.

3. Characterization of the modifications with optical microscope. Refractive index modifications are observed, type of the modifications is determined, microcracks are registered.

4. Characterization of the gratings with HeNe laser. Place your sample that HeNe laser beam passes through the gratings. Observe difraction image on the screen which is located at fixed distance from yuor sample. Evaluate distances between difraction miximums. Use provided difraction equation:

$$m * \lambda = \Lambda * \sin(\theta); \tag{1}$$

   where m – a number of the difraction maximum, λ – wavelength, Λ – a period of the grating, θ – an angle between normal and difraction maximum. Use a powermeter to detect average power of the difracted beams. Compare difraction efficiency when different exposure parameters for fabrication of the gratings were applied.

6 Theoretical background

Modification of transparent materials

The existence of a threshold intensity at which laser damage occurs opens up unique application possibilities for processing transparent materials. Controlling the laser pulse intensity, conditions may be selected so that the threshold intensity is exceeded only in the focus of the focusing lens. In this way, the area of laser-induced damage will be strict defined in the volume of the transparent material. Gradually changing the position of the focus in a transparent medium it is possible to form various three-dimensional objects, photonic elements or integrated optical systems with micrometric or submicrometric resolution.

In the literature, the term laser-induced material damage is commonly referred to an irreversible change in the properties of medium caused by laser radiation, normally detected optical methods. However, under certain conditions, a structure will form under matter violation, stands out with extremely high regularity, is homogeneous and can be clearly classified. Such structures are formed because of a laser pulse whose intensity is close to the damage threshold, can regularly change and modify the structure of the material. So to single out these derivatives from another, the term laser-induced material modification will be used in this description.The concept of material damage continues to be used only when it is meant irregular formations, visually detectable cracks in the material, and so on.

Volumetric material modification

To achieve laser pulse intensities greater than TW / cm2 required for the material modified, the laser beam inevitably has to be focused. Focusing, on the other hand, allows selectively select spaces where the radiation intensity is sufficient for nonlinear absorption.

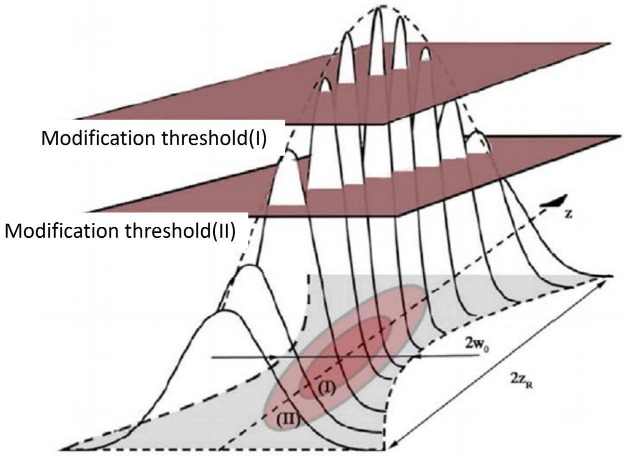

Fig. 2 Gaussian beam intensity distribution in the focus (z -beam propagation direction). Modification of the material is only possible in a limited area of the threshold intensity. Given threshold value (or radiation intensity), the size of the modified area itself may be less than the diffraction limited diameter (2w) or peak length (2z$_r$).

