Probing densified silica glass structure by molecular oxygen and E’ point defect formation under irradiation

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Article

Keywords:

Posted Date: January 3rd, 2023

DOI: https://doi.org/10.21203/rs.3.rs-2398011/v1

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Abstract

The aim of the paper was to learn more about the structure of densified silica, in particular about the metamict-like silica phase (density = 2.26 g/cm$^3$) by examining the radiation-induced formation of E’ point defects and interstitial molecular oxygen. The large amount of the molecular oxygen produced after 11 GGy integrated dose irradiation in the metamict-like phase is destroyed when this one is submitted to electron irradiation. It infers a particular behavior to this silica phase compared to the other densified silica where the amount of O$_2$ is reduced compared to silica. The position and shape of the O$_2$ emission line support the idea that the void configuration of metamict phase is close to silica. A strong correlation exists between the formation of 3-membered rings of Si-O bonds and E’-centers in the densification process between 2.20-and 2.26 density.

Introduction

Silica glass, also known as amorphous silica, continues to serve as indispensable material in many technological applications, such as optical communications, electronics, UV and laser optics, sensor technologies, medicine, materials processing.

The densification of silica glass under high pressure (HP) [1], by shock waves or irradiation (laser [2], ions, electrons, neutrons) has been extensively studied. Compression of silica gives rise to permanent densification with a densification ratio of 20% (for HP > 15 GPa) while irradiation does not lead to values exceeding 3–4% [3]. We recently showed the convergence to a common “metamict-like” silica phase after irradiating with 2.5 MeV high-energy electrons amorphous silica samples having different initial densities, up to 11 GGy [4]. The metamict densified silica phase has density of 2.26 g/cm$^3$, and its structure shows a large amount of 3-membered rings, as indicated by the intense 606 cm$^{-1}$ ("D$_2$"") band in the Raman spectrum [4]. Those characteristics are very similar to ones evidenced by Bates et al. in neutron-irradiated quartz and amorphous silica [5]. This metamict phase could be considered as a “Medium Density Amorphous” (density = 2.26 g/cm$^3$) phase in addition to the Low Density Amorphous and High Density Amorphous Phases. Hence, it presents interesting aspects regarding the still open question of polyamorphism in silica glass [6]. However, the structure and properties of the metamict phase are not known in detail, mostly because reaching this phase requires drastic irradiation conditions (i.e. 10 days of irradiation with high-energy electrons or 2×10$^{20}$ n/cm$^2$ fast neutrons flux). Moreover, it has been demonstrated by Hobbs, using electron diffraction measurements [7] that the structure of metamict phase is slightly different, when obtained from different polymorphs - quartz, cristobalite or tridymite, or when obtained by different irradiations – fast neutrons or electrons. This shows that there is no single unique metamict state of SiO$_2$ and that the problem is more complex.

Almost all, crystalline polymorphs of SiO$_2$ and silica glass are built from corner-sharing SiO$_4$ tetrahedra of roughly the same size in all phases. Different phases are distinguished by different connection topologies of SiO$_4$ units. Hence, their different densities are caused by differently sized inter-tetrahedral (interstitial)
voids. In the case of silica glass, these voids cause density fluctuations and Rayleigh scattering. The latter is identified as presently the main obstacle to further reduction of losses in optical communication waveguides and provides for direct applied interest in densified forms of amorphous silica [8]. If the interstitial voids are sufficiently large, they can accommodate oxygen molecules O$_2$, formed in irradiated silica glass by dimerization of two interstitial oxygen atoms created in Frenkel process [...] . Whether this process is energetically feasible, it is determined by the size of voids: O$_2$ easily forms by 13 MGy γ-irradiation in glassy silica (density 2.20 g/cm$^3$) and, in contrast, is completely absent in similarly irradiated α-quartz (density 2.65 g/cm$^3$) [9]. There is no measurable O$_2$ concentration in α-quartz, even after much higher (7 GGy) dose of MeV electrons [10]. In this way, the creation of radiolytic O$_2$ is very sensitive to the void size and can yield information on the changes of configuration of interstitial voids in densified silica glass.

