Void formation in glasses

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\textbf{Abstract.} Void formation as a result of a single tightly focused femtosecond pulse irradiation has been systematically studied in commercial optical-grade glasses of different composition. Correlations between the composition, mass density, glass transition temperature and Young modulus of glass with the void formation threshold have been revealed. The pulse energy necessary to form a void was found reciprocal to the amount of glass-forming oxide in the case of silicate, phosphate and borate glasses. The larger is the bond strength (the cohesion energy per bond) of the glass-forming oxide, the lower is the threshold energy of the pulse, at which the void is formed after a single pulse irradiation.

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1. Introduction

Glasses have evolved into key technological materials for construction, science and communications over the last four millennia of usage and are becoming increasingly relied upon in this century of photonics [1]. The emerging of optics and, recently, laser technology and their current growth in importance in a variety of ways are inseparable from the evolution of glass fabrication and processing, which have become state-of-the-art nano-/micro-technologies in their own right. Apart from the optical, the control of mechanical and structural properties of glasses has paramount importance, especially for micro-opto-mechanical chip and sensor applications. By controlling micro-patterns formed/recorded inside glass, a reinforcement for compressive and tensile load applications can be achieved as has been well established for ceramic materials [2]. As a result of mass conservation, the formation of a three-dimensionally localized densified micro-region inside glass is accompanied with mass-density decrease around the micro-pattern.

The void inside glass represents a kind of ultimate density modulation created by a laser pulse: the empty volume surrounded by a shell of densified material [3, 4]. It is technologically important to establish the conditions of formation of such photo-modification for micro-structuring, creation of new phases inside the densified region [5, 6] with altered chemical properties [7], as well as to assess damage resistance of glasses at extremely high irradiance (>10 TW cm\(^{-2}\)). Voids of sub-micrometre cross-sections can be recorded inside glass by tightly focused single ultra-short pulses without crack formation [8]. The mechanism of void creation is a micro-explosion [9] which triggers shock and rarefaction waves from the focus [10]. Recently, the scaling between the void diameter and the pulse energy has been established in the case of crystalline sapphire and a high-purity vicosil silica [8, 10]. It has been demonstrated that the radius of a shock-affected region, \(r_{sh}\), is given by [11]:

\[
    r_{sh} \approx \sqrt[3]{\frac{E_{abs}}{\pi Y}},
\]

where \(E_{abs}\) is the absorbed energy and \(Y\) is the Young modulus. This dependence was corroborated experimentally and by numerical simulations using a realistic equation-of-state [11]. The absorbed energy deposited within a skin (absorption) depth of approximately \(l_a \approx 100\) nm at the ionized focal volume was a source of a micro-explosion. Since the skin depth in a fully ionized (metallic) plasma is weakly dependent on the properties of the initial material, the radii of the shock-affected volume and void are mainly determined by the Young modulus according to equation (1) and the conditions of void formation by a micro-explosion can be compared in different glasses regardless of their linear optical properties important only for an initial focusing [11].

Here, we present a systematic study of the void recording by tightly focused femtosecond laser pulses in glasses of different compositions. Departure from equation (1) in description of the optically recognizable final void size has been found due to refill of the void by a back-relaxation of the shock-displaced material after the micro-explosion. The linear optical properties of the refractive index, \(n\), absorption coefficient, \(\alpha\), and quality of surface polishing of all 24 glasses were comparable. The employed tight focusing conditions had achieved similar diameters of the focal spots with few exceptions where self-focusing (due to a nonlinear refractive index, \(n_2\)) become important. Correlations between the physical and compositional properties and the void formation shows a direct dependence of the void formation threshold and the concentration of a glass-forming oxide X–O (where X is Si, P and B).

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Figure 1. Correlations between the void formation threshold energy, $E_{\text{th}}$, and the concentration of glass former (a), mass density (b), Young modulus (c) and glass transition temperature (d). The inset shows the optical image of voids in a phosphate sample no. 19. Lines are drawn as eye guides to highlight tendencies common for the silicates (Si), phosphates (P) and borates (B). The nomenclature of glasses and color notations are in accordance with figure 2. The marker boxes are larger than the $x$- and $y$-error bars.

