Preliminary results on non-linear effects in Au-ion-doped glass materials irradiated by femtosecond laser pulses

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Abstract. Our research was motivated by the specific properties of noble-metal nanoparticles and their wide applications. The resonance frequency for noble-metal nanostructures is in the near-UV and visible spectral ranges, where most of the commercially-available lasers oscillate. This makes these materials attractive candidates for studying their properties in view of efficient applications. We investigated filaments formation in Au-ion-doped glass materials, transparent in the visible range, during irradiation by femtosecond laser pulses. Second harmonic generation in the media was observed as well. This proved the formation of polycrystalline structures inside the media after femtosecond laser radiation. Further, self-phase modulation and continuum were observed. Thus, the nonlinearity of the media is higher than that of glass not doped with noble-metal particles. The nonlinear effects in the samples were investigated in terms of the laser beam parameters. The laser energy applied was between 10 – 40 μJ. The wavelengths used were in the range 240 – 2600 nm, as generated by an optical parametric amplifier system (TOPAS). The regenerative Ti:Sapphire amplified laser system emits at a central wavelength of 800 nm with a pulse duration of 35 fs and 1-kHz repetition rate.

1. Introduction

The ultrafast laser is one of the greatest breakthroughs in the laser technologies and among the greatest inventions of the humankind in the last century radically changing many aspects of our life. Recently, the 2018 Nobel Prize in Physics was awarded to G. Mourou and D. Strickland "for their method of generating high-intensity, ultra-short optical pulses". With the ultrafast laser technology maturing over the years, extensive attention has been attracted to its use in many fields of science and technology. This led to a rapid growth in the development of applications such as surface and bulk modification, nanostructure generation and formation, bio-sensing, optical data storage, photonics, chemical reaction acceleration [1-4]. Focusing on the field of optoelectronics, the main research activities have been devoted to the fabrication of photonics devices embedded in the bulk of transparent solid dielectrics. The opportunity to fabricate nanostructures, such as nanoclusters, is crucial for the development of new materials and multifunctional microsystems and devices. The structural modification inside the

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bulk of transparent materials initiated by focusing fs laser pulses is a result of complicated nonlinear processes that include multiphoton absorption, ionization, self-phase modulation, and diffraction physical phenomena. When a laser pulse with power exceeding the critical power for self-focusing propagates in a Kerr medium, such as fused silica, filaments appear due to the dynamics competition between Kerr self-focusing and defocusing induced by ionization and nonlinear absorption. The structural modification induced in the transparent materials can be applied to fabricating gratings, 3D integrated optical devices inside optical materials and waveguides in a variety of glasses.

Composites of glasses containing noble-metal nanoparticles are among the very promising materials for technological applications in photonics and optics and continuously attract special attention. Although several methods are available to induce and generate nanoparticles in glass (ion exchange, melt-quenching, sol-gel, chemical vapor deposition), none of them offer spatial control of the nanoparticles formation. At present, only femtosecond lasers allow the generation of metallic nanoparticles under a 3-dimensional control. Furthermore, there are several advantages of femtosecond laser induced nanoparticle formation in transparent materials over other fabrication structural techniques: the absorption process is independent of the materials; the nonlinear nature of the optical absorption confines the induced changes to the focal volume leading to a well-defined modified region with minimum damage and heat affected zone.

The main objectives of the present study are:

- preliminary observation of the non-linear effects induced by femtosecond laser pulses in borosilicate glasses doped with Au ions
- investigation of the structure of the non-centrosymmetric glasses doped with Au ions (generation of second harmonics)
- adjustment, modification and calibration of the z-scan technique of determining non-linear parameters, such as non-linear refractive index and multiphoton absorption coefficient.

To fulfill the objectives of the study, several tasks were accomplished. Sections 2 and 3 present information on the setup configuration and preliminary results. Section 4 summarizes the main conclusions and the plans for future work.

