

Observation of O₂ inside voids formed in GeO₂ glass by tightly-focused fs-laser pulses

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Abstract: Unusual generation of molecular oxygen confined in a void inside the bulk of GeO₂ glass is observed with the Raman spectroscopy. The voids are formed by single tightly-focussed femtosecond laser pulses, converting a host glass material into a high temperature plasma, which explodes creating a void and inducing unexpected phase transformations. The intensity of the 1556 cm⁻¹ Raman line, that is a signature of molecular oxygen, increases with pulse energy. The mechanism of O₂ formation and material synthesis in plasma is presented and its relevance to fundamental problems of matter at high-pressure and temperature conditions and subject to geo-physical sciences is discussed.

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OCIS codes: (160.2750) Glass and other amorphous materials; (350.3850) Materials processing; (140.3390) Laser materials processing; (140.3440) Laser-induced breakdown; (160.1245) Artificially engineered materials.

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1. Introduction

Laser structuring of materials by ultra-short laser pulses has become a versatile tool of three-dimensional (3D) nano- and micro-fabrication with applications in optofluidics, micro-optics, and photonic crystals [1–7]. The mechanisms of fs-laser structuring is still an active research field revealing subtle control methods of material processing via engineering an interplay of thermal, linear and nonlinear absorption processes [8–17]. Recently, it has been demonstrated that high pressure and temperature conditions (high- p, T) created by a single fs-laser pulse inside sapphire Al_2O_3 lead to a spatial separation of the constituting Al and O ions and subsequent formation of a high-density phase of the body-centered cubic (bcc) Aluminium [18]. The obvious but still unanswered question remained - where the oxygen had been deposited since the Raman signature of the molecular O_2 had not been found inside the post-explosion voids. As different oxidation states of aluminium are known and complexes with different stoichiometry of neutral and ionic compounds Al_xO_y can be formed [19], it is highly probable that O_2 is accommodated in sapphire [18]. Oxygen-rich and depleted regions were observed in ripple-like nanostructures formed by fs-laser pulses in silica [20]. In fused silica, a strong network alteration was observed by synchrotron X-ray diffraction and changes of an average Si-to-O distance distribution in the laser structured regions with a faint diffraction signatures of a possible crystalline phase [21]. What is the fate of oxygen formed by laser induced micro-explosion and how it affects stabilization of newly formed nano-crystalline materials is a good motivation for further studies of this new method of material synthesis in a strongly-ionized hot plasma [18].

Glasses such as GeO_2 and SiO_2 are good model systems to investigate fs-laser induced changes and their applications to waveguide formation by direct laser writing [14]. We found recently that fs-laser induced modifications in GeO_2 glass are consistent with those induced by hydrostatic pressure [22] and formation of a crystalline GeO_2 due to thermal accumulation from a close proximity of the laser irradiated sites. In SiO_2 glass, the high refractive index is formed along the irradiation path of fs-laser pulses due to a fictive temperature effect [23]: silica becomes more dense at higher temperature, at which the glass is quenched and retrieved [14]. New chemical pathways of material synthesis might be envisaged using the fs-laser driven plasma method which is applicable for breaking some of the nature's strongest chemical bonds in oxides.

Here we demonstrate formation of molecular oxygen in the voids induced by tightly focused fs-pulses in the bulk of GeO_2 glass. We chose GeO_2 due to favorably large Ge-to-O mass ratio: Ge (72.61 a.u.) is considerably heavier as compared with Si (28.09 a.u.), which is close to Al (26.98 a.u.) already investigated in the sapphire breakdown [18]. Hence, GeO_2 glass is a good material to check the mechanism of spatial separation of ions proposed recently [18]. Detection of O_2 further corroborated the method of synthesis and spatial separation in a strongly non-equilibrium plasma [18]. It is noteworthy that Ge-nanocrystallites expected to be formed are inactive in Raman scattering. Potential of this pathway of material synthesis via plasma state for structuring of materials and its relevance to fundamental problems of matter at high- p, T

