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The influence of codoping on optical properties and glass connectivity of silica fiber preforms.

M.R. Cicconi^{1,2*}, W. Blanc³, D. de Ligny¹, D.R. Neuville²

1 – Department Werkstoffwissenschaften, Lehrstuhl für Glas und Keramik, Universität Erlangen-Nürnberg, Martensstrasse 5, D-91058 Erlangen, Germany

2 – Institut de Physique du Globe de Paris, 1, rue Jussieu, F- 75005 Paris, France

3 – Université Côte d'Azur, CNRS, Institut de Physique de Nice, UMR 7010, Parc Valrose, Nice, Cedex 2, France

Keywords: REE, Raman, Photoluminescence, glass structure, cations structural role

*Corresponding author: Dr. Maria Rita Cicconi

e-mail: maria.rita.cicconi@fau.de

phone: +49 9131 85-27567

Friedrich-Alexander-Universität Erlangen-Nürnberg, Martensstrasse 5, D-91058, Erlangen (Germany)

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Confirmation of Authorship

As corresponding author, I Maria Rita Cicconi, hereby confirm on behalf of all authors that this manuscript is original and unpublished, and is not being or having been submitted for publication to any other journal, and that all the authors have read the manuscript and agree with its submission to Ceramics International.

Dr. Maria Rita Cicconi

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M.R. Cicconi^{1,2*}, W. Blanc³, D. de Ligny¹, D.R. Neuville²

1 – Department Werkstoffwissenschaften, Lehrstuhl für Glas und Keramik, Universität Erlangen-Nürnberg, Martensstrasse 5, D-91058 Erlangen, Germany

2 – Institut de Physique du Globe de Paris, 1, rue Jussieu, F- 75005 Paris, France

3 – Université Côte d'Azur, CNRS, Institut de Physique de Nice, UMR 7010, Parc Valrose, Nice, Cedex 2, France

Abstract

REE-doped glasses have applications in many fields, and for example, Al and Ce codoping in SiO₂ fiber preforms is usually done to attenuate the optical degradation (photodarkening) of *e.g.* Yb and Tm doped silica optical fibers. In this study, we investigated a SiO₂ fiber preform having a gradual increase of the CeO₂ + Al₂O₃ content from 1.5 to 6.3 mol% and a CeO₂/Al₂O₃ molar ratio varying from 0.04 to 1.4. Raman and photoluminescence spectroscopies have been used to evaluate changes in the short- and medium-range order both in the cladding and in the core portions, and the evolution of the glass optical properties, respectively. The variations of the excitation and emission bands have been linked to modifications in the vibration bands of the Raman spectra, and in turn, the relationship between optical properties and glass connectivity has been carefully considered. Our results show that there is a strong positive linear relationship between the increase of the Raman bands in the high-frequency range and the red-shift of the excitation maxima. Therefore, the change of <Ce-O> distances and covalency character influences, in the same way, both the photoluminescence behavior of the core, and the connectivity of the amorphous network.

Keywords: REE, Raman, Photoluminescence, glass structure, cations structural role

Introduction

Since the 1960s, when the first commercially available silica-based optical fiber was developed, the applications of this material have greatly widened from telecommunication to sensors, to biomedical applications [1,2]. In a recent review, Ballato and coauthors [1] report an overview of the main characteristics of optical fibers, and about the development of new

materials and processes that will enable the design of advanced optical fibers suited to further uses. Above and beyond the development of new bulk chemistries or of composite materials (*e.g.* nanoparticles), researcher have first tried to enhance our understanding of SiO₂-based optical fibers by studying the occurrence of defects under various conditions, or by investigating the effect of doping on the formation or suppression of defects *e.g.* [3–5]. Many other studies were focused on the core composition, in order to avoid the clustering of Rare Earth Elements (REE), and enhance REE solubility, *e.g.* [6,7]. Al and/or P and/or Ce codoping, besides increasing REE solubility, has been recognized as a very effective way to mitigate Yb- or Tm-based fibers optical degradation (aka photodarkening) [8,9]. For instance, a combination of Al or P, or the codoping of Al, P and Ce is able to reduce the photodarkening of Si-based fibers. This mitigation, in Ce-codoped fibers have been attributed to the coexistence of cerium with two stable oxidation state (trivalent and tetravalent), and the occurrence of two processes: either Ce³⁺ that by trapping a hole may lose the 4*f* electron to form Ce⁴⁺ species or Ce⁴⁺ trapping an electron to form Ce³⁺ species [8–12]. Significantly fewer studies have been devoted to the understanding of how elements enter into the silica network, and how the different properties of the SiO₂ optical fibers are modified *e.g.* [6,13]. Because of the strong link between glass structure and properties, an understanding of the cations speciation would lead not only to the understanding of the mitigation of the photodarkening, but also to the understanding of the glass fibers properties on a broader scale. Indeed, this lack of knowledge hampers the development of new materials and applications. Consequently, we started an investigation of silica optical fiber preforms codoped with cerium and/or aluminum, focusing on the element structural role and glass connectivity. In a recent study, we assessed the role of aluminum in influencing Ce speciation (valence, coordination, bond character) in aluminosilicate glasses and Ce-doped or Ce/Al codoped silica fiber preforms, collapsed under different conditions [14]. The addition of aluminum prompts the stabilization of reduced Ce species, and induces variations of the Ce local environment, causing a blue shift of the photoluminescence emission band. Furthermore, it was established a Ce redox ratio limit ($\text{Ce}^{3+}/\text{Ce}_{\text{tot}} > 0.85 \pm 0.07$) that marks the clear occurrence of additional bands in the UV region. Based on the results, it was evaluated that the photodarkening attenuation is most probably due to the ability of trivalent Ce to trap hole centers. Since Ce redox ratio and bond covalency change depending on Al concentration/structural role, cerium photoluminescence properties were correlated by considering the glass bulk composition (in terms of optical basicity), and Al average coordination [14]. Despite the remarkable results obtained, codoping at the dilute scale may influence differently the response of the properties.

