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

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A R T I C L E   I N F O
Article history:
Received 19 April 2016
Received in revised form 30 May 2016
Accepted 26 June 2016
Available online xxxx

Keywords:
Silicate
Glass ceramics
Optical breakdown
Spectroscopy

A B S T R A C T
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.

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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

http://dx.doi.org/10.1016/j.jnoncrysol.2016.06.037
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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 $1.8 \pm 0.1 \mu m$ 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 $\lambda/4$ 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 $\approx 1 \mu m$). The spectral resolution of the spectrometer was $\pm 1 \text{ cm}^{-1}$ and the recorded spectra had an accuracy of $\pm 2 \text{ cm}^{-1}$. The same laser was used for photoluminoscence (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 ($\text{Ga}^+$) 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 $\text{Ga}^+$ 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 ($\lambda = 1.5405 \text{ Å}$).

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...
surrounding the narrower half of the void suggest high density of the energy deposited in this area resulting in a very high pressure and strong material tensions (Fig. 1). In contrast, the broader part of the cavity is accompanied only by individual, long, radial cracks being the typical indication of more relaxed conditions. Distinguished mechanical and optical features of the dense material layer are easily deduced from the inset in Fig. 5. The SEM image shows bulk damage of soda-lime sample that underwent mechanical cleavage. The shell region surrounding the void is smoother, if compared to the pristine (before irradiation) or fractured material. This would suggest increased hardness and resistance to the mechanical damage.

Transmission electron microscopy (TEM) was used to analyze properties of the shock-affected area in a broader perspective of the phase transitions. Fig. 2 shows HRTEM image of the region near to the void. We found nano-crystals (crystallites), with a size of several nanometers in diameter, precipitated in a thin layer (~150 nm) of amorphous matrix at the shell/void interface. This is a glass-ceramics, a material important for practice due to preservation of the glass transparency level while demonstrating mechanical strength of classical ceramics [7]. Moreover, considering the crystallites size, one can deduce that the precipitated nano-crystals create a mesoscopic phase. The distribution of the crystallites across the shell is of primary importance for crystallization of glass. The extreme thermodynamical conditions (the pressure on the order of 100 GPa and the average temperature close to 10⁴ K) result from the process of optical breakdown in a limited focal volume within a time interval of 30–40 ns. This time scale suggests that the crystallization process occurs after the breakdown beginning as nucleation phase in the pure thermal process is estimated as starting after 10–20 ns [8]. The crystallization process seems to be independent of the surface as the border line between the mesostructured layer and the pure densified glass does not reflect the shape of the void wall. The heat generated by the energy deposition is partly conducted into the pristine material giving a smoothed temperature distribution in the radial direction. Additionally, the peak pressure of the shock wave itself, exceeds a pressure value required to induce structural changes (usually a few GPa). It is also expected that shock could enhance the motion of atoms and hence reduce necessary activation energy of the crystallization process in its first step - nucleation. The time scale and the crystallization character suggest homogeneous nucleation with the amorphous phase separation. These conditions are preferable for obtaining the observed type of the mesostructure as they promote rich nucleation with very limited crystal growth [9].

Both, the HRTEM image and selective-area electron diffraction (SAED) pattern of the sample are presented in Fig. 3. The presence of fine spherical rings around the central bright region of the SAED pattern results from existence of nano-crystallites in the glassy matrix. The SAED pattern were indexed using cristobalite crystal structure and the correctness of the method was verified by X-ray diffraction analysis. On the search for the structural information, X-ray diffraction of the irradiated sample was performed by making a regular scan-array of the sub-regions modified in the process. The distance between the two such sub-regions was large enough to avoid overlapping of the consecutively irradiated areas. The XRD pattern of the pristine region exhibits a broad hump pronouncing its amorphous structure (Fig. 4). However, after the laser-irradiation, two narrow diffraction peaks appeared to signify product of crystallization. Only the strongest peaks of the X-ray
diffraction image recorded due to small partial content of the crystallites in the glass as well as very limited area of the mesoscopic zone. Nevertheless, the registered peaks showed the pattern belonging with very high probability to a mixture of cristobalite [10] and stishovite [11]. (See Fig. 4.)

It was attempted to determine the average crystallite size using the Scherrer formula \(D = \frac{K\lambda}{\beta \cos \theta}\) and the recorded diffraction orders. In the formula, \(\lambda\) is the wavelength of X-ray radiation (in our case CuK\(\alpha = 1.5406\) Å), \(\beta\) is the full width at half maximum (FWHM) of the peak at a diffraction angle \(2\theta\) and \(K = 0.89\) is a correction factor. FWHM of the most intense diffraction peak of cristobalite gave the crystallite size \((D)\) equal to 10 ± 1 nm.

Compositional analysis of the pristine and irradiated regions was conducted using Raman spectroscopy. Raman spectrum of the pristine region shows peaks located at 520 cm\(^{-1}\), 630 cm\(^{-1}\), 800 cm\(^{-1}\), 950 cm\(^{-1}\), and 1090 cm\(^{-1}\) (see Fig. 5). The band around 520 cm\(^{-1}\) results from Si–O–Si symmetric stretching vibration modes of Q\(^4\) and Q\(^3\) species [12]. The 600 cm\(^{-1}\) band is attributed to the same Si–O–Si vibration mode but in the Q\(^2\) species [13]. The 800 cm\(^{-1}\) band corresponds to Si motion in its tetrahedral oxygen cage [12] and the bands around 950 cm\(^{-1}\) and 1080 cm\(^{-1}\) are related to Si–O stretching vibration modes of Q\(^2\) and Q\(^3\) species, respectively [14].