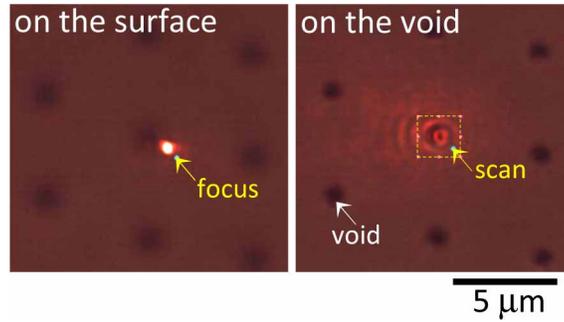


Fig. 1. Backscattered image of a typical sample: a single layer of separated void-structures at 5-7 μm depth below the surface (here in BaF_2). Focused 633 nm cw-laser was used in Raman detection of micro-modifications around void-structures: an optical image of the focal spot on the surface and on the void-structure. The region of interest is selected by a square (marked) for mapping.

conditions encountered in planets' interiors and subject to geo-physical sciences are discussed.

2. Methods and samples

Powder of germanium dioxide (99.98% pure from Alfa Aesar) was melted at 1400°C in a Pt crucible during 36 h and quenched by dripping the bottom of the crucible into water. Pt crucible was used since it does not react with GeO_2 melt. Transparent and bubble free glass was obtained, cut, polished and used in experiments.

Voids were formed in sub-surface region of GeO_2 glass at few micrometers depth by single tightly focussed fs-laser pulses. Typical pulse energy of $\lambda_p = 800$ nm wavelength and $t_p = 150$ fs duration (FWHM) pulses at the entrance of the microscope was $E_p = 250 - 800$ nJ; an overall transmission of the system with an oil-immersion lens of numerical aperture $NA = 1.42$ was 0.4. Pulses were pre-chirped to achieve 150 fs duration at the focal spot. Only at the maximum pulse energy the power ~ 2 MW/pulse approached the threshold of self-focusing and filamentation in glass [24]; hence, we can exclude self-focusing from consideration of an energy delivery to the focal spot. Neglecting optical aberrations and non-linear absorption, the focal volume can be approximated by an ellipsoid with transverse and axial radii of $r_{tr} \approx 202$ nm and $r_{ax} \approx 4r_{tr}$ [25] respectively, estimated at a full-width at half-maximum (FWHM) intensity level. Assuming Gaussian intensity distribution at the focus, intensity $I(r) = \frac{2(E_p/t_p)}{\pi w^2} \exp(-2r^2/w^2)$ with the amplitude, $I_0 = \frac{2(E_p/t_p)}{\pi w^2} \simeq 721$ TW/cm², estimated here for $E_p = 200$ nJ (corresponding to 500 nJ at the entrance of microscope), where the waist of the beam is w ; $r_{tr} = \sqrt{\ln 2/2}w$.

Raman scattering was measured directly from the void-structures (Fig.1) using Aramis (Nano-Optic Devices) dedicated microscope-based setups at a $NA = 0.9$ focusing. The wavelength of excitation in Raman scattering was 633 nm due to low background luminescence. Figure 1 shows representative void-structures in the sample (in this case BaF_2) where the Raman excitation beam was focused on the surface and on the void recognizable by a doughnut intensity distribution: a result of interference between the laser beam and the void. Focusing of laser beam on a structure with a radial symmetry generates optical vortex recognizable by the doughnut intensity distribution [26]. The depth at which this doughnut shape appeared was chosen as the reference depth at which further horizontal (x,y) map were collected. As to get the best spatial resolution, the maps were realized using a $0.5 \mu\text{m}$ steps in both lateral direc-