The presence and concentration of interstitial O$_2$ molecules in SiO$_2$ can be determined by their photoluminescence (PL) peak at 1272 nm (0.974 eV). Concentrations as low as $10^{14}$ O$_2$/cm$^3$ can be measured [11]. This PL has reasonably high quantum yield (> 0.1), however, the sensitivity is still limited by the extremely small absorption cross sections (~ $10^{-23}$ cm$^2$ [12] for photo-exciting this luminescence). This problem can be circumvented by measuring in situ cathodoluminescence, instead of PL, where O$_2$ is excited by energy transfer. This was first applied by Stevens-Kalceff in 2000 for amorphous and crystalline SiO$_2$. However, relatively low-energy (30 keV) electrons were used, which induced unintended and rapid quartz amorphization in the surface layer [13]. To avoid this, we probe and compare silica samples with different initial densities using cathodoluminescence analysis by high-energy (2.5 MeV) electrons (SIRIUS accelerator) in the 0-200 MGy dose range, much below the amorphization threshold.

In addition, we studied the formation of E’ point defects (Si dangling bonds) in densified silica glasses. The splitting of the hyperfine $^{29}$Si doublet of the E’$_\gamma$ point defect in electron paramagnetic resonance (EPR) spectra can be used to probe the local order around the defect. Buscarino et al. [14] by studying the evolution of the E’ point defect concentration and $^{29}$Si hyperfine coupling in silica irradiated up to doses of 5 GGy, evidenced a heterogeneous and “local” densification [14]. Devine [15] studied the point defect formation in densified silica and their recombination under thermal annealing. He concluded that formation of E’-centers is enhanced due to the existence of strained bonds in densified glass. Further, he observed a large difference between the thermal annealing-induced conversion of E’-centers ($\equiv$ Si• to peroxy radicals $\equiv$ Si − O−O•), when measured in undensified and densified silica. The rate-limiting factor for this conversion is the diffusion of interstitial O$_2$ molecules in silica. Hence it could be deduced that diffusion coefficient of O$_2$ at 450° C in densified silica samples is between $10^7$ and $10^9$ times smaller than that in pristine silica.

The present study is dedicated to comparing different amorphous silica types (including metamict silica glass and silica glasses with higher density) concerning the E’ point defect and O$_2$ formation under irradiation in order to get structural information.
The aim of the present work is to obtain additional structural information on densified silica glasses and metamict silica glass by comparative studies of radiation-induced formation of interstitial O₂ molecules and E'-point defects.

**Results**

Figure 1 reports the intensity of the emission line at 1272 nm caused by \(^1\Delta_g \phi^3 \sum^- g\) transition of O₂ [9] as a function of the irradiation dose (up to 60 MGy). The irradiation time was converted into an integrated dose.

Three groups of O₂ growth curves can be seen in Fig. 1 related to the silica glass stoichiometry and density. In all cases, the saturation is not reached at 60 MGy. The formation of O₂ is much more efficient in pristine silica than in densified silica glasses or O-deficient one. The curves of silica glasses with initial density equaling 2.42 and 2.34 quasi overlap with the plot of O-deficient silica (2.20), whereas the amorphous silica with the highest initial density (2.58) exhibits a quasi-linear growth with a much lower O₂ formation rate. We estimated the initial slope for each curve: for silica it is 10 times larger than for P5T350 and the ratio between slopes equals 250 comparing silica to the highly densified silica (P5T1000).

Figure 2 compares the evolution of the O₂ emission line intensity during irradiation in three samples, all containing sizeable amounts of interstitial O₂ before the start of the irradiation. The pristine “O-rich” silica contained \(\sim 10^{18} \text{O}_2/\text{cm}^3\) introduced by synthesis in oxygen plasma. The two other, initially stoichiometric samples contained interstitial O₂ introduced by high-dose (11 GGy) pre-irradiation. One of them was pristine, density 2.21 g/cm³ the other was densified to 2.61 g/cm³. However, after the 11 GGy irradiation, they both converged to similar density 2.26 g/cm³ and thus correspond to metamict silica samples.