In the present study, by using a SiO₂ fiber preform having a gradual change of the Al₂O₃/CeO₂ molar ratio codoping, we correlate cerium photoluminescence properties to the variations occurring in the glass connectivity, and in turn on the codopant structural role (valence, bond distances, and coordination). Raman spectroscopy was used to identify changes in the short- and medium-range order of cladding and codoped cores, and these results were associated to the variations observed in the luminescence properties, and in turn, to the Ce species structural environment.

In addition to photodarkening attenuation, the luminescence properties of cerium (and REE in general) are quite important in many other fields, including phosphors, scintillators and generation of fiber gratings [15–19]. Hence, understanding the evolution of cerium (REE) valence and local environment and the effects on the host structure has a key role in the development of new materials and technical applications.

Experimental Methods

Preform was prepared by the conventional modified chemical vapor deposition (MCVD) technique. In order to obtain a gradual change of the codopant molar ratio along the preform, aluminum and cerium were incorporated with the gradual solution doping technique [20]. Two doping solutions were prepared: solution A contains 1 mol/l of AlCl₃:6H₂O; in solution B, CeCl₃:6H₂O and AlCl₃:6H₂O concentrations were 1 and 1 mol/l, respectively. The pure silica core porous layer was soaked first with solution A. Then, solution A is removed and the solution B is injected in the preform and slowly drained until the bottom (draining time: 20 minutes) to induce a change in cerium concentration. After drying of the solvent, the core layer was sintered down to a dense glass layer in O₂ flux. Then, the tube was collapsed under the same flux into a solid rod, referred to as preform, at an elevated temperature higher than 1800 °C.

Small disks (1 mm thickness) of the solid rod (9 mm diameter) have been cut at different positions along the preform. Each disk represents a different CeO₂/Al₂O₃ molar ratio in the codoped core, starting from the sample cut at 4 cm (CeO₂/Al₂O₃ = 0.04), up to the sample cut at 32 cm (CeO₂/Al₂O₃ = 1.4) as well as a variation of the CeO₂ + Al₂O₃ content from 1.5 to 6.3 mol% (see Table 1). The surrounding cladding is composed almost exclusively by SiO₂ (99.98 - 99.89 mol%), with small impurities of Al₂O₃. Disks are labeled according to the distance, and then to the increasing CeO₂/Al₂O₃ molar ratio. A schematic drawing (Figure 1) reports sample labels, and codopant molar ratios, whereas the core composition is reported in Table 1. Images and chemical analyses have been obtained by Energy dispersive X-ray (EDX) and scanning

electron microscope (SEM) analysis at the Institute de Physique du Globe de Paris (France). The SEM-EDX mapping allowed checking the homogeneous distribution of the dopants in the core portions. Photoluminescence spectra of each disk core have been collected with a spectrofluorometer equipped with double monochromators (Czerny-Turner) in excitation and emission (Fluorolog3, Horiba Jobin Yvon), using a 450 W Xe-lamp as the excitation source (excitation and emission spectral resolution ≤ 1.5 nm). Spectra have been normalized to the maximum intensity. Raman spectra have been collected both with laser excitations at 488 nm and 532 nm at the Department of Materials Science and Engineering (WW3, FAU Erlangen-Nürnberg, Germany). The Thermo Scientific Nicolet™ Almega Raman spectrometer (532nm) coupled with a high-quality Olympus visible microscope (objective 100x), and a high-resolution grating (2400 lines/mm) provides a very good spatial and frequency resolution, respectively of ~ 1 μm and 1 cm^{-1} . All spectra have been normalized to the total area, after removal of a polynomial background. Moreover, Raman spectra were also collected with a different excitation line (488nm) in order to check the presence of any contribution arising from luminescence centres.

Figure 1: Schematic drawing of the core portion of the SiO₂ preform (silica cladding not represented). Each bold number indicates the position where the disks have been cut (cm) along the preform, which also represents samples labeling. Darker color indicates a higher CeO₂ content. On top is reported the CeO₂/Al₂O₃ molar ratio in the codoped core.

Results and discussion

Ce³⁺, contrary to the oxidized Ce⁴⁺ species, is optically active and has fluorescence emission that originates from a transition from one (or more) of the *5d* levels, to the 2F ground state [7,21,22]. Trivalent cerium has a [Xe] 4f¹ ground electronic state, which is split into two sublevels (doublet ²F_{5/2} and ²F_{7/2}), separated by about 2200 cm^{-1} , and the excited levels *5d* lie about 40000 cm^{-1} above the ground state [22,23]. Despite the well-shielded inner electronic shell, the *f-d* transitions are strongly dependent on the chemical and structural environment. Hence, both Ce³⁺ excitation (Ex) and emission (Em) spectra might shift depending on Ce content, temperature, glass polymerization and connectivity [7,14,22,24,25]. For example, in a previous study on Na aluminosilicate glasses we observed that both Ce³⁺ excitation and emission bands shift depending on the Al/Na molar ratio, and drastically change for peraluminous compositions [14].

Figure 2 shows the photoluminescence spectra for all codoped core samples. Excitation spectra were collected at the maximum of the emission, and *vice versa*. By increasing Ce content, and in turn, the CeO₂/Al₂O₃ molar ratio, there is a gradual shift of both Ex and Em

bands toward lower frequencies. The excitation band is an asymmetric broad band that can be deconvoluted in three contributions, with the first two, respectively at $\sim 35000 \text{ cm}^{-1}$ ($\sim 285 \text{ nm}$; $G_{3\text{Ex}}$), and $\sim 32300 \text{ cm}^{-1}$ ($\sim 310 \text{ nm}$; $G_{2\text{Ex}}$), remaining nearly at the same frequency, despite the different compositions (Table 2). On the contrary, the third band is a very small feature centered at $\sim 30900 \text{ cm}^{-1}$ ($\sim 324 \text{ nm}$; $G_{1\text{Ex}}$) in Ce-poor preform (sample 4), which represents only 11% of the whole excitation band area (Figure 2). By increasing the CeO_2 content, this feature gradually shifts toward lower frequencies and increases its intensity, becoming the stronger contribution in sample 32 (representing $\sim 50\%$ of the whole excitation band). The Ce-rich preform (sample 32) has this contribution centered at $\sim 29600 \text{ cm}^{-1}$ ($\sim 339 \text{ nm}$) (Table 2).