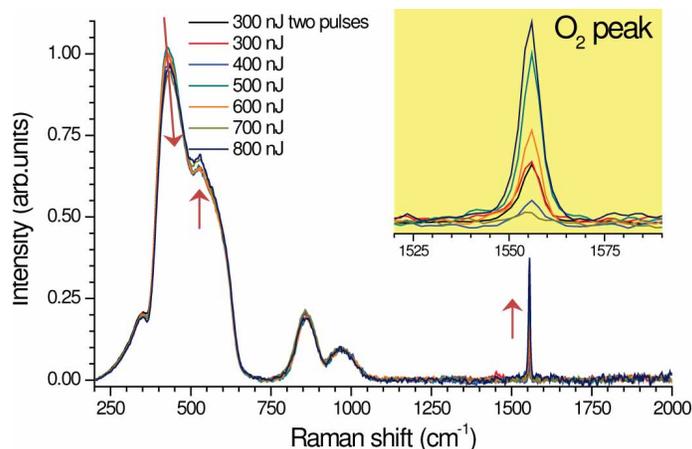


Fig. 2. Raman spectrum of single void structures recorded at different 150 fs/800 nm pulse energies. The arrows show tendency at increasing pulse energy. The inset present evolution of O_2 line intensity.

tions, below the theoretical lateral spot size of $0.9 \mu\text{m}$. The depth of the spot obtained here with a confocal pin hole is estimated at $5 \mu\text{m}$.

3. Results

Voids were formed in sub-surface region of GeO_2 glass at few micrometers depth by single tightly focussed fs-laser pulses. Typical pulse energy of 800nm/150 fs pulses were $0.2\text{--}0.5 \mu\text{J}$. Separation between voids was $3\text{--}5 \mu\text{m}$ in order to avoid modification of the already formed void-structures by heat diffusion from the neighboring sites. For Raman scattering measurements a focal spot of 633 nm laser beam was placed onto the void-structure by focusing at the doughnut depth which was measured to be similar to the depth of the focussed fs-laser pulses (Fig. 1).

Figure 2 shows an extended Raman spectrum of GeO_2 sample with voids measured at 633 nm excitation. The D_2 -band at 520 cm^{-1} is increasing in intensity signifying increase of density in the three-ring tetrahedral- $(\text{GeO})_4$ structures. Usually Raman spectra are collected from Boson peak at $\sim 40\text{--}100$ up to 1000 cm^{-1} where the longitudinal and transverse phonon modes LO and TO, respectively, are identified. This spectral region identifies glass modifications induced by temperature and pressure [22]. No crystallization signatures were observed. Unexpectedly, at longer wavenumbers a distinct molecular O_2 peak was identified at 1556 cm^{-1} .

The extracted pulse energy dependence of the O_2 line at 1556 cm^{-1} is given in Fig. 3. The maximum O_2 intensity obtained on each map was plotted, and coincided with the focal spot of 633 nm cw-laser at the exact void position (see below). To assure that O_2 was embedded inside the voids, atmospheric oxygen intensity background level observed by focusing on the surface (Fig. 1) is reported as the grey region. Strong intensity fluctuation of the 1556 cm^{-1} was observed, however, the correlation between the pulse energy used for the void formation and Raman intensity of O_2 has been determined. However, when cracks are formed at the highest pulse energies, generated oxygen can sometime escape the void through nano-cracks (see data point at 700 nJ in Fig. 3). If cracks do not reach surface, O_2 signature become spatially dispersed around the void as was revealed by spatial mapping discussed below.

