Femtosecond laser direct writing in SiO 2 -Al 2 O 3 binary glasses and thermal stability of Type II permanent modifications

Yitao Wang, Shuen Wei, Miss R. Cicconi, Yuta Tsuji, Masahiro Shimizu, Yasuhiko Shimotsuma, Kiyotaka Miura, Gang-Ding Peng, Daniel R. Neuville, Bertrand Poumellec, et al.

Femtosecond laser direct writing in SiO_2-Al_2O_3 binary glasses and thermal stability of *Type II* permanent modifications

Y. Wang[1], S. Wei[2,*], M.R. Cicconi[3], Y. Tsuji[4], M. Shimizu[4], Y. Shimotsuma[4], K. Miura[4], G.-D. Peng[2], D.R. Neuville[3], B. Poumellec[1] and M. Lancry[1]

[1] Institut de Chimie Moléculaire et des Matériaux d'Orsay, CNRS-Université Paris Sud, Université Paris Saclay, 91405 Orsay, France

[2] School of Electrical Engineering & Telecommunications, University of New South Wales, Sydney, NSW 2052, Australia

[3] CNRS-IPGP, Géomatériaux, 1 rue Jussieu, 75005 Paris, France

[4] Graduate School of Engineering, Kyoto University, Kyoto, Japan

* corresponding author: shuen.wei@unsw.edu.au

Abstract: We investigate the potential of fabricating thermally stable refractive index contrasts using femtosecond (fs) near-infrared (IR) radiation in aluminosilicate glasses. A set of pure SiO_2-Al_2O_3 glasses are manufactured, characterized (density and Raman) and investigated after being irradiated by fs laser within the *Type II* regime. The formation of nanogratings is identified and studied using quantitative birefringence measurements. Their thermal stability is then investigated through 30min step isochronal annealing (up to 1250°C). For both SiO_2 and $50SiO_2$-$50Al_2O_3$ compositions, the normalized birefringence does not decrease when tested up to 1100°C, while for the 4,6 mol% GeO_2-SiO_2 erased for 20% at 1000°C.

1. Introduction

Since the discovery of the laser-induced periodic surface structure (LIPSS) by Birnbaum nearly a half-century ago [1], many interesting researches have been carried out from the experimental and theoretical perspectives [2]. One of the intriguing phenomena induced by the femtosecond (fs) laser pulses is the formation of the polarization-dependent sub-wavelength nanostructures [3]. As opposed to the LIPSS written onto the surface of various materials (e.g., metals, semi-conductors, dielectrics), formation of nanogratings within the bulk has been observed mostly in silicate and germanates glasses with a limited alkali content [4, 5, 6, 7, 8, 9]. In the case of SiO_2 or GeO_2 glasses, self-organized nanogratings, which are composed of stripe-like regions with oxygen deficiencies including nanovoids [10, 11], are perpendicularly aligned to the laser polarization.

The very high intensity fields achievable using femtosecond laser pulses can lead to highly localized plasma ionization and deoxygenation, resulting in strong sub-diffraction interference effects between the plasma and the optical field, generating complex condensed structures such as nanogratings. These are based on glass decomposition that resolidifies into a nanoporous [10], usually silicon-rich, structure, creating a strong and highly stable refractive index contrast [12]. Based on such photo-induced structures showing localized birefringence in glass, various applications ranging from embedded micro-reflectors, retardation plates, microfluidic channels, to rewritable 5D optical storage, polarization imaging have been investigated as review in Refs. [13, 14].

Besides these applications mentioned above, nanogratings in SiO_2 due to its remarkable

