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Effects of ionizing radiations on the optical properties of ionic copper-activated sol-gel silica glasses

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Studying the impact of radiations on doped silica glasses is essential for several technological applications. Herein, bulk silica glasses, activated with various concentrations of luminescent monovalent copper (Cu^+), have been prepared using the sol-gel technique. Thereafter, these glasses were subjected to X- or γ−rays irradiation at 1 MGy(SiO_2) accumulated dose. The effect of these ionizing radiations on the optical properties of these glasses, as a function of the Cu-doping content, were investigated using optical absorption and photoluminescence spectroscopies. Before any irradiation, the glass with the lowest copper concentration exhibits blue and green luminescence bands under UV excitation, suggesting that Cu^+ ions occupy both cubic and tetragonal symmetry sites. However, at higher Cu-doping level, only the green emission band exists. Moreover, we showed that the hydroxyl content decreases with increasing copper doping concentration. Both X and γ radiation exposures induced visible absorption due to HC_1 color centers in the highly Cu-doped glasses. In the case of the lower Cu-doped glass, the Cu^+ sites with a cubic symmetry are transformed into sites with tetragonal symmetry.

1. Introduction

Nowadays, monovalent copper-activated silica glasses are the subject of intensive investigations as promising material for radiation dosimetry. Indeed, they exhibit a strong visible luminescence under UV or X irradiation [1,2]. Moreover, these vitreous materials can be drawn into optical fibers. This renders possible their integration in optical fiber-based dosimeters, which are considered as innovative solutions when a spatial resolution is required, like in conformational radiotherapy [3,4] or when a remote measurement is compulsory, as it is the case in certain kinds of space applications [5], in high energy physics [6], in Megajoule-class lasers [7] or in civil nuclear industry [8]. Compared with other information transmission channels, the use of optical fiber offers several advantages making them more attractive: electromagnetic immunity, broad pass-band, small size and low information loss [9]. Recently, using the sol-gel method, we have successfully prepared ionic copper doped silica glasses that have been used as sensitive materials in radioluminescence (RL)-based fibered dosimeters [10]. Besides, we have investigated the optical stimulation luminescence (OSL) signal of such a materials, which is non-negligible after irradiation under X-ray or proton beam. Those preliminary results justify our interest in sol-gel Cu-doped silica for applications such as dosimetry in radiotherapy or protontherapy [10,11]. Moreover, even if a darkening of the glass appears at X-ray dose level of about 50 kGy (SiO_2), due to the creation of defect centers, the material remains X-sensitive after exposure to several kGy. The effect of X- or γ-radiation on multicomponent glasses has been widely studied [12–14]. The ionizing radiation produces electron-hole pairs, which for some of them become individually trapped at various defect sites in the glass structure. This induces visible coloration of the irradiated glasses. It has been shown that nonbridging oxygen hole centers (NBOHCs) were mainly responsible for the irradiation-induced visible absorptions of silicate glasses [15]. The induced deep color could be stable for months, but can be almost thermally bleached by heat-treatment. The recent advent of new glass compositions has revived studies of the radiation-induced changes in the optical properties of glasses for radiation monitoring and dosimetry applications [16]. Nevertheless, the impact of ionizing radiations on copper-doped glasses was hardly investigated.

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Recently, the effect of γ-radiation on structural and optical absorption properties of Cu^{2+}-doped multicomponent glasses, prepared using the melt-quenching method, has been reported [17]. Yet, this kind of glass does not present an immediate interest for radiation dosimetry, as Cu^{2+} ion is optically inactive under UV, X or γ-excitation when compared to Cu^{+} ion. In this paper, we report on the effects of X- or γ-ray irradiation on the optical properties of the active Cu^{+}-doped silica glasses fabricated using the sol-gel technique. The main aim of this paper is to study the impact of such ionizing radiation on the optical properties of the doped silica glasses as a function of copper concentration.

2. Experimental

2.1. Glass syntheses

All reactants and solvents were purchased from Aldrich Chemical Company. They were used as-received without further purifications. Porous monolithic silica rods were prepared from tetraethylorthosilicate (TEOS), using the polymeric sol-gel route, as already described previously [18]. These nanoporous monoliths, whose pores are interconnected, were post-doped by solution doping method. To adjust the copper concentration inside the final glass, several alcoholic (Ethanol) solutions with different copper salt (copper (II) hexafluoroacetylacetonate hydrate) concentrations were used. Subsequently, the samples were taken out from the soaking solutions and dried at 50 °C for 24 h in order to remove the solvent, before densification under helium atmosphere at 1200 °C for 2 h to obtain dense doped silica glasses [19]. For comparison, non-doped silica glasses were also prepared in the same conditions. Hence, four sets of glass samples were obtained and hereafter labeled: SiO_2, SiO_2Cu50, SiO_2Cu250, and SiO_2Cu500 for 0, 50, 250 and 500 at-ppm copper contents, respectively. The copper concentration in the glass sample SiO_2Cu250 was determined by Electron Probe Micro-Analysis (EPMA) using a CAMECA SX 100 microprobe. For the samples SiO_2Cu50 and SiO_2Cu500, the copper concentrations were estimated from the one (measured by EPMA) of SiO_2Cu250 glass and the copper concentration ratios in the alcoholic solutions used for impregnation.