The asymmetric luminescence is related to the allowed electronic transition $5d \rightarrow 4f$, and two sublevels of Ce^{3+} transitions from the $5d$ to $2F_{7/2}$ and $2F_{5/2}$ states are clearly discernible (Figure 2). The emission bands have been analyzed and deconvoluted in two Gaussians that are split by $\sim 2300 \text{ cm}^{-1}$ apart, in agreement with the L-S splitting of Ce^{3+} ions [22,23]. Sample 9 presents the minimum split of $\sim 2180 \text{ cm}^{-1}$ (see Table 2), and has the lowest Stokes shift ($\sim 5100 \text{ cm}^{-1}$). By increasing the Ce content, there is a general decrease of the Em asymmetry, and an increase of both Stokes shifts and ground level splitting. Additionally, the emission shows a red shift, with the Em maximum moving from 27400 cm^{-1} to 24000 cm^{-1} (~ 366 and 416 nm , respectively), by increasing Ce content (Figure 2). Band position and results from the bands' deconvolution of both excitation and emission spectra are reported in Table 2.

Figure 2: Normalised excitation (Ex) and emission (Em) spectra for the different samples, and deconvoluted Gaussian bands. By increasing the CeO_2 molar content both Ex and Em bands show a red shift, and an increase of Stokes shifts and of the ground level splitting. The luminescence properties of sample 4 are different. See text for details.

Absorption bands of Ce ions in glasses, attributed to the $4f_i \rightarrow 5d_i$ transition, have been reported in the wide-ranging region $28500 - 50000 \text{ cm}^{-1}$, depending on the bulk chemistry. In this region, two broad contributions related to charge transfer (CT) transition of Ce^{4+} overlap with the Ce^{3+} ions $4f_i \rightarrow 5d_i$ bands [7,22,26–28]. The position and the intensity of Ce^{4+} CT absorption bands change remarkably depending on glass (host) composition [24,29,30]. Ce^{3+} emission band as well may cover a wide range of frequencies, depending on glass composition, and in particular, the presence of aluminum causes a marked blue shift of the luminescence band in Ce-doped glasses (e.g. [7]), along with a change in the cerium average oxidation state [14]. Based on the previous investigations on the influence of bulk chemistry (optical basicity) and Al content on Ce redox state [14,31,32], we do not expect a very high amount of oxidized species in the preform cores. Because of the low basicity of the glass (very high amount of

SiO₂) and a CeO₂/Al₂O₃ molar ratio > 0.1, we estimate a Ce³⁺/Ce_{tot} ratio ≤ 0.8 for all glasses, except for the Ce-poor one (sample 4). The latter has > 98 mol% of SiO₂, and a CeO₂/Al₂O₃ ratio of 0.04, and an expected Ce³⁺/Ce_{tot} ratio ≥ 0.9. In addition, since the excitation bands of samples 32 to 9 are very similar to those previously reported for aluminosilicate and (Ce, Al) codoped silica fiber preforms [14], we are confident that they should have a similar average estimated Ce³⁺/Ce_{tot} ratio. In contrast, sample 4 excitation has the two strongest contributions at higher frequencies: In particular, the contribution at ~ 35700 cm⁻¹ (~ 280 nm), has a frequency compatible with the occurrence of band(s) related to charge transfer transitions. In peraluminous silicate glasses and (Ce, Al) codoped silica fibers this band has been observed to become predominant for high amount of reduced Ce species [14]. Since sample 4 has an expected Ce³⁺/Ce_{tot} ratio ≥ 0.9, following optical basicity considerations, we might associate as well the high-frequency band in the excitation signal to trapped hole centers, and in turn, to trivalent cerium that may lose the 4f electron: Ce³⁺ + h⁺ = Ce³⁺⁺ + e⁻.

In order to exclude any possible contribution from the silica glass, the photoluminescence signals of some of the cladding portions have been measured as well, by using the same experimental conditions used for the codoped cores. It was observed the occurrence of some bands in the outer silica claddings, with visible intensity variations across the portion analyzed. The broad contributions observed have maxima centered at ~ 27000 and ~ 22700 cm⁻¹ (excitation and emission maxima, respectively). These bands may be related to some impurities, and most likely to the occurrence of Si defects in the cladding. The most intense bands observed have been compared to the signals collected in the core (Figure 3). Photoluminescence spectra of the codoped cores have been collected at the maximum of the excitation or of the emission signals, indicated by the vertical black arrows in Figure 3. The signal intensity increases by increasing the Ce molar content, both in the excitation and in the emission. The strongest excitation signal observed in the different cladding (grey solid line) consists of a broad asymmetric band centred at ~ 370 nm and a minor contribution at ~ 300 nm (orange vertical arrow). Two emission spectra are reported for the cladding, one collected with an excitation wavelength of 300 nm (orange solid line, a position almost overlapping the maximum of sample 4) and one collected at 350 nm (grey solid line). Even if the emission of Ce-doped samples (9 to 32) overlaps the one of the cladding, the contribution that the cladding might provide is at least 6 times smaller and shifted at lower frequencies. The Ex signal of the cladding is partially overlapping the cores Ex bands, and may contribute to the signal only on the tail at lower frequencies, thus without influencing the three main contributions (Figure 2). Therefore, the influence of the silica cladding on Ce bands is very limited.

