



HAL
open science

Erasure of nanopores in silicate glasses induced by femtosecond laser irradiation in the Type II regime

Maxime Cavillon, Yitao Wang, Bertrand Pommellec, François Brisset,
Matthieu Lancry

► **To cite this version:**

Maxime Cavillon, Yitao Wang, Bertrand Pommellec, François Brisset, Matthieu Lancry. Erasure of nanopores in silicate glasses induced by femtosecond laser irradiation in the Type II regime. Applied physics. A, Materials science & processing, 2020, 126, 10.1007/s00339-020-04062-8 . hal-03093803

HAL Id: hal-03093803

<https://hal.science/hal-03093803>

Submitted on 4 Jan 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 Title: Erasure of nanopores in silicate glasses induced by femtosecond laser irradiation in
2 the Type II regime

3 Authors : Maxime Cavillon ^{†,*}, Yitao Wang [†], Bertrand Poumellec [†], François Brisset [†], and
4 Matthieu Lancry [†]

5 [†] Institut de Chimie Moléculaire et des Matériaux d'Orsay (ICMMO/SP2M/MAP),
6 Université Paris-Saclay, CNRS, 91405 Orsay Cedex, France

7 * corresponding author: maxime.cavillon@universite-paris-saclay.fr

8 **Abstract:** Optical devices fabricated by femtosecond (fs) laser within the Type II regime
9 are of interest for high temperature applications (> 800°C). fs-Type II regime is
10 characterized by the formation of self-organized nanogratings, which are composed of
11 regularly spaced porous nanolayers with nanopores having a typical size of a few tens of
12 nm. In this work, we first investigate the evolution of the nanopores size distribution as a
13 function of fs-laser writing speed and pulse energy, as well as a function of annealing
14 temperature after fs-laser irradiation. Then, the thermal stability of such nanopores is
15 numerically investigated through the use of the Rayleigh-Plesset (R-P) equation, and is
16 compared with experimental data. The R-P equation provides insights into the temperature
17 range at which the nanopores would ultimately collapse, serving as a design tool for future
18 high temperature fs-Type II based devices. The key role of glass viscosity and nanopore
19 size diameter on the overall thermal stability is also discussed.

20 **Keywords:** femtosecond laser; nanogratings; silicate glasses; thermal stability

21

22 1. Introduction

23 Optical devices capable to withstand and operate at high temperatures (> 800°C) for a
24 long period of time (e.g. hundreds of hours) are attractive for many applications, including
25 aircraft engine monitoring, fuel bed combustors, long lifetime optical data storage or fiber
26 lasers[1–3]. Within the tools at one's disposal to fabricate devices in both fiber and bulk
27 glass materials, femtosecond laser-direct writing (FLDW) is particularly interesting.
28 Indeed, FLDW is a versatile technique that enables high peak powers to induce local three-
29 dimensional (3D) modifications inside the glass substrate, due to the nonlinear absorption
30 processes involved during the laser light – matter interaction. One of the unique features of
31 FLDW is the possibility to induce self-organized nanogratings, within the so-called Type II

32 regime [4]. In addition, nanogratings have been reported in a variety of glasses, including
33 silica, germanates, silicates, borosilicates [5, 6].

34 In silica, these nanogratings can survive beyond 1000 °C for several hours [7], and are
35 composed of regularly spaced porous nanolayers (typically few tens of nm thickness, with
36 a period of about 300 nm). The latter are filled with nanopores having their size and number
37 being a function of the laser parameters as well as the glass material [8]. Upon an increase
38 in temperature, Type II regime laser-induced modifications would yield changes in the
39 glass structure (e.g., point defects, stress, specific volume) and in the related physical
40 properties (e.g., refractive index, birefringence, light absorption and scattering). Such
41 modifications will ultimately dictate the response and the lifetime of a fabricated optical
42 device (e.g., a grating used as a sensor [2] or a dot used for 5D optical data storage [3]).

43 Thus, it is critical to understand what are the underlying mechanisms that drive the
44 evolution of these aforementioned modifications at high temperatures. The annealing of fs-
45 laser induced nanogratings yield to some modifications, at different temperature ranges,
46 which have previously been investigated and reported. For instance, the presence of laser
47 induced defects, such as non-bridging oxygen hole centers (NBOHC), fully erased at 600°C
48 within a few minutes [9]. Additionally, in silica the typically large amount of 3- and 4-
49 membered rings, characteristic of densification and the presence of an intense compressive
50 stress induced by Type II laser irradiation, is found to decrease and to anneal away within
51 the 800°C - 900°C temperature range [9, 10]. Moreover, the stress field associated with the
52 formation of nanogratings (see for instance Ref. [11]) is typically relaxed slightly below or
53 at the glass transition temperature ($\approx 1100^\circ\text{C}$ for silica) [10, 12, 13]. Ultimately, the fs-
54 induced modifications correspond to a permanently decomposed glass with nanopores
55 embedded inside it [14, 15]. As a note, the presence of defects in the glass, as discussed
56 above, is partly associated with the dissociation of SiO_2 into $\text{SiO}_{2(1-x)} + x\text{O}_2$ [14]. The
57 Raman peak intensity, centered at 1556 cm^{-1} in Ref. [14], is characteristic of free O_2 inside
58 the glass nanopores [16]. Increasing the temperature in the $300^\circ\text{C} - 600^\circ\text{C}$ range causes
59 bleaching of defects, which would yield a decrease of the O_2 pressure. **The signature of free**
60 **O_2 is detected up to $\approx 600^\circ\text{C}$ using Raman spectroscopy (see Figure 3.14 of Ref. [17]), and**
61 **agrees well with the aforementioned defect bleaching.**

62 In this work, we first investigate the nanopores size distribution, in silica glass, for
63 different writing conditions (speed and pulse energy), as well as the erasure of the
64 nanopores through heat treatments at different temperatures. Variations in the average

65 nanopore size diameter are observed [18]. Following this, the thermal stability of the laser
 66 induced nanopores is investigated using the Rayleigh-Plesset (R-P) equation [19], assuming
 67 the nanopores to have a spherical shape. In practice, the nanopores can take the form of
 68 ellipsoids or more complex shapes [20, 21]. However, this work intends to set the basis for
 69 future work to include these difficulties and therefore only spherical particles is considered.