It is amazing to observe that those glasses display a different behavior than glasses displayed in Fig. 1. In all cases, a quick decrease of the oxygen peak intensity is observed up to 10 MGy followed by a flat regime for both silica glasses with 2.26 density and a slight increase for the O-rich silica. In metamict like phases, molecular oxygen has been formed under irradiation by the dimerization of oxygen created during Frenkel process or bond dissociation. The diminution of peak intensity when the sample is placed under the electron beam means that in those samples, molecular oxygen has been permanently released into the voids during the formation of metamict-like phase and secondly destroyed under the electron beam. The inset compares the shape of the emission lines of P5T1000 and non-densified SiO₂ irradiated at 11 GGy at the beginning of the CL measurement and at the end (after 100 MGy). The shape of the four spectra perfectly overlap meaning there is no evolution of the O₂ environment after additional 100 MGy irradiation and that in both 11 GGy irradiated glasses, the molecular oxygen gets a comparable environment.
Figure 3 displays the emission peak corresponding to the $^1\Delta_g \phi^3 \sum_{-g}$ transition of O$_2$ for four densified amorphous silica samples, one pristine silica and neutron irradiated α-quartz (density = 2.65 g/cm$^3$) for comparison. In two samples, O$_2$ emission line is peaking at 1272 nm while a red shift of the peak can be seen for three samples: 1276 nm for P5T350 and 1281 nm for P5T1000 and quartz. It must be underlined that those three samples have the highest density. The shift of the peak position follows the density variation. Compared to silica glass, an asymmetric broadening of the peak is visible for all samples even those with densities of 2.28 and 2.29 but it is worth noticing that it is larger for P5T1000 sample.

Figure 4 shows the EPR spectra of P5T350 glass irradiated at different doses. Examining, the shape of the E’ EPR spectra, we notice that for all densified glasses, it becomes broader from $10^8$ Gy, when increasing dose. Figure 4 illustrates this result for the P5T350 glass. Moreover, we checked that the spectra of E’ centers of all 11 GGy irradiated samples overlap. The broadening of the shape can be mainly due to the dipolar interaction between the paramagnetic centers getting closer when increasing their concentration and/or to the densification of the glass. However, it can be noticed that the density of the densified silica glasses is constant up to $10^9$ Gy and decreases when larger than 2.26 with increasing dose from 1 GGy as reported in [16]. As the broadening is of the same order from $10^8$ Gy, it seems therefore reasonable to attribute it to the dipolar interaction. This result is in agreement with the evolution of the hyperfine splitting of the $^{29}$Si doublet of the E’$^\gamma$ versus dose. For P5T350 sample similarly to other glasses, the hyperfine splitting remains stable in the $10^5$-$10^8$ Gy interval. This means that structural change linked to densification are not responsible for the broadening of the E’ line shape inferring the role of dipolar interaction.

The shape of the E’ EPR line of P5T350_10$^7$ Gy is compared with P5T1000_11 GGy sample (metamict) before and after annealing at 475°C where E’ point defect recovery reaches almost 80% (Fig. 5).

We can observe that before annealing, the broadening of the 11 GGy sample spectrum is higher whereas its density is lower compared to P5T350_10$^7$Gy. After annealing at 475°C, the shape of both samples evolves, the broadening decreases for both glasses and becomes nearly the same. This result suggests that the main origin for the broadening could be the E’ concentration increase and dipolar effect, rather than the densification which remains stable after annealing at 475°C (Raman spectra and densities).

As the shape of the E’ point defect evolves with dose, the double integration of the signal was taken into account to evaluated the E’ concentration (instead of the peak to peak intensity). Figure 6 displays the evolution of the E’ concentration in the 0–11 GGy dose range for SiO$_2$, P4T450, P5T1000 and P5T350 glasses. Silica glass exhibits a different growth curve than densified silica. Densified glasses reach a saturation concentration of E’ centers around 1 GGy whereas for silica this value is around 5 GGy.