thermal stability up to ~ 1200°C [12, 15], they are now extensively studied for applications like long lifetime optical data storage and for sensing applications in extreme environments. For example, *Type II fs-IR* modifications which are attributed to the formation of self-organized nanogratings made of oxide decomposition [10, 11], demonstrate remarkable thermal stability up to ~ 1000°C for 150 hours after a stabilization for 1 hour at 1000°C [16], while operating for 100 hours at 1050°C reveals a slight (5%) intensity decay. This is likely associated with thermal relaxation of the bulk glass at these temperatures. It should be noted that, in this work, we categorize the type of modifications from the perspective of the nature of refractive index modifications induced by IR femtosecond laser irradiation. More specifically, *Type I IR-fs* modification is featured by an isotropic growth of the refractive index with respect to the non-irradiated regime. The *Type II* IR-*fs* modification, characterized by a high level of anisotropic index change [8] and resulting birefringence, is typically induced by the presence of nanogratings. As relates to applications, fs-FBGs have recently been tested as temperature sensors for monitoring fluidized bed combustors [17], as well as for radiation resistant temperature sensors [18, 19]. The refractive change is 3D localized and involves significant stress-induced changes around the irradiated regions. For this reason, the higher temperature regime is limited by the thermal response of both the surrounding regions and the fiber itself, which has not been relaxed prior to application. Recent results indicate the need of >30mol% Al_2O_3 [20] to improve FBG thermal stability above standard fibers like SMF28 from Corning. To go beyond the thermal stability limit [16] imposed by standard SiO_2-based optical fibers, FBGs can be inscribed in SiO_2-Al_2O_3 optical fibers using femtosecond laser direct writing [20, 21, 22]. The doping that determines the optical fiber core soften the glass far

too much and so are not directly involved in the high temperature processing that allows gratings to operate at higher temperatures. The usual dopants like Germanium (Ge), Fluorine (F) or Boron (B) in the fiber core determine the high temperature processing. Therefore, most commercial fibers will be unlikely to be designed for long-term operation above 1000°C [16]. However, if one examines the softening point (T at which log(η)=7,1 dPa.s) or the melting point (T at which log(η)=1 dPa.s), it is suggested that the introduction of a high melting point compatible oxide with SiO_2 like Al_2O_3 (which melts above 2000°C) could overcome to above-mentioned thermal stability limits imposed by silica-based optical fibers.

This paper mainly explores how the substitution of SiO_2 by Al_2O_3 up to 50 mol% in the glass impacts the formation and thermal properties of *Type II* modifications [23] written by IR femtosecond laser. The binary SiO_2-Al_2O_3 glass system was chosen because a) pure aluminosilicate glasses are known to exhibit high melting temperatures [24] and b) aluminosilicate glasses containing high Al_2O_3 concentrations typically present an increase in Al coordination number (namely 5 and 6 fold-coordination [25, 26, 27, 28]), increasing glass network cross-linking density and bond strength. SiO_2-Al_2O_3 glasses are therefore expected to be a good glass candidate for applications in high temperature environments. In this view, we prepared a set of aluminosilicate glasses using aerodynamic levitation with CO_2 laser heating. To further investigate the impact of dopants on thermal stability of *Type II* modification, Suprasil® CG silica, GeO_2-doped SiO_2, TiO_2-doped SiO_2 (ULE® 7972, Corning) and borosilicate (Borofloat® 33, Schott) were also investigated. Then we irradiated them by femtosecond laser and we studied the *Type II fs-IR* modifications by isochronal heat-treatments up to 1250°C, in order to determine

the effect of different dopants on the “thermal stability” of silicate glass.

2. Experimental details

Aluminum oxide (alumina, Al_2O_3) and silicon dioxide (silica, SiO_2) ultrapure raw powders based on the stoichiometry $x.SiO_2$ - $(1-x).Al_2O_3$ (x = 50, 60, 70, 80) were mixed in alumina mortar and pressed into pellets. The pellets were sintered for 12 h at 1100°C in air, and crushed and used as a preform for aerodynamic levitation with CO_2 laser melting. The calcined preforms were levitated using a flow of dry air (N_2: 79 %, O_2: 21 %) and melted through focusing of 100 W CO_2 laser via a ZnSe lens (f = 254mm). To ensure homogeneity of the melt, the temperature was kept above the melting point for tens of seconds. Then, the melt was rapidly cooled by turning off the laser power while gas levitating. Colorless and transparent spherical samples with a diameter of approximately 1-2 mm were obtained. Imperfections, such as bubbles, would interrupt laser propagation, thus, hot fully homogeneous sphere were melted again. The glass phases of all prepared samples were verified by Cu K X-ray diffraction (XRD, Rigaku; RINT-2500HFK/PC) and SEM-EDS chemical analysis. Volumetric mass density (which will be referred to as density for short) of all samples was measured at room temperature by Archimedean method, using toluene as an immersion liquid. The relation between these weights and density and temperature of toluene is well known. For each composition, measurements were performed on five different samples.

