Research Article

Structure and Optical Properties of Doped SiO$_2$ Mesoporous Glasses

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1. Introduction

Nowadays, a number of novel materials have been investigated, from organometallics, catalysis [1], semiconductors [2], carbonaceous materials [3], to optical fibers, and so forth, aiming to develop a new generation of nanotechnology-based mesosystems [4]. The development of nanostructured materials represents special significance for optical applications. Among the materials widely investigated due to their optical properties, silica ion-doped have been proved to be competitive candidates [5]. In addition, they represent very attractive materials for selective separation and adsorption of chemical for sensing [6].

The modification of its surface to design silica materials provides a wide range of special applications. Their proper development allows studying the structural behavior at molecular level and their interactions. The sol-gel process [7–9] has acquired much interest in recent years for providing inorganic materials in which it is possible to control particle size and shape, as well as the final arrangement of the colloidal particles, in order to obtain interesting materials with improved properties. In this work, we show the nanostructure differences between of several materials synthesized by two alternative routes that employ sol-gel process.

FT-IR and surface-enhanced Raman scattering (SERS) spectroscopies have been employed as auxiliary techniques for the study of structure at the molecular level of the optical glasses based on silica [10]. Raman scattering and IR were used to determine the interaction and the structural and molecular modifications induced by the doping element and the heat treatment. IR spectroscopy was used to determine the incorporation Cu$^{2+}$ in the silica network.

The structural properties, particle size distribution, porous size, and surface area depend strongly of the condensation and hydrolysis rate of the gelation; therefore, the
heat and/or use of doping metal must be tightly controlled to obtain an ordered structural arrangement.

The thermoluminescence phenomena occurred when a phosphor material is heated previously exposed to ionizing and nonionizing radiation. This is considered as an effective technique to understanding of the creation of defects generates a glow curve which is a graphical representation of light emission as a function of temperature and is related with trapping levels in the band gap, the main goal of analyzing trapping levels is to obtain several kinetic parameters [11].

The glow curves obtained for each material are different, and each glow peak is ascribed to the recombination centres and is related to the traps [12]. The luminescence properties of several silicate as gemstone exhibit good response thermoluminescent (TL), and a number of methods to synthesize TL materials have been reported based on traditional approaches to modify the band structure of the materials as well as the characteristic of their electron traps, thus controlling to some extent the corresponding TL response [13, 14].

In this work, a series of SiO\textsubscript{2} xerogels, some of them doped with Cu\textsuperscript{2+} and Fe\textsuperscript{3+} ions, are synthesized by the sol-gel procedure. Porous glasses are created by precursor gels after thermal treatment at 500°C. The surface and pore morphology characteristics depicted by porous glasses are studied by surface-enhanced Raman scattering (SERS), TEM, and N\textsubscript{2} sorption analyses. Some optical properties were measured as the behavior of the glow curve through the technique of thermally stimulated luminescence and luminescence spectrum response.

## 2. Experimental

Mixtures of tetraethylorthosilicate (TEOS) (98% Aldrich), triple distilled water and ethanol produced SiO\textsubscript{2} gels. Doping cations came from either Cu(NO\textsubscript{3})\textsubscript{2}·2.5H\textsubscript{2}O (Aldrich 99 wt.%) or Fe(NO\textsubscript{3})\textsubscript{2}·9H\textsubscript{2}O (Baker 99 wt.%). Each sol synthesis was performed in a Nalgene flask at room temperature by dissolving the appropriate amount of TEOS in ethanol under a gentle stirring. Separately, suitable quantities of Cu\textsuperscript{2+} or Fe\textsuperscript{3+} nitrates were dissolved in water. The Cu\textsuperscript{2+} or Fe\textsuperscript{3+} solution was then poured inside the flask containing the TEOS mixture. The reaction system was subjected to stirring during 20 min; afterward 0.25 cm\textsuperscript{3} of concentrated HCl mixed with 0.25 cm\textsuperscript{3} of concentrated HF were added drop by drop while continuing the stirring for further 30 min. The resulting SiO\textsubscript{2} sol was then poured into a Nalgene cylinder where gelation rapidly occurred. Each gel was dried at 110°C for 48 h and the resulting xerogel calcined at 500°C during 24 h then obtaining SiO\textsubscript{2} cylindrical monoliths.

Molar TEOS: H\textsubscript{2}O: ethanol ratios of: 1:4:6 (MG\textsubscript{1}), 1:1:4 (MG\textsubscript{2}) and 1:3:6 (MG\textsubscript{3}) were chosen to produce an assortment of transparent monolithic glass materials. For all samples, the amounts of Cu(NO\textsubscript{3})\textsubscript{2}·2.5H\textsubscript{2}O or Fe(NO\textsubscript{3})\textsubscript{2}·9H\textsubscript{2}O employed for the synthesis of cation-doped xerogels corresponded to 10\textsuperscript{−3} and 6 × 10\textsuperscript{−4} mol per one mol of TEOS, respectively. Figure 1, shows the samples MG\textsubscript{1}-Cu, MG\textsubscript{2}-Cu, MG\textsubscript{3}-Cu, and MG\textsubscript{1}-undoped at 110°C, respectively. On the other hand, Figure 2 shows the samples MG\textsubscript{1}-Cu, MG\textsubscript{2}-Cu, MG\textsubscript{3}-Cu, and MG\textsubscript{1}-undoped at 500°C.