Figure 3: Photoluminescence spectra collected in the codoped cores are compared to the most intense signals observed in the cladding (grey solid lines). Black vertical arrows indicate the Ex and Em wavelength used to collect the signals in the codoped core samples. For the cladding, two emission bands are reported, one collected with an excitation wavelength (λ_{Em}) of 300 nm (close to the Ex maximum of sample 4 – orange vertical arrow), and the other one collected at 350 nm (grey vertical arrow).

In order to better understand the frequency shifts and the photoluminescence evolution depending on the Ce content, we have taken into account the possible occurrence of different cerium populations. Figure 4 shows the excitation spectra of samples 4 and 32 (black solid lines), and the three Gaussian functions used for signal deconvolution (dotted lines). Emission spectra have been collected for different excitation wavelengths (vertical arrows) for both samples. When the excitation increases from 280 to 335 nm (~ 35700 to ~ 29900 cm^{-1} , respectively) the emission of sample 32 barely shifts (~ 620 cm^{-1}), and the two Emission bands have a very similar shape. Therefore, it is reasonable to consider that we are exciting the same electronic level. On the contrary, in the Ce-poor glass (sample 4) the Em maximum drastically shifts (up to ~ 3900 cm^{-1}) for the same excitation wavelengths reported above. Furthermore, besides the change of the Em maximum depending on the excitation wavelength, there is also a variation of band symmetry (Figure 4). In the case of crystalline materials, it has been reported that the distortion of Ce^{3+} sites affects the crystal field splitting of the $5d$ configuration, and that the occurrence of vacancies might contribute in changing Ce charge distribution. Consequently, both would lead to red shift emission and changes in band symmetry [33–35]. In case of amorphous materials, stronger crystal field splitting would lower the energy level of the $5d$ configuration. Moreover, the increase of bond covalency character as well might affect the $5d$ orbital. Hence, both covalency and crystal field increases induce a red shift. Following these considerations, we might expect that the different emission signals of sample 4 derive from the distribution of Ce in different sites, and in turn, to the different chemical environments surrounding Ce^{3+} ions (*i.e.* $\langle \text{Ce-O} \rangle$ distances and bond covalency). In particular, we could consider that the shorter wavelength emitting site is less covalent in nature, whereas the longer wavelength emitting site is less ionic. The increase of Ce content induces a red shift of the excitation because the longer wavelength emitting site becomes predominant.

Because of the very low doping level of Ce in sample 4, it is required to consider the combination of other effects, such as the occurrence of i) trapped hole centers-related transitions, with Ce^{3++} ions having different energy states, and ii) the presence of part of the Ce^{3+} ions localized around point defects. The latter hypothesis might explain why the observed photoluminescence signals are so different.

Figure 4: (a) Normalized excitation spectra for samples 4 and 32 (black solid lines) and Gaussian bands used for signal deconvolution (dotted lines). The Emission spectra (colored solid lines) were collected at different excitation wavelengths marked by the vertical arrows.

The Raman spectra of silicate glasses can be divided in different major regions, and we will consider two of them: the high and the low-frequency regions. The low-wavenumber region from ~ 350 to 650 cm^{-1} , gives information on the T-O-T rocking, bending mode and ring distributions (see [36] and references therein). The high-wavenumber portion extending from ~ 860 to 1300 cm^{-1} (also referred as Q -range) contains stretching motions of tetrahedral cations T (*e.g.* T = Si^{4+} , Al^{3+}) [36]. The short-range order of silicate glasses can be described through the abundance of the Q^n species, where n is the number of bridging oxygen atoms (BO) and Q represents the four-fold coordinated cation (*i.e.* fully polymerized = Q^4). A fully polymerized SiO_2 glass network has only weak bands in the frequency range $\sim 950 - 1300 \text{ cm}^{-1}$, whereas it has a strong asymmetric band in the low-frequency region ($350 - 500 \text{ cm}^{-1}$). Moreover, highly polymerized glasses have two well-pronounced peaks, usually referred to as defect lines, D_1 ($\sim 490 \text{ cm}^{-1}$) and D_2 ($\sim 600 \text{ cm}^{-1}$), associated, respectively, with the breathing modes of $(\text{SiO})_4$ - and $(\text{SiO})_3$ -rings [37,38]. In general, by increasing the number of non-bridging oxygen (NBO), the main band in the low-frequency region decreases in intensity and shifts to higher wavenumbers, whilst the Q -range shifts toward lower frequencies and increases its intensity because other bands (related to other Q species, such as Q^3 , Q^2) appear in the $850\text{-}1300 \text{ cm}^{-1}$ portion ([36] and references therein). SiO_2 glass vibrations in the Q -range can be deconvoluted with three main contributions that represent different types of stretching vibration of the SiO_4 tetrahedra [39–42], and here we use the same terminology adopted in our previous work (see [14] and reference therein). Indeed, to describe the vibration of the SiO_4 tetrahedra in silica glass we use $Q^{4,I}$, and $Q^{4,II}$ species (at frequencies higher than 1100 cm^{-1}), and the T_2 stretching mode at $\sim 1050 \text{ cm}^{-1}$ (the latter related to two oxygen atoms that move closer to the central T atom, while the other two oxygens of TO_4 tetrahedra move away) [43].