Raman spectra of the samples were recorded at room temperature with a T64000 Jobin-Yvon-Horiba® spectrometer equipped with an Olympus® microscope. A confocal system

and a 1024 Charge-Coupled Detector cooled by nitrogen were used, allowing a spatial resolution of 1-2 µm² with a x100 objective. The spectral resolution is ~0.7 cm^{-1}. A Coherent® Argon laser is used with an excitation wavelength of 488,1 nm with 50 mW on the sample. A commercial Suprasil® CG glass from Heraeus (a synthetic Type III pure SiO_2 glass [29]) has been chosen to serve as a reference to calibrate the sample spectra. All sample spectra were acquired in the frequency range 17 - 1400 cm^{-1} with the same experimental conditions in order to minimize experimental errors. The intensities of the spectra have been normalized over the total integrated area.

Femtosecond laser irradiation (λ = 1030 nm, 250 fs) was performed on the SiO_2-Al_2O_3 samples to investigate the writing kinetics of *Type II* modifications. In order to irradiate with a specific depth, and to make testing easier, samples were glued on a glass slide with a transparent resin, then polished using diamond lapping film (ø = 6 µm, 3 µm, 1 µm, 0.25 µm, 0.1 µm) until reaching optical quality. The polished surface was then placed on a xyz motorized translation stages and irradiated. Laser experiments include writing series of lines along the x-axis with a linear laser polarization oriented either parallel (Xx configuration) or perpendicular (Xy configuration) to the scanning direction. The laser pulse repetition rate was fixed to 100 kHz and the scanning speed to 100 µm/s. The laser beam was focused 300 µm below the surface using a 0.6 NA aspheric lens. The pulse energy was varied by step in different range of energy: ranging from 0.1 to 0.5 µJ with step of 0.1 µJ; ranging from 0.6-1 µJ with step of 0.2 µJ; ranging from 1.5-4 µJ with step of 0.5 µJ. The gap between two consecutive lines was fixed to 25 µm. Then in order to measure the optical retardance *R,* we use an Olympus BX51 polarizing optical

microscope equipped with a de Sénarmont compensator. The retardance R is defined as $R=B.L$, where B is the linear birefringence (n_e-n_o) and L is the length of the birefringent object being measured. The de Sénarmont compensator couples a highly precise quarter wavelength birefringent quartz plate with a 180º rotating analyzer to provide retardation measurements having an accuracy that approaches one thousandth of a wavelength.

3. Results

Density measurement of SiO_2-Al_2O_3 samples

Figure 1 shows the evolution of the density of the SiO_2-Al_2O_3 samples for different Al_2O_3 contents. Data from the literature [30, 31, 32] are reported for the sake of comparison. There is a clear trend where density increases as alumina content increases. From this graph, it is intuitive that the densities of our home-made SiO_2-Al_2O_3 samples are consistent with the literature. The standard deviations shown in Figure 1 result from the measurements for five pellets (10 measurements for each pellet) with the same target composition. It can be seen that deviation becomes gradually stronger when the pellet contains more alumina. It might be related to the increasing difficulty to vitrify the glass, which likely results in nanoscale phase separation and voids in the high-alumina-containing samples.

Raman spectra of SiO_2-Al_2O_3 samples

Raman spectra of SiO_2-Al_2O_3 samples with different concentrations of aluminum oxide (namely 20%, 30%, 40%, and 50% mole of Al_2O_3) are reported in Figure 2, along with the spectrum of Suprasil® CG glass, used as reference. The most intense contribution is located around 430 cm^{-1} (R band) and is associated to T–O–T symmetric stretching modes (T represents

the centered tetrahedron cation) [33]. By increasing the Al_2O_3 content, there is a clear intensity decrease of this band, related to both variations of the number of SiO_4 tetrahedra as well as to variations of T-O-T inter-tetrahedral angles and T-O average distances [30]. The sharp peaks, also called D_1 and D_2 defect lines, at around 490 and 600 cm^{-1}, are ascribed to the breathing modes of 4- and 3- membered rings, respectively [34]. According to Figure 2, both peak intensities relatively decrease with a higher content of alumina, which indicates that the addition of alumina causes modifications of the ring statistic in the silica glass network [30, 31]. In the mid-frequency area, the asymmetric band near 800 cm^{-1} results from the motion of Si atoms in their tetrahedral oxygen cage [35], and slightly decreases in intensity and move toward lower wavenumbers upon addition of Al_2O_3. This decrease could be associated to a decrease of Si-BO (Silicon-bridging oxygen).