Diffraction limits the minimum area of space in which the laser beam can be focused. If we focus on a flat-wave lens with a numerical aperture of NA, then the minimum possible beam radius in the beam waist would be approximately equal $w = 0,61 M^2 \lambda / NA$, where λ – wavelength, n – refractive index, M^2 – beam quality parameter.This size actually determines the radius of the formed Airy disk. The profile of the laser beam is usually closer to the Gaussian distribution, but if compared spatial energy distribution of such fibers, this difference would be very small. In the case of the flat-wave, 83% of the energy is concentrated in the Airy disk, and in the case of the Gaussian fiber, 86% of the energy falls below the Gaussian envelope at level $1/e^2$. Therefore, previous formula describes quite accurately the size of the focus spot, however, excluding the aberration of the focusing optics. Beam waist length of the Gaussian beam, the so-called confocal parameter, corresponds to twice the Rayleigh length (distance, when the radiation intensity decreases twice): $2z_r = 2nw^2\pi/\lambda$. As already mentioned, in order to modify a material, it is necessary to achieve such an intensity of radiation that which would be above a certain threshold. As can be seen from Figure 2, it is easy it is possible to implement a situation where the threshold intensity is exceeded only in the focus. Thus, it is possible to create modified derivatives without completely damaging the material its surface. When choosing intensity, close damage threshold, it is possible to create derivatives that are smaller than the diffraction constraint fiber diameter. Such a technology is particularly successful in the creation of three - dimensional derivatives with submicrometric resolution in polymers. Similar resolution is also available for glasses achieved, but due to nonlinear processes such as light filament formation the area of the modified material increases. Nevertheless, the formation of three-dimensional microarrays is successfully implemented.

Types of the modifications

By selecting different parameters of the laser radiation, various types of modifications can be created in a transparent material. Although the nature of the modified area itself often depends on physical properties of the substance, certain types of modifications can be distinguished (Fig. 3. By acting on a substance with an impulse of intensity lower than the modification threshold, short-lived unstable may already occur in the medium derivatives that are excreted by altered absorption or refractive index. Such modifications are called unstable. When the radiation intensity only exceeds the threshold of the formation of residual modification, a homogeneous area with an altered refractive index is produced, also known as type I modification. By increasing the intensity, the homogeneity of the modified area begins to decrease, and there is a double refraction of light (type II modification). Increasing intensity even more and selecting of appropriate focusing conditions, microcavities can be formed in the material. Illiustrations of the modifications are provided in Fig. 4 In some materials, one type of modification may predominate and another type not at all. In other materials, such as fused quartz, all types can be realized modifications.

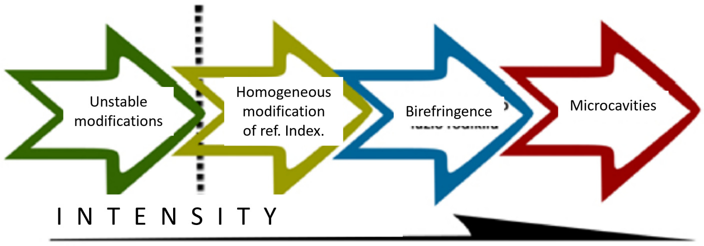

Fig. 3 Nature of modified derivatives induced by ultrashort laser pulses

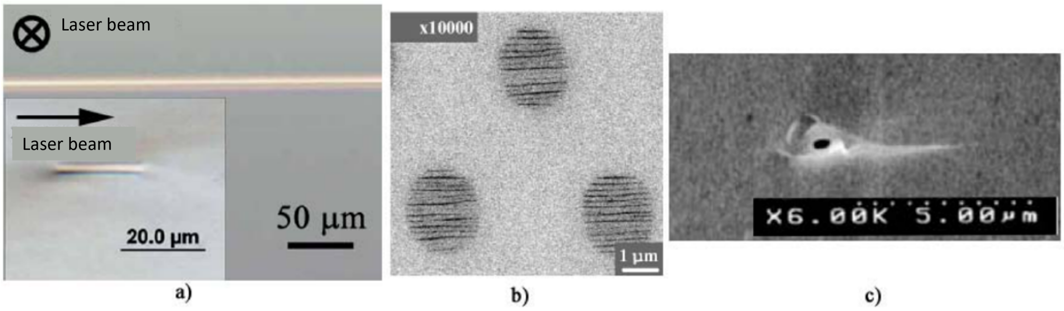

Fig. 4 Material modified by ultrashort laser pulses. (a) Optical fiber recorded in phosphate glass (longitudinal and transverse view, type I modified derivative); b) nanograting in fused quartz (type II modified derivative); c) microcavities in fused quartz.

