Raman investigation of germanium- and phosphorus-doping effects on the structure of sol–gel silica-based optical fiber preforms

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ABSTRACT

This works reports the structural investigation of homogeneously doped sol–gel-derived silica optical fiber preforms. Crack-free germanosilicate (2.7 wt% Ge) and phosphosilicate (2.5 wt% P) glasses, suitable for optical fiber fabrication, have been prepared using the polymeric sol–gel route combined with the sol-doping technique. Space homogeneity of the doping oxide (GeO_2 or P_2O_5) in the cylindrical preforms has been checked by chemical analysis. The structure of these glasses have been studied using Raman spectroscopy and compared to pure silica glasses. It is shown that phosphorus has a much more sensitive effect on the glassy structure than germanium, both at small and medium scales. Indeed, in the low-wavenumber region (7–100 cm^{-1}), the phosphorus-doping was found to affect the intensity of the boson peak, suggesting an enhancement of heterogeneity at the nanometer scale. At a shorter scale, both germanium- and phosphorus-doping were found to reduce the number of three- and four-membered rings in the silica glass network.

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1. Introduction

Germanosilicate and phosphosilicate glasses, composed of two network-former oxides, have acquired increasing interest and active research because of their potential applications in optical fiber technologies. While Ge-doped silica glass is the basic material for conventional optical fibers [1], phosphosilicate fibers are used in stimulated Raman lasers and amplifiers [2]. Moreover, co-doping with P_2O_5 makes it possible to increase the rare-earth content of silica glass by preventing rare-earth clustering and thus reducing light emission quenching. Thereby, rare-earth doping of the phosphosilicate core allows the fabrication of highly efficient optical amplifiers and laser sources [3,4]. In addition, the photosensitivity of both germanosilicate and phosphosilicate glasses to UV irradiation allows to write Bragg gratings in the corresponding fibers [5,6]. Up to now, the vapor based techniques, such as Modified Chemical Vapor Deposition (MCVD), are the widely used techniques to prepare such glass preforms. However, sol–gel process has become a new promising route that offers several advantages, such as simple implementation, low cost, high purity and chemical homogeneity of the products, besides much lower sintering temperatures [7]. This low temperature technique is particularly interesting in the case of phosphosilicate glass because melt forming of high phosphorus oxide (P_2O_5) content glasses would be difficult, owing to the strong volatility of P_2O_5 at high temperature [8]. However, preparation of crack-free bulk glasses containing this oxide remains difficult by the sol–gel process: attempts to synthesize bulk and dense phosphosilicate glasses generally led to powders or non-dehydrated small glass pieces, non-suitable for optical fiber fabrication [9,10]. Recently, we have demonstrated that polymeric sol–gel route is a versatile and reliable method to produce pure or rare-earth doped silica glasses with high purity and quality [11]. Moreover, the obtained doped silica rods overcome the dimension limitation inherent to conventional glass fabrication methods, since their large diameters are suitable for Large Mode Area solid-core photonic bandgap fibers fabrication. These glasses have been successfully integrated inside microstructured optical fibers that may be used as amplifiers or laser media [12,13].

This paper reports the preliminary results of an effort undertaken to prepare silica-based multi-component rod glasses using the polymeric sol–gel route. In this work, germanosilicate and phosphosilicate glasses suitable for optical fiber fabrication were synthesized and studied. The aim of this work is to analyze the

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effects of Ge and P doping on the structure of the silica glass network. The comparison is also focused on the influence of the densification atmosphere, since a sol–gel dehydration process (under chlorine atmosphere) is necessary to obtain low attenuation microstructured fibers (<5 dB/km). A particular attention has been paid to the low-frequency range of Raman spectra and the non-continuous model proposed by Duval et al. [14] has been used to compare at the nanometer scale, also called intermediate scale order in glasses, the structural organization of doped and pure silica glasses.

2. Experimental

Porous monolithic germanosilicate and phosphosilicate rods were prepared using a "particulate" polymeric sol–gel route under base catalysis conditions (by adding ammonium hydroxide). Tetraethylorthosilicate (TEOS), germanium isopropoxide and triethylphosphate were used as silica, germania and phosphorus precursors, respectively, with molar ratios Ge/Si = 0.02 and P/Si = 0.3. The obtained xerogels were dehydrated under chlorine/oxygen atmosphere to reduce OH content, before densification at 1200–1300 °C under helium atmosphere, leading to dense transparent germanosilicate or phosphosilicate glass rods. The procedure is similar to that used to prepare pure silica glass rods and is described elsewhere [15]. To study the influence of OH groups on the glass structure, other doped xerogels have been densified under air atmosphere without dehydration at 900 °C. Pure silica glasses have also been prepared by dehydration-densification or densification under air for comparison. Hence, six kinds of glass samples were obtained, namely pure silica, germanosilicate and phosphosilicate, labeled Si, Si–Ge, Si–P, for dehydrated samples and Si-Air, Si–P-Air, Si-Ge-Air for non-dehydrated samples, respectively.