70 The role played by both the glass material (including silica – *Infrasil and PCVD types*,
 71 Borofloat 33 – $81\%SiO_2-B_2O_3-Na_2O-Al_2O_3$, and ~~Ultra low expansion~~—ULE glass – glass
 72 *Ultra Low Expansion 93%SiO₂-TiO₂*) and the initial nanopore size diameter on the overall
 73 thermal stability of the fs-induced nanogratings are modeled using the R-P equation, and
 74 compared with experimental data. This work is aimed to provide preliminary insights on
 75 the ultimate stability of the nanopores present in the glass. This may be used as a means to
 76 ease the selection of glass material and laser parameters to enhance thermal stability in
 77 future optical designs operating in a high temperature environment.

78 2. Materials and Methods

79 First, the nanopore size distribution within the porous regions is investigated for three
 80 different glass samples (labeled S1, S2 and S3), which are reported in Table 1, along with
 81 the different laser irradiation conditions. In S1 sample the writing speed is varied from 0.01
 82 mm s⁻¹ to 10 mm s⁻¹. In S2, the pulse energy is varied from 0.2 μJ to 1.0 μJ, and in S3 Type
 83 II laser-induced modifications are consecutively annealed for 30 minutes at 1000°C,
 84 1100°C, and 1200°C. In order to investigate the nanopores and their size distribution, each
 85 sample was cleaved perpendicularly to the laser light polarization direction (for instance see
 86 Ref. [1]) and imaged by a scanning electron microscope (FEG-SEM Zeiss Supra 55 VP).

87
 88 **Table 1** Glass samples and laser irradiation conditions investigated for nanopore
 89 size distribution characterization

Materials	Silica SuprasilCG	Silica PCVD	Silica suprasilCG
Parameters Sample Labelling	S1 ¹	S2	S3
Pulse energy (μJ)	2.0	0.2; 0.4; and 1.0	1.0
Writing speed, v (mm s ⁻¹) ²	0.01; 0.1; 1; 10	0.1	0.1
Repetition rate, f (kHz)	100	100	100

Number of pulses per μm	10,000; 1,000; 100; 10	1,000	1,000
Wavelength (nm)	1030	1030	1030
Pulse duration (fs)	250	300	300
Numerical aperture, NA	0.6	0.6	0.6
Focusing depth (μm)	-	± 300	± 300
Configuration ³	-	//	//

90 ¹This sample is the same as in Ref. [8].

91 ²Varying the laser writing speed v with a constant repetition rate f is equivalent to changing
92 the pulse density v/f , or the “number of pulses per μm ” as defined in the table.

93 ³ // or \perp : Laser polarization parallel (//) or perpendicular (\perp) to the writing direction.

94 Following the investigation of the nanopore sizes, a numerical approach, using the
95 Rayleigh-Plesset (R-P) equation, is undertaken to simulate the erasure of the nanopores
96 during the thermal annealing. The R-P equation is derived from the Navier-Stokes equation
97 and physically describes the evolution of a spherical bubble inside an incompressible
98 Newtonian fluid. The R-P equation takes the following form [19, 22, 23]:

$$\frac{\Delta P}{\rho} = R_{pore} \frac{d^2 R_{pore}}{dt^2} + \frac{3}{2} \left(\frac{dR_{pore}}{dt} \right)^2 + \frac{4\eta(T)}{\rho R_{pore}} \frac{dR_{pore}}{dt} + \frac{2S}{\rho R_{pore}}. \quad (1)$$

99 In this equation, ΔP is the pressure difference (in Pa) between the inside of the nanopore
100 (supposed spherical) and far away from it, ρ is the glass density (in kg m^{-3}), R_{pore} the radius
101 (in m) of the spherical nanopore, t the time (in s), $\eta(T)$ the glass viscosity (in Pa.s), and S is
102 the surface energy (around 0.3 J m^{-2} for silica [24]). Both ρ and S are set independent to the
103 temperature for sake of simplicity. The viscosity is extrapolated from glass manufacturer
104 datasheets (Borofloat33, SuprasilCG, Infrasil and PCVD) and from Ref. [8] for ULE glass,
105 using a Vogel-Tammann-Fulcher (VTF) law in the form $\log(\eta)=A+B/(T-T_0)$. Initial
106 conditions are R_{pore} (at $t = 0$) = R_0 and dR_{pore}/dt (at $t = 0$) = 0. The equation is solved
107 numerically using an ordinary differential equation (ODE) built-in solver from Matlab
108 software. This work only intends to provide preliminary understandings on the ultimate
109 stability of nanopores using the R-P equation. Therefore, several assumptions and
110 simplifications are made. First, we set $\Delta P = 0$, as the decrease in O_2 concentration inside the
111 nanopore, due to bleaching of defects as described in the introduction below 600°C . It would
112 result in a rather small O_2 pressure, which will be subsequently neglected throughout the
113 paper. The R-P equation is used to compute the nanopore size evolution for different glasses,

114 including pure silica (PCVD, Infrasil301), Borofloat33 and ULE, which have been reported
 115 in Ref. [8]. In these experiments, the thermal stability of Type II nanostructures is
 116 investigated through step isochronal measurements ($\Delta t = 30$ minutes, ΔT typ. 25°C or 50°C)
 117 and by monitoring the retardance induced by the birefringent nanogratings. The Retardance
 118 (R) is defined as the product of the Birefringence (B) with the length (L) of the birefringent
 119 object ($R = B \times L$). In Ref. [8], the aforementioned $R(\Delta t, T)$ values measured at room
 120 temperature after each annealing step are normalized relative to the initial (not annealed) $R(t$
 121 $= 0, 20^\circ\text{C})$ value. In this work, the experimental data are normalized with respect to the R
 122 value at the temperature above which the retardance experiences a steep decay rate (e.g., $T =$
 123 1225°C for Infrasil301 in figure 5a in Ref. [8]). The latter normalization enables to
 124 investigate only the last step of nanograting erasure.