2. Void recording

Voids were recorded inside glass samples at approximately 50 $\mu$m depth. The focusing was optimized to have the smallest threshold of recognizable optical damage, a dielectric breakdown, which is caused by ionization of the focal volume. This was achieved by an afocal focusing: a slight change of the laser beam divergence using a relay telescope. The damage threshold was optically recognized by an in situ observation. This apparently subjective method of threshold determination was made qualitative by measuring statistics of the breakdown [12], i.e. the probability of an optical damage occurrence was established at different laser pulse energies and the threshold had typically 5% uncertainty caused by laser stability.

The threshold of void formation was higher than the threshold of the dielectric breakdown in terms of pulse energy and was revealed by a comparison of optical image and the cleaved cross-section of the sample [8]. The bright central spot in an optical image was confirmed to be a signature of the void. It should be noted that the size of the void cannot be determined by this procedure. However, only the fact of the void creation was under question in this study. The inset in figure 1(a) shows an optical contrast corresponding to the void approximately 200 nm...
in diameter (size was determined by scanning electron microscopy (SEM) after cleaving the sample [8]). The typical threshold diameter of the optically recognizable void was 100–150 nm in all glasses. This void’s threshold size is determined by the optical resolution of the employed imaging. It is noteworthy that there were no voids observed in few silicate glasses (figure 2) under the maximum pulse energy of 300 nJ used in our studies, most probably, due to self-focusing which had dispersed pulse energy axially. The self-focusing was not significant for the lower pulse energies in all glasses since power per pulse was below 2 MW [13].

3. Correlations: glass properties versus the void formation threshold

A simple relation between the absorbed energy and the void diameter has been established for crystalline sapphire [10, 11] and high-purity silica (viosil) [8]. It was based on the model that the volumetric absorbed energy density (i.e. the pressure $Jm^{-3} = Nm^{-2} ≡ Pa$) determines the void size according to the Young modulus (a ‘cold’ pressure) of the host material in correspondence to equation (1). However, this model only considers a micro-explosion phase of void formation and does not take into account a post-explosion relaxation of material. We found that glasses of different composition and physical properties do not obey the dependence of void formation established for sapphire and silica. We explore, here, correlations between different glass characteristics and the void formation.

The glass samples were characterized by standard methods (see section 5) and the obtained values are listed in figure 2. The uncertainties of the measured values were typically less than 2% (see figure 2). The most distinct correlation is between the void creation threshold and the total concentration of a glass former as shown in figure 1(a). The total concentration of glass formers is considered, though they form separate networks. The efficiency of re-establishment of the glassy network during re-solidification was found to be an important factor in void formation. The larger the amount of a glass former the smaller threshold of the void formation. Experimental data, the property maps, are clustered according to the main glass types: silicates, phosphates and borates (germanium-silicates, samples no. 10 and 11, join the dependence obeyed by the silicate family). Since 24 different glasses were investigated, the data in figure 1 should be analyzed for the observable trends and correlations and are expected not to obey exact dependencies. There were no voids observed in few silicate glasses with glass former concentrations 0.73–0.86 (figure 2) even under the maximum pulse energy of 300 nJ used in our studies. One can expect the dependence plotted in figure 1(a) to be even steeper for silicates since the creation of a void would require even higher pulse energy for decreasing Si concentration. Most probably, the self-focusing was responsible for the axial energy smearing and conditions for a point-like breakdown were not reached. The pulse energy of 300 nJ at a pulse duration of 180 fs comprises 1.7 MW power per pulse and this is already close to the typical self-focusing threshold in glasses at 2–3 MW depending on the nonlinear refractive index, $n_2$, of material [13].