The high frequency region (HF: 850 – 1300 cm^{-1}) shows bands related to the Si-O asymmetric stretching vibrations. The HF envelop can be studied by using mathematical function, and in the case of pure SiO_2 glass, three Gaussians can be used to represents the Si centered tetrahedra connected with four bridging oxygens (at ~ 1060 cm^{-1}, ~1155 cm^{-1} and ~1200 cm^{-1}). The HF region of the SiO_2-Al_2O_3 samples has been studied as well by using mathematical functions, and Figure 2b-e show the Gaussian decomposition of the 850-1300 cm^{-1} frequency region, and the necessity of four components in order to reproduce the envelope. Indeed, besides the three high frequency bands described for SiO_2, the addition of alumina in the silica glass leads to the rise of an additional contribution at ~ 975 cm^{-1}, which increases in intensity by increasing Al_2O_3. Furthermore, the band at ~1155 cm^{-1} shifts toward lower frequencies and increases in intensity upon addition of alumina, and this can be related to the stabilization of

4-fold or 5-fold coordinated Al^{3+} units, and the formation of Si-O-Al bonds. Indeed because of the high amount of Al_2O_3, besides the presence of AlO_4 tetrahedra, it is expected the presence of higher coordinated species (Al^{3+} 5-fold and/or 6-fold coordinated), which would cause the formation of non-bridging oxygens, and strong modifications in the glass connectivity. In particular based on the literature [25, 26], we expect that around 50% of Al are 5-fold coordinated in these glasses. This results in a depolymerization of the silica network (in agreement with the changes of the Boson peak at low frequency) and to the creation of Q_{n-1} species in agreement with the low frequency shift.

Writing kinetics of Type-II modifications in SiO_2-Al_2O_3 samples

Figure 3 shows the measurements of the retardance *R* for all investigated pellets with different compositions as a function of the laser pulse energy in μJ/pulse. Note we added the results obtained in Suprasil® CG glass (SiO_2) as a reference here. Above the *Type II* threshold, optical properties of the irradiated regions are modified. The average refractive index usually decreases, and the refractive index contrast continues to maintain even after a high temperature processing (typically an annealing for a few hours at 1000°C) in SiO_2 [12]. Moreover, a strong linear birefringence (mostly attributed to a form birefringence) is observed and can be easily detected using any birefringence imaging system.

Analysis of the curves shown in Figure 3 indicates that all samples exhibit a similar trend in their writing kinetics. Note that the threshold T1 [23], related to the formation of permanent index changes without form birefringence, is about 0.3 μJ as we can observe a contrast in natural light

but not between crossed polarizers. We did not observe any variation of T1 with the increasing content of Al_2O_3 in the investigated range. For higher pulse energy, occurrence of form birefringence was revealed using the full order waveplate technique, which allows detecting the slow/fast axis orientation of the photo-induced birefringence. Since we observed a 90° rotation of the slow axis orientation when switching from Xx to Xy writing configuration, we can attest the formation of orientable birefringence that is usually related to the formation of nanogratings [6, 8]. Therefore, it was observed that the threshold T2 [23], which is related to the *Type II* modifications, appears around 0.4 μJ in SiO_2 for our experimental conditions. It depends slightly on the Al_2O_3 concentration and increases up to 0.6 uJ for 50 mole% Al_2O_3. Typically, a strong retardance increase appears above T2 for short pulse energy increment and plateaus around 0.8-1 μJ (1.5 uJ for Suprasil® CG glass). Observing the trends in Figure 3, it is possible to notice two features: as the Al_2O_3 concentration increases both the slope at the origin and the maximum retardance gradually decrease. With respect to silica, SiO_2-Al_2O_3 samples exhibit much lower retardance values by a factor 4 for the $80SiO_2$-$20Al_2O_3$ sample and by a factor of 10 for the $50SiO_2$-$50Al_2O_3$ one.

Thermal stability of Type-II IR-fs modifications in SiO_2-Al_2O_3 samples

To investigate the thermal stability of the written *Type II* modifications, the samples were heat-treated following Δt = 30min step isochronal annealing up to extreme temperatures to observe the evolution in their birefringence. In this context, we have thus monitored retardance *R* (which is related to the birefringence through the length of the object) at room temperature after each annealing step. The retardance was normalized relative to its initial value at room T i.e.