125 In order to compare the computed results from the R-P equation with the experimental
 126 normalized R values, the nanopore **size** diameter (from R-P equation) is converted to a
 127 normalized retardance value following the procedure described below. First, we calculate the
 128 average refractive index of the porous nanolayer (n_{pl}) using the Maxwell-Garnet equation
 129 [25]:

$$n_{pl} = \sqrt{n_G^2 \frac{n_G^2 + \frac{(1 + 2FF)}{3}(n_{pore}^2 - n_G^2)}{n_G^2 + \frac{(1 - FF)}{3}(n_{pore}^2 - n_G^2)}}. \quad (2)$$

130 In the above equation, n_G is the glass refractive index (taken as 1.4599, i.e., index of silica at
 131 551 nm), which is assumed independent of temperature (small dn/dT of $\approx 10 \times 10^{-6} \text{ K}^{-1}$ [26]).
 132 This value is taken equal both inside the porous nanoplanes (i.e., around the **nanopores**) and
 133 between the porous nanoplanes. **This simplification is acceptable in the conditions of this**
 134 **work, as we principally focus on the erasure of the nanopores for temperatures at, or above,**
 135 **the glass transition temperatures of the glass materials investigated. Therefore, the**
 136 **contributions to the refractive index due for instance by the presence of a stress field or a**
 137 **permanent densification of the glass are annealed away.**

138 FF is the filling factor, defined here as the relative volume taken by the **nanopores** per unit
 139 volume of porous nanolayer (labeled V), and n_{pore} is the **nanopore** refractive index, taken
 140 equal to 1. The filling factor is related to the averaged nanopore radius (R_{pore}) through the
 141 following equation:

$$FF = N \frac{4\pi R_{pore}^3}{3V}. \quad (3)$$

Here N is the number of nanopores (with an averaged nanopore radius R_{pore}) per unit volume V of porous nanolayer. A 2D filling factor (i.e., taking the area taken by the nanopores per unit surface of porous nanolayer) can be determined from SEM micrographs and is usually in the order of 20% - 40% [18]. The latter (labeled FF_{2D}) will be used in section 3.1. When discussing the normalized retardance in section 3.23, the FF defined in Equation 3 is computed. Additionally, in this work, the refractive index of the glass in between the porous nanolayers is set equal to n_G as in Ref. [18]. Hence, the birefringence $B = n_o - n_e$, where n_o and n_e are the refractive indices of the ordinary and extraordinary axes, respectively, is calculated from [7, 18]:

$$B = n_o - n_e = \sqrt{\left[1 - \frac{\delta}{\Lambda}\right] n_G^2 + \frac{\delta}{\Lambda} n_{pl}^2} - \left[\sqrt{\frac{\left[1 - \frac{\delta}{\Lambda}\right]}{n_G^2} + \frac{\frac{\delta}{\Lambda}}{n_{pl}^2}} \right]^{-1}. \quad (4)$$

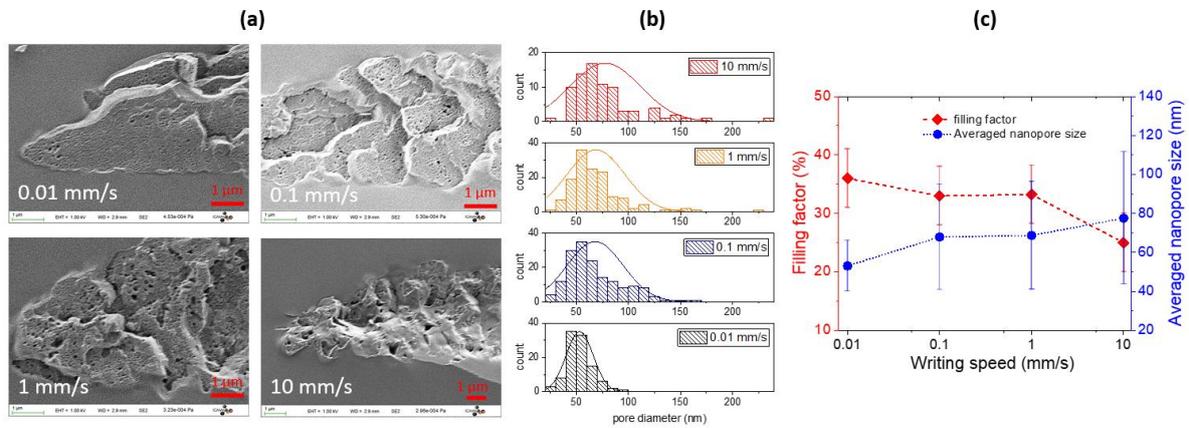
142 Λ is the average spacing between nanolayers, δ is the porous nanolayer thickness, and $(\Lambda - \delta)$
 143 is the interlayer thickness. Finally, the linear retardance can be calculated using the
 144 expression $R = B \times L$ as defined above.