Since void formation is related to a mass transfer by micro-explosion, one should expect dependence of the void formation threshold on the mass density of glass. Indeed, the heavier the glass the larger void formation threshold was observed for the same family of glasses as shown in figure 1(b). It is difficult to predict scaling of the final void size on the mass density due to the reflow of glass initially expelled by the micro-explosion. The visco-elastic glass transformations in the case of liquid-to-solid transition are very complicated in the presence of strong temperature gradients [14] and would require special studies for this particular
**Figure 2.** Glass composition, properties and void formation thresholds in terms of pulse energy at the focus of single 800 nm/180 fs pulses at tight focusing (the numerical aperture NA = 1.35). The annealing point temperature is presented instead of the actual $T_g$ for the glass nos. 1–3 and 15. The refractive index was measured at the wavelength 587.56 nm ($d$-line). The uncertainties of the measured values were: $\Delta n = \pm 5 \times 10^{-4}$ for refractive index, $\Delta Y = \pm 1$ GPa for Young modulus, $\Delta \rho = \pm 5 \times 10^{-3}$ g cm$^{-3}$ for mass density.

| Name         | YODSIL | ULE | Pyrex |
|--------------|--------|-----|-------|
| Sample No.   |        |     |       |
| Series       | S      | S   | S     |
| SiO$_2$      | 100.0  | 95.0| 82.4  |
| AlO$_2$      | 1.7    | 4.3 | 4.0   |
| MgO          | 0.8    | 28.6| 47.9  |
| Li$_2$O      | 0.02   | 0.04| 0.02  |
| Na$_2$O      | 4.0    | 0.8 | 0.8   |
| K$_2$O       | 0.01   | 0.02| 0.02  |
| CaO          | 0.01   | 0.02| 0.02  |
| SrO          | 0.01   | 0.02| 0.02  |
| BaO          | 0.01   | 0.02| 0.02  |
| TiO$_2$      | 5.0    | 0.0 | 0.1   |
| ZrO$_2$      | 0.11   | 0.11| 0.11  |
| Total        | 100.0  | 100.0| 100.0 |
| Glass former | 100.0  | 95.0| 82.4  |
| Void/no.     |        |     |       |
| Void creation threshold (nJ pulse$^{-1}$) | 26.5 | 24.5| 12.0 |
| Refractive index ($n_d$) | 1.4860 | 1.4800| 1.4720 |
| Abbe number ($v_d$) | 67.7 | 53.1| 65.7 |
| Mass density (g cm$^{-3}$) | 2.20 | 2.17| 2.13 |
| Young modulus (GPa) | 75   | 68  | 66   |
| Bulk modulus (GPa) | 52   | 58  | 58   |
three-dimensionally confined micro-explosion geometry. For a qualitative estimate, the timescale of a reflow of liquidized glass into the void is given by $\tau_f \approx l^2/\nu$, where $l \sim 1 \mu m$ is the characteristic size of the reflow distance and $\nu \approx 10^{-7} \text{–} 10^{-6} \text{m}^2 \text{s}^{-1}$ is the kinematic viscosity of high-temperature melts. Then, $\tau_f \approx 1\text{–}10 \mu s$ with a re-solidification following on a timescale longer by an order of magnitude [14].

The prediction by equation (1) is compared with experimental data shown in figure 1(c). The void formation threshold was judged from an optical transmission image and is determined by the optical resolution; hence, the threshold volume, $\sim r_{sh}^3$, can be assumed to be the same. Then, the absorbed pulse energy, $E_{abs}$, determines the onset of void formation and is proportional to the Young modulus according to equation (1) with prediction $E_{th} \sim Y$. Poor linearity between the pulse energy and Young modulus was observed; moreover, it was different for each glass family. Since the void formation is judged by a post-explosion observation, the relaxation of a shock-affected volume is important; however, it is not reflected in equation (1). Sapphire and silica have the highest melting temperatures compared with the tested samples; hence, the melting and its reflow after micro-explosion are the least expected. Also, the cohesion energy (the bond strength) of silica and sapphire are among the highest of the used materials, facilitating an effective bonding recovery after the micro-explosion as discussed below in more details. This makes the equation (1) appropriate for description of shock-affected volume and void formation only in the case of strong bond formers Si and Al.