The cladding portion of all samples is nearly completely composed of SiO_2 (Al_2O_3 impurities $\leq 0.13 \text{ mol\%}$), thus the Raman spectrum of a pure SiO_2 glass (QSIL®), collected with the same experimental conditions, has been used as reference (dashed line in Figure 5A). In the cladding portions analyzed, Raman spectra show some small variations compared to the reference SiO_2 , mainly on the intensity of the defect lines, and on the relative intensity of the bands in the Q -range. In SiO_2 -rich amorphous materials having less than $4 \text{ mol\% Al}_2\text{O}_3$, NMR

data indicates the occurrence of Al^{3+} mostly 4-fold coordinated (${}^{[4]}\text{Al}^{3+}$) with small contributions from distorted ${}^{[6]}\text{Al}^{3+}$ (6-fold coordinated) [44]. Al, as network former, mainly enters the more distorted $Q^{4,II}$ sites causing an intensity increase and a small negative shift of this band [14,45]. These considerations fit well with the signal collected in the cladding, and thus, we can relate the small variations observed among the different claddings to the inclusion of Al^{3+} in the tetrahedral sites, which induces different average $\langle\text{T-O}\rangle$ distances and small changes in the ring statistic (insets in Figure 5A). The mathematical average of the seven different claddings (hereafter called $\overline{\text{Clad}}$) was done in order to have a reference spectrum that takes into account the chemical variability found in the outer cladding. The $\overline{\text{Clad}}$ spectrum is reported in Figure 5B (solid black line) and compared to the spectra collected in the core areas.

In the core portions analyzed, the (Ce, Al) codoping induces much more visible changes in the glass network, both in the short-and medium-range order. At low frequencies, the main T-O-T band and the defect bands decrease in intensity and the latter become broader, compared to SiO_2 and $\overline{\text{Clad}}$ (Figure 5B). Moreover, there is a small shift ($\sim 2\text{-}3\text{ cm}^{-1}$) toward higher frequencies of the maximum of the low-frequency region. These changes indicate a lower quantity of smaller $(\text{SiO})_4$ - and $(\text{SiO})_3$ -rings with the increase of the doping, and the shift to higher wavenumbers of the Main Band suggests a small decrease of the ring intertetrahedral angles T-O-T. The strongest variations observed in the cores are in the $860\text{ - }1300\text{ cm}^{-1}$ frequency region, where new contributions systematically rises (between ~ 860 and 1050 cm^{-1}) by increasing the CeO_2 content (inset Figure 5B).

Figure 5: Raman spectra collected in the cladding (A), and in the codoped core (B) of the different disks. A) The Raman spectrum of pure SiO_2 glass (dashed black line) is compared to signals from the cladding portions .B) An average spectra of all claddings ($\overline{\text{Clad}}$, black solid line) is reported as reference and compared to the core signals. Insets provide a magnification of the D_2 defect line, and of the Q -range.

In order to evaluate the modifications occurring in the glass structure upon incorporation of Ce and Al oxides, and the influence of the different Ce contents, we studied in detail the high-frequency region by means of two approaches. The first one is a subtractive method where the signal of the cladding has been subtracted to the signal collected in the core, and the difference spectrum has been deconvoluted by mathematical functions. The second approach involves the more classical deconvolution of the whole high-frequency portion.

In order to separate the contributions to the Raman spectra due only to the Al/Ce codoping, the signal collected into the cladding has been subtracted to the one collected in the core region, for each sample. The resulting difference spectra highlights the distinct portions

where the vibrational bands are affected by the incorporation of Al_2O_3 and CeO_2 (Figure 6A). In the low-frequency region, the relative intensity of the defect lines changes depending on the amount of codoping. Furthermore, the shift of the main band at $\sim 434 \text{ cm}^{-1}$ is evident (Figure 6B). In the high-frequency portion, the contribution in the Q -range, $860\text{-}1050 \text{ cm}^{-1}$, strongly increases by increasing the Ce and Al content (Figure 6C). The modifications observed in the asymmetric band centred at $\sim 800 \text{ cm}^{-1}$ will not be discussed here, preferring to focus on changes in the Q -range. Figure 6D reports an example of the subtractive method used here. The cladding and core spectra collected for sample 32 are shown in Figure 6D, along with the difference spectrum obtained (symbols). The latter has been fitted, and four contributions can be distinguished for high codoping: two well defined bands that are related to the two main peaks (named P_2 and P_3), and two smaller side bands associated with the shoulder observed for each of the main peaks (P_1 and P_4 , respectively at lower and higher frequencies in Figure 6D). The difference spectrum of sample 4 presents a single contribution centred at $1120.2(2) \text{ cm}^{-1}$ (Figure 6E). The difference spectrum is well fit with a Lorentzian function with a full-width half-maximum $\text{FWHM} = 45.5(3) \text{ cm}^{-1}$ (the use of a Gaussian for this sample would imply the use of other two side bands, and we prefer to use the minimum number of bands to achieve a satisfactory fit). The difference spectrum obtained between pure SiO_2 and a reference glass having 98.8 mol% SiO_2 and 1.2mol% Al_2O_3 indicates a residual contribution with a nearly identical shape and position ($1120.9(10) \text{ cm}^{-1}$; unpublished data). Since sample 4 core has 1.5 mol% of Al_2O_3 , and only 0.05mol% of CeO_2 we can affirm with confidence that this contribution is only due to the Al^{3+} cations entering the tetrahedral sites. By increasing the Ce content to $\sim 1 \text{ mol\%}$, another main contribution appears, which represents 50% of the whole area. Indeed, sample 9 difference spectrum requires two Gaussian bands, named P_2 and P_3 , respectively centered at $988.5(2) \text{ cm}^{-1}$ and $1118.7(4) \text{ cm}^{-1}$ to fit the two dominant contributions (see Figure 6E). Additionally, a small shoulder is visible in the high-frequency portion (P_4 band). Further addition of CeO_2 induces the increase of the P_2 band, and the appearance of the shoulder at lower frequencies (P_1). Thus, these two bands (P_1+P_2) contribute to more than 60% of the total difference spectra (see Table 3).

The subtractive method here used allows underlining that the main variations in the Q -range are related to the appearance of the P_1 and P_2 contributions (respectively at ~ 917 and $\sim 985 \text{ cm}^{-1}$) and their rise by increasing the CeO_2 and Al_2O_3 content. Based on this data analysis, we propose the following assignment for the two main contributions: P_3 to Al-O stretching modes and P_2 to the presence of cerium ions.

