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Optical breakdown-driven mesostructure in bulk of soda-lime glass

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ABSTRACT

A study of structural changes in soda-lime glass irradiated with a tightly focused nanosecond laser pulse is presented with center on the material area strongly affected by pressure of a shock wave and the induced temperature. Different forms of microscopy, together with photoluminescence and Raman spectroscopy were used in characterization of the structural transitions induced by the optical breakdown in the bulk of soda-lime glass. Inspection of the irradiated region and its vicinity confirmed existence of an elongated void surrounded by a shell of densified material and the outer cracks. Laser-induced material densification was also identified by μ-Raman spectroscopy. High-resolution transmission electron microscopy (HRTEM) of the shock-affected region revealed nano-crystallization. Nanocrystals (crystallites) with an average diameter of 4–5 nm were precipitated in a matrix of densified glass and formed in this way a mesoscopic phase embedded in an amorphous host medium. This phase was spatially limited to a layer with a thickness of 100–150 nm at the shell/void interface.

1. Introduction

Due to their relatively simple composition, easy availability and processing, vitreous material is often used as a model to study the physics of amorphous solids. The vitreous state needs some amount of activation energy to change from its metastable form to the crystalline state. In practice, standard crystallization of glass is realized as a quasi-stationary process on a long (from seconds to hours) time scale. It starts with nucleation followed during a sufficiently long time interval by crystal growth at sufficiently high, strictly controlled temperature (isothermal process). Crystallization under laser irradiation has become increasingly attractive for engineering and science due to its potential to shorten the process markedly. Moreover, laser heating in the bulk could be advantageous to space-selective precipitation of nanocrystals inside transparent material with the aim of glass ceramics (GC) fabrication. Nanocrystalline GCs have certain advantages, as they are usually fully transparent to visible light (particularly useful in optical applications) and show higher mechanical durability, when compared to glass.

The heating rate, during the nanosecond laser pulse irradiation exceeding 10^{10} K/s, is followed by equally fast quenching process and both easily generate either overheated or overcooled state of the matter. On the other hand, the local stress induced by the laser may reduce the necessary activation energy required for nucleation. Reported experimental results on laser-supported crystallization gave the crystallites of size ≤100 nm [1–3].

Nonlinear energy absorption within the focal volume of a tightly focused laser beam in bulk of a wide-bandgap dielectrics leads to the energy density level easily exceeding an optical breakdown threshold. The generated extreme temperature and pressure used to drive shock and rarefaction waves in the deposition area [4]. As a consequence, physical modifications of the material occur within a complex chain of physical processes originating in the area of the energy deposition and lead to the glass densification and refractive index change, accompanied by phase transitions (crystallization or amorphisation) [5]. The area where the influence of the laser irradiation occurs is denoted as the laser-affected area. It consists of an empty space called void, surrounded by the shell of the densified material and the outermost fractures or cracks.

Our interest in investigating the laser-induced phase transitions in soda-lime glass was triggered by two reasons. First, by ubiquity of the material in modern technology. Second, by its multi-element composition and strong willingness to stay in the amorphous state. In this work we show that the structural changes induced in bulk of soda-lime glass by a single, tightly focused nanosecond laser pulse are more complex than it appears at the first glance, and differ from those initiated by the moderate laser heating. A part of the apparently amorphous shell area shows on closer inspection noticeable level of nanocrystallization with the crystallites dispersed in amorphous matrix. The scale of the effect suggest creation of a mesoscopic phase. We ascribe the phenomenon to the extreme value of the main thermodynamic parameters during the optical breakdown. The dominant physical mechanisms involved in the transformation process are discussed and

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the features of the locally created glass ceramic are extracted from the data obtained with diversity of the diagnostic tools.

2. Experimental detail

A 4 ns-long laser pulse from a Q-switched Nd:YAG laser oscillator (Quantel's Brilliant model) working in the regime of second harmonic (532 nm) was used as the source of the driving radiation. Energy of the incident laser beam was varied by an attenuator working in the reflection regime to keep the radial intensity distribution unchanged. The laser beam was focused in the bulk of sample to a diameter of 1.8 ± 0.1 μm by a microscope objective having numerical aperture (*NA*) of 0.40. All measurements were performed in the air with a sample mounted on a precise XYZ motorized stage ensuring fresh material for each shot. Samples polished to a surface quality of 60/40 scratch/dig induced a limited wave-front distortion of λ/4 at 632.8 nm. The energy bandgap of soda-lime glass is 3.9 eV, while its Young's modulus is equal to 72 GPa. The irradiated samples were post-processed by cutting, etching or milling techniques to reveal details of the morphological changes with microscope imaging.

The surface morphology was recorded by scanning electron microscope (SEM). Compositional study was performed with the micro-Raman spectroscopy applying an argon laser (514.15 nm) combined with a Raman spectrometer (Labram Aramis, Jobin YVON) and a microscope objective (MO) of 100× magnification (beam spot ≈ 1 μm). The spectral resolution of the spectrometer was ± 1 cm^{-1} and the recorded spectra had an accuracy of ± 2 cm^{-1}. The same laser was used for photoluminouscence (PL) studies of the samples at a room temperature. The PL spectrum was highly reproducible with the estimated standard deviation lower than 0.5%. All the spectra (Raman and PL) were corrected for the instrumental spectral response. The lamellae needed for high resolution transmission electron microscopy (HRTEM) were prepared by the focused ion beam (Helios Nanolab 450 F1) technique with a gallium ion (Ga^{+}) source milling the sample down to a thickness of 100 nm. A platinum film was deposited over the sample surface to protect its volume from the Ga^{+} ion beam. Cross-sectional analysis of the photo-modified region was carried out using transmission electron microscope (Tecnai TF30 ST). Furthermore, X-ray diffraction analysis of the sample was performed with Cu-Kα radiation ($\lambda = 1.5405$ Å).