145 3. Results

146 3.1. *Experimental observation of the evolution of the nanopore size in nanogratings-Impact* 147 *of laser writing conditions on the evolution of nanopores size*

148 The impact of the writing speed in the nanopore distribution is depicted in Fig. 1,
 149 where SEM micrographs, nanopore size distribution, 2D filling factor and averaged
 150 nanopore size-diameter as a function of writing speed, are displayed (using Sample S1). We
 151 observed that the average nanopore diameter increases when writing speed increases (from
 152 53 nm to 77 nm from 0.01 mm s^{-1} to 10 mm s^{-1} , respectively, corresponding to a \square 45%
 153 increase). As the writing speed increases, the spread of the nanopore diameter distribution
 154 also becomes larger (e.g. standard deviation is increased from 13 nm to 34 nm between
 155 0.01 mm s^{-1} and 10 mm s^{-1}). While the average nanopore size is increased when speed is
 156 increased, the 2D filling factor comparatively decreases. The evolution of FF_{2D} observed in

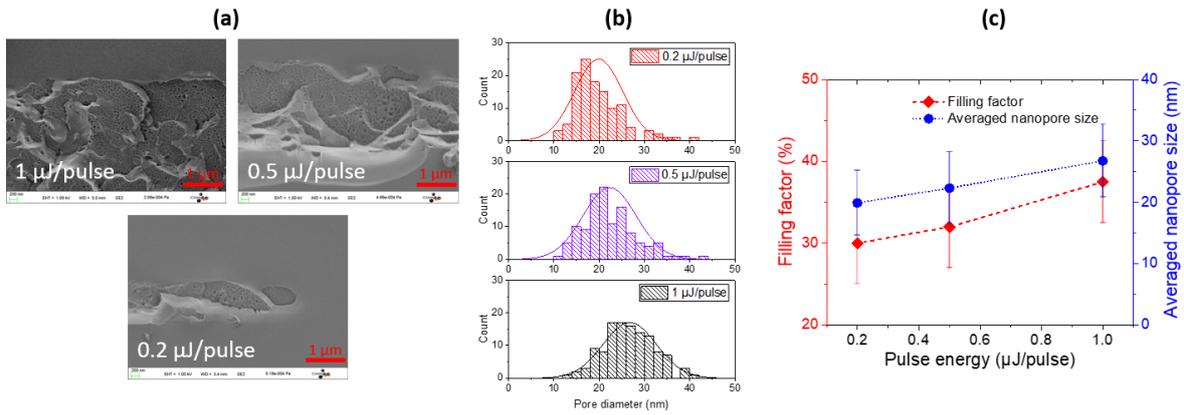
157 Fig. 1 is qualitatively in agreement with retardance values reported in Ref. [8]. However, it
 158 is worth pointing out that other contributions factor into the measured retardance value,
 159 such as laser track length, porous nanolayer thickness or periodicity.



160

161 **Fig. 1** Effect of the writing speed on nanopore size, distribution and filling factor,
 162 using Sample S1. (a) Scanning electron micrographs of the porous regions for
 163 different writing speeds; (b) Nanopore size diameter distributions with respect to
 164 the writing speed; (c) Evolution of the 2D porosity filling factor and the average
 165 nanopore size diameter as a function of writing speed. The lines are here only as
 166 guide-to-the-eye

167 The evolution of the nanopore size and distribution, as presented in Fig. 1 with respect
 168 to varying writing speed conditions, is now investigated through the variation of the laser
 169 pulse energy, everything else being set constant (from Sample S2). The results are reported
 170 in Fig. 2. An increase of the pulse energy is associated with an increase in the nanopore size
 171 diameter, which exhibits an almost linear rate within the investigated interval (□8.6 nm
 172 diameter increase per μJ). There is almost no evolution of the standard deviation (5.3 nm
 173 and 5.9 nm for 0.2 μJ and 1.0 μJ, respectively). However, as opposed to the results from
 174 Fig. 1a, the increase in energy is associated with an increase of the filling factor, and is in
 175 agreement with a higher retardance value (for instance in Ref. [27]).



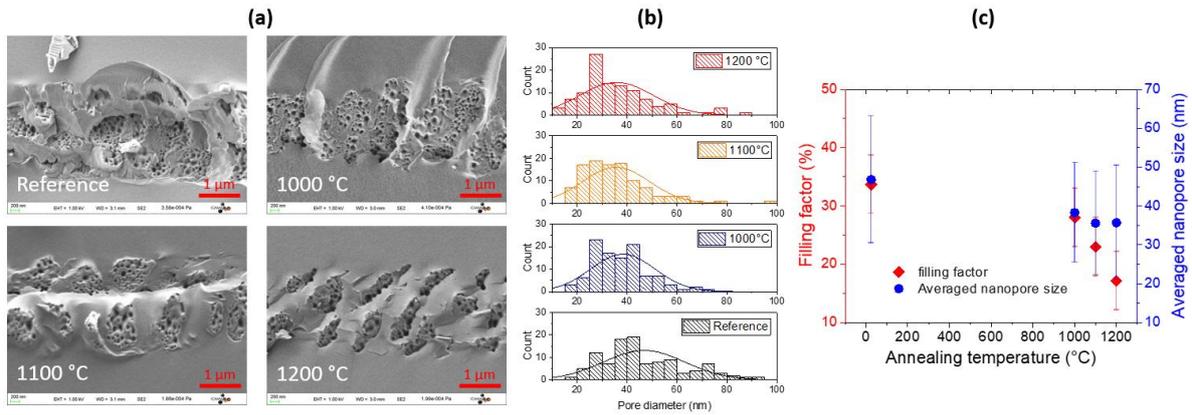
176

177 **Fig. 2** Effect of the laser pulse energy on nanopore size, distribution and filling
 178 factor, using Sample S2. (a) Scanning electron micrographs of the porous regions
 179 for different pulse energies; (b) Nanopore size diameter distributions with respect
 180 to pulse energy; (c) Evolution of the 2D porosity filling factor and the average
 181 nanopore size diameter as a function of pulse energy. The lines are here only as
 182 guide-to-the-eye

183 3.2. *Experimental observation of the evolution of the nanopore size in nanogratings*

184 *Experimental observation of the decrease in nanopores size in annealing process*

185 ~~Finally, the~~ The evolution of the nanopores' morphology and size distribution as a
 186 function of annealing temperature (for isochronal time steps Δt of 30 minutes, and using
 187 sample S3) is reported in Fig. 3. In this experiment, we observe that the nanopore size
 188 diameter decreases first as the temperature increases, but appears to plateau at the highest
 189 temperature. This effect can be interpreted from the results given by the R-P equation, and
 190 is discussed in the following section. On the other hand, we observe a diminution of FF_{2D}
 191 that is characteristic of a decrease in the birefringence response (hence the measured
 192 retardance). Other SEM micrograph analysis, not presented here, also showed that both
 193 planes' thickness and spacing between planes were independent of temperature.