$R_{norm}(\Delta t, T) = R(\Delta t, T) / R(0, 25°C)$. Figure 4 displays the normalized retardance $R_{norm}(\Delta t, T)$ as a function of temperature. Here we have chosen to perform annealing of samples written at 2.0 µJ/pulse, which corresponds to the stable range of *Type II* modifications (in term of writing kinetics) and can facilitate the reliable measurements of the retardance. The thermal stability of $70SiO_2$-$30Al_2O_3$ and $50SiO_2$-$50Al_2O_3$ samples were displayed in Figure 4 together with some additional samples namely SiO_2 (Suprasil® CG, T_a ~ 1150ºC), GeO_2-SiO_2 (4.6 mole% GeO_2; T_a ~ 1070ºC), and TiO_2-SiO_2 (ULE® 7972; 7 mole% TiO_2; T_a ~ 900ºC) and Alumino-borosilicate (Borofloat® 33; 81 mole% SiO_2, 13 mole% B_2O_3, 4 mole% Na_2O/K2O, 2 mole% Al_2O_3; T_a ~ 652ºC). The glass viscosity at 10^{13} dPa.s defines here the annealing point T_a values.

Some typical characteristics of normalized $R_{norm}(\Delta t, T)$ can be observed from the Figure 4, which typically reveals at least three different erasure mechanisms, which are hypothesized and discussed in the next section. However, they have different trends and contributions for each chemical composition. For both Borofloat® 33 and ULE®, the decay starts after the heat-treatment at 300°C. Typically R_{norm} decreases smoothly until 600°C corresponding to a 20% decay. Then the decline is accelerated for higher temperatures until the laser tracks are not visible under polarizing optical microscope. This corresponds to full erasure after a 30min thermal treatment at 650°C in Borofloat® 33 and 1025°C in ULE® glass. These values are quite close to their respective annealing points T_a: 652°C for Borofloat® 33 and 1000°C for ULE®. Note the temperatures mentioned here are dependent on the duration of the isochronal plateau and a longer duration will shift down this “full erasure” temperature, which is somehow at the image of the glass transition temperature range, and revealing in such a way that the erasure

mechanisms are in fact distributed [36].

On the contrary, the R_{norm} of both GeO_2-doped SiO_2 and $70SiO_2$-$30Al_2O_3$ exhibit a higher thermal stability and quite similar trends. The decay starts slowly at 650°C leading to 10% erasure at 850°C in $70SiO_2$-$30Al_2O_3$. Then it begins to fall within 850-1000°C range and there is a very sharp erasure process above 1000°C. Finally, the *Type II* modifications disappear completely at 1075°C in 4.6 mole% GeO_2-doped SiO_2 whereas it survives up to 1175°C in $70SiO_2$-$30Al_2O_3$. Note this value is much higher than the reported glass transition temperature of 865°C (determined from thermal expansion curve) for a 5 wt.% Eu_2O_3-doped $70SiO_2$-$30Al_2O_3$ glass melted within a gold image furnace and quenched using twin roller technique [37].

Finally, the highest temperature resistance can be found for $50SiO_2$-$50Al_2O_3$ pellet and SiO_2 glasses. They show similar trends, and initially the R_{norm} value increases significantly (typ. 30%) above 550°C to reach a maximum around 650°C in SiO_2 and 800°C in $50SiO_2$-$50Al_2O_3$. Then, similarly to the other samples, the R_{norm} value starts to decrease slowly for temperature higher than 800°C. In SiO_2, this feature is well correlated with the structural relaxation of densified silica formed within the nanograting regime [38] that as confirmed by the three and four-folds rings anneal out at the range of 700-900°C [39, 40]. Finally, the further increase in the isochronal annealing temperature above 1100°C leads to a very steep decrease of the birefringence, and the R_{norm} value drops to zero at about 1225°C in both SiO_2 and $50SiO_2$-$50Al_2O_3$ samples.