3. Results and discussion

Energy deposited in a transparent dielectric typically generates damage structure in the bulk on a micrometer size scale. The lateral view of the breakdown area in the bulk of soda-lime glass recorded for different irradiation energies with a confocal microscope is shown in Fig. 1. The damage morphology in the images has a few common features as the void and dense shell with a size increasing dominantly in the axial direction. Interestingly, the layer of the densified material surrounding void (shell) and compressed by the shock wave extends well behind the geometrical focus in a form of crooked tail (best seen for shots with energy of 1826 μJ and 2029 μJ). This feature was observed only in gases [6] and ascribed to fast ionization in the primary stages of the breakdown.

Radial, circular or circumferential cracks surround the apparently homogeneous shell. It is worth noting that the massive damages

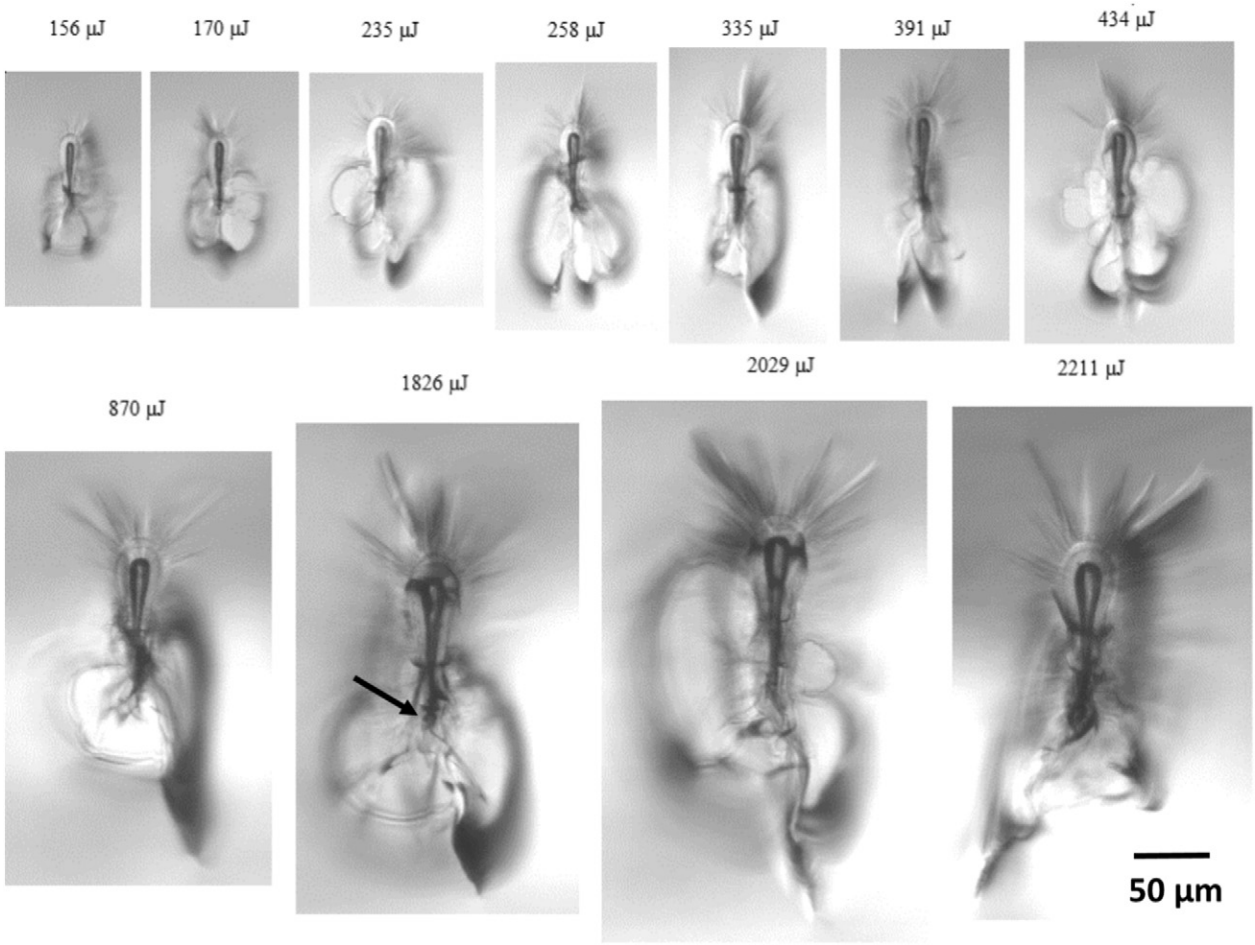

Fig. 1. Lateral view of damage morphology in soda-lime glass recorded with a laser scanning confocal microscope. Values of the incident energy are indicated at the top of each panel and the irradiation direction was from the top to the bottom. The scale bar is valid for the whole image. Black arrow points to the region whose TEM image is shown and analyzed in Fig. 2.