195

196

197

198

199

200

201

Fig. 3 Effect of thermal annealing on nanopore size, distribution and filling factor, using Sample S3. (a) Scanning electron micrographs of the porous regions for different annealing temperatures ($\Delta t = 30$ minutes); (b) nanopore size diameter distributions with respect to annealing temperature; (c) Evolution of the 2D porosity filling factor and the average nanopore size diameter as a function of annealing temperature

202

3.3. ~~Understanding thermal stability of nanopores using the Rayleigh-Plesset equation~~

203

~~Simulation study of the decrease in nanopores size in annealing process by the Rayleigh-~~

204

~~Plesset equation~~

205

206

207

208

209

210

211

212

213

214

215

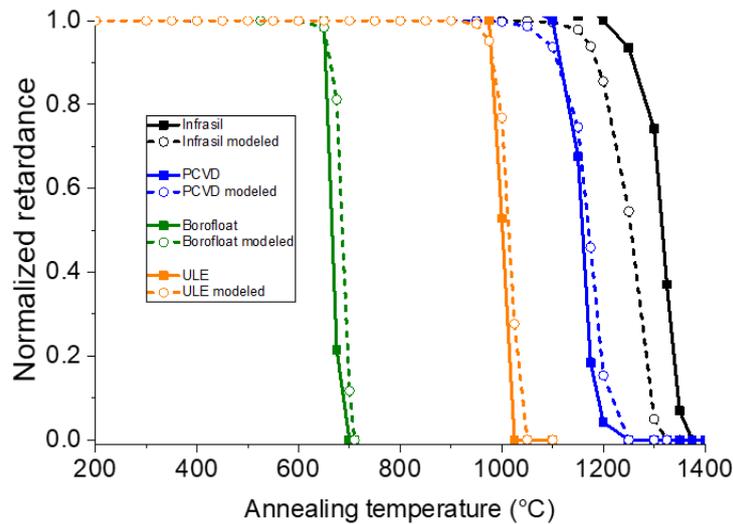
216

217

218

Thermal stability of Type II nanogratings inscribed in various glasses (silica and silicate glasses) were investigated and reported in Ref. [8], using step isochronal annealing experiments ($\Delta t = 30$ minutes, $\Delta T = 25^\circ\text{C}$). These data are displayed in Fig. 4, but renormalized relative to the sharp retardance decrease at the highest annealing temperature values that we hypothesized here to be characteristic of the nanopore erasure. It is worth pointing out that in order for each data point to be independent to the other, the criterion $(\Delta t \times k_0)^{-(\Delta T/T_{max})} \ll 1$ must be fulfilled [28] (with k_0 estimated to be around 5×10^5 to 5×10^7 s^{-1} for nanogratings erasure in silica [29]). In this work, this criterion is not satisfied and therefore the thermal stability in this condition is expected to be slightly underestimated with respect to a stability curve having independent data points. In this paper only the final erasure step of the measured retardance $R(\Delta t, T)$ is investigated. Following the same experimental conditions as in the experiment, the Rayleigh-Plesset (R-P) equation was used to simulate the nanopore erasure, and the evolution of the retardance was calculated based the nanopore size diameter, the filling factor FF and using the form birefringence equations

219 (Equations 2, 3, and 4) shown above. Here we assume that the nanolayers thickness (δ), the
 220 average spacing (A), and the interlayer thickness ($A-\delta$), and the laser track length (L) did not
 221 change with the annealing steps ~~in agreement with our SEM observations~~. The comparison
 222 between experimental data and the simulated data (using R-P equation) are reported in Fig.
 223 4. It is worth pointing out that the R-P equation computed here is for a single initial
 224 ~~nanopore size~~ diameter. However, as was previously discussed, the ~~nanopore size~~ diameter
 225 is distributed in a fairly wide interval, depending on the laser writing conditions but also
 226 with the chemical composition [6, 30]. However, as a first approximation, one can note that
 227 evolution of the simulated retardance, related to the erasure of the nanopores using the R-P
 228 equation, agrees rather well with the experimental data. This is indicative that viscosity is a
 229 first order property in the erasure mechanism of nanogratings and their associated
 230 birefringence in a high temperature regime.

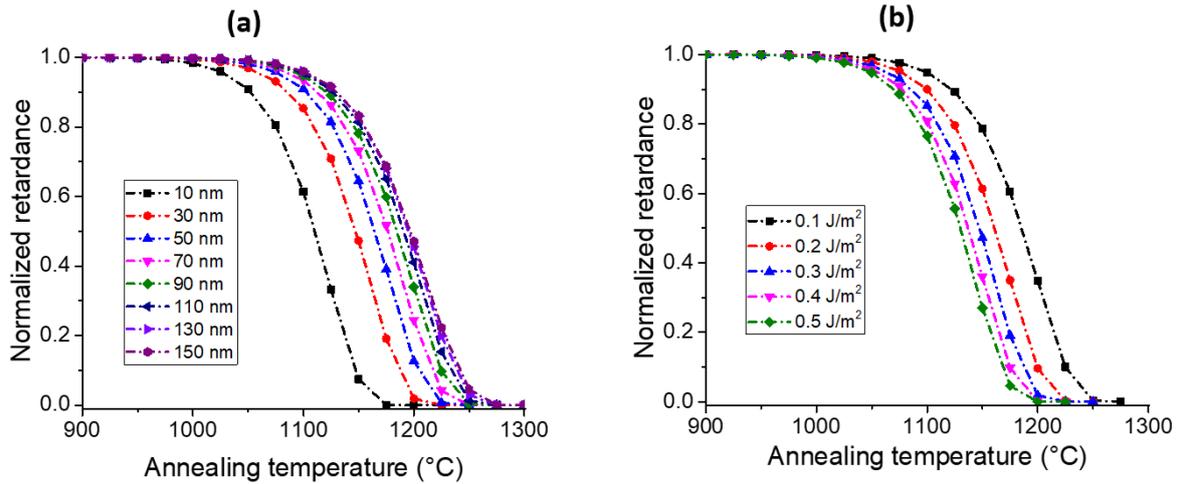


231

232 **Fig. 4** Evolution of the normalized retardance during step isochronal annealing
 233 experiments for various glasses (taken and re-normalized from Ref. [8]) compared
 234 with the Rayleigh-Plesset (R-P) equation used to simulate the nanopores' erasure.
 235 Conditions used in the simulation: $\Delta P = 0$ Pa; $S = 0.3$ J m⁻²; $\rho = 2200$ kg m⁻³;
 236 ~~Initial nanopore radius used during calculation: $R(t = 0) = 25$ nm~~; $\eta(T)$ fitted using
 237 a VTF law for each glass (Infrasil, PCVD, Borofloat33, and ULE)