4. Discussion

Typically, $R_{norm}(\Delta t, T)$ decreases smoothly until 600°C corresponding to a 20% decay in

Borofloat® 33 and ULE® glasses whereas it does not change significant in SiO_2, GeO_2-SiO_2 and SiO_2-Al_2O_3 samples This indicates that the contribution of point defects centers (E', ODC, NBOHC) to the refractive index contrast of the nanogratings themselves remain quite limited. As another example waveguide formed in silica with an infrared femtosecond laser [41] showed photo-induced absorption peaks at 213nm and 260nm corresponding to the respective center defects E 'and NBOHC. However, most of these two defects were completely erased after annealing at 400°C, although the waveguide retained its guiding properties up to 900°C. As a result, color centers are unlikely to have played a strong role in the refractive index change [41]. Other results lead to the conclusion that the thermal stability of colored centers produced in borosilicate and silica glasses is not compatible with that of the change in refractive index [42]. Their contribution might explain the slight erasure of the measured retardance that is observed below 600°C especially in Borofloat® 33 and ULE® glasses but point defects cannot account for the observed "abnormal" increase of $R_{norm}(\Delta t, T)$ within 600-800°C in both SiO_2 and $50SiO_2$-$50Al_2O_3$ samples.

The next point is the abnormal behavior that is observed in the intermediate temperature range (600-800°C). Bricchi et al. [12] and Grobnic [16] have already observed such unusual behavior within *Type II* regime respectively in SiO_2 or in slightly Ge-doped optical fibers. We suggest this could be related to some changes in the strain field resulting in an additional stress-induced birefringence, but this hypothesis needs to be further investigated. More specifically, this hypothesis is based on the imposed sequence of step isochronal annealing associated with quenching to room temperature (after each step), which leads to the occurrence of an additional

stress field. This suggestion is supported by a recent publication of Y. Bellouard group [43]. In this recent work the authors report that while densified zones (so-called *Type I* regime) display a decrease of thermal expansion coefficient, nanogratings (*Type II* regime) show the opposite trend, with respect to the pristine material. In addition, the authors highlight that an annealing treatment of 10 hours at 300°C leads to a significant increase in the coefficient of expansion α within *Type II* affected zone. In the framework of our step isochronal annealing experiments, this should lead to an increase in the residual stresses and thus traditional stress-induced birefringence resulting in the observed increase of the overall retardance in the 600-800°C range.

The last point is the contribution to the birefringence that exhibits a very high thermal stability in SiO_2 and SiO_2-Al_2O_3. This part, typically above 1000°C in Figure 4, is attributed to the nanogratings internal structure itself (e.g. nanoporous silica in SiO_2). A first comment about Figure 4 is that the $50SiO_2$-$50Al_2O_3$ glass shows similar high temperature stability as the pure silica glass (Suprasil). However, Type II modifications erase at much lower temperature in $70SiO_2$-$30Al_2O_3$. We think that the problem here can mostly be seen in term of glass viscosity and glass structure relaxation. Indeed the limiting factor at high temperature is related the stability of the nanogratings and in particular the "nanopores" within the nanolayers themselves. In a simple view, the thermal stability of these nanopores can be described by the Rayeigh-Plesset equation as suggested by Rudenko et al. [44]. Assuming a constant surface tension with T, the key term of this equation is thus related to the glass viscosity η at high T. We suggested that the observe difference is mostly related to $\eta(T)$ that is likely higher for 50% Al_2O_3 than for 30 mol% Al_2O_3 in agreement with the reported values of glass melting T_m temperatures.

This could be attributed to an increase in Al coordination number (4, 5, and 6 fold-coordination [25, 26, 27, 28]), increasing glass network cross-linking density and bond strength. Note that additional measurements of the viscosity-tempertaure dependence would be nice to validate this view.

In addition based on nanogratings chemical changes observed in other multicomponent oxide glasses [9, 45, 46], we suggest that nanogratings in our aluminosilicate samples are made of Al_2O_3-rich phase that separates from the SiO_2-rich matrix phase. Backscattered electron image and element distribution maps shown in Figure 5 have confirmed this view. In particular the high thermal stability of laser-induced phase separation could be related to immiscibility, which has been reported for example in annealed solgel glasses containing >10 mol% Al_2O_3 and this immiscibility appears to increase with Al_2O_3 content as reported in [47, 48]. This immiscibility can be ascribed to the difference in the coordination number between oxygen ions bonded to Si and those bonded to Al. Indeed, when one Al^{3+} ions replaces Si^{4+} in a tetrahedral coordination site, one oxygen ion must ideally tri-bridge three tetrahedra to maintain the charge balance, leading to a densification of the glass network. This could lead to nanoscale separation between Si and Al-rich glassy phases. Based on literature the Al-rich phase would have a typical composition ranging from $3Al_2O_3$-$2SiO_2$ to $2Al_2O_3$-SiO_2 [49], for which the edge-shared AlO_6 octahedral chains are interconnected by AlO_4 or SiO_4 tetrahedra [50, 51]. Thus, immiscibility increases the structural connectivity in the "residual" Si-rich matrix. Furthermore, the separation of Al-rich phase likely favors the formation of Mullite nuclei [49], and it is not excluding that nanolayers are partly nano-crystallized in the form of Mullite, which would need further investigations.