Figure 6: A-C) Raman spectra collected in the core region and the subtracted spectra obtained by the difference between core and cladding of the same sample. Magnifications of the defect lines and of the Q -range are reported, respectively, in panel B and C. In A, a Cladding spectrum is reported as reference in black. D) Example of the subtractive method used. The Raman signal of each cladding has been subtracted to the one collected into the core region. The difference spectrum obtained has been deconvoluted with mathematical functions, and based on their positions we use the labels P_1 , P_2 , P_3 and P_4 . E) Stacked difference spectra and position of the mathematical functions for some of the samples.

The second method used to study the variations occurring in the Raman signals involves the more classical fit of the whole high-frequency region. The deconvolution has been done for all samples, both in the cladding and codoped core portions. As a reference, the analysis of the Raman signals of the SiO_2 glass and of the average cladding $\overline{\text{Clad}}$ was done as well in the range 950-1300 cm^{-1} . As reported above, pure SiO_2 glass weak bands in the Q -range can be deconvoluted with three main contributions related to Q species with four bridging oxygens. In the cladding portions, these three bands are assigned to $Q^{4,I}$, $Q^{4,II}$ and T_2 stretching modes (see Figure 7). A small negative frequency shifts of the $Q^{4,II}$ species is probably due to Al^{3+} cations entering the tetrahedral sites. The results of the fit of SiO_2 and of the average cladding ($\overline{\text{Clad}}$) Q -range Raman signals are reported in Table 4. In the codoped core, besides these three main contributions, other two bands appear in the lower part of the Q envelope ($< 1050 \text{ cm}^{-1}$), and increase in intensity by increasing the (Ce, Al) doping (see Figure 7). These two contributions below 1050 cm^{-1} are not related to electronic transitions (luminescence) because they have the same intensities and Raman shift position even when collected with a different excitation line. In order to give stable fits, the full-width half maximum (FWHM) of the Gaussian functions should be constrained below 60 cm^{-1} [46], thus, a further contribution between 1090 - 1110 cm^{-1} should be added. This supplementary band would take into account the occurrence of Q^3 species possibly due to both Ce ions and higher coordinated Al^{3+} species acting as network modifiers. However, due to pure fit stability, we decided to avoid including this further contribution. Therefore, only five Gaussian functions were used to deconvoluting core Raman spectra: the three related to TO_4 tetrahedra (hereafter called G_1 to G_3) and two additional contributions at lower frequencies (hereafter called G_4 and G_5).

By increasing the codoping, the bands G_1 to G_3 show a minor increased intensity compared to the cladding, and a shift of the component at $\sim 1150 \text{ cm}^{-1}$ (G_2). On the other hand, the two additional bands at lower frequencies (G_4 , G_5) strongly increase by increasing the cerium content. Thus, particular attention will be given to the frequency and intensity evolution of the bands at $\sim 925 \text{ cm}^{-1}$ (G_4) and $\sim 980 \text{ cm}^{-1}$ (G_5). This increase in G_4 and G_5 intensities leads the whole Q envelope to move toward lower frequencies. To represent this tendency we used the center of mass C (or centroid) of the analyzed range, calculated as (see Table 4):

$$C = \frac{(G^1 * A_{G^1}) + (G^2 * A_{G^2}) + (G^3 * A_{G^3}) + (G^4 * A_{G^4}) + (G^5 * A_{G^5})}{A_{tot}}$$

(where A_{tot} is the total area of the Q -range; see Table 4) resulting in $\sim -60 \text{ cm}^{-1}$ shift of the high-frequency band by increasing the Ce, Al codoping from 1.5 to 6.3 mol%. As reference, the center of mass of pure SiO_2 has been estimated at $\sim 1119.7 \text{ cm}^{-1}$, whereas the one related to the average cladding signal is $\sim 1116 \text{ cm}^{-1}$ (see Table 4). Sample 32 core has a very high amount of CeO_2 ($\sim 3.7 \text{ mol\%}$) and does not follow the trend observed for the other codoped cores. A possible explanation takes account of the clustering taking place because of the high Ce content.

This deconvolution method, as the subtractive one, highlights that the higher doping induces strong changes in the glass topology, and the rise of the bands in the lower frequency of the Q -range is associated to the higher content of Ce ions. Despite the increase of codopant amount in the core (and in turn, the decrease of silica), it seems that there is not a strong depolymerization since the Raman Main Band was only slightly affected. A decrease of Q^4 species is anyway restricted since Al^{3+} ions tend to enter preferentially the $Q^{4,II}$ site. The main role of cerium ions is then uncertain. It could be charge-compensator of Al^{3+} ions, and/or directly connected to the tetrahedral network. Then, the contributions G_4 and G_5 could be associated to a weakening of the stretching of the bond Si-O when Ce is nearby, by analogy of recent assignments done by Nesbitt et al. [47].

Figure 7: Details of the Raman spectra and deconvolution of the high-frequency regions of some of the samples investigated. In the codoped core, for CeO_2 contents $\geq 1 \text{ mol\%}$, two additional vibrations rise, respectively at $\sim 916 \text{ cm}^{-1}$ and $\sim 970 \text{ cm}^{-1}$. The chemical compositions of both cladding and core are reported for sake of clarity (as mol% oxide).

In order to assess and link structural changes to macroscopic properties in the codoped cores, we correlated the variations observed in the glass connectivity to the cerium photoluminescence properties, by taking into account the center of mass and the integrated areas of the deconvoluted bands in the Q -range, and the frequency position of Excitation and Emission signals.