Raman spectra were recorded at room temperature using a Jobin-Yvon T64000 spectrometer coupled with a nitrogen-cooled charge-coupled device camera. The spectral range 10–1400 cm^{-1} was investigated with a typical precision of 0.5 cm^{-1}. Samples were excited by the 514.5 nm line of an Ar$^+$ laser.

Electron Probe Micro-Analysis (EPMA) was performed using a CAMECA SX 100 microprobe.

3. Results and discussion

3.1. EPMA analysis

The average Ge and P percentages in the glass samples and their radial distribution were measured by EPMA (Fig. 1). The average doping levels of Ge and P were 2.7 and 2.5 wt%, respectively.

Regarding the amount of Ge and P in the starting sol, one can note the conservation of Ge and a loss of P inside the doped glasses. This could be explained by the high reactivity of germanium isopropoxide with TEOS, and the lower reactivity of triethylphosphate with TEOS. However, across both glass samples, the doping distribution profiles are shown almost uniform.

The obtained glass rods have diameters of about 5 mm and 8 mm for Ge-doped and P-doped samples, respectively. Apart from the homogeneity of the doping, they present no cracks and exhibit a very good transparency, as shown in the insets of Fig. 1. Moreover, the obtained sol–gel glasses show light scattering level comparable to the one arising from the Suprasil glass, as previously reported [10].

3.2. Raman analysis

Fig. 2 exhibits the Raman spectra of two pure sol–gel silica samples, one being dehydrated under chlorine atmosphere (Si) and another being simply densified in air (Si-Air). The spectrum of Suprasil F300 (Heraeus), a silica glass with a very low OH content, is also presented for comparison. All spectra have been normalized by their prevailing band around 430 cm^{-1}.

The three spectra are very similar, all presenting the typical bands associated to the vibrations enumerated in Table 1.

The low-frequency band, lying between 5 and 140 cm^{-1} and called the "boson peak", is a universal characteristic of amorphous dense transparent materials (essentially glasses and a few polymers). In their non-continuous model, Duval et al. [13] have assigned the Boson peak to localized acoustic vibrations in cohesive domains at the nanometer scale. The size distribution of the corresponding cohesive domains in our glasses will be evaluated and discussed in the end of this section.

The main Raman band located between 150 and 550 cm^{-1} is generally associated with a network Si–O–Si vibration, involving a motion of the oxygen atom along the line bisecting the Si–O–Si angle θ. The broad distribution of the values taken by θ within the structure causes the large width of this band around its central wavenumber 435 cm^{-1}. In the sample densified in air atmosphere (Si-Air), this band is slightly broadened and shifted toward low frequencies as compared to samples with low OH concentration. This sample thus presents higher Si–O–Si angles in its densified structure, which is indicative of a system less strained than in dehydrated samples. It can be noted that, qualitatively, the same conclusions can be drawn about the dehydrated samples Si–Ge and Si–P.

The sharp bands D$_1$ and D$_2$ at ~492 and ~604 cm^{-1}, known as defect modes, have been associated to symmetric breathing
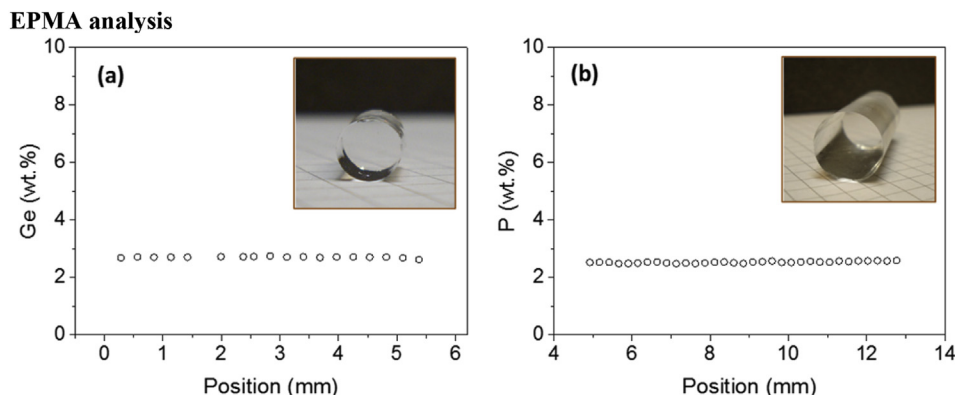

Fig. 1. Distribution of (a) Ge within Si–Ge and (b) P within Si–P glasses section. Insets: the binary glass rod images.