



Cerium/aluminum correlation in aluminosilicate glasses and optical silica fiber preforms



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ABSTRACT

Optical, structural properties and redox were studied for Ce-bearing silicate and aluminosilicate glasses and Ce-activated silica (SiO₂) fiber preforms, by X-ray Absorption, Raman and Photoluminescence Spectroscopy.

The introduction of Al₂O₃ in Ce-bearing silicate glass strongly stabilizes reduced species in agreement with the optical basicity concept and additionally induces modifications in the Ce³⁺ surrounding. In Al-free silica preforms, depending on the collapsing conditions, the Ce³⁺/ΣCe ratio has the highest variability (Ce³⁺/ΣCe = 0.7–0.85 ± 0.07), whereas in Al-bearing fiber preforms, Al codoping induces a strong stabilization of Ce³⁺ species, despite the collapsing atmosphere.

Al presence induces modifications on Ce local environment, and thus variations of the distance between Ce³⁺ and its ligands, and/or to variations of the covalency of the bonds. Absorption bands in the UV region, ascribed to Charge-transfer (CT) bands, in our samples, occur only for low amount of Ce⁴⁺ (Ce³⁺/ΣCe > 0.85 ± 0.07). Indeed, in silicate and aluminosilicate glasses the higher amount of Ce⁴⁺ does not give rise to UV absorption bands ascribed to CT processes, whereas, in fiber preforms, Ce³⁺ species can induce the trapping of hole centers, and enhance the photoluminescence efficiency. More generally, these results enhance our understanding of REE structural and chemical roles in amorphous materials and increase our knowledge for technical applications.

1. Introduction

Rare-earth elements (REE)-bearing materials are economically and technologically important and they have a strong impact in many fields, including geo- and materials sciences and, especially in the development of high-power laser, solid-state devices, electronic and optical devices, as well as in the ceramic industries [1–5]. To improve these technological applications, it is necessary to increase our understanding of REE structural and chemical roles in amorphous materials. Among REE, Ce³⁺ has attracted much attention thanks its 5*d* → 4*f* emission [6], whereas the presence of Ce⁴⁺ is an issue for luminescent applications because this ion does not emit light. Indeed, cerium in glasses may be present both in tri- and tetravalent states, and the proportion between them, as for many other multivalent elements, depends on several factors, including cerium content, oxidizing–reducing conditions during glass synthesis, temperature, and glass bulk chemistry [4,7–10].

Optical absorption and luminescence spectroscopy are widely used

lab techniques to investigate REE- and transition elements-bearing glasses, and have been extensively employed to study Ce-doped glasses [7,8,10–12]. However, the quantification of Ce redox state in glasses by these spectroscopic techniques is very controversial. Indeed, both Ce species present absorption in the UV-region with an overlap of broad bands, which increases or decreases depending on many factors. Ce⁴⁺ does not show luminescence due to closed electronic shell ([Xe] 4*f*⁰), whereas trivalent cerium ([Xe] 4*f*¹) is optically active and has fluorescence emission that originates from a transition from one (or more) of the 5*d* levels, to the 2*F* ground state [7,13,14]. Ce³⁺ may lose the 4*f* electron to form Ce⁴⁺ by direct ionization or by trapping a hole, Ce³⁺ + h⁺ → Ce⁴⁺, and Ce⁴⁺ may trap an electron, Ce⁴⁺ + e⁻ → Ce³⁺, and the charge-transfer (CT) gives rise to a broad absorption band in the UV region (around 4.8 eV).

Recently, in Yb or Tm-based glass fibers, the co-doping of Al and Ce has been studied, for different host compositions, as an effective way to reduce photodarkening (PD) [15,16]. Indeed, PD is mitigated by co-doping with P or Al, or a combination of Al, P, and Ce [15,17,18]. Shao

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and coauthors [16] demonstrated that trapped electron centers and trapped hole centers were inhibited by Ce doping, and they suggested that the coexistence of the redox couple $\text{Ce}^{3+}/\text{Ce}^{4+}$ in glasses provides means for trapping both hole- and electron-related color centers. Jet-schke et al. [17] have shown that a small portion of Ce^{3+} ions are temporarily oxidized to Ce^{4+} by trapping released holes in the pump process, which ensures that the hole related color centers are suppressed. The ability to trap electrons/holes has been the most used explanation to explain the photodarkening mitigation in Yb-activated fibers [15–17], and recently, also in Tm-based fibers [18]. However, the role of Ce, and the redox ratios that favor the suppression of photodarkening have not been clarified. To gain insight into the favored mechanisms, it is necessary to accurately determine the $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio, and provide insights into the codopant(s) structural role, and on the effect of manufacturing conditions (e.g. collapsing atmosphere). The study of the element speciation in fiber preforms is particularly complex due to the limited dimension of the doped core, and to the low concentration of the dopants.

In order to better quantify the variations occurring in Ce-activated silica fiber preforms codoped with Al, in this study, glasses in the ternary $\text{SiO}_2\text{-Na}_2\text{O-Al}_2\text{O}_3$ system, with constant molar content of SiO_2 (~66.6 mol%) and with Al/(Al + Na) ratios varying from 0 to 0.54, have been used to study Ce structural role and redox, depending on Al presence and content. Data obtained from X-ray absorption spectroscopy (XAS) at the Ce L_{III} -edge, photoluminescence (PL), and Raman spectroscopy are presented. The sensibility and the resolution achievable with these spectroscopy techniques allowed obtaining reproducible results. Discussions of the outcomes are based on the quantified $\text{Ce}^{3+}/\Sigma\text{Ce}$ ratios, on the structural variations occurring in the glass network, and on the chemistry (optical basicity) of the glasses.