By changing the codopant amount in the core portions, it is possible to observe a common trend for all the parameters taken into account, related both to the glass structure and to the optical properties. The decrease of the Q -range center of mass is very well correlated with the red shift of both Excitation and Emission maxima. Indeed, by increasing the codoping, the center of mass of the Q -range drop, similar to the drop observed in the photoluminescence maxima (Figure 8A). Furthermore, we can observe that sample 4 has the highest value of the

Q -range center of mass, which in turn corresponds to the highest values of Ex and Em. Sample 4 presents the most different photoluminescence properties and its C value is very close to the one calculated for the average cladding. A plausible explanation could be that a very low doping level of Ce^{3+} ions induces these species to associate not to the aluminosilicate network but to dangling point defects. Instead, when in higher amounts Ce ions tend to associate to the aluminosilicate network before reaching the limit of cerium clusters formation. This could be appreciated by looking at the increase of the integrated area of the bands in the lower portion of the Q -range (Figure 8B), and especially to the practically linear correlation between the sum of the integrated area of the P_1 and P_2 bands and the frequency of the excitation maxima (Adjusted Coefficient of Determination $R^2 = 99.92$):

$$y(x) = (-34.5 \pm 2.6) \cdot x + 32772 \pm 202$$

This positive relationship means that the change of $\langle \text{Ce-O} \rangle$ species covalency character influences, in the same way, both the photoluminescence behavior of the core, and the connectivity of the amorphous network.

The correlation observed between glass short-range order and optical properties endorses that Ce species are strongly connected to the glass network, and the small changes in the medium-range order supports the conclusion that Ce^{3+} ions partially act as charge-compensator to neighboring Al polyhedral (AlO_4^- , AlO_5^{3-}). Consequently, $\langle \text{Ce-O} \rangle$ connectivity changes depending on Al coordination/content, in agreement with previous experimental and molecular dynamic studies [14,48] and references therein.

Figure 8: Correlations between parameters from Raman data analysis and Photoluminescence studies of the codoped cores. A) the Raman center of mass C vs. the Emission (Em) and Excitation (Ex) maxima. B) the frequency Excitation maxima are related to the sum of the integrated areas of the contributions P_1 and P_2 , obtained following the subtractive method. The latter shows a nearly perfect linear correlation (Adjusted $R^2 = 99.92$).

Conclusions

We investigated a series of silica preforms having different codopant contents in the core, and variations of the $\text{CeO}_2/\text{Al}_2\text{O}_3$ molar ratios from 0.04 to 1.4. Raman spectroscopy has been used to evaluate changes in glass connectivity and modifications in the short- and medium-range order both in the cladding and in the core portions. Photoluminescence studies of the codoped cores allowed evaluating the evolution of the glass optical properties.

This work allowed determining a correlation between glass topology and optical properties and to better understand the short-range order variations depending on the silica fiber preform codopant ratios. In particular, we observed that:

- by increasing the $\text{CeO}_2\text{-Al}_2\text{O}_3$ content, there is a red shift of both excitation and emission spectra, and at the same time, a clear shift toward lower frequencies of the Raman Q -range;
- very low doping level of Ce^{3+} ions (0.05 mol%) probably induces these species to associate not to the tetrahedra network but to point defects;
- when in higher amounts Ce ions behave differently, and the positive correlation between glass short-range order and optical properties endorses that Ce species are strongly associated to the aluminosilicate glass network;
- the change of $\langle\text{Ce-O}\rangle$ bonding character influences, in the same way, both the photoluminescence behavior of the core, and the connectivity of the amorphous network.

The combined use of photoluminescence and Raman spectroscopy enabled discriminating the distinct influence of the two codopants depending on the $\text{CeO}_2\text{-Al}_2\text{O}_3$ content. These results will allow to better design the codopant ratios needed to avoid photodarkening of silica fiber, but also to shed some light on the mechanisms involved in the attenuation of this unwanted optical degradation. Besides application in optical fibers, the understanding of the relationship between macro and micro-scale properties is a necessary step in the way of developing material with *ad hoc* properties.

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Tables

Table 1: Chemical composition (as mol%) of the codoped core measured by SEM-EDS.

Sample position/label	SiO ₂	Al ₂ O ₃	CeO ₂	CeO ₂ /Al ₂ O ₃
32	93.7	2.6	3.71	1.44
29	94.9	2.4	2.67	1.11
24	95.7	2.1	2.16	1.02
19	96.1	2.0	1.87	0.93
14	96.5	1.9	1.58	0.84
9	97.4	1.6	1.03	0.63
4	98.5	1.5	0.05	0.04

Table 2: Results from the photoluminescence studies. Excitation (Ex) and emission (Em) maxima, and parameters obtained from the deconvolution of the bands with Gaussian (G*) functions are reported. SS: Stokes shifts. All values as cm⁻¹. The Ce/Al molar ratios are reported for sake of clarity.

Sample	Excitation				Emission			splitting ground levels	SS	Ce/Al
	Ex max	G _{1Ex}	G _{2Ex}	G _{3Ex}	Em max	G _{1Em}	G _{2Em}			
32	30024	29498	32160	35095	24017	24741	22370	2371	6007	1.44
29	30077	29524	32166	34969	24452	25234	22838	2396	5625	1.11
24	30235	29751	32503	35268	24724	25420	23112	2309	5511	1.02
19	30512	29721	32235	35003	24643	25363	23064	2299	5869	0.93
14	30390	29638	32060	34724	24709	25395	23084	2311	5680	0.84
9	30816	29985	32380	34931	25526	26324	24142	2181	5290	0.63
4	32969	30958	32531	34931	27360	28164	25734	2381	5609	0.04

Table 3: Results of the study of the difference Raman spectra reported in Figure 5E. Ce and Al oxides molar contents are reported for sake of clarity. The position of each peak, the total integrated area of the difference spectra, and the integrated area (as %) of the two contributions at lower frequencies (P₁ + P₂) are reported.