Modification of the refractive index

When an intensity exceeds a certain critical value, a derivative of a modified substance becomes stable. Regularly formed transparent derivatives in various types of glass demonstrated for the first time by Davis et al. in 1996. The resulting derivatives have been found to have isotropic change in the refractive index that can reach up to 10^{-2}. Such a change is sufficient to accommodate the media operating waveguides demonstrated by the same group of scientists should be realized in later works. These works have greatly pushed the development of integrated optical technology. Despite abundant research, the physical mechanisms that lead to changes in refractive index are present today not fully understood. A lot can happen in a solid medium when exposed to an intense laser pulse, different processes that can change the refractive index in one way or another. There are three possible models describing changes in refractive index: thermal model, long - term defect model, and lattice deformation model (Fig. 5.

Thermal model

This model is based on the fact that the temperature of the material in the focus can be reached high enough to allow phase transformation of the material. The thermal conductivity of the dDielectric medium is low, the hot zone is concentrated in a small area of space, therefore, even at low pulse energies (500 nJ), the material can be heated up to 2000 K and more. After heating, the area cools rapidly due to the high temperature gradient (typical relaxation time> 1 μs). In this way, the media is remelted having properties of a refrigerated liquid that are different from the unaffected material properties. The refractive index of fused quartz is known to be higher (10^{-3}) if high temperatures state quartz is rapidly cooled. This change is due to an anomaly of this material compaction: the fused quartz lattice has an annular derivative

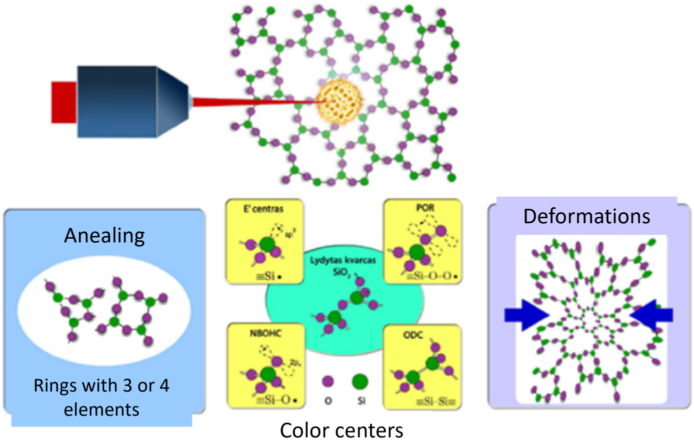

Fig. 5 Mechanisms of refractive index change in fused quartz. Material affected by intense radiation may condense after remelting. Due to a change in the chemical structure 3 and 4 element rings are formed instead of the dominant 5, 6 element ring derivative. Also available point defect - the formation of a color center. The substance forms on rapid heating internal pressure, resulting in deformation of the lattice. All of these phenomena affect the rate of fracture change in material.

formed from an -O-Si-O- element. Ordinary quartz is dominated by 5 and 6 element rings, but is rapidly cooled by hot cooling state quartz multiplies significantly in the ring of 3 and 4 elements, making the material denser. In fact, Raman spectroscopic studies of the laser-modified zone confirm this ring and experimental work demonstrates an increase in the refractive index in fused quartz.

Such an interpretation of the modification of the refractive index based on the thermal behavior of the material allows qualitatively predict possible changes in the refractive index of the material, but far from sufficient to explain all the features of the modified area. Microscopically modified areas analysis shows that the distribution of the refractive index in the area affected by the laser pulse is quite complex, various variations in refractive index are observed, which, moreover, are highly dependent on irradiation parameter. Typically, if there is an increased refractive index at the center of the modification,areas of reduced fracture index are observed in the periphery, and vice versa. Selecting the appropriate pulse parameters, zones with the opposite sign of refraction can be induced in the same materialr. This situation suggests that laser pulse absorption induce rapid dynamic processes that additional lattice deformations, which also do influence on the change in refractive index.

Deformation model

Relaxation of free electrons generated by a femtosecond pulse proceeds very rapidly (<1 ps). Immediately after relaxation, a large amount of energy is quickly transferred to the grid, therefore its temperature is raised and a high thermoelastic preasure is created in a confined space. Relaxing tension in the material can cause strong acoustic waves that can induce plastic lattice deformations. The existence of such waves is confirmed experiment. The propagating wave interacts with the heated lattice and creates a heterogeneous density variations that have an effect on the change in refractive index. For such compression to occur, also confirms the change in molecular bond angle in the SiO2 molecule recorded by Raman spectra. Local changes in density inevitably cause a tension field visible under a polarizing microscope. However, simulations of the change in refractive index showed that lattice deformations account for only about 10% of the total change in observed refractive index, hence such a model alone cannot explain in detail the reason for the occurrence of the fracture index.

