Cooling rate calibration and mapping of ultra-short pulsed laser modifications in fused silica by Raman and Brillouin spectroscopy

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Abstract

This paper focuses on the preparation of a new extended set of calibrations of cooling rate (fictive temperature) in fused silica determined by inelastic light scattering and its subsequent use to characterize the local cooling rate distribution in ultra-short pulsed (USP) laser modification. In order to determine the thermal history (e.g. cooling rate and fictive temperature) of fused silica, high-resolution inelastic light-scattering experiments (Raman and Brillouin spectroscopy) were investigated. Calibrations were performed and compared to the existing literature to quantify structural changes due to a change of fictive temperature. Compared to existing calibrations, this paper provides an extension to lower and higher cooling rates. Using this new set of calibrations, we characterized a USP laser modification in fused silica and calculated the local fictive temperature distribution. An equation relating the fictive temperature ($T_f$) to cooling rates is given. A maximum cooling rate of 3000 K min$^{-1}$ in the glass transition region around 1200 $^\circ$C was deduced from the Raman analysis. The Brillouin observations are sensitive to both the thermal history and the residual stress. By comparing the Raman and Brillouin observations, we extracted the local residual stress distribution with high spatial resolution. For the first time, combined Raman and Brillouin inelastic light scattering experiments show the local distribution of cooling rates and residual stresses (detailed behavior of the glass structure) in the interior and the surrounding of an USP laser modified zone.

Keywords: glass structure, ultra-short pulsed laser, fused silica, cooling rate, fictive temperature, Raman spectroscopy, Brillouin spectroscopy

Some figures may appear in colour only in the online journal
1. Introduction

The processing of glass with ultra-short pulsed (USP) lasers for cutting [1], ablating, welding [2] or modifying, on the surface as well as inside the volume [3], is a well-researched topic with the potential for novel applications [4]. The localized modification in the physical and chemical properties of transparent media allows various applications, such as photonic, microfluidic and micro mechanical devices. A better understanding of photonic applications, like direct waveguide writing in transparent media, presents the possibility for improvements in the communication sector [5]. Industrial processes use USP laser for surface polishing or ‘finishing’ to achieve specific roughness requirements [6]. In the medical sector, the internal modification and subsequent selective etching of the laser-modified zone generates specific geometries of microfluidic devices used in merging lab-on-a-chip devices [7]. The final properties of the laser-modified zones depend on the pulse duration, average power, pulse repetition rate and feeding speed which affect the physical conditions present during the laser-glass interaction such as temperature and pressure in glass media [8]. As a result, the irradiation conditions used during the modification process ultimately determine the network structure.

The localized change of properties, (i.e. density and refractive index) is based on rearrangements of the glass network which is influenced by the cooling rate and residual stress within the medium [9]. Cooling rate and residual stress affect the atomic structure of glass. To understand how either cooling rate or residual stress effect the behavior of the glass network, it is necessary to analyze both effects separately [10]. This has been done for residual stress with isostatic or uniaxial compression and monitoring the response of the glass network in-situ or after treatment at a certain pressure (often in the range of several gigapascal) [11–13]. In order to assess the effects of different cooling rates, glass is heated well above the glass transition temperature ($T_g$) and cooled at a set cooling rate using a differential scanning calorimeter (DSC) or a conventional annealing process [14, 15].

Since it is not always possible to monitor or determine the cooling rate of a glass, the fictive temperature ($T_f$) is used to describe the thermal history of a glass. During the cooling process, the viscosity of a glass-forming material increases as the temperature decreases until the glass-forming material can no longer adjust to the low temperature state. At this point, the material transitions from its liquid state and into a frozen, non-equilibrium (glassy) state [16]. In the glass transition range, the $T_f$ is thermodynamically defined as the point at which the enthalpies of the solid (glassy) and the liquid states intersect. Since this is a time-dependent process, $T_f$ depends on the cooling rate. A fast cooling rate leads to a high $T_f$, and conversely, a slow cooling rate to a low $T_f$. This fact is used in conventional annealing processes where glass is heated at certain temperatures in the glass transition range, relaxed and subsequently quenched in water. The relaxation time of the glass structure (i.e. the time required to reach an equilibrium state in the network) depends on the viscosity of the glass at a specific temperature [17]. This results in shorter relaxation times for materials with lower viscosity and longer relaxation times for highly viscous materials. If the glass is fully relaxed at a certain temperature and then quenched significantly faster than the relaxation time, the $T_f$ of that glass is its annealing temperature [18]. For example, using faster cooling rates in fused silica yields denser glass structures.

We used fused silica in our study since most commercial glass is silica-based and the glass structure is thus not affected by network modifying additives. To find the physical conditions at which the glass was modified, we used the so called ‘memory effect’ of the thermal history of the glass network [18]. This means, the glass network changes according to the applied pressure, cooling rate or radiation and can be analyzed afterwards.