Sample	Al ₂ O ₃ cladding mol%	Al ₂ O ₃ core mol%	CeO ₂ core mol%	P ₁ (cm ⁻¹)	P ₂ (cm ⁻¹)	P ₃ (cm ⁻¹)	P ₄ (cm ⁻¹)	Tot Integrated area	% Int. Area P ₁ +P ₂
32	0.03	2.58	3.71	907.5	985.2	1121.8	1200.8	3.16	74.5
29	0.06	2.41	2.67	905.3	980.9	1115.8	1185.5	4.13	78.1
24	0.02	2.12	2.16	926.8	985.7	1116.5	1163.8	1.44	72.0
19	0.02	2.00	1.87	912.2	985.6	1116.2	1180.0	2.30	65.6
14	0.02	1.88	1.58	937.2	988.1	1116.0	1159.5	0.90	64.0
9	0.11	1.62	1.03		988.5	1118.7	1176.6	0.78	49.5
4	0.13	1.47	0.05			1120.2*		0.37	0.0

* Single Lorentzian function. See text for details

Table 4: Results from the Raman signal deconvolution of the Ce/Al codoped cores, in the high-frequency range. Each Gaussian function integrated area (A_G), and total integrated area (A_{tot}), along with the Center of mass (C) of the whole Q -range are reported. Data obtained for the average Cladding ($\overline{Clad}$) and reference SiO_2 are reported for comparison.

Sample	Ce/A l	G^1 (cm^{-1})	A_{G^1}	G^2 (cm^{-1})	A_{G^2}	G^3 (cm^{-1})	A_{G^3}	G^4 (cm^{-1})	A_{G^4}	G^5 (cm^{-1})	A_{G^5}	A_{tot} t	C (cm^{-1})
32	1.44	1051.5	42.3	1153.4	19.7	1211.1	13.3	915.8	8.0	972.0	16.7	3.9	1068.8
29	1.11	1054.5	40.9	1151.0	18.3	1210.9	10.4	919.7	11.2	978.5	19.2	5.1	1058.7
24	1.02	1054.0	46.0	1143.2	17.2	1203.1	16.6	924.1	9.9	979.3	10.3	4.1	1073.5
19	-	1055.1	45.6	1157.7	29.5	1218.5	6.6	917.7	6.1	972.5	12.3	4.7	1077.5
14	0.84	1060.6	51.9	1154.6	21.9	1211.0	11.3	919.5	5.5	977.4	9.3	3.6	1082.8
9	0.63	1061.5	52.6	1147.4	21.0	1206.2	17.4	927.3	5.2	978.3	3.7	3.9	1094.7
4	0.04	1058.0	45.7	1132.8	27.1	1203.5	27.2	-	-	-	-	3.0	1117.9
$\overline{Clad}^{\S}$	-	1059.9	55.8	1159.4	21.3	1212.9	23.0	-	-	-	-	2.7	1116.2
SiO_2	-	1059.4	53.8	1161.5	20.6	1212.9	25.6	-	-	-	-	2.1	1119.7

$\S$ Average signal of all cladding portions analyzed.

Figures Caption

Figure 1: Schematic drawing of the core portion of the SiO₂ preform (silica cladding not represented). Each bold number indicates the position where the disks have been cut (cm) along the preform, which also represents samples labeling. Darker color indicates a higher CeO₂ content. On top is reported the CeO₂/Al₂O₃ molar ratio in the codoped core.

Figure 2: Normalised excitation (Ex) and emission (Em) spectra for the different samples, and deconvoluted Gaussian bands. By increasing the CeO₂ molar content both Ex and Em bands show a red shift, and an increase of Stokes shifts and of the ground level splitting. The luminescence properties of sample 4 are different. See text for details.

Figure 3: Photoluminescence spectra collected in the codoped cores are compared to the most intense signals observed in the cladding (grey solid lines). Black vertical arrows indicate the Ex and Em wavelength used to collect the signals in the codoped core samples. For the cladding, two emission bands are reported, one collected with an excitation wavelength (λ_{Em}) of 300 nm (close to the Ex maximum of sample 4 – orange vertical arrow), and the other one collected at 350 nm (grey vertical arrow).

Figure 4: (a) Normalized excitation spectra for samples 4 and 32 (black solid lines) and Gaussian bands used for signal deconvolution (dotted lines). The Emission spectra (colored solid lines) were collected at different excitation wavelengths marked by the vertical arrows.

Figure 5: Raman spectra collected in the cladding (A), and in the codoped core (B) of the different disks. A) The Raman spectrum of pure SiO₂ glass (dashed black line) is compared to signals from the cladding portions .B) An average spectra of all claddings ($\overline{Clad}$, black solid line) is reported as reference and compared to the core signals. Insets provide a magnification of the D_2 defect line, and of the Q -range.

Figure 6: A-C) Raman spectra collected in the core region and the subtracted spectra obtained by the difference between core and cladding of the same sample. Magnifications of the defect lines and of the Q -range are reported, respectively, in panel B and C. In A, a Cladding spectrum is reported as reference in black. D) Example of the subtractive method used. The Raman signal of each cladding has been subtracted to the one collected into the core region. The difference spectrum obtained has been deconvoluted with mathematical functions, and

based on their positions we use the labels P₁, P₂, P₃ and P₄. E) Stacked difference spectra and position of the mathematical functions for some of the samples.

Figure 7: Details of the Raman spectra and deconvolution of the high-frequency regions of some of the samples investigated. In the codoped core, for CeO₂ contents ≥ 1 mol%, two additional vibrations rise, respectively at ~ 916 cm⁻¹ and ~ 970 cm⁻¹. The chemical compositions of both cladding and core are reported for sake of clarity (as mol% oxide).

Figure 8: Correlations between parameters from Raman data analysis and Photoluminescence studies of the codoped cores. A) the Raman center of mass C vs. the Emission (Em) and Excitation (Ex) maxima. B) the frequency Excitation maxima are related to the sum of the integrated areas of the contributions P₁ and P₂, obtained following the subtractive method. The latter shows a nearly perfect linear correlation (Adjusted R² = 99.92).

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Figure 2

Figure 3

Figure 4

Figure 5

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Figure 7

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