**Discussion**
From Fig. 4, it is visible that the formation of E’ center in densified silica is more efficient than in silica in agreement with Devine results [15;17]. He measured a factor 100 in a sample compacted at 5 GPa, 600°C and irradiated at 1 MGy [15] while our data shows a maximum ratio of 40 for the 5GPa, 350°C at the same dose. This result is due to the fact that strained bonds leads to a more efficient creation of E’ point defect by bond cleavage like suggesting by Kajihara et al. [18]. We can estimate from Fig. 4 that the ratio E’conc (densified) vs E’conc (undensified) decreases when dose increases. This may be related, i.e, increasing dose leads to a less dense sample in densified silica samples.

However, we observe that E’ kinetic growth with dose does not seem very sensitive to the densification rate of the samples. It is thus worth noticing that a more strained bond i.e in a denser silica glass with a lower Si-O-Si angle does not imply a higher efficiency to produce E’ (i.e P5T1000 vs P4T450). Moreover, it can be underlined that all silica glasses converge towards the same amount of E’ when they reach the same “metamict” phase at 11 GGy. The growth of point defects in dense silica is fast and reaches a maximum of E’ centers at 6x10^8 Gy whereas in this [0-6x10^8 Gy] dose range, we showed that the density and the glass network of all densified silica glasses remain constant [4]. We remind that from 1 GGy to 11 GGy, the glass network of dense silica evolves towards a less dense glass with a progressive threefold rings amount increase [4;16] while the production of E’ point defect is stable. So it means that there is no direct correlation between the E’ concentration increase and the formation of small membered rings when density is higher than 2.26. This result tends to confirm Devine suggestion in [19] implying that “once the strained bond is cleaved, the network may relax to a new equilibrium which does not necessarily involve recombination of the Si—O—Si linkage that has been opened.” In addition, we measured the Si primary hyperfine structure of E’ center evolution with the irradiation dose for the same 4 samples. For a clearer analysis, we plotted the epsilon parameter equaling (A_{iso}^0-A_{iso}^)/ A_{iso} as a function of the silica density (Fig. 7). The A_{iso}^0 is a reference value of 41.8 mT that was obtained for a silica irradiated at very low dose in [20], confirmed as well by our measurements. We clearly see in Fig. 6, two regimes delimited by the 2.30 value. The first one corresponds to a linear increase of epsilon in agreement with a strong variation of the local order around the E’ center. Concerning the values, it is worth noticing that the extrapolation of the straight line visible in Fig. 5 in [16] gives a 5% of epsilon value for the metamict phase identically to ours. Concerning densities higher than 2.26 g/cm^3, hyperfine constant (A_{iso}^) are reported in only one paper of Devine [21]. The values from this paper and the evolution of hyperfine versus densification rate are similar to ours when rescaled (The reference A_{iso}^ from Devine equals 41 mT instead of 41.8 mT).

It is relevant to mention that a two-step curve as a function of density was already evidenced in [16]. This figure reported in Fig. 7B shows the evolution of the D_2 intensity as a function of the density with 2 regimes, a linear one up to 2.26. The increase of the 3-membered-rings in the 2.20–2.26 region seems to be clearly associated to local rearrangement after Si-O-Si bond breaking reflected by the increase of the Si primary hyperfine parameter of the E’ center.

Analyzing the formation of molecular oxygen, we evidenced by our CL measurement that the amount of produced molecular oxygen in densified silica is much lower than in SiO_2.
Even if the Frenkel process predominates in SiO$_2$, with the larger number of strained bonds in densified silica, the bond dissociation mechanism part increase could explain why the E’ number increases so much whereas the O$_2$ formation decrease.