Following the laser exposure, the intensities of 520 cm\(^{-1}\) and 630 cm\(^{-1}\) bands in the Raman spectrum decreased. This is contradictory to the claims that variation of the bands around 600 cm\(^{-1}\) should be attributed to change in the Q\(^{2}\) ratio with the pressure. It was namely implied, that the band about 600 cm\(^{-1}\) (concentration of the Q\(^2\) units) increases at the expense of the 560 cm\(^{-1}\) band (determined by the Q\(^3\) units) as a visible signature of the densification process [15]. In our soda-lime glass, the 560 cm\(^{-1}\) band does not exist at all, even in the pristine material, and essentially, after the irradiation the band with the peak at 631 cm\(^{-1}\) slightly reduced its intensity but clearly showed spectral narrowing and increased sharpness at the peak, suggesting development towards crystallization. The high-frequency part of the spectrum was modified much stronger. Reports suggesting that with densification intensity of the 950 cm\(^{-1}\) band increases, whereas that of the band around 1100 cm\(^{-1}\) decreases [15] have been fully confirmed. Additionally, the peak of the 1090 cm\(^{-1}\) band has been shifted by 18.3 cm\(^{-1}\) towards the lower frequencies. Such a shift is usually ascribed to increase in the fictive temperature [16] but this parameter seems to be inadequate as it is difficult to adapt the definition of the fictive temperature (\(T_f\)) to the situation when presence of structural equilibrium of the fluid is very unlikely due to high and transient pressure, by nature reducing a temperature value at the melting point. The last
argument would be consistent with the suggestions that the observed changes are predominantly due to densification and that the fictive temperature effects, if present, give a minor contribution [17]. Reduction in the band intensity is interpreted as a result of pressure-induced formation of Q$^1$ at the expense of Q$^3$ species. Majority of these effects was observed in quasi-static experiments. We have to stress that in our experiment both factors, temperature and pressure apart from their extreme values acted simultaneously on the nanosecond scale, while the previously reported results considered these parameters separately. The new effects as a very strong increase in the intensity of the band about 800 cm$^{-1}$ and strongly pronounced appearance of the low-frequency edge of the 1090 cm$^{-1}$ band need more detailed and dedicated analysis. It is also interesting that the laser-induced shift of the 1090 cm$^{-1}$ band revealed quite strong sub-band about 1111 cm$^{-1}$, related to Q$^4$ and hence representing more order in the structure by very high polimerisation level. In this situation, we think that the shift of Raman peak towards lower frequency is attributed rather to increase in material compression and its densification due to pressure, but the influence of the temperature cannot be ignored. Interestingly, the discussed shift can also be caused by presence of the devitrinite in the shell [18].

Luminous spectra obtained from bulk region of the pristine soda-lime glass sample are shown in the Fig. 6a. The spectra feature typical structure with broad peaks around 1.8 eV and 2.25 eV. The PL band at 1.8–1.85 eV is attributed to structural defects due to the non-bridging oxygen hole center (NBOHC) [19]. The reported peak energies of this red emission are extended usually from 1.8 to 1.95 eV, depending on the excitation condition and a particular SiO$_2$ structure. The 1.8 eV PL band is different from the PL band related to the oxygen deficiency-associated defect centers (typical for Si clusters or SiO$_x$ structure with x<2) that are introduced usually during the manufacturing process. The band at 2.25 eV is typically associated with the defects and surface flaws present in material [20]. For more detailed analysis, the spectrum was de-convoluted into the Gaussian components. This revealed an additional weak band centered at 2.2 eV usually attributed to interstitial O$_{2-}$ ions trapped in subsurface micro fractures in the vicinity of E$_{2g}$ centers with positive charge compensating the O$_{2-}$ ions [21].

The sample of soda-lime silicate glass irradiated with ns-laser pulse yielded luminous bands in the energy interval between 1.5 and 2.21 eV (Fig. 6b), with significantly enhanced overall intensity. Recorded signal was analyzed with a multi-parameter Gaussian fit function and that revealed broad PL sub-bands centered around 1.6 eV, 1.7, 1.9 and 2.1 eV. The composition of the NBOHC band (1.8 eV) of the irradiated region was analyzed with a multi-parameter Gaussian fit function and that revealed broad PL sub-bands centered around 1.6 eV, 1.7, 1.9 and 2.1 eV. The composition of the NBOHC band (1.8 eV) of the irradiated region was de-convoluted into the Gaussian components. This revealed an additional weak band centered at 2.2 eV usually attributed to interstitial O$_{2-}$ ions trapped in subsurface micro fractures in the vicinity of E$_{2g}$ centers with positive charge compensating the O$_{2-}$ ions [21].

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Fig. 6. Photoluminescence spectrum of: a) pristine soda-lime glass sample and b) after the sample is exposed to laser-irradiation. Spectra of laser treated region were taken from the same point as marked by arrow in (Fig. 5). The goodness of the fit given by the adj. R-square value is 0.99.
IBS-R012-D1 and by the Gwangju Institute of Science and Technology through the Top Brand Project (TBP). Z. U. Rehman was supported by IBS-R012-D1.

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