5. Conclusion

Here, femtosecond laser direct writing in a set of binary SiO_2-Al_2O_3 glasses (no alkali) up to 50mol% Al_2O_3 was investigated. It was shown that *Type II* (i.e. nanogratings likely made of phase separation) can be photo-induced in these aluminosilicate glasses. Additionally, isochronal thermal annealing of $50SiO_2$-$50Al_2O_3$ shows a similar thermal stability of *Type II* modifications compared to SiO_2 and improved compared to Ge-doped SiO_2. Indeed, the normalized retardance shows no decrease in magnitude at temperatures lower than 1100°C. In contrast, in the GeO_2-SiO_2 glass, the retardance has already decreased by ~20% at 1000°C. More generally there is a trend indicating that *Type II* thermal erasure is strongly related to the glass transition temperature range as suggested by our comparison involving Borofloat® 33, ULE®, GeO_2-SiO_2 and SiO_2 glasses. These results suggest that inscription of such "*Type II fs-IR*" modifications in SiO_2-Al_2O_3 could be employed to make fiber Bragg gratings with high thermal stability. This opens the door toward the fabrication of a new range of "fiber Bragg gratings host fibres" (Al_2O_3 but also ZrO_2 or YAG-derivated [22]) suitable for ultra-high temperature operation.

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Conflict of interest

We declare that we do not have any commercial or associative interest that represents a conflict

of interest in connection with the work submitted.

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Figure, and Table Caption List

Figure 1: Density of the SiO_2-Al_2O_3 samples compared with the results extracted from the literature [30, 31, 32].

Figure 2: a) Raman spectra of SiO_2-Al_2O_3 samples + phase SiO_2 for sake of comparison b) Sample $80SiO_2$-$20Al_2O_3$;

c) Sample $70SiO_2$-$30Al_2O_3$; d) Sample $60SiO_2$-$40Al_2O_3$; e) Sample $50SiO_2$-$50Al_2O_3$.

Figure 3: Retardance *R* as a function of pulse energy for SiO_2-Al_2O_3 glasses (20%, 30%, 40%, and 50% mole of Al_2O_3). Blue arrow (right scale) indicates the decreasing content of Al_2O_3. Laser parameters are: 1030 nm, 300 fs, 100 kHz, 100 µm/s, NA=0.6, polarization parallel to the scanning direction i.e. Xx writing configuration. Inset: Retardance R as a function of pulse energy from 0.3 to 1 µJ. Arrows in inset indicate the advent of *Type II* modifications of pure silica (green), low Al_2O_3 glasses (red) and 50 SiO_2-50 Al_2O_3 glass (pink).

Figure 4: Normalized retardance $R_{norm}(\Delta t, T)$ as a function of temperature for Suprasil® CG (SiO_2), $70SiO_2$-$30Al_2O_3$, and $50SiO_2$-$50Al_2O_3$. GeO_2-SiO_2 (4.6 mole% GeO_2), ULE® (7 mole% TiO_2) and Borofloat® 33 glasses are also shown for sake of comparison. Laser conditions are: 1030 nm, 300 fs, 100 kHz, 100 µm/s, NA=0.6, Xx writing configuration i.e. laser polarization wad parallel to the writing direction.

Figure 5: Backscattered electron image and element distribution maps obtained by an electron probe micro analyzer. (EPMA) equipped with a Schottky field emission (FE) electron gun (JXA-8530F, JEOL). Glass: $50SiO_2$-$50Al_2O_3$. Laser conditions: 1030 nm, 1 ps, 1 µm/s and 2,5 µJ/pulse, Xy writing configuration.