2.2. Ionizing irradiations

The X irradiations were performed at room temperature (RT) using the X-ray source facility (MOPERIX) in Laboratoire Hubert Curien operating at 100 kV, with a 40 keV energy peak. A dose rate of 20 $Gy(SiO_2).s^{-1}$ was used for exposure time leading to an accumulated dose of 1 MGy in silica. The γ irradiations were performed at RT at an absorbed dose of 1 MGy with 1.2 MeV photons with a dose rate of 0.4 $Gy(SiO_2).s^{-1}$ using the Brigitte facility at SCK-CEN (Belgium). All irradiations were performed in air. It is worthy to note that, despite an identical accumulated dose in both X and γ irradiation experiments, the dose rate are very different. Furthermore, the distribution of the deposited dose along the penetration direction is inhomogeneous in the case of X-ray irradiation. For these reasons, we emphasize that a rigorous quantitative comparison between the two kinds of radiations is out of the scope of this paper.

2.3. Absorption measurements

UV–visible absorption spectra were obtained at room temperature using a Cary 5000 double-beam spectrophotometer (Agilent Technologies).

2.4. PL and PL kinetics measurements

Photoluminescence spectra were recorded at room temperature via confocal microscopy luminescence configuration using a LabRam Aramis spectrometer (Jobin-Yvon) equipped with a He-Cd (325 nm) probe laser, a CCD camera and micro-translation stages. The spectra were recorded employing a 40× UV objective and a 150 grooves/mm grating in a back-reflected geometry.

Time-resolved luminescence measurements were performed using an optical parametric oscillator equipped with a second harmonic generation nonlinear crystal pumped by the third harmonic of a Nd:YAG laser with pulse width of 5 ns and repetition rate of 10 Hz. The light emitted by the samples was spectrally resolved by a grating with 300 grooves/mm and recorded by a gated intensified CCD equipped with a delay generator.

3. Results and discussion

3.1. Before irradiation

Fig. 1 shows the Raman spectra of all studied samples. They present the well-known bands of SiO_2 glass [20], including the large band centered around 440 cm^{-1} and assigned to the Si-*O*-Si network deformation vibration (ω_1). The asymmetric band located around 810 cm^{-1} (ω_3) is attributed to a complex vibration involving substantial silicon motion in addition to a bending movement of oxygen in a vitreous network. The two smaller bands at 490 cm^{-1} (D_1) and 603 cm^{-1} (D_2) are assigned to symmetric stretching modes of three- and four-member siloxane rings, respectively, in the silica network. Finally, in the low-frequency region, clearly appears a band around 56 cm^{-1}, that is called the “Boson peak” and which is characteristic of the vitreous state [21]. No trace of crystalline phase can be detected in these spectra, even after X-ray or γ-ray irradiation.

The optical absorption spectra of the non-doped and Cu^{+}-doped silica glasses are presented in Fig. 2a. The non-doped glass (SiO_2) does not show any absorption band in the UV domain. On the contrary, the glasses doped with ionic copper present a relatively broad absorption band, covering the spectral range 275–375 nm, and peaking at 296 nm. This band can be attributed to single Cu^{+} ions occupying different sites in the host glass, as it has been reported in the case of Cu^{+}-doped silica-based glasses [22]. One can note that the absorption coefficient associated with this band

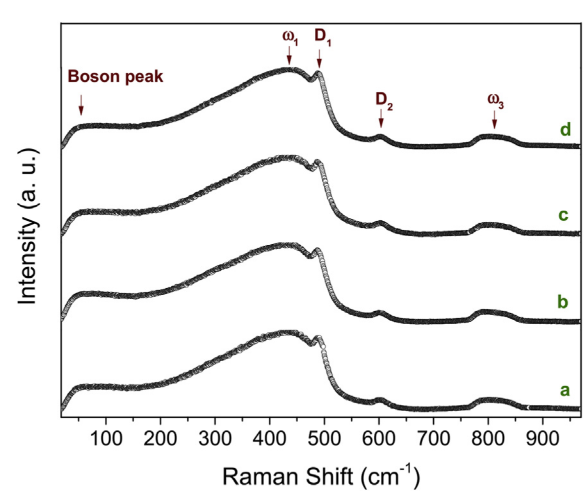

Fig. 1. Normalized Raman spectra of (a) SiO_2, (b) SiO_2Cu50, (c) SiO_2Cu250, and (d) SiO_2Cu500 glasses before irradiations.