238 The effects of both ~~nanopore size~~ diameter and surface energy S (from R-P equation)
 239 are investigated and reported in Fig. 5 (a and b). As the initial ~~nanopore size~~ diameter is
 240 increased or the glass surface energy is decreased, the annealing curves shift to higher
 241 temperatures. With a 100 nm ~~nanopore diameter~~ change, thermal stability curve is expected

242 to shift by $\approx 100^\circ\text{C}$ (for a value of $R = 0.5$). In contrast, the surface energy plays a less
 243 significant role in the process since a large change of surface energy ($\Delta S = 0.4 \text{ J m}^{-2}$) shifts
 244 only by $\approx 50^\circ\text{C}$ the annealing curves. The discrepancy between the experimental data and
 245 the model observed in Fig. 4 for the Infrasil301 could potentially be attributed to a variation
 246 of surface energy, although further investigations would be necessary to verify this
 247 hypothesis.
 248



249
 250 **Fig. 5** Evolution of the Retardance (only taking into account the evolution of the
 251 nanopores) for step isochronal annealing experiments ($\Delta t = 30$ minutes, $\Delta T = 25$
 252 $^\circ\text{C}$) for SuprasilCG glass simulated by Rayleigh-Plesset (R-P) equations. (a) Effect
 253 of initial nanopore size diameter (from 10 nm to 150 nm), with a constant value of
 254 $S = 0.3 \text{ J m}^{-2}$. (b) Effect of surface energy S (from 0.1 J m^{-2} to 0.5 J m^{-2}), with a
 255 constant value of $R(t = 0) = 15 \text{ nm}$

256 4. Discussion

257 In the previous section we have shown that the thermal stability of nanogratings
 258 (evaluated through optical retardance measurements) induced by IR fs-laser (so called Type
 259 II regime) is not only a function of the silicate glass chemical composition but also of the
 260 nanogratings morphology. The use of various laser-writing parameters, including writing
 261 speed (hence linear pulse density) and pulse energy, directly influence the distribution and
 262 the size of the nanopores within the porous nanolayers. A direct consequence of this is the
 263 change in the thermal stability of optical devices fabricated by Type II fs-laser writing. As
 264 an example, the average refractive index changes along the “fringes” of a Type II fiber

265 Bragg grating (such as the ones in Ref.[2]) would be equal to $(n_e + n_o) / 2$. In contrast
266 polarizing based devices like radial-azimuthal polarization converter [31], achromatic
267 polarization rotator [32], fs-laser induced waveplates [13, 33] or 5D “eternal” optical
268 memories [3] are based on the optical retardance amplitude and thus proportional to $(n_e -$
269 $n_o)$. Hence, the optical response of these devices at high temperatures would be related to
270 the magnitude of birefringence induced by the overall porous structure, and among which
271 the nanopore size plays an important role.

272 Additionally, the chemical composition of the glass material has a critical role in the
273 erasure of the nanopores, as its viscosity behavior is found to mostly dictate the overall
274 nanopores’ erasure, as shown from the results using R-P equation. For instance, low OH
275 and Cl impurity-containing materials, such as Infrasil301 silica, present high viscosity at
276 high temperatures, which is expected to promote thermal stability of the nanopores. The
277 differences observed in optical properties, here in term of linear birefringence, are in fairly
278 good agreement between experimental and simulated data using the R-P equation as shown
279 in Fig. 4.

280 From Fig. 1, the average nanopore diameter increases from 53 nm to 77 nm between
281 low and high writing speeds (0.01 mm s^{-1} to 10 mm s^{-1}), and the steep decay of the
282 associated isochronal annealing curves is shifted by $\square 15^\circ\text{C}$ to higher temperatures (Ref.
283 [8]). By using the R-P equation with the experimental conditions described in the same
284 reference, a shift of $\square 15^\circ\text{C}$ is also predicted.

285 In Fig. 3c, we observe that, as the irradiated glass is progressively annealed, the
286 nanogratings filling factor FF decreases while the averaged nanopore size remains nearly
287 constant. This can be explained on the basis of the R-P equation, where we observe that
288 small nanopores being erased more quickly than the larger ones (see Fig. 5a). As a result,
289 the fully erased small nanopores are not included in the counting to determine the average
290 nanopore size-diameter. This has an effect of shifting up the average nanopore size diameter
291 to larger values. However, the filling factor still decreases as nanopores are progressively
292 erased, which are in agreement with the observation of a decrease in retardance. One a
293 more speculative note and based on results from Fig. 5b, a possible way to further promote
294 thermal stability could be by minimizing the glass surface energy.

295 As was mentioned in the introduction, it is worth pointing out that the shape of the
296 nanopore is rather ellipsoidal than spherical, as was brought to evidence in Ref. [20] using
297 small angle X-ray scattering (SAXS) measurements. In our conditions and to reveal the

298 porosity of the nanopore layers, the sample are cleaved along the short axis direction and
299 placed under an SEM for observation. It is this axis that will determine the kinetics of
300 erasure of the nanopores (based on R-P equation) as the long axis of the nanopores will take
301 a longer time to erase. Although the shape of the annealing curve is expected to be slightly
302 modified, using an ellipsoidal geometry to model the dynamics of the nanopore erasure
303 should not be drastically different with respect to a spherical geometry.