FT-IR silica glass spectra were measured on a Bruker Vector 33 spectrometer by means of the Diffuse Reflectance
Figure 4: FT-IR spectra at 700–400 cm\(^{-1}\) interval, for MG\(_3\)-Cu doped and MG\(_3\)-Fe doped.

Figure 5: Raman scattering spectra of MG\(_3\), MG\(_3\)-Cu, and MG\(_3\)-Fe.

Figure 6: Raman scattering spectra at 80–700 cm\(^{-1}\) of MG\(_3\)-Cu and MG\(_3\)-Fe doped.

Figure 7: \(\text{N}_2\) sorption on (a) MG\(_3\)-Cu.

3. Results and Discussion

3.1. FT-IR and Dispersive Surface-Enhanced Raman Scattering. Figure 3 shows IR spectra of cation-undoped MG\(_1\), MG\(_2\)-Cu, and MG\(_2\)-Fe silica samples treated at 500°C. These...
spectra present a sharp peak at 3746 cm$^{-1}$ due to the fundamental OH stretching vibration of the surface silanol groups (Si-OH). The wide band appearing between 3600 cm$^{-1}$ and 3500 cm$^{-1}$ corresponds to OH vibrations of Si-OH groups existing on the surface or hydrogen-bonded to molecular water. The peak at 1370 cm$^{-1}$ has been interpreted as a signal proceeding from a highly disordered structure [15]. Signals characteristic of silica glass are found at 1085 cm$^{-1}$ and 800 cm$^{-1}$ and correspond to symmetric and asymmetric Si-O stretching modes while the band displayed at 450 cm$^{-1}$ is due to the Si-O-Si bending mode [15, 16].

In the case of FT-IR spectra of Cu-doped silica glasses (Figure 3), the vibration modes of the Cu-O groups [17, 18] should appear at 420, 425 and 528 cm$^{-1}$; however, these peaks are hidden by the wide band centered at 450 cm$^{-1}$ and which is assigned to Si-O-Si groups. The vibrations modes of Fe-O groups should appear at 636 and 560 cm$^{-1}$ [19]. For Cu-doped MG$_1$ and Fe-doped MG$_2$ samples, the absence of the 1370 cm$^{-1}$ band is indicative that these samples possess a more ordered structure than the cation-undoped specimens. Finally, three-member Si-O rings are detected at 3746 cm$^{-1}$.

Observing the Cu-O and Fe-O groups for the doped monolithic glasses in Figure 4, it is possible to see the spectra at 700–400 cm$^{-1}$ interval to observe the Cu-O and Fe-O groups of the MG$_3$-Cu-doped and MG$_3$-Fe-doped samples, respectively.

The Raman scattering spectra of MG$_3$, MG$_3$-Cu, and MG$_3$-Fe calcined samples are shown in Figure 5. The Si-O-Si and SiO$_4$ characteristic bands depicted at 980 cm$^{-1}$ and 430 cm$^{-1}$, respectively, are indicative of the existence of a 3D glass network. The two signals occurring at 485 and 610 cm$^{-1}$ are called D$_1$ and D$_2$ defect bands; D$_1$ is attributed to the emergence of 4-member Si-O rings, while D$_2$ is interpreted as a symmetrical stretching vibration of O atoms.
constituting the Si-O three-member rings [20]. The Raman scattering spectrum of sample MG<sub>1</sub>-Cu depicts a band at 280 cm<sup>-1</sup>; this signal can be due to the crystalline lattice of Cu(NO<sub>3</sub>)<sub>2</sub> [21]. In this case, is possible to observe the spectra at 700–80 cm<sup>-1</sup> interval, as shown in Figure 6, the Cu-O and Fe-O groups for the MG<sub>3</sub>-Cu-doped and MG<sub>3</sub>-Fe-doped samples, respectively.

3.2. N<sub>2</sub> Sorption. Table 1 shows the textural properties of nine SiO<sub>2</sub> glasses: in this results, we can see that the porosity glasses is adequate for catalysis system, and these properties were obtained using a mixed of two different catalyst (HCl and HF) that obtained with only one catalyst. The biggest areas were obtained of the porous glasses with Cu-doped cation, and the best textural properties were obtained with the MG<sub>3</sub> group. On the other hand, with the Fe-doped cation was decreased the pore sizes of the SiO<sub>2</sub> glasses.

The N<sub>2</sub> sorption isotherms and pore-size distributions (PSD) of three SiO<sub>2</sub> glasses one Cu-doped (MG<sub>1</sub>-Cu) and two cation-undoped (MG<sub>1</sub> and MG<sub>2</sub>), are shown in Figures 7, 8, and 9. Also, they display the PSD functions that have been calculated by the nonlocal functional density theory.
Figure 15: TL glow curves of MG3-Fe at different doses in the interval 100–800 Gy.