2. Experimental configuration and settings

2.1. Setup configuration

The main part of the experimental setup is a femtosecond laser system consisting of several units – oscillator, amplifier, pumping laser and optical parametric amplifier (OPA). The Ti:Sapphire regenerative amplifier has a pulse width of ~35 fs, pulse energy of ~6 mJ and operates at 1-kHz repetition rate. The TOPAS Prime automated OPA system has wavelength extension from the deep UV range through the infrared (240 – 2600 nm). To perform z-scan measurements, the femtosecond laser is further equipped with a high precision planar XY stage, a CCD camera, and optical and opto-mechanical elements.

The distribution of the energy in the laser beam spot is detected by a two-dimensional CCD camera (SPIRICON CCIR) having 1200(H)×1200(V) pixels (pixel size 80 μm×80 μm). The variations of the beam radius are measured by a laser beam profiler (Spiricon, Inc. LBA-PC Laser Beam Analyzer). A schematic of the experimental setup is shown in figure 1.

![Figure 1. Experimental setup configuration with the main lasers parameters and a schematic drawing on the right-hand side, and a photograph on the left-hand side.](image-url)
2.2. Material

Three groups of borosilicate glasses were studied (see figure 2): (i) samples doped with Au ions (annealed); (ii) samples with Au ions (not annealed), (iii) sample without Au ions as reference. The samples were synthesized by conventional melt-quenching with different concentrations (0.1 and 1 wt %). Detailed information on the sample concentration and composition was provided in our previous works [5, 6].

A fused silica glass sample was used to calibrate the z-scan technique making use of its well-known non-linear refractive index.

Figure 2. Glass samples doped with Au ions used in the experiments.

3. Results

Generally speaking, amorphous media, such as glass, have a centrosymmetric structure, which precludes the generation of second harmonic. Therefore, the appearance of second harmonic indicates the formation of polycrystalline structures in the bulk medium leading to quasi phase-synchronism, which in turn points to the appearance of clusters of nanoparticles. We observed filaments formation in all samples in the wavelength region from 260 – 1600 nm. Figure 3 presents examples of filament structures in the cases of wavelengths of 266 nm, 800 nm and 1064 nm. As seen, the filaments are well defined. The femtosecond pulse energy needed to generate filaments was below the ablation threshold for each wavelength [7], and above that for observing multifilament structures.

Figure 3. Examples of filament structures for wavelengths of (a) 266 nm, (b) 800 nm and (c) 1064 nm.

Second harmonic generation was achieved by focusing the laser beam by an achromatic lens with a focal distance of 15 cm and was observed at different wavelengths (266 nm, 532 nm, 600 nm, 800 nm, 1064 nm, 1500 nm and 1600 nm). All three groups of samples were irradiated by a 1064-nm laser pulse. A green glow was observed in all cases. Figure 4 presents an example of second harmonic generation in the annealed sample with 1 % Au. The spectra were registered by a spectrometer detecting the generation at 532 nm. The laser pulse energy applied was in the range 15 – 30 µJ. Furthermore, second harmonic was generated at the main wavelength of the femtosecond laser (800 nm) at a repetition rate of 1 kHz and a pulse duration of 35 fs. The beam profile was a circular Gaussian one with $M^2 = 1.03$. Figure 3 (b), bottom left image, illustrates the appearance of multifilament structures above the ablation threshold.

Figure 4. Generation of second harmonic by 15-µJ pulse energy at 1064 nm in 1% Au glass.
our study was to adjust the experimental setup configuration for the planned implementation of z-scan measurements. The technique is based on the transformation of phase distortion to amplitude distortion during beam propagation. The z-scan method allows one to determine the main non-linear parameters, such as non-linear refractive index and multi-photon absorption coefficient. For this purpose, we extended the experimental configuration by placing a CCD camera. We should emphasize the use of a CCD camera instead of a diaphragm, as in the standard z-scan method, which eliminates the effects of the laser pulse energy instabilities. This also avoids the use of an aperture that is normally placed in front of the power meter and gives rise to diffraction distortions, which is another undesirable effect.