Color centers

The development of electron paramagnetic resonance (EPR) began in the middle of the last century, luminescence, light absorption measurement methods allowed the identification of various glass defects, to observe the change of their dynamics by exposure to various radiation, firing large particles of energy and etc. The glasses have amorphous structures, which makes them rich in various lattice defects. Thermal status of glass consistency can vary, so the nature and amount of defects also vary. So defect testing is quite complicated.

In the case of pure fused quartz, the four most common groups of defects can be distinguished: E 'centers (≡Si•, where • stands for a free electron), non bondend oxygen hole centers – NBOHC (≡Si-O•), peroxy radicals – POR (≡Si-O-O•), oxygen deficiency centers – ODC (≡Si-Si≡).

All of the listed defects can be induced by both ultraviolet laser radiation and femtosecond infrared radiation. Defects of a similar type are found in other glasses: germaniosilicate glass is dominated by germanium-oxygen hole centers, borosilicate glass in glass - boron-oxygen hole centers and so on.

The influence of the color center on the change in the refractive index is debatable. EPR measurements show that up to 10^{19} cm^{-3} of defect may occur in the excited material, causing fracture accordingly indicator change to 10^{-3}. On the other hand, direct measurement of absorbance is recorded due to a defect much smaller change in refractive index (10^{-8}) that the color centers do not stand out in the long run stability and may be destroyed by heat treatment (annealing at 200 °C). However, the modifications of the refractive index itself are relatively stable up to 700 °C.

The real reason for the change in refractive index can be explained by all three models. The change in refractive index is usually thought to be due to the thermal action of the material, which in turn causes lattice deformations. However, the thermal model cannot fully explain the occurrence of a change in the refractive index under low intensity (insufficient to cause phase transition), but with a high pulse repetition rate laser radiation. On the other hand, the deformation or color center model predicts much lower change than is observed.

Birefringence. Nanogratings

At higher energies, the homogeneity of the modified zone decreases, moreover, these derivatives are characterized by birefringence of light. To distinguish them from others, these modifications were named for type II modifications. Only very recently the causes of a birefringence have been founded. It has been found to result from ongoing nanostructuring in the area affected by the laser.

The physics of the formation of such nanostructures is not yet understood, as there is still a lack of the experimental data. One interpretation is based on the fact that intense electromagnetic waves and the interference of the electric field generated by the electron plasma can form similar derivatives. Because of these interferences, laser light modulates the plasma density and essentially divides the plasma into separate nanoplanes, which are separated from each other by a period equal to half the light wavelength. In other works, the grid periodicity is much less than half a wavelength. In addition, it is observed that the lattice period is affected by the frequency of pulse repetitions. These results call into question the interfering lattice formation theory and the plasma nanoplanet formation is explained by plasmonic effects. Conditions required for plasma density distribution are unclear. It should be noted that the periodicity of the grids and regularity is maintained at macroscopic distances by slow transmission of the sample during recording with respect to a fixed focal position. Therefore, it can be said that the plasma density redistribution can also be led by material defects. Material defects created by one laser pulse "remembers" primary plasma distribution and retransmits this information to other pulses in the same place or during slow transmission of the sample.

This presence of nanoparticles oriented in one direction explains the emergence of a birefringrence in type II modifications. By changing the radiation polarization, intensity and modified area this birefringrence effect can be manipulated. It is already showen that phase plates can be formed on this principle.