We analyzed different cooling rates observing $T_f$ with inelastic light scattering, Raman, and Brillouin spectroscopy. Different calibration methods linking these spectroscopies to $T_f$ were already reported for fused silica in the literature at a small temperature range around $T_g$ (1200 °C). New samples of fused silica were equilibrated at different $T_f$ by the annealing method. As shown in section 3, we expanded the relationship between cooling rate and fictive temperature to include lower and higher cooling rates than those reported in existing literature. The new calibrations obtained were extrapolated and used to evaluate the behavior of extremely high cooling rates matching the conditions encountered after USP laser modification. A modified zone was inscribed with 3 W average power, 2 MHz repetition rate, and 200 mm s$^{-1}$ feeding speed and was mapped at high spatial resolution using inelastic light scattering. The optical and acoustic responses of the modified glass structure were evaluated before the local $T_f$ distribution was estimated [19]. The local cooling rates were calculated by relating the $T_f$ distribution to the viscosity of fused silica. Comparing the observations obtained from Raman spectroscopy to the Brillouin analysis, we determined the local residual stresses caused by the USP laser modification.

2. Experimental procedure and methods

The fused silica used in the experiments (specification EN08) were electrically molten natural quartz glass with a SiO$_2$ content above 99.98% and a hydroxyl content below 150 ppm. A complete chemical characterization is listed in [20]. The glass samples were 1 mm thick with both sides polished to optical standards.

2.1. Correlation of fictive temperature to the cooling rate

One way to evaluate the cooling rate ($q_e$) in the temperature domain of the glass transition, is to determine the $T_f$, at which structural relaxation does not have enough time to take place. When the liquid is taken as a Maxwell body, its relaxation time ($\tau_r$) is related to the shear modulus ($G_\infty$) and the viscosity ($\eta$) by the following relation:

$$\tau_r = \frac{\eta}{G_\infty}$$  \hspace{1cm} (1)
Furthermore, following [21–23], \( T_f \) can be directly related to \( q_E \) using the viscosity–temperature dependence with:

\[
\log (q_E(T_f)) = 13 - \log (\eta(T_f)) = 13 - A + \frac{B}{(T_f - T_0)} = -5.66 + \frac{19433}{(T_f - 364.15)}
\]

where \( q_E \) will be in K/min, \( \eta \) in Pa \cdot s, \( T_f \) and \( T_0 \) in K. The three variables \( A, B \) and \( T_0 \) are the traditional coefficients of the Vogel–Fulcher–Tammann (VFT) equation. The numerical values reported in the equation above were obtained from the SciGlass database.

2.2. Calibration of fictive temperature to vibrational spectra

Isothermal treatment is an effective method for preparing calibration samples with different \( T_f \). Isothermal treatment was performed by placing the glass sample inside a platinum crucible within an annealing furnace, which was kept at the desired \( T_f \). The annealing time was chosen to be longer than the relaxation time \( \tau_r \) and calculated using equation (2). The samples were kept in the annealing furnace three times longer than the \( \tau_r \) (3 \( \cdot \) \( \tau_r \)). After annealing, the samples were quenched in direct contact using distilled deionized water to ensure fast cooling. If the cooling time (the duration of the quenching procedure) at the end of the isothermal treatment is significantly shorter than the relaxation time, the prepared glass samples will have the desired fictive temperature \( T_f \)—which equals the annealing temperature.

In this way, samples with \( T_f \) ranging from 990 °C to 1250 °C were prepared. The corresponding cooling rates (in the domain of the glass transition) range from 0.001 K min\(^{-1}\) to 78 K min\(^{-1}\). Using distilled deionized water at room temperature yielded a short quenching duration (\( t < 1 \) s) and prevented further relaxation. Compared to previous studies, using the calibrations reported in this paper, we obtained samples with lower \( T_f \) ranges than those reported in previous studies.

We prepared three other samples at 1300 °C, 1350 °C and 1400 °C, as reported in previous studies. At these high temperatures, the cooling rates necessary to obtain the corresponding \( T_f \) is above 390 K min\(^{-1}\) and thus too high to be achieved under typical quenching conditions [17]. These samples did not maintain the desired \( T_f \). The observations from these three samples appear in red on the calibration curves. These observations were excluded from the fit (see figures 1 to 4) to avoid overestimating \( T_f \) by quenching the calibration samples not fast enough. The temperature ranges used in previous studies reported in literature are represented in figures 2 to 4 as blue dashed lines. All of the compared studies observed temperatures that far exceeded 1250 °C—the highest temperature reported in our experiments. This discrepancy explains why our calibrations show a larger slope than the literature values. Indeed, our results showed a similar slope after fitting our observations in the temperature interval reported in previous literature and including results for samples with high \( T_f \). The error of the fit reported in literature is represented as a grey background in figures 1–4.