The samples were placed on an XY planar stage ensuring a smooth and precise translation of the sample across the laser beam focused by a lens with a focal distance of 10 cm. The radius of the laser beam waist was measured to be \( r_0 = 65 \mu m \), while the Rayleigh length was in the order of 3 mm. Applying the z-scan method requires a preliminary calibration using a medium with a well-known non-linear refractive index. We used fused silica glass samples with thickness of 1 mm and parameters quoted in [8, 9]. The preliminary measurements showed values in the order of \( 3 \times 10^{-20} \) m\(^2\)/W. This is in good agreement with the data from literature. Thus, at this stage, the z-scan method is calibrated, and the first measurements of the nonlinear refractive index and the multi-photon absorption coefficient were performed. Further calculations and novel results concerning the nonlinear parameters studied will be published in future articles.

4. Conclusions
We studied the formation filaments in glass materials doped with Au ions at different concentrations, which are transparent in the visible range, during irradiation by femtosecond laser pulses. Second harmonic generation in the media was observed as well, proving the formation of polycrystalline structures inside the media. Self-phase modulation and continuum were also observed. Thus, the degree of non-linearity of the media was higher than in undoped glass. The non-linear effects arising in the doped glass samples were investigated as a function of the laser beam parameters. Preliminary measurements and calibration of the z-scan method were performed. We plan to continue and widen this research by measuring the non-linear refractive index and the multiphoton coefficient and studying the relationship between the formation of filaments and the local changes in the refractive index in glasses doped with Au ions.

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References
[1] Guo Z, Qu S, Ran L, Han Y and Liu S 2008 Formation of two-dimensional periodic microstructures by a single shot of three interfered femtosecond laser pulses on the surface of silica glass Optics Letters 33 2383
[2] Zhang Y, Chen Q, Xia H and Sun H 2010 Designable 3D nanofabrication by femtosecond laser direct writing Nano Today 5 435
[3] Tan D, Sharafuddeen K N, Yue Y and Qiu Y 2016 Femtosecond laser induced phenomena in transparent solid materials: fundamentals and applications Prog. Mater. Sci. 76 154
[4] Zhang Z, Cerkauskaitė A, Drevinskas R, Patel A, Beresna M and Kazansky P G 2016 Eternal 3D data storage by ultrafast laser writing in glass Proc. SPIE 9736 Laser-based Micro- and Nanoprocessing X 97360U
[5] Nedyalkov N, Stankova N E, Koleva M E, Nikov R, Atanasov P, Grozeva M, Iordanova E, Yankov G, Aleksandrov L, Iordanova R and Karashanova D 2018 Optical properties modification of gold doped glass induced by nanosecond laser radiation and annealing, Optical Mater. 75 646
[6] Nedyalkov N, Koleva M E, Nikov R, Stankova N E, Iordanova E, Yankov G, Alexandrov L and Iordanova R 2019 Tuning optical properties of noble metal nanoparticle-composed glasses by laser radiation Appl. Surface Sci. 463 968

[7] Nedyalkov N, Stankova N E, Koleva M E, Nikov R, Alexandrov L, Iordanova R, Iordanova E and Yankov G 2019 Laser processing of noble metal doped glasses by femto- and nanosecond laser pulses Appl. Surface Sci. 475 478

[8] Yankov G, Stefanov I, Dimitrov K, Piroeva I, Dimowa L T, Tarassov M P, Shivachev B L, Yoneda L and Petrov T 2013 Measurement of nonlinear refractive index and multiphoton absorption by the subpicosecond z-scan method of tellurite multicomponent glassy matrixes having nonlinear susceptibility Physica Scripta T157 014026

[9] Pálfalvi L, Tóth B C, Almási G, Fülöp J A and Hebling J 2009 A general Z-scan theory Appl. Phys. B 97 679