Influence of radiation parameters on modifications

Modifications induced by ultrashort laser pulses were discussed in the previous section.Hhowever, we did not completely analyze the laser radiation parameter required for such modifications to create. Radiation intensity, wavelength, pulse duration, pulse repetition frequency, focusing sharpness, optical and physical properties of the material and other parameters may affect the type or quality of inducible modifications. Also, not yet fully understood physical mechanisms that determine the occurrence of modifications complicate such light and material interaction analysis. Therefore, to induce the desired type of modifications with the selected laser system, it is still necessary to experimentally select the required radiation parameters. As a result, a relatively wide range of research on modification of transparent media, allows to understand the influence of essential recording parameters on the development of modifications.

Most of the study was conducted using the most popular, Ti: sapphire-based laser systems. They generate pulses of 800 nm wavelength, the duration of which reaches less than 100 fs. In such systems, the repetition rate of the pulses is low and reaches 1 kHz. Homogeneous modifications of the refractive index in fused quartz are observed using this type of system at a pulse intensity of about 40 to 200 TW / cm^2 (radiant energy density 4 to 20 J / cm^2). Type II modifications start to occur at intensities between 200 and 600 TW / cm^2 (20-60 J / cm^2), and micro-lesions occur at intensities greater than 600 TW / cm^2 ($>$ 60 J / cm^2). Such values are obtained by focusing the radiation with a lens with a numerical aperture of 0.65.

The intensity can be varied using a different sharpness focusing optics, but the the focal length of lens itself can greatly change the nature of the modification created. Using small numerical aperture lenses (NA $<$ 0.2), the threshold for modification is reached only when when the irradiation power already exceeds the focusing threshold of the material. The resulting materials modifications are already heavily affected by the phenomenon of filamentation. During filament formation the energy is redistributed over a large area, so the longitudinal dimensions of the modification change significantly, its longitudinal dimension can reach even a few millimeters. Increased in focus the concentration of free electrons reduces the dielectric constant of the material, so radiation is always partially dispersed and occurs at the beginning of filamentation even with the use of medium sharpness lenses (NA 2 (0.4 - 1)). For this reason, the morphology of the modification becomes heterogeneous. In the area close to the focus, the change in the refractive index is usually greater, and the dimensions close to or even smaller than the constricted width of the focus spot or the depth of focus. For a less modified area of length along the direction of propagation of the pulse depends on the focusing lens setting. Thus, the formation of regular microcavities is possible only with ultra-sharp focusing lenses (NA> 1). Because in order to initiate micro-explosions, all radiation energy must be concentrated in the smallest possible unit. Therefore phenomenon of filamentation must be kept to a minimum.

As already mentioned, the relaxation times of a substance when exposed to ultrashort laser pulses reaches microsecond scales. Therefore, using laser systems with high pulse repetition rate, the thermal accumulation effect is possible because the material is no longer fading cool until another pulse comes. This accumulation changes the nature of the modification. It is observed that under such conditions the modified derivative becomes larger and its dimensions take over depend on the duration of laser exposure. It is important to note that this effect is not observed in all materials: it is particularly pronounced in borosilicate glasses but completely weak in fused quartz. This selectivity of the effect on the substance is not fully understood, but it is believed that the reason could be a larger band-gaP of fused quartz and a higher phase transition temperature (1800 ° C). Frequency of laser pulse repetition at which already the noticeable thermal accumulation effect is 0.5 MHz (pulses fall into the material every 2 μs). At lower frequencies (<0.2 MHz), this effect is only observed at intensities, significantly exceeding the damage threshold.

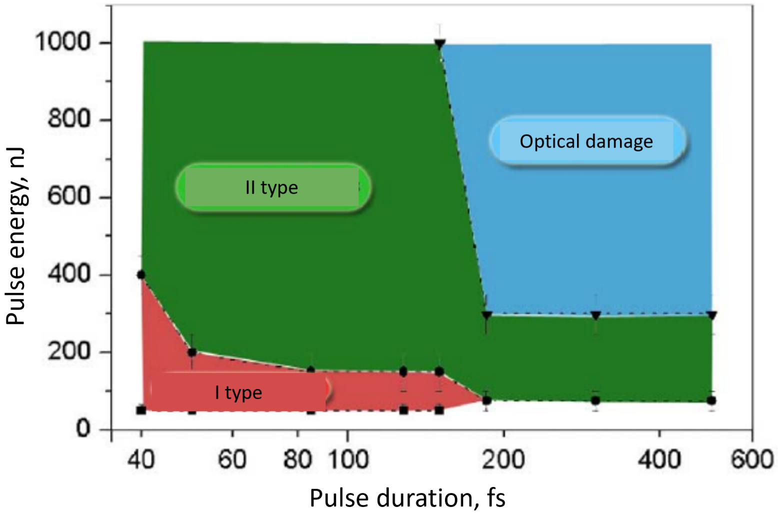

Fig. 6 Influence of laser pulse durations on the type of modification in fused quartz (radiation waves length - 800 nm, focused with a 0.65 NA lens).