The calibration samples subjected to different cooling rates were characterized with vibrational spectroscopic analysis methods, which observed both the acoustic vibrations (Brillouin shift) and optical vibrations (Raman shift) at room temperature.
2.3. Vibrational analysis

The vibrational analysis was performed with the in-house built ARABICA (Associated Raman Brillouin Calorimeter) spectrometer [24]. A single frequency 488 nm CW laser source (coherent sapphire SF) was used to excite optical and acoustic vibrations inside the glass network at the laser focal point. For further description purposes we will refer to this laser as Raman–Brillouin analysis (RBA) laser. In a 180° reflective measurement setup the scattered light contains the Rayleigh (elastically scattered light), the Raman (optically scattered light) and the Brillouin (acoustically scattered light) contributions. The Brillouin signal was observed using a tandem Fabry–Perot interferometer (TFP). The Raman signal was analyzed with a CCD camera after passing a monochromator with a high spectral resolution grating. The exact technical specifications as well as a precise description of the setup was published by Veber et al [24]. Combining a focusing objective (NA 0.42, WD 20.5 mm) with a three-axis stage assembly allows scanning of large 2D areas.

Our work focuses on four different observables for the vibrational analysis. Three observables were obtained from the Raman signal: the σ-parameter (1st observable), the main band position (2nd observable) and the $D_2$ area (3rd observable). The fourth observable was the Brillouin shift.

2.3.1. Raman spectroscopy. An example of Raman spectra of fused silica EN08 subjected to different cooling rates ranging from slow-cooled (obtainable with conventional annealing methods) to fast- and extreme-fast-cooled (obtained after ultra-short pulsed laser irradiation). 2.3.1 explains the assignment of the different bands in the spectra above. The inset shows the raw Raman signal (black) for the slow-cooled sample with the fourth order polynomial baseline (red) applied for background correction.

![Figure 3](image1.png)  
**Figure 3.** Evaluation of the main band position calculated from the Raman spectra. The symbols (black points) indicate the observations of our work including a linear fit (red line) of the data from 980 °C to 1250 °C, excluding the data from 1300 °C to 1400 °C (red points) due to uncertainties in the production process. The blue dashed line shows the previous literature calibration, the interval used for the fit as well as the error as a grey background.

![Figure 4](image2.png)  
**Figure 4.** Brillouin spectrum evaluated for the average shift position of the signal. The symbols (black points) indicate the observations of our work including a linear fit (red line) of the data from 980 °C to 1250 °C, excluding the data from 1300 °C to 1400 °C (red points) due to uncertainties in the production process. The blue dashed line shows the previous literature calibration, the interval used for the fit as well as the error as a grey background.

![Figure 5](image3.png)  
**Figure 5.** Example of Raman spectra of fused silica EN08 displayed with different cooling rates ranging from slow-cooled (obtainable with conventional annealing methods) to fast- and extreme-fast-cooled (obtained after ultra-short pulsed laser irradiation). 2.3.1 explains the assignment of the different bands in the spectra above. The inset shows the raw Raman signal (black) for the slow-cooled sample with the fourth order polynomial baseline (red) applied for background correction.
The displayed spectra show typical bands for amorphous SiO$_2$ previously described in the literature. The so-called ‘main band’ ($\omega_1$), around 445 cm$^{-1}$, is associated with the intertetrahedral Si-O-Si bond angle distribution. With increasing cooling rate, the band broadens and shifts to higher frequencies resulting in a decrease of the mean Si-O-Si bond angle and a widening of the distribution [25]. $D_1$ at 490 cm$^{-1}$ and $D_2$ at 605 cm$^{-1}$ are assigned to 4- and 3-membered SiO$_4$ defect rings, respectively. These ring structures appear sensitive to permanent densification [12, 13], residual stress [26], cooling rate [27], and irradiation. All these phenomena induce a general rearrangement of the network structure [28, 29]. $\omega_3$ and $\omega_4$ can be found in the literature and will not be further discussed in our work [30]. All spectra were collected in a wavenumber range from 50 to 1450 cm$^{-1}$. No vibrational contributions of the glass network of fused silica were present above the observed range.