Figure 4(a) shows the Raman intensity map scanned at the 1556 cm^{-1} band measured at the

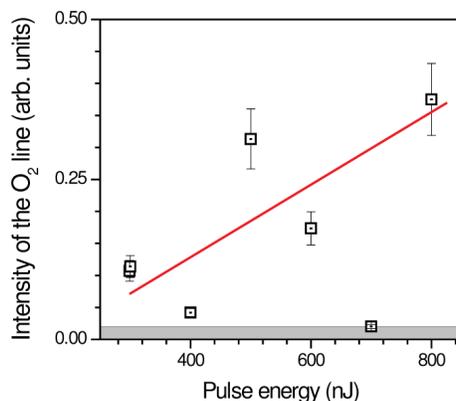


Fig. 3. The correlation of the Raman signature at 1556 cm^{-1} (see, Fig. 2) vs pulse energy. The line is an eye guide; the gray profile shows the background signal of oxygen by focusing on the surface.

depth of the voids on a larger scale. Clear correlation between the O_2 presence and location of the voids is confirmed. One cannot exclude also the other possibility for the molecular oxygen location in the solid phase adjacent to the void (Fig. 4). The O_2 could be formed in the glass where concentration of atomic oxygen has a maximum. The Raman band at 520 cm^{-1} corresponds to the D_2 band of GeO_2 glass and signifies densification. It was found to be more delocalized around the irradiation locations as shown in (b). Departure of the shape of densified regions from an expected circular symmetry is, most probably, caused by interplay of a spherical aberration [27], pulse front tilt [28] and the beam intensity distribution.

4. Discussion

Formation of oxygen out from GeO_2 at the conditions of confined micro-explosion where high- p, T zone is created by tightly focused laser inside a pristine glass, might be understood via scenario similar to that explaining the spatial separation of Al - O ions in sapphire [18]. Indeed, under conditions of the experiments when a $E_p = 500\text{ nJ}$ single pulse energy is absorbed in the volume, which is much smaller than the focal volume due to plasma formation and dramatic shrinking in the absorption depth (note, this E_p value is above the largest energy used in experiments when crack formation and self-focusing had to be avoided and is used here for estimation of the upper bound conditions of the plasma formation).

Let us estimate the energy density for the absorption in the plasma of absorption coefficient $A \simeq 0.6$ within the skin depth $z_s \simeq 70\text{ nm}$, typical for the employed micro-explosion conditions [25]. One would find a huge energy density of $\frac{E_p}{z_s \pi r_f^2} = 55\text{ MJ/cm}^3$ is created inside a cylindrical volume generating maximum pressure of 55 TPa (volumetric energy density J/m^3 is the pressure in Pa) and temperature of 100 eV ($\sim 10^6\text{ K}$) [25]. These are typical conditions of the *warm dense matter* [29] which is here formed by an ultrafast laser pulse in a confined micro-explosion. In these conditions the molecular bonds are broken early in the pulse and constituent Ge and O are ionized to the high degree with ion charge of 3-4 (3,4 electrons are stripped off each ion).

The strong shock wave generated after the end of the laser pulse propagates inside a pristine glass compressing and heating material in an area twice larger than the energy deposition region. Requirements for an elemental separation in plasma is following [18]: (i) the solid density