Another important parameter that determines the type of modification is the pulse duration. We will discuss here only experimental results related to the induction of refractive index modifications. Modification of morphology on the change in pulse duration has not been consistently studied. There is a ferry work that has delved into this problem, but they are quite different in modification fabrication modes. In the study of modifications in fused quartz, an induced filament of light, using weakly focusing optics (NA <0.1), it was found that the modification of the refractive index (in this work it has not been investigated what type this modification is) can be induced only when the duration is less than 250 fs. At longer pulse durations, an intensely light-scattering optical violation is formed. Impact of pulse durations on the morphology of modifications using sharper focusing objective was investigated by researcher Hnatovsky et al. It can be seen in Fig. (6), that type I modifications are formed only at durations of less than 200 fs. When pulse durations are longer, modifications are already distinguished by a birefringence. In borosilicate glass, in which no type II modifications are observed, homogeneous changes in the refractive index are also obtained with pulses lasting a few picoseconds.

The effect of radiation wavelength on the induction of modifications remains highly debatable. When measuring the thresholds for the occurrence of modifications induced with different wavelengths in different in transparent materials, no significant difference is observed - the difference in threshold between 800 nm and 400 nm induced threshold was only 10 %. According to Keldysh theory, shorter wavelengths increases the probability of multiphoton ionization, but increases tunneling ionization rate accordingly at longer waves. Based on these considerations, it can be said that the general the nonlinear absorption coefficient varies little with varying wavelength. However, it is still lacking research that could provide a stronger basis for this claim.

Photonic elements in transparent materials

It has been observed that ultrashort laser pulses can be used to modify optical properties of the transparent media. Even without a definitive understanding of the nature of this phenomenon, the potential applications of this technology were demonstrated a high abundance of various photonic elements recorded in a variety of type glass. A detailed overview of the elements created by this method can be found in Della Valle and etc. and the references therein. Therefore, in this section we will review only the essentials applications demonstrating the use of various types of modifications for practical purposes.

The very first works on the modification of transparent media carried out by the Hirao groups have already been demonstrated fiber optic effect due to locally altered refractive index of the material. Slowly tranlsating the specimen relative to the focal position automatically forms a fiber of the shape and the structure depends on the transmission geometry of the sample and the parameter of the writing beam. Although different materials respond differently to femtosecond impulses, different technologies solutions allow the creation of fiber optics in various types of materials: fused quartz, borosilicate glass, multicomponent glass, non-linear crystals, polymers and etc. The flexibility of such technology is demonstrated by more complex photonic elements such as integrated fiber-optic multichannel hubs, accumulators, interferometers and other microdevices. Such elements still lag behind in their efficiency from the fiber-optic integrated on silicon substrate, but such a methodology is not so universal and its application possibilities are quite limited. Direct recording technology is promising for the production of unique elements.As an example may be given of a fiber recorded in fused quartz during the same processing, together with Bragg grating.

Another wide field of application is the production of diffractive elements. Thin one-dimensional gratings, volumetric Bregg gratings, Daman gratings, Fresnel lenses, holographs inscribed with femtoseconds pulses were displayed in various types of glass. Usually such photonic elements are not very effective as there is currently no method that can accurately control the required rate of refractive index change and the homogeneity of the derivative itself. Despite this, applied works done using modification of transparent materials by ultrashort laser pulses show the great importance of this technology perspective.

The main literature for this lab work was adapted from PhD dissertation of Dr. Domas Paipulas: https://epublications.vu.lt/object/elaba:2004292/2004292.pdf