In our work, we focused on a spectral range from 150 to 700 cm$^{-1}$ because this range shows the strongest influence on structural rearrangements compared to the relatively small changes in ranges exceeding 700 cm$^{-1}$. Changes of the main $D_1$ and $D_2$ bands were integrated to determine the $\sigma$-parameter defined by Deschamps et al [12] (see equation (3)).

$$\frac{\int_{\alpha_1}^{\sigma} I_{\text{Raman}}(\alpha) \, d\alpha}{\int_{\alpha_1}^{\alpha_2} I_{\text{Raman}}(\alpha) \, d\alpha} = \frac{1}{2}. \quad (3)$$

Equation (3) describes the $\sigma$-parameter (1st observable) with $\alpha_1$ as the lower border of the integral (in our work set to 150 cm$^{-1}$) and $\alpha_2$ as the higher border of the integral (in our work set to 690 cm$^{-1}$). The position of the main band (2nd observable) peak was calculated at the maximum intensity of the $\omega_1$ band. The main band was fitted by a fourth order polynomial between 380 and 430 cm$^{-1}$ to denoise the spectrum and minimize the calculation error. The $D_1$ area (3rd observable) was calculated between 570 and 650 cm$^{-1}$. All observables were calculated after baseline correction and normalization to the total area of the spectrum.

2.3.2. Brillouin spectroscopy. Figure 6 contains examples of Brillouin spectra. The incident laser on the measured sample interfered with the acoustic vibrations parallel to the incident laser (z-direction). The observed signal (Brillouin shift) represents the diffracted portion of the incident RBA laser at the wave fronts of the induced vibrations, which correlate with the sound velocity of the observed material. The shown Brillouin shifts and Raman measurements were collected simultaneously. The displayed spectra in figure 6 for slow-, fast- and extreme-fast-cooled glass show both negative (anti-Stokes signal) and positive (Stokes signal) Brillouin shifts. Due to experimental restrictions, the arithmetic mean value of the anti-Stokes and Stokes signal was calculated to determine the Brillouin shift (4th observable). A rearrangement in the network structure due to difference in pressure or cooling rate, alters the Si-O-Si bond angle distribution. The change of the bond angle distribution modifies the sound velocity of the glass network, and therefore, induces a shift in the observed Brillouin signal [13].

Figure 6. Example of Brillouin spectra of fused silica EN08 displayed with different cooling rates ranging from slow-cooled (obtainable with conventional annealing methods) to fast- and extreme-fast-cooled (obtained after ultra-short pulsed laser irradiation). Negative shifts are related to the anti-Stokes signal (left) and positive shifts to the Stokes signal (right) respectively.

Figure 7. Schematic representation of the experimental setup used for the USP modification process. The sample surface is aligned perpendicular to the incident laser using the CCD camera.

2.4. Ultra-short pulsed laser modification

The glass modification experiments in our work were performed using a mode-locked Nd:YVO$_4$-laser (Fuego, Time-Bandwidth Products, Switzerland). This system emits pulses with a FWHM-duration of 10 ps at 1064 nm wavelength with an adjustable repetition rate from 50 kHz to 8 MHz and a nominal average output power up to 30 W. In our work, the repetition rate was set to 2 MHz and the output power was set to 3 W (see [31]).
The laser was focused using a wavelength corrected ELWD microscope objective with a numerical aperture (NA) of 0.7 and a correction collar to compensate for spherical aberrations and to achieve a focus-depth independent focal spot size. A schematic representation of the setup used for the internal USP laser modification is provided in figure 7. The USP laser was incident from above (y-direction) and focused into the volume of the sample. The laser focal spot remained in a fixed position and the fused silica sample was moved along the x-axis at a constant speed (200 mm s⁻¹). The acceleration and deceleration occurred outside of the sample to ensure constant irradiation conditions during the modification process.

For all samples, the focal spot was set to a depth of 250 μm below the surface. A correction of the focusing depth due to the refractive index of fused silica (n = 1.4496 at 1064 nm [32]) as well as an adjustment of the correction collar of the focusing objective was incorporated.

The laser modified sample from figure 8 was mapped in an x-y direction. The mapping depth (z-direction) was chosen to be directly in the center of the modified zone. Since the gas bubbles are located in the center (z-direction), they were used to place the focal spot of the RBA laser on this plane. This is done using reflections from the generated gas bubbles. The modified zones were mapped with an RBA laser with a focus diameter of 1.4 μm and a step size of 2.5 μm. The entire area was mapped with a total of 20 × 30 measurement points.

3. Results and discussion

The inscribed modification was optically analyzed to evaluate the lateral behavior of the inscribed modification (figure 8). The focal point of the laser beam induces dynamic plasma formation, which grows quasi-periodically in the direction of the incoming laser [33, 34]. The complete heat-affected zone (HAZ) is visible by a slight change of the refractive index between the unmodified glass and the modified zone. In the upper part of the modified zone, a gas bubble (black dot in figure 8), typical for fused silica but also observed in Borofloat 33 glass types, is generated. This due to agglomeration of smaller bubbles generated during the plasma state of the modification process near the focal spot of the USP laser.