One way also to explain the low amount of produced O$_2$, particularly in P5T1000 (initial slope is 250 times lower compared to silica) is considering the microstructure limiting the diffusion of oxygen. Devine et al. [15] by analyzing the creation of peroxo-radicals from the recombination of E’ and O$_2$ (after thermal treatment) in HP compacted silica concluded that the diffusion coefficient of O$_2$ in compacted silica is several order of magnitude lower than in pristine silica, between $10^7$ and $10^9$ times smaller at 450°C than in uncompact ed silica. The reduction of the size voids was attested in densified samples by Positron Annihilation Spectroscopy (PAS) [22]. A linear decrease of the void volume with density was evidenced. For a 22% increase of density, it reaches less than 10 Å$^3$ against 65 Å$^3$ for silica. The density of P5T1000 glass is close to quartz 2.61 compared to pristine quartz 2.65.

As a matter of fact, the peak position displayed by a neutron irradiated alpha quartz studied in [23] and measured during the same CL experiment is overlapped with the P5T1000. The only difference concerns the larger broadening of the P5T1000 due to a larger variety of O$_2$ environment compared to quartz (not fully amorphized into metamict phase at $10^{19}$ neutrons/cm$^2$).

All 11 GGy irradiated samples display the same characteristics in terms of E’ center (same line shape and amount, and same hyperfine parameter). It is also important to notice that the F300 suprasil silica and P5T1000 samples both irradiated at 11 GGy show the same O$_2$ curve kinetic and emission shape (Fig. 2). This confirms that the local order is similar in both samples whatever their different initial structure, furthermore than the medium range evidenced by Raman spectroscopy in [3]. The fact that O$_2$ is destroyed like in O-rich silica means that a large amount of O$_2$ was created in the metamict phase inside the voids. This could explain the similitude with the O-rich silica behaviour. A study by PAS [24] described a large open structure seems with an estimated average size of microvoids close to 0.3 nm in silica and metamict phase obtained from quartz amorphization by neutrons. The position and shape of the O$_2$ emission line, overlapping with P4T450 sample displaying a 2.29 density supports this (Fig. 3). Indeed, it means that the environment of O$_2$ (in links with the voids size) is not so different than in silica and in P4T450 silica glass. Further analyses are needed to precise the metamict phase structure, a $^{17}$O and $^{29}$Si NMR ones are undergoing.

**Methods**

Synthetic silica glass samples of Suprasil F300 type (< 1 ppm of OH, 2000 ppm Cl) were studied. Some samples were densified before irradiation by using High Pressure, High Temperature (HP-HT) belt press. The experimental details for the HP-HT samples are reported elsewhere [4]. Pressure of 4 GPa was applied at 450°C and 5 GPa was applied at temperatures 350 and 1000°C. The obtained samples are
labeled as P4T450, P5T350 and P5T1000. O-rich and O-deficient silica samples were also irradiated. The pristine “O-rich” silica contained \( \sim 10^{18} \text{O}_2/\text{cm}^3 \) introduced by synthesis in oxygen plasma.

Density measurements were performed at Institut de Physique du Globe de Paris. Density was measured using the sink-float method based on the Archimedean technique following the law (density \( (T) = 0.8845 - 0.9159 \times 10^{-3} \times T + 0.368.10^{-6} \times T^2, T \) in °C). The samples were weighed in air and immersed in toluene which was the immersion liquid used. The sample characteristics are displayed in Table 1.

Table 1 reports the characteristics of the samples. Initial and final irradiation doses as well as their initial and final density (final meaning the density reached after integrating the dose at the end of the cathodoluminescence experiment).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial dose</th>
<th>final dose</th>
<th>initial density (g/cm(^3))</th>
<th>density after irradiation (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suprasil F300</td>
<td>0</td>
<td>62 MGy</td>
<td>2.2</td>
<td>2.204</td>
</tr>
<tr>
<td>P5T350</td>
<td>0</td>
<td>56 MGy</td>
<td>2.422</td>
<td>2.41</td>
</tr>
<tr>
<td>P4T450</td>
<td>0</td>
<td>100 MGy</td>
<td>2.294</td>
<td>2.344</td>
</tr>
<tr>
<td>P5T1000</td>
<td>0</td>
<td>199 MGy</td>
<td>2.612</td>
<td>2.5817</td>
</tr>
<tr>
<td>O-deficient silica</td>
<td>0</td>
<td>186 MGy</td>
<td>2.217</td>
<td>2.202</td>
</tr>
<tr>
<td>O-rich silica</td>
<td>0</td>
<td>104 MGy</td>
<td>2.214</td>
<td>/</td>
</tr>
<tr>
<td>F300 11 GGy</td>
<td>11 GGy</td>
<td>+ 103 MGy</td>
<td>2.257</td>
<td>2.256</td>
</tr>
<tr>
<td>P5T1000 11 GGy</td>
<td>11 GGy</td>
<td>+ 94 MGy</td>
<td>2.282</td>
<td>2.288</td>
</tr>
</tbody>
</table>