304 Type III regime, associated with the formation of nanovoids (typically in the 100s nm
305 to 1 μm diameter range [34–36]), is known to be slightly more stable than type II
306 nanogratings, provided that associated stress and densified shell surrounding the nanovoids
307 can be stabilized. From this work, the larger size of the nanopores is expected to be a
308 principal contributor to this higher thermal stability. Hence, in the realm of high thermal
309 stability devices, one would want to maximize the nanopore size diameter. Additionally, a
310 single void structural modification induced by femtosecond laser may be advantageous
311 over nanopores as one would not have to take into account a nanopore size distribution,
312 which may ease thermal stability predictions. Finally, the viscous behavior of the glass
313 material will ultimately set the upper limit of the thermal stability of the device. Hence the
314 current interest is to develop high viscosity glasses and optical fibers [1, 37].

315 **5. Conclusions**

316 In this work, the effect of glass composition and laser parameters upon fs-laser
317 direct writing in the Type II regime (formation of nanogratings), are reported in silica and
318 silicate glasses. The evolution of nanopores diameter as a function of laser writing speed,
319 pulse energy, and temperature (through step isochronal annealing) is investigated and
320 discussed. The Rayleigh-Plesset (R-P) equation is then used to compute the collapse of
321 such nanopores as a function of glass chemical composition and with varying initial
322 nanopore size diameters or surface energy values. The R-P equation shed light on the major
323 role played by the temperature dependence of the glass viscosity on the thermal stability of
324 fs-induced Type II modifications. The viscous behavior of the glass, at high temperature, is
325 the major parameter that drives the nanogratings erasure and related form birefringence.
326 The initial nanopore size diameter is also found to play a significant role in the overall
327 thermal stability of the fs-laser induced modified region. On a final note, this work aims to
328 serve as a roadmap for the development of components stable at high temperatures, by

329 mean of both glass property tailoring (e.g., viscosity, surface energy) and the mastering of
330 laser-induced structural modifications (such as the formation of large nanopores or voids).

331 **Funding**

332 The authors would like to acknowledge the following institutions for funding their research:
333 Agence Nationale pour la Recherche, FLAG/IR project, grant number ANR-18-CE08-
334 0004-01 and CNRS Défi Instrumentation aux Limites, Ultrabragg project.

335 **Conflicts of Interest**

336 The authors declare no conflict of interest.

337 **Availability of data and material** (Not applicable)

338 **Code availability** (Not applicable)

339 **References**

- 340 1. Cavillon M, Lancry M, Poumellec B, et al (2019) Overview of high temperature
341 fibre Bragg gratings and potential improvement using highly doped aluminosilicate
342 glass optical fibres. *J Phys Photonics* 1:042001(1)-042001(12).
343 <https://doi.org/10.1088/2515-7647/ab382f>
- 344 2. Mihailov SJ, Grobncic D, Hnatovsky C, et al (2017) Extreme Environment Sensing
345 Using Femtosecond Laser-Inscribed Fiber Bragg Gratings. *Sensors* 17:.
346 <https://doi.org/10.3390/s17122909>
- 347 3. Zhang J, Gecevičius M, Beresna M, Kazansky PG (2014) Seemingly unlimited
348 lifetime data storage in nanostructured glass. *Phys Rev Lett* 112:1–5.
349 <https://doi.org/10.1103/PhysRevLett.112.033901>
- 350 4. Shimotsuma Y, Kazansky PG, Qiu J, Hirao K (2003) Self-organized nanogratings in
351 glass irradiated by ultrashort light pulses. *Phys Rev Lett* 91:247405(1)-247405(4).
352 <https://doi.org/10.1103/PhysRevLett.91.247405>
- 353 5. Richter S, Miese C, Döring S, et al (2013) Laser induced nanogratings beyond fused
354 silica - periodic nanostructures in borosilicate glasses and ULETM. *Opt Mater*
355 *Express* 3:1161–1166. <https://doi.org/10.1364/OME.3.001161>

- 356 6. Lancry M, Zimmerman F, Desmarchelier R, et al (2016) Nanogratings formation in
357 multicomponent silicate glasses. *Appl Phys B Lasers Opt* 122:1–8.
358 <https://doi.org/10.1007/s00340-016-6337-8>
- 359 7. Bricchi E, Kazansky PG (2006) Extraordinary stability of anisotropic femtosecond
360 direct-written structures embedded in silica glass. *Appl Phys Lett* 88:2–4.
361 <https://doi.org/10.1063/1.2185587>
- 362 8. Wei S-E, Wang Y, Yao H, et al (2020) Thermal stability of type II modifications by
363 IR femtosecond laser in silica-based glasses. *Sensors* 20:1–14.
364 <https://doi.org/10.3390/s20030762>
- 365 9. Witcher JJ, Reichman WJ, Fletcher LB, et al (2013) Thermal annealing of
366 femtosecond laser written structures in silica glass. *Opt Mater Express* 3:502–510.
367 <https://doi.org/10.1364/OME.3.000502>
- 368 10. Lu J, Yang M, Wang DN, et al (2009) Fiber Bragg gratings with enhanced thermal
369 stability by residual stress relaxation. *Opt Express* 17:19785–19790.
370 <https://doi.org/10.1364/oe.17.019785>
- 371 11. Thomson RR, Gillet P, Mukherjee S, et al (2016) Stress-state manipulation in fused
372 silica via femtosecond laser irradiation. *Optica* 3:1285.
373 <https://doi.org/10.1364/optica.3.001285>
- 374 12. Bhardwaj VR, Corkum PB, Rayner DM, et al (2004) Stress in femtosecond-laser-
375 written waveguides in fused silica. *Opt Lett* 29:1312–1314.
376 <https://doi.org/10.1364/OL.29.001312>
- 377 13. Tian J, Yao H, Cavillon M, et al (2020) A comparison between nanogratings-based
378 and stress-engineered waveplates written by femtosecond laser in silica.
379 *Micromachines* 11:1–11. <https://doi.org/10.3390/mi11020131>
- 380 14. Lancry M, Poumellec B, Canning J, et al (2013) Ultrafast nanoporous silica
381 formation driven by femtosecond laser irradiation. *Laser Photonics Rev* 7:953–962.
382 <https://doi.org/10.1002/lpor.201300043>
- 383 15. Canning J, Lancry M, Cook K, et al (2011) Anatomy of a femtosecond laser