During the process the bubbles are trapped within the laser-plasma-interaction mechanism and dragged in the direction of the moving USP laser [35]. During USP laser modification process, fused silica reaches temperatures between 3000 °C and 4000 °C [34], forming gaseous SiO₂ inside the molten area. The rapid dissociation of gaseous SiO₂ into silicon and oxygen forms the bubbles [35]. At a high feeding speed (e.g. 200 mm s⁻¹), the quasi-periodic plasma motion generates separate molten zones along the feeding direction (x-direction) (see figure 8). For description purposes, we will refer to one such cycle (see red box in figure 8) generated during this process as the ‘gas bubble cycle zone’ (GBCZ).

Using a feeding speed of 200 mm s⁻¹ (see figure 8), single GBCZs along the moving direction of the laser are visible. All GBCZs were tilted in the feeding direction (x-direction) of the USP laser. The formation of these GBCZs occurred in the following manner: The initial laser pulses ionize the glass network by multi-photon absorption, initiating plasma formation. Inside the plasma, SiO₂ begins dissociating into its component elements. This process forms small oxygen bubbles that agglomerate and move towards the incoming laser beam (y-direction). The laser beam drags the bubbles which are agglomerating inside the plasma along with the plasma (against the motion of the sample) due to a thermal gradient effect described in [36]. With increasing size, the agglomerating bubbles start to block the incident laser beam partially up to a point where the incident energy is no longer sufficient to ionize the network causing the plasma to be extinguished and, consequently, to stop the thermal accumulation in the modification area [34, 35]. Cooling the network increases the viscosity of the glass, freezing the bubble in place. Due to the constant feeding speed, the laser focal spot moves past the blocking bubble, and the described process restarts. For the process parameters used in figure 8 of 3 W average power, 2 MHz repetition rate and 200 mm s⁻¹ feeding speed, the average length of a separated structure is 26.36 μm with 10 pulses per μm. At the starting point of the USP laser, the GBCZ shows the formation of randomly distributed cracks.

This defect formation can be attributed to high internal pressure at the initial plasma formation working against a cold and brittle material [31]. For modified zones at high repetition rates or fast feeding speeds—which generate the GBCZs—a defect formation at the focal spot is visible for every GBCZ, because with quasi-periodic laser-plasma-interaction each new GBCZ is generated in yet unmodified and still cold and thus brittle material.

3.1. Fictive temperature calibration curve with a conventional annealing method

A diagram of the σ-parameter depending on $T_f$ is shown in figure 1. The σ-parameter was calculated for the spectral range from 150 to 690 cm⁻¹, as described in 2.3.1. The σ-parameter increases monotonically with $T_f$ from 980 °C to 1250 °C. This $T_f$ range was linearly fitted, excluding values above 1250 °C, as shown in figure 1. It appears impossible to generate higher cooling rates with our conventional annealing method (section 2.2) due to the handling times of the sample.
and the short relaxation times (below 1 s) of the glass network above 1250 °C [36]. For calibration purposes, our conventional annealing method limited the obtainable cooling rates; therefore, we excluded results obtained at a \( T_f \) above 1250 °C. Data using the \( \sigma \)-parameter for \( T_f \) calibration has not been previously reported. As a result, we could not make a direct comparison between our calibration and those reported in the literature.

The following fit equation of our calibration correlates \( T_f \) to the \( \sigma \)-parameter. The relationship is valid in a stress regime from 0 to 1 GPa.

\[
T_f(\degree C) = \frac{\sigma \left( cm^{-1} \right) - 361 \pm 3 \left( cm^{-1} \right)}{0.041 \pm 0.003 \left( \frac{cm^{-1}}{e} \right)}.
\] (4)

The observation of the \( D_2 \) band area of our work is shown in figure 2 and compared to the results of Martinet et al [37]. The evolution of the \( D_2 \) area shows a monotonic trend with increasing \( T_f \) in the temperature range from 980 °C to 1250 °C. Including the new observations in the low \( T_f \) range (980 °C and 1000 °C) and considering only the results which are not limited by our conventional annealing method (e.g. below 1250 °C), a different evolution of the \( D_2 \) area is visible compared to literature. The linear behavior reported in the literature underestimates the \( T_f \). If the results of our work are fitted in the same \( T_f \) range reported in the literature, the prediction of the \( T_f \) is similar. We expected reliable observations from the low \( T_f \) range due to the long relaxation times (>3 h) of the glass network in the sub \( T_f \) range (<1200 °C) [38].

The following fit equation of our calibration correlates \( T_f \) to the \( D_2 \) area—abbreviated as \( D_2 \) in the equation—after a normalization to the total area of the spectrum (total area = 100). The relationship is valid in a stress regime from 0 to 1 GPa.

\[
T_f(\degree C) = \frac{D_2 - 3.9 \pm 0.4}{0.0058 \pm 0.0003 \left( \frac{1}{e} \right)}.
\] (5)

The observation of the main band position of our work is shown in figure 3 and compared to the calibration done by Martinet et al [37]. The position of the main band behaved monotonically with increasing \( T_f \). Our fit considers the range from 980 until 1250 °C. Our calibration and the reported data from literature show a similar behavior with \( T_f \) in the observed temperature range.