- Data availability statement

The data that support the findings of this study are available from corresponding authors upon request.

Near infrared cathodoluminescence spectra were obtained under a 2.5 MeV electrons excitation provided by SIRIUS accelerator (LSI) with a home-made system [25]. The detection is performed by using an InGaAs ANDOR camera operating between 900 nm and 1.6 \( \mu \)m associated with a spectrometer (grating line 1200t/mm).

The developed Matlab code for extracting the peak intensity of the 1272 nm emission line of \( \text{O}_2 (^1\Delta_g \rightarrow 3\Sigma_g^-) \) consists of correcting, automatically, all the obtained spectra from the artefact of the ANDOR camera. For each spectrum, we perform the correction following two steps. First, we subtract the baseline
of the intensity at the range around 1400 nm, since the optical fiber transmitting the signal is not transparent at this range (due to the O-H absorption). After that, we normalize the spectra to the intensity of emission in the shortwave region (Cherenkov) at around 1160 nm.

EPR measurements were carried out at room temperature with a X-Band JES-X310 JEOL spectrometer working at frequency of 9.2 GHz and with magnetic-field modulation frequency of 100 kHz detecting the E’ signal in unsaturated conditions (1 µW) and in high power second harmonic mode (50 mW) to detect the $^{29}\text{Si}$ hyperfine doublet.

**Declarations**

**Acknowledgments:** I sincerely thank G. Jullian de la Fuente for the help in data analysis during his free time. We are grateful to D. Neuville for his density measurements device. In addition, the Master 2 students I. Brahimi and A. Mouhoub are acknowledged also for their contribution to EPR measurements at high temperature. The authors acknowledge support from the EMIR&A French network (FR CNRS 3618) on the platform SIRIUS.

- **Author contribution statement**
  N.O. wrote the main manuscript text, prepared the figures and performed all experiments assisted by I.R and M.M for some of them. S. Le F. performed the densifications under high pressure. A.A helps in the measurement of hyperfine structure of E’ center (EPR) and O.C assists the authors for electron irradiations. L.S takes part in the relevant scientic discussion, in the analysis of the results and the writing of the paper.

- **Additional Information (including a Competing Interests Statement)**
  The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

- **Data availability statement**
  The data that support the findings of this study are available from corresponding authors upon request.

**References**


**Figures**
Figure 1

Irradiation dose-dependence of $O_2$ cathodoluminescence intensity
Figure 2

Growth kinetic for O\textsubscript{2} as a function of irradiation dose. The inset shows the O\textsubscript{2} emission lines of SiO\textsubscript{2} 11GGy and P5T1000 11GGy and the perfect overlapping before between them and before and after the measurement.
Figure 3

Cathodoluminescence emission spectra of radiolytic O$_2$ in electron-irradiated densified and non-densified silica glasses, and neutron-irradiated α-quartz. The respective densities (g/cm$^3$) are indicated in the legend.
Figure 4

EPR spectra of E' center for P5T350 irradiated at different doses
Figure 5

EPR spectra of E' center for P5T350 $10^7$ Gy and P5T1000 11 GGy before (bottom) and after annealing at 475°C (top).
Figure 6

Concentration of E’ center as a function of integrated dose in GGy
Figure 7

\((A_{\text{iso}} - A_{\text{iso}}^0) / A_{\text{iso}}\) = epsilon (A) and \(D_2\) intensity (B) from [16] as a function of silica glass density