2. Experimental methods

The starting material has been prepared from dried pure Al_2O_3 , SiO_2 and Na_2CO_3 in stoichiometric proportions. The mixtures were homogenized in an agate mortar and melted twice in air, at 1400 °C, in order to obtain a homogeneous bubble-free glass. The bulk glasses obtained have compositions corresponding to aluminosilicate glasses in the $\text{SiO}_2\text{-Na}_2\text{O-Al}_2\text{O}_3$ system, with constant SiO_2 molar content (~66.6 mol%) and Al/Na ratios from 0.0 to 1.17. Ce-free glasses are named NA66.y, with $y = \text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O} = 100 - (66 + y)$. 10 g of each was finely ground, doped with 0.36 mol% CeO_2 , then remelted in air. Ce-bearing aluminosilicate glasses are labeled NAC66.y. The glasses obtained were checked by Raman and optical microscope to ensure homogeneity and absence of crystalline phases. Glass compositions and synthesis conditions are listed in Table 1.

Ce-activated silica (SiO_2) preforms were fabricated by the conventional modified chemical vapor deposition (MCVD) technique [19], and the so-called solution doping technique [20] was applied to incorporate aluminum and REE (cerium and thulium): the pure silica core porous layer was soaked with a solution of water containing chlorides salts of desired concentrations to prepare Ce, Ce-Al and Ce-Tm-Al doped samples. $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{TmCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ concentrations were 0.08, 0.02 and 0.7 mol/l, respectively. After drying of the solvent, the core layer was sintered down to a dense glass layer in O_2 , He or N_2 flux (except for the first pass which was always made under O_2 atmosphere). 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. Ce-activated silica preforms are labeled depending on the dopant/codopant, and on the flux during collapsing (He, O_2 , N_2 , Table 1). Sections of the preforms were cut and polished to optical quality. The preform discs obtained are ~0.9 mm in diameter, with the doped cores in the range of 280–400 μm .

X-ray absorption spectroscopy (XAS) experiments at the Ce L_{III} -edge (5723 eV) were carried out at BM25A beamline (ESRF, France). Ce model compounds (Ce^{4+}O_2 and Ce^{3+} -pyrochlore) and powdered

glasses were prepared by smearing finely ground powder on a Kapton tape. The flat sample surface was placed 45° with respect incoming beam and detector. Ce spectra were acquired in fluorescence mode by using a Si 13-elements detector and the energy was calibrated by defining the first derivative peak of a metallic Cr reference foil (5989 eV) acquired, simultaneously to the samples, in transmission mode. A Si (111) crystal monochromator was used, providing an energy resolution of ~0.8 eV at 5.8 keV, but considering the finite core-hole width of Ce at the L_{III} -edge, the resulting convoluted energy resolution is around 4 eV. A few experiments, in order to describe the evolution of Ce XAS spectra depending on the redox, have been done at high temperatures (HT) via Dispersive-XAS (D-XAS). Spectra for a Na-disilicate glass (Na66.00) containing 1.8 mol% CeO_2 were acquired in transmission mode at ODE beamline (SOLEIL, France). ODE is an energy-dispersive beamline with a Si(111) bent polychromator crystal at the focal point of which the sample is placed. The beam size was ~30 × 30 μm (FWHM). Due to the fixed energy–position correlation in the diffracted energy band, a complete spectrum was obtained from measurements of the intensity distribution on a position-sensitive detector. For high-temperatures (HT) experiments the samples were loaded as microgram-powders in a 0.5 mm hole of the Pt-Ir10% heating wire of the micro-furnace previously used for in situ high-temperature studies of Eu and Fe in silicate glasses i.e. [21–23]. Because a spectrum is recorded in the order of milliseconds, this beamline is particularly well suited to investigate reduction/oxidation kinetics processes at HT. The closed micro-furnace allows also the use of different gases (Ar/H_2 , Ar, O_2) to obtain different redox environments. For all XAS spectra background was subtracted using a linear function and then normalised for atomic absorption on the average absorption coefficient of the spectral region from 5750 to 5780 eV. The threshold energy was taken as the first maximum of the first derivative of the spectra, whereas the main peak positions were obtained by calculating the second derivative of the spectra.

Analyses of optical emission and excitation behaviour (PL) were performed with a spectrofluorometer equipped with double monochromators (Czerny-Turner) in excitation and emission (Fluorolog3, Horiba Jobin Yvon), using a 450 W Xe-lamp as excitation source. All measurements were carried out with excitation and emission spectral resolution of 1 nm. The photoluminescence measurements for aluminosilicate glasses were carried out on polished glasses with dimension of ~0.8–1.0 cm, whereas for silica preforms discs the cladding portion was masked by a black tape (matt black foil), in order to collect the signal almost exclusively from the doped core. Several measurements were repeated in order to ensure the reproducibility.

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). The Thermo Scientific Nicolet™ Alpha Raman spectrometer coupled with a high-quality Olympus visible microscope, and a high resolution grating (2400 lines/mm) provided a very good spatial and frequency resolution, respectively of ~1 μm and 1 cm^{-1} .

Aluminosilicate glasses and fiber preforms were analyzed by scanning electron microscopy (SEM) (Merlin™, Carl Zeiss AG, Germany). The chemical composition was evaluated with an energy dispersive X-ray spectrometer (EDS) (X-Max^N, Oxford Instruments plc., UK).

3. Results and discussion

3.1. XAS and D-XAS

Ce crystalline compounds used as trivalent and tetravalent Ce references are, respectively, Ce-pyrochlore and CeO_2 [24]. As shown in Fig. 1a trivalent and tetravalent Ce compounds display strong differences in the Ce L_{III} -edge X-ray absorption near-edge structure (XANES) region. The Ce^{3+} -pyrochlore has a relatively narrow white-line at ~5727 eV arising from the transition (vertical dashed line a), whereas

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