The following fit equation of our calibration correlates \( T_f \) to the main band position (MB). The relationship is only valid in ambient pressure conditions.

\[
T_f(\degree C) = \frac{MB \left( cm^{-1} \right) - 414 \pm 3 \left( cm^{-1} \right)}{0.022 \pm 0.003 \left( \frac{cm^{-1}}{e} \right)}.
\] (6)

As for the Raman observables, the Brillouin shift was evaluated using the same \( T_f \) range from 980 °C to 1250 °C. The Brillouin shift exhibited a linear behavior. Our new calibration deviates only slightly from the prediction of literature [39].

The following fit equation of our calibration correlates \( T_f \) to the Brillouin shift (BR). The relationship is only valid in ambient pressure conditions.

\[
T_f(\degree C) = \frac{BR \left( GHz \right) - 34.9 \pm 0.1 \left( GHz \right)}{0.00071 \pm 0.00009 \left( \frac{GHz}{e} \right)}.
\] (7)

The calibration curves reported in previous studies use a different temperature range compared to our study. The range reported by Martinet et al [37] (see range of blue dashed lines in figures 2 and 3) observed a temperature range from 1150 °C to 1350 °C. Le Parc et al [39] determined the Brillouin shift (see range of blue dashed line in figure 4) in a temperature range from 1100 °C to 1450 °C.

Compared to our observed temperature range (980 °C to 1250 °C) the previously reported studies use a significantly higher temperature domain. If our new set of calibration is linearly fitted in the temperature range reported in previous studies, the slope of the linear fit is similar. Therefore, our new set of calibration does not contradict the validity of previous calibrations in their interval of determination. However, our new set of equations should be more reliable in case of extrapolation to hyperquenched (extreme-fast-cooled) glass conditions for the here investigated observables. This is because a \( T_f \) calibration procedure at lower temperature domains allows easier and more reliable heat treatment due to the longer relaxation times (\( \tau_r \)) of the network. This way, undesired but systematic calibration errors that occur in high temperature domains can be excluded. The interval of determination (observed \( T_f \) range) plays an important role for the reliability of the calibration curve. An increase in the determination interval could further improve the accuracy of our provided calibrations.

3.2. Extreme-high-cooling rates

For all following observables, the correlating \( T_f \) was calculated using the calibrations described above. In figure 9, the evaluation of the \( \sigma \)-parameter is represented by a superposition of the vibrational analysis mapping and the optical microscope transmission image of the modified zone. A \( T_f \) of 1150 °C was calculated for the unmodified glass. The glass transformation temperature (\( T_{tr} \), defined for a cooling rate of 10 K min\(^{-1}\)) for industrially produced fused silica is 1200 °C [20]. Our observations for the base glass agree with the expected \( T_f \). Significantly higher \( \sigma \)-parameters, correlating with a higher \( T_f \), were observed in the modified zone. The observations increase radially from the edges (1180 °C) to the center (1327 °C). The observations of the \( \sigma \)-parameter of the USP laser modified zone indicate a \( T_f \) in the extrapolation range of our calibration method. A maximum \( T_f \) was observed in the center of the modified zone indicating a higher cooling rate which can be attributed to higher temperatures during the plasma activity [33, 40, 41]. We expected that heat dissipation via thermal radiation, as opposed to thermal conduction, would have a stronger influence on the cooling rate during the formation of the higher \( T_f \) in the center of the modified zone. A stronger contribution of thermal conduction would lead to higher \( T_f \) at the edges of the modified zone [37, 42].

The evaluation of the \( D_2 \) area (see figure 10) shows a \( T_f \) distribution similar to the evaluation of the \( \sigma \)-parameter. A \( T_f \)
of around 1150 °C was calculated for the unmodified glass. The $T_f$ for the modified zone shows a radial increase from the edges (1180 °C) to the center (1375 °C). The maximum $T_f$ was observed at 1375 °C, which corresponds to a cooling rate of 2900 K min$^{-1}$ in the glass transition domain.

Compared to the $\sigma$-parameter, the center of the modified zone shows a slightly higher $T_f$ within its error bars. The evaluation methods of the $D_2$ area and the $\sigma$-parameter show the same $T_f$ distribution for the base glass as well as the modified zone. This can be explained by calculating the $\sigma$-parameter (see equation (3)). If the Raman spectra are compared, the biggest change in the range from 150 to 690 cm$^{-1}$ is observable in the increasing $D_2$ band. Neither the main band nor the $D_1$ band show changes on the same order as the $D_2$ band with $T_f$. Therefore, the evolution of the $\sigma$-parameter is mainly based on the increase of the $D_2$ band resulting in similar results for both methods.