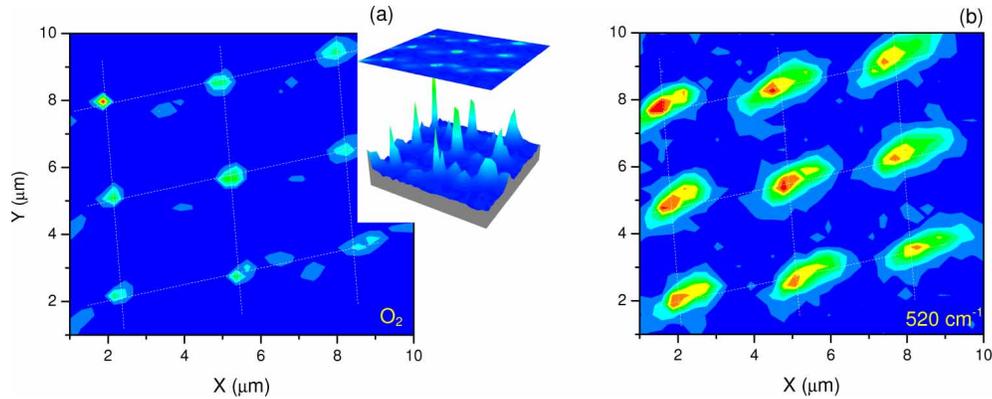


Fig. 4. Spatial map of the voids at the O_2 1556 cm^{-1} (a) and 520 cm^{-1} (b) Raman lines. Depth of scan is centered on the voids plane. The dashed eye-guides shows alignment of the voids. Inset in (a) shows 3D rendering of the plot. Pulse energy $E_p = 500\text{ nJ}$.

plasma should be of high ionization degree ($Z \simeq 2 - 3$) and temperature $> 10\text{ eV}$ ($> 10^4\text{ K}$). Then, (ii) light ions can overcome heavy ions under condition of a directed motion (a shock wave in our case) and, (iii) once the shock wave stops because the micro-explosion is confined inside bulk of cold glass, (iv) the ion separation is finally frozen during the fast cooling.

These conditions occur during the shock formation in the high temperature/density plasma, where the Coulomb interactions dominate and allows for the ion separation even at the solid state density, which is unusual. Ion motion begins when electrons initially absorbed all energy transfer the energy to ions via the Coulomb collisions. Time for the energy transfer $t_{e-O} = (M_O/m_e)\tau_{e-i}$ by these collisions is directly proportional to the ion mass, here τ_{e-i} is the electron-to-ion momentum transfer time, M_O and m_e are oxygen ion and electron masses, respectively. Therefore light oxygen moves first during the several picoseconds after the pulse end while the heavier Ge ion starts to move later $t_{e-Ge} = (M_{Ge}/M_O)t_{e-O}$. Thus the shock wave in this case has an unusual structure of two-fluids hydrodynamics: light oxygen moves faster and earlier in time while germanium trails behind thus ensuring their separation in space.

Additional contribution to the ions separation comes after the shock stopping from the mass dependent diffusion dominated by the Coulomb collisions. Thus one may suppose that oxygen moved far away from the void. It is reasonable suggesting that gradient of oxygen concentration is formed (concentration decreases in direction of the central void). Such situation is favorable for atomic oxygen diffusion in direction to the void center. Because the molecular diffusion is too slow it appears to be most probable that the oxygen diffuses in an atomic state. We suggest that molecular oxygen might be formed in the void long after the pulse end in a relatively cool state. This conjecture is qualitatively in agreement with the experimental finding of the increase in the Raman signal from the sample irradiated at higher fluence. Indeed, higher fluence means higher temperature, higher gradient of oxygen concentration, thus more oxygen diffused into the void. This conjecture needs to be further scrutinized by experiment and theory.

Presence of O_2 in the void structures provides the key evidence of elemental separation in a hot plasma. Further studies will be directed to establish pressure of oxygen in the void and search for other prospective systems where new nanomaterials can be formed via micro-explosion and plasma pathway of synthesis. The range of the pressure and temperature conditions which can be reached by a laser-triggered micro-explosion [30, 31] is entering realm of the high-energy density physics [29]. It is appealing that new materials can be formed using

table-top laser setups and recreate conditions present deep in the Earth. Currently the diamond anvil cells [32] and just a handful state-of-the-art high power laser facilities are used for high-p,T studies of exotic materials [33–36]. Synthesis of new materials [37–40] as well as research of the Earth’s geo-system functioning [41–44] can become experimentally more accessible.

5. Conclusions

We demonstrate oxygen generation inside voids formed in Ge-oxide glass by confined micro-explosion triggered by single ultra-short laser pulses. Large mass difference of Ge and O in GeO₂-glass facilitated ion separation during the plasma stage of the process. Ge and O separation has been evidenced by a simple and accessible Raman scattering and supports earlier findings of elemental separation in the plasma observed in sapphire where characterization was carried out using synchrotron X-ray diffraction [18].

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