It appears that, in the case of glasses with a lesser amount of glass former, the formation of a rigid glassy network during post-explosion phase of relaxation is less effective and shock-liquidized material refills the void initially formed by the micro-explosion. As a result, much higher pulse energies are necessary to finally observe the void after the post-explosion relaxation is finished as shown in figure 1(a). Though a smaller absorbed energy is required to initially create the void during micro-explosion in glass with smaller Young (bulk) modulus (equation (1)), the post-explosion relaxation and refilling of a void is strongly dependent on glass former concentration. This is corroborated qualitatively by the correlation between the threshold of the void formation and $T_g$ (figure 1(d)) for each family of glasses. The glasses of smallest $T_g$ showed the highest thresholds, expectedly, due to the void refill. It is noteworthy that the $T_g$ can have variations from the in-bulk values at the void edge of a few tens of nanometres [15]. The re-establishment of chemical bonds after a micro-explosion phase of duration $\sim 0.2 \text{ ns}$ [10] is the most effective in glasses with a large concentration of glass former, since the glass formers have bond strength $> 3.5 \text{ eV}$ per X–O bond and coordination number $2 \leq n \leq 4$ favoring the network formation [16] (the bond strength is a cohesive energy, $E_{coh}$, per bond). The glass formers Si, P and B have decreasing X–O bond strength $4.60 \text{,} 4.32$ and $3.86 \text{ eV bond}^{-1}$ (all for $n = 4$) [16], a tendency clearly discernable in figure 1(a) (see the eye guides).

The observed phenomenon is qualitatively discussed below in terms of $E_{coh}$ and intratomic distance, $d$. The cohesive energy of material (the energy necessary to separate a solid into isolated atoms), $E_{coh}$, corresponds to the minimum of the Lennard–Jones potential. According to an accepted view that the components other than glass formers (the modifiers [16]) enter the glass as interstitials, the decrease in glass former concentration usually corresponds to the decrease of the average interatomic separations, $d_{av}$, and an increase in the interatomic distance of the glass network former, $d_{net}$ [16]. In terms of bond strength, the glass modifiers have typically $< 2.5 \text{ eV bond}^{-1}$ (in oxides) [16]. Thus, the most pure silicate, borate and phosphate glasses have the minimal $d_{net}$ and correspondingly the largest $E_{coh}$. Once the glass network is destroyed by a shock wave the large $E_{coh}$ (the potential minimum) facilitates effective restoration.
of the network after the micro-explosion phase (from approximately 0.2–0.5 ps onwards [11]). The smallest void creation thresholds were observed in the large $E_{coh}$ glasses (figure 1(a)) due to weak reflow of molten material into the void formed by a shock wave.

The smaller $d_{av}$ renders an increase in elastic moduli $Y$ and $B$. It is well known in glass technology that the smaller $d_{av}$ (additions of non-glass formers) favors the technologically favorable decrease in melting temperature, $T_m$. According to the Lindeman criteria of melting (though derived for crystalline materials and discussed here qualitatively), the $T_m$ is given by [17]:

$$T_m = \frac{x}{9h^2} M k_B T_D^2 d_{av}^2,$$

where $M$ is the atomic mass, $k_B$ is the Boltzmann constant, $T_D$ is the Debye temperature (it is assumed $T > T_D$) and $0.2 \leq x \leq 0.25$ is the Lindemal parameter (a median departure of an atom from its equilibrium position). The empirical relation between the $T_m$ and $T_g$ in inorganic glasses is $T_g \simeq \frac{2}{3} T_m$ [18]. The data in figure 1(d) qualitatively supports this basic tendency showing the multi-component glasses having the larger void formation thresholds due to effective refill of the void due to low $T_g$ (in terms of bond strength, glass modifiers reduce the energy-per-bond [16, 18]).

It is noteworthy that the dependence of the void formation threshold on the refractive index has not been observed, partially, due to optimized focusing (comparable focal spots were obtained in all samples) as well as due to small difference in the indices of the glasses used. The difference in refractive index can be easily accounted for by calculation of the focal light intensity distribution at the focus due to spherical aberration caused by the index mismatch [11, 19].