The reader might notice that there are some cracks present at the starting points of the GBCZs in figures 8–10. This brings up the question whether or not these cracks have an influence on the Raman observables because they might change the vibrational behavior of optical phonons. As can be seen from the results in figures 9 and 10 either they have no influence on the Raman observables or cannot be resolved with the used evaluation methods.

Compared to the $\sigma$-parameter and $D_2$ area, the evaluation of the main band position (see figure 11) shows a different distribution of the $T_f$ in the modified zone. Compared to figures 9 and 10, no clear pattern-like distribution of the $T_f$ was observed inside the modified zone. Nonetheless, the maximum $T_f$ was visible in both the center of the modified zone and near the focal spot of the USP laser. Compared to the $\sigma$-parameter,
the $T_f$ calculated with the main band position was generally lower. The maximum $T_f$ calculated for the main band position was 1293 °C. Unfortunately, the precision of our calibration function (see figure 3 and our measurement of the main band position limits our possible interpretations. The evaluation of $T_f$ using the $\sigma$-parameter or $D_2$ area is better than using the main band position. Moreover, in-situ high pressure experiments have shown that both the $\sigma$-parameter and the $D_2$ area are virtually unaffected by pressure up to 1 GPa [43]. Therefore, we can assume that figures 9 and 10 give the purely thermal response of the glass structure.

Figure 12 shows the evaluation of the acoustic vibrations, the Brillouin shift. The Brillouin shift indicates a different behavior compared to the Raman observations. The Brillouin shift in the GBCZ (1 in figure 12) as well as in the area below, (2 in figure 12) shows very high values of up to 35.9 GHz. The unmodified base glass 3 has an intermediate value of 35.75 GHz. Finally, the starting point of the GBCZ 4 shows a lower shift down to 35.5 GHz. The direct application of our calibration (see equation (7)) contradicted the values obtained from the Raman calibrations. The maximum $T_f$ (1442 °C) occurred in the unmodified zone 2, while the lowest cooling rate would have been predicted in zone 4, where the plasma initiation took place. Only zone 3, with a $T_f$ of 1150 °C, was similar to the results of the $\sigma$-parameter and the $D_2$ area. After careful observation, the area under the laser focal spot (zone 4) presents microscopic cracks, visible as fringes in the optical image, as well as possible nanobubbles. The cracks are likely a result of the shockwave formation induced by the incident USP laser on the cold and brittle base glass [44].

The cracks and the possibly inherent nanobubbles can lower the density and the sound velocity of the network, resulting in a lower Brillouin shift compared to the unmodified glass.

Conversely, only the existence of residual stress can influence the Brillouin shift and modify its dependence on $T_f$. As Sonneville et al [11] reported, using in-situ Raman and Brillouin spectroscopy, the Brillouin shift decreases under pressures up to 2 GPa. The Brillouin shift shows increases in the tensile regime [11]. In the same pressure interval, the Raman spectra of fused silica remains unchanged [43]. The observed Brillouin shift at the USP laser focal spot could be interpreted as compressive stress that is not detectable by Raman spectroscopy. The Brillouin shift of the modified zone 1 can be attributed to the change in $T_f$ present in the Raman observables. The Brillouin shift of the USP laser focal area 4 observes both the thermal history effect and compressive stress linked to the crack formation. No change of $T_f$ was expected in the surrounding of the modified zone (zone 2) due to the absence of thermal accumulation. However, volume variation of nearby GBCZ could have induced a local gradient in the stress distribution between 4 and 2, resulting in tensile stress in 2.

From the Raman observables, we expected a $T_f$ change in the modified area with no influence on the surrounding base glass. The observed Brillouin shift indicates the change of $T_f$ with additional influences due to residual stress. By correlating the $\sigma$-parameter to the Brillouin shift, it is possible to separate the influence of $T_f$ from the influence of pressure (residual stress). The correlation of the $\sigma$-parameter with the Brillouin shift was expected in the sur-