Figure 16: Excitation and emission spectra of MG2-Fe, MG3-Cu, and MG3-Fe taken at room temperature.

(NLDF) procedure [22]. All isotherms correspond to IUPAC Type IV shapes while depicting IUPAC H2 hysteresis loops. An important characteristic of these isotherms is the existence of a plateau during the development of desorption boundary curve (DBC) of the hysteresis loop; on the other hand, the adsorption boundary curves (ABC) display a sloping behavior. Main textural parameters (i.e., surface area, pore volume, and mean pore size) of the glass specimens are presented in Table 1.

An interesting characteristic of porous glasses consists of the appreciable overlap between the PSD functions obtained from the ABC and DBC isotherms. The DBC-PSD result depicts a mode value higher than the ABC-PSD outcome in all cases; this means that a pore-blocking phenomenon is taking place along the DBC.

Another interesting feature of all PSD distributions consists in pointing out that the DBC percolation peak protrudes above the ABC curve by about one third of its total area (compare the shaded peak area versus the crosshatched area in Figure 5); this means that an average connectivity (C) of about four corresponds to the cavities of porous glass. This is due to the fact that according to percolation theory [23], the shoulder of the DBC isotherm requires a fraction of $1/C - 1$ open bonds in order to create a percolation vapor path into the inner pores of the glass substrate. Therefore, the pore structure of glasses prepared by the sol-gel method resembles a fractal 3D network of interconnected (deformed) tetrahedral [24].

TEM photographs (Figure 10) of porous glasses reveal the fractal nature of the precursory SiO$_2$ gels: the morphologies of the vitreous solids are similar to structures created by diffusion-limiting processes for the samples the Cu-O and Fe-O groups for the MG3-Cu-doped and MG3-Fe-doped samples, respectively.

3.3. Optical Measurement. The TL response induced by an irradiation dose of 400 Gy in SiO$_2$ glasses with impurities: MG2-Fe, MG3-Cu, and MG3-Fe, is presented in Figure 9. Specimens display complex TL glow curve structure and support exposure to high doses [25]. Those Fe-doped show TL glow curve with two maxima, while MG3-Cu has only one TL peak around of 420 K. Silica glasses TL glow curves after successive exposures to beta particles are present in Figure 10. Each was obtained by irradiating the same monolith during a dose of 100 Gy. The reproducibility of the TL glow curves for MG3-Fe irradiated 5 times is ±2% better samples realized with other reagent concentration. Figures 11–15 illustrate the TL glow curves of the irradiated samples, respectively, at different laboratory doses, in the interval of 100–800 Gy. As can be seen, the maxima of the curves for the Fe-doped samples appear in the same position regardless doses, which indicates that first-order processes are involved in the TL phenomenon [26]. On the other hand, the Cu-doped specimen not have the same conduct; however, all samples do not present saturation of the TL response for the used doses. Therefore, cation-doped directly influences in the creation of various traps and recombination centres of SiO$_2$ nanostructures mesoporous glasses.

Figure 14 shows the luminescence spectrums comparison of MG2-Fe, MG3-Cu, and MG3-Fe taken at room temperature without annealing. Silica glasses MG3 excitation band is centered at 314 nm, and the emission is centered at 525 nm, while the MG2 monolith present excitation and emission band centered in 330 and 550, respectively (Figure 16). There are small shift in the spectra for each specimen type, but there are not important differences between the spectra for distinct doping. In both samples, the main emission occurs around the green.
4. Conclusions

The sol-gel process assisted by supercritical drying is an efficient method to fabricate highly porous monolithic silica materials. A variety of porous glasses of outstanding surface areas and mesopore volumes can be synthesized by the sol-gel procedure. Thermal treatment of precursory gels produces mesoporous substrates free of micropores and of well-defined pore volumes. The effect of doping cations consists in decreasing the pore sizes of the resultant glasses.

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Table 1: Textural properties of porous glasses.

| Sample | MG1 | MG1-Fe | MG1-Cu | MG2 | MG2-Fe | MG2-Cu | MG3 | MG3-Fe | MG3-Cu |
|--------|-----|--------|--------|-----|--------|--------|-----|--------|--------|
| $A_{\text{BET}}$/$\text{m}^2$ g$^{-1}$ | 449 | 352 | 680 | 766 | 134 | 711 | 298 | 970 | 629 |
| $V_p$/$\text{mm}^3$ g$^{-1}$ | 440 | 322 | 609 | 706 | 181 | 605 | 3630 | 1908 | 1749 |
| $W_{\text{DBC}}$/nm | 4.7 | 3.4 | 6.0 | 4.8 | 3.5 | 3.7 | 4.8 | 6.0 | 6.8 |

$A_{\text{BET}}$ = BET area; $V_p$ = pore volume; $W_{\text{DBC}}$ = DBC mean pore widths.
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