One of the smallest void formation thresholds was observed in viosil at $26.5 \pm 0.5 \text{nJ}$, which corresponds to $104 \text{TWcm}^{-2}$ for the employed focusing conditions. The total energy of the chemical bonds was $13.8 \text{nJ}$ calculated as four Si–O bonds (two double bonds of SiO$_2$) with $4.6 \text{eV bond}^{-1}$; the focal volume was calculated by formulae given in [11] and viosil properties from figure 2. The absorbance in a fully ionized plasma is approximately $A = 0.6$ for our experimental conditions [11]; thus, the average energy consumed for the formation of an optically recognizable void is $15.4 \text{nJ}$, just slightly larger than the energy of chemical bonding.

The phenomenon of void formation in wide-band-gap materials and its temporal evolution is expected to reveal more details for a better understanding of light–matter interaction, nonlinear light propagation, filamentation, shock wave formation, ionization and breakdown, as well as for the mechanisms of new phase formation in highly non-equilibrium conditions of post-micro-explosion. New materials [5] with chemically altered properties [7] are formed in shock-affected regions; for example, stishovite formation on the surface of ablated silica glass has been observed [6]. Photo-structuring of chemically inert dielectrics used in UV-optics, blue GaN-based light-emitting diodes and micro-fluidic chips are prospective fields for new material processing solutions used in light-extraction, micro-channel formation [7] and recording of micro-optical components.

4. Conclusions

The threshold of void formation in glasses was found to be reciprocal to the concentration of a glass former $X$–$O$ ($X$ = Si, P, B). The direct laser writing of voids inside dielectric
materials (including glasses) is expected to become a useful tool for miniaturization of micro-optical/fluidic/mechanical applications via an inherent 3D functionality of such a process.

5. Samples and experimental procedures

Samples of optical-grade commercial glasses (Ohara Inc.) were used in this study along with well-known brands of pyrex (Corning Inc.), viosil (Shinetsu Chemical Co. Ltd) and ultra-low expansion (ULE; Corning Inc.) glasses which differ also in their glass former (Si, Ge, P and B) concentrations \cite{16}. Some of the glass samples (No. 6, 10–13 and 15–24) were melted from reagent-grade raw materials in a platinum (for silicate- and germanate-rich glass) or SiO$_2$ (for phosphate- or borate-rich glass) crucible in an electric furnace for 5 h with stirring. The casted glasses (typical volume of 200–300 cm$^3$) were annealed around $T_g$ for 2 h. The optical and physical properties of glasses relevant to the investigated correlations were directly measured and are presented in figure 2.

The Young modulus was measured according to the Japanese Industrial Standard (JIS) using a pulse-echo-overlap method based on the measurement of the longitudinal, $v_l$ (10 MHz) and transverse, $v_s$ (20 MHz) wave velocities with an ultrasonic precision thickness gauge (Model 25DL, Panametrics-NDT). The Young modulus is $Y = \rho v_s^2 (3v_l^2 - 4v_s^2/v_l^2 - v_s^2)$, $\rho$ is the mass density. The Poisson ratio is $\sigma = \frac{1}{2}(v_l^2 - 2v_s^2/v_l^2 - v_s^2)$. The bulk modulus, $B$, discussed in the text is related to the Young modulus, $Y$, by $Y = 3B(1 - 2\sigma)$ in isotropic material. The refractive index was measured on a prism-shaped glass by a refractometer (PR-2, Carl Zeiss Jena). The mass density was measured by a standard Archimedes method using water. The glass transition temperature, $T_g$, was measured by a differential thermal analysis.

Standard set-up consisting of a laser providing amplified femtosecond pulses (Hurricane, Spectra Physics) and an optical microscope was used for recording voids inside glasses under tight focusing conditions using an objective lens with a numerical aperture of NA = 1.35. The diameter of the focal spot was estimated as $D = 1.22\lambda/NA$ at the 1/e$^2$-level by intensity. The corresponding irradiance is calculated at the full width at half maximum (FWHM), i.e. the diameter was $\sqrt{\ln 2/\pi}D$ at the wavelength $\lambda = 800$ nm and for a $\tau_p = 180$ fs pulse duration at the focus (achieved by a chirp pre-compensation). The pulses were set tilt-free for best focusing. A single-pulse irradiation per void was used for all experiments. Morphology of voids was inspected by optical electron microscopy and SEM (more details on experimental procedures are given elsewhere \cite{8,11}). The pulse energy given in the text is measured at the focus.

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