- 384 processed silica waveguide. *Opt Mater Express* 1:998–1008.
385 <https://doi.org/10.1364/ome.1.000998>
- 386 16. Berger AJ, Wang Y, Sammeth DM, et al (1995) Aqueous Dissolved Gas
387 Measurements Using Near-Infrared Raman Spectroscopy. *Appl Spectrosc* 49:1164–
388 1169. <https://doi.org/10.1366/0003702953965047>
- 389 17. Zimmermann F (2017) Ultrashort pulse induced nanostructures in transparent
390 materials. Friedrich-Schiller-Universität Jena
- 391 18. Desmarchelier R, Poumellec B, Brisset F, et al (2015) In the Heart of Femtosecond
392 Laser Induced Nanogratings : From Porous Nanoplanes to Form Birefringence.
393 *World J Nano Sci Eng* 5:115–125. <https://doi.org/10.4236/wjnse.2015.54014>
- 394 19. Rudenko A, Colombier JP, Itina TE (2018) Nanopore-mediated ultrashort laser-
395 induced formation and erasure of volume nanogratings in glass. *Phys Chem Chem*
396 *Phys* 20:5887–5899. <https://doi.org/10.1039/c7cp07603g>
- 397 20. Richter S, Plech A, Steinert M, et al (2012) On the fundamental structure of
398 femtosecond laser-induced nanogratings. *Laser Photonics Rev* 6:787–792.
399 <https://doi.org/10.1002/lpor.201200048>
- 400 21. Sakakura M, Lei Y, Wang L, et al (2020) Ultralow-loss geometric phase and
401 polarization shaping by ultrafast laser writing in silica glass. *Light Sci Appl* 9:1–10.
402 <https://doi.org/10.1038/s41377-020-0250-y>
- 403 22. Plesset MS (1949) The Dynamics of Cavitation Bubbles. *J Appl Mech* 16:277–282.
404 <https://doi.org/10.1080/15435075.2018.1431546>
- 405 23. Brennen CE (1995) Cavitation and bubble dynamics. Oxford University Press
- 406 24. Boyd K, Ebendorff-Heidepriem H, Monro TM, Munch J (2012) Surface tension and
407 viscosity measurement of optical glasses using a scanning CO2 laser. *Opt Mater*
408 *Express* 2:1101–1110. <https://doi.org/10.1364/ome.2.001101>
- 409 25. Markel VA (2016) Introduction to the Maxwell Garnett approximation: tutorial. *J*
410 *Opt Soc Am A* 33:1244–1256. <https://doi.org/10.1364/JOSAA.33.001244>
- 411 26. Weber MJ (2003) Handbook of Optical Materials. CRC Press

- 412 27. Lancry M, Canning J, Cook K, et al (2016) Nanoscale femtosecond laser milling and
413 control of nanoporosity in the normal and anomalous regimes of GeO₂-SiO₂ glasses.
414 Opt Mater Express 6:321. <https://doi.org/10.1364/OME.6.000321>
- 415 28. Poumellec B, Lancry M (2015) Kinetics of Thermally Activated Physical Processes
416 in Disordered Media. Fibers 3:206–252. <https://doi.org/10.3390/fib3030206>
- 417 29. Gecevičius M (2015) Polarization Sensitive Optical Elements By Ultrafast Laser
418 Nanostructuring of Glass. University of Southampton
- 419 30. Zimmermann F, Lancry M, Plech A, et al (2016) Femtosecond laser written
420 nanostructures in Ge-doped glasses. Opt Lett 41:1161–1164.
421 <https://doi.org/10.1364/ol.41.001161>
- 422 31. Beresna M, Gecevičius M, Kazansky PG, Gertus T (2011) Radially polarized optical
423 vortex converter created by femtosecond laser nanostructuring of glass. Appl Phys
424 Lett 98:1–4. <https://doi.org/10.1063/1.3590716>
- 425 32. Desmarchelier R, Lancry M, Gecevicius M, et al (2015) Achromatic polarization
426 rotator imprinted by ultrafast laser nanostructuring in glass. Appl Phys Lett
427 107:181111(1)–181111(4). <https://doi.org/10.1063/1.4934866>
- 428 33. Gecevičius M, Beresna M, Kazansky PG (2013) Polarization sensitive camera by
429 femtosecond laser nanostructuring. Opt Lett 38:4096–4099.
430 <https://doi.org/10.1364/ol.38.004096>
- 431 34. Williams RJ, Krämer RG, Nolte S, et al (2013) Detuning in apodized point-by-point
432 fiber Bragg gratings: insights into the grating morphology. Opt Express 21:26854–
433 26867. <https://doi.org/10.1364/oe.21.026854>
- 434 35. Glezer EN, Milosavljevic M, Huang L, et al (1996) 3-D Optical Storage Inside
435 Transparent Materials. Opt Lett 21:2023–2026
- 436 36. Gamaly EG, Juodkasis S, Nishimura K, et al (2006) Laser-matter interaction in the
437 bulk of a transparent solid: Confined microexplosion and void formation. Phys Rev
438 B - Condens Matter Mater Phys 73:1–15.
439 <https://doi.org/10.1103/PhysRevB.73.214101>

440 37. Wang Y, Wei S, Yuta RC, et al (2020) Femtosecond laser direct writing in SiO₂ -
441 Al₂O₃ binary glasses and thermal stability of Type II permanent modifications. J
442 Am Ceram Soc 1–9. <https://doi.org/10.1111/jace.17164>
443