Figure 13. Correlation of the $\sigma$-parameter with the Brillouin shift. The black symbols show the results of our calibration, the red symbols indicate the results of the modified zone. All values of the calibration are linearly fitted (black line). The red line indicates the shifted linear fit of the calibration to fit the results of the modified zone. The difference between the calibration and the modified zone is shown by the blue segment, indicating the residual stress. 1 indicates the center of the GBCZ, 2 the region between and below the GBCZ, 3 the unmodified region and 4 the focal area of the USP laser and starting point of the GBCZ.
shift as well as the calibration results are shown in figure 13. The different areas defined in figure 12 are also reported. The observations for the unmodified base glass above the GBCZ 3 show almost no variation in both the Brillouin shift and the σ-parameter. However, area 2 shows a strong variation in the Brillouin shift at constant σ-parameter, indicating a pure stress induced behavior. The results for the modified zone are visible in 1, showing a linear behavior between the Brillouin shift and the σ-parameter. The linear fit (red line) of this zone is parallel to our calibration curve (black line) by an offset of +0.05 GHz (see blue segment). This indicates that area 1 is predominantly affected by a gradient of the fictive temperature effect, but that it is under low, constant tensile stress. It is in this area where the highest $T_f$ was observed. At the starting point of the GBCZ 4, non-linear changes occurred in both the Brillouin shift and the σ-parameter. A combined influence of compressive stress and $T_f$ was observable since the results showed higher σ-parameter (correlated only to $T_f$) and smaller Brillouin shifts (correlated to the compressive stress) at the same time. The high scattering of the points in area 4 can be easily explained by the presence of cracks.

As exemplified in area 1, it is possible to differentiate the cooling rate effects from residual stress effects by comparing the Raman signals to the Brillouin shift. Sonnevile et al reported a pressure dependence of the Brillouin shift of $-2.5 \text{ GHz GPa}^{-1}$ [11]. The offset of +0.05 GHz corresponds to a tension of 20 MPa. This can be generalized to every point of our mappings. By subtracting the $T_f$ contribution obtained from the σ-parameter from the global Brillouin shift (containing the contribution of $T_f$ and residual stress) only the contribution of the residual stress (RS) was extracted. The residual stress expressed by the Brillouin shift (in GHz) can be quantified in GPa using the aforementioned calibration [11]. A residual stress calibration is given as follows:

$$RS (\text{GPa}) = \frac{BR (\text{GHz}) - 0.0173 \left( \frac{\text{GHz}}{\text{cm}^2} \right) \cdot \sigma (\text{cm}^{-1}) - 28.6 (\text{GHz})}{-2.5 \left( \frac{\text{GHz}}{\text{GPa}} \right)} \quad (8)$$

Applying this calibration, a residual stress map shown in figure 14 was obtained. Excess stresses were observed at the focal spot of the USP laser and along some of the discontinuities visible at the bottom of the GBCZ, which are probably cracks. The tensile regions are poorly defined as they were defused between and below the GBCZ.

The above-mentioned combination of $T_f$ and residual stresses on the Brillouin shift may not completely cover the whole picture. As is reported in the literature, high-energy particles (x-ray photons, electrons, ions) also lead to changes in the Raman spectra without any additional mechanical stress or heat input [28, 29, 45]. USP laser interaction with plasma produces fast electrons that generate x-ray photons [46]. While the laser peak fluence used in our experiments was not as high as in [46], we cannot completely exclude the potential effects electrons, in the laser-generated plasma, have on structural network changes.

![Figure 14](image-url) Calculation of the residual stress for a modified zone inscribed with an average power of 3 W, a repetition rate of 2 MHz and a feed speed of 200 mm s$^{-1}$. The residual stress is obtained by combining the Brillouin shift of figure 12 with the σ-parameter of figure 9 by using equation (8). The calculated residual stress is color coded and overlaid with an optical image of identical scale.

4. Conclusion

In our work, fused silica was prepared at different fictive temperatures, similar to cooling rates, by using a conventional annealing method. Different observables obtained from inelastic light scattering (optical and acoustic vibrations of the glass network) were correlated to the $T_f$ and calibration curves. Concerning our experimental study, the observed $T_f$ range reported in the literature was expanded to lower $T_f$ values. This provides a more reliable extrapolation for all the observables studied. The expanded range of $T_f$ shows a slightly different behavior compared to literature.

A USP laser modified zone in fused silica was produced and mapped with high spatial resolution by Raman and Brillouin spectroscopy. The mapping of the modified zone provides a detailed view of the $T_f$ distribution within the modified zone. We observed, by the Raman signal, a higher $T_f$ in the center of the modified zone indicating a higher cooling rate. Using the USP laser, it was possible to generate higher $T_f$ compared to our conventional annealing method. The results of the σ-parameter and the $D_2$ area were found to be very suitable for a local mapping of the $T_f$ across the USP laser modified zone. The Raman main band position by itself was less accurate. Moreover, the σ-parameter and the $D_2$ area only show the response to changes in $T_f$ and are not influenced by residual stress. The observation of the Brillouin signal shows additional effects besides the $T_f$ due to residual stress. However, if the residual stresses are low enough (<2 GPa) the combination of the Raman signal (σ-parameter) and the Brillouin shift can be used to separate and quantify the influence of residual stress.
on the glass network. The measured cooling rate and residual stress in our study can be used to validate future simulations of the GBCZ and USP laser modified zones in fused silica.

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