Research Article

Structure and Optical Properties of Doped SiO₂ Mesoporous Glasses

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Monolithic mesoporous silica glasses were synthesized. The presence of Cu²⁺ and Fe³⁺ cations during the synthesis of sol-gel precursors leads to different morphologies and pore sizes. The materials are characterized via IR and Raman scattering spectra to detect surface groups and -Si-O-Si- rings (i.e., 3–6 Si atoms) and morphology is examined through electron microscopy. N₂ sorption isotherms reveal details of the mesoporous structure of the materials, which are endowed with significantly large surface areas and pore volumes. Vapor percolation occurs in these samples because of a void arrangement consisting of pore bulges delimited by narrower necks. The optical characterization shows the luminescence spectrum and thermoluminescent behavior subjected to successive exposures of beta particles.

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 pro-

viding 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 Cu²⁺ 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

FIGURE 1: MG₁-Cu, MG₂-Cu, MG₃-Cu, and MG₁-undoped at 110°C.

FIGURE 2: MG₂-Fe and MG₂-Cu at 500°C.

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 SiO₂ xerogels, some of them doped with Cu²⁺ and Fe³⁺ 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),

FIGURE 3: FT-IR spectra of MG₁, MG₂-Cu doped, and MG₂-Fe doped.

TEM, and N₂ 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 SiO₂ gels. Doping cations came from either Cu(NO₃)₂·2.5H₂O (Aldrich 99 wt.%) or Fe(NO₃)₂·9H₂O (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 Cu²⁺ or Fe³⁺ nitrates were dissolved in water. The Cu²⁺ or Fe³⁺ solution was then poured inside the flask containing the TEOS mixture. The reaction system was subjected to stirring during 20 min; afterward 0.25 cm³ of concentrated HCl mixed with 0.25 cm³ of concentrated HF were added drop by drop while continuing the stirring for further 30 min. The resulting SiO₂ 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 SiO₂ cylindrical monoliths.

Molar TEOS: H₂O: ethanol ratios of: 1:4:6 (MG₁), 1:1:4 (MG₂) and 1:3:6 (MG₃) were chosen to produce an assortment of transparent monolithic glass materials. For all samples, the amounts of Cu(NO₃)₂·2.5H₂O or Fe(NO₃)₂·9H₂O employed for the synthesis of cation-doped xerogels corresponded to 10⁻³ and 6 × 10⁻⁴ mol per one mol of TEOS, respectively. Figure 1, shows the samples MG₁-Cu, MG₂-Cu, MG₃-Cu, and MG₁-undoped at 110°C, respectively. On the other hand, Figure 2 shows the samples MG₁, MG₁-Fe, and MG₁-Cu 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 $\text{MG}_3\text{-Cu}$ doped and $\text{MG}_3\text{-Fe}$ doped.

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

FIGURE 5: Raman scattering spectra of MG_3 , $\text{MG}_3\text{-Cu}$, and $\text{MG}_3\text{-Fe}$.

FIGURE 7: N_2 sorption on (a) $\text{MG}_3\text{-Cu}$.

technique. Glasses were also analyzed by Raman scattering spectroscopy by mounting the cylindrical glass specimens transversally in the sampling compartment of a Senterra Bruker Raman scattering instrument with at laser 785 nm. Transmission electron microscopy (TEM) of powdery glass samples was performed in a JEOL JEM-1010 instrument.

N_2 sorption isotherms at 76 K of powdery samples were measured in a Quantachrome Autosorb 1 instrument. The N_2 and He gases were UHP grade (Praxair, 99.99%). All samples were outgassed at 200°C overnight prior to the sorption run.

TL measurements and beta irradiation were performed in a Risø TL/OSL model TL/OSL-DA-15 unit equipped

with a ^{90}Sr beta source 3.33 Gy min^{-1} dose rate. The TL signal was integrated from room temperature up to 650 K under N_2 atmosphere using a heating rate of 1°C s^{-1} . The luminescence spectra were obtained prior to the UV excitation by using a Perkin Elmer spectrofluorometer model LS50-B at room temperature.

3. Results and Discussion

3.1. FT-IR and Dispersive Surface-Enhanced Raman Scattering. Figure 3 shows IR spectra of cation-undoped MG_1 , $\text{MG}_2\text{-Cu}$, and $\text{MG}_2\text{-Fe}$ silica samples treated at 500°C. These

FIGURE 8: N_2 sorption on (a) MG_1 undoped. FIGURE 9: N_2 sorption on (a) MG_2 undoped.

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 model [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]

(a)

(b)

FIGURE 10: TEM micrographs of (a) MG_3 -Cu and (b) MG_3 -Fe.

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

FIGURE 11: TL glow curves of SiO_2 glasses with different doping concentrations irradiated using a 400 Gy dose.

FIGURE 12: Reproducibility of the TL glow of silica glasses after being expose 5 times to beta particles for 100 Gy dose each.

constituting the Si-O three-member rings [20]. The Raman scattering spectrum of sample $\text{MG}_1\text{-Cu}$ depicts a band at 280 cm^{-1} ; this signal can be due to the crystalline lattice of $\text{Cu}(\text{NO}_3)_2$ [21]. In this case, is possible to observe the spectra at $700\text{--}80\text{ cm}^{-1}$ interval, as shown in Figure 6, the Cu-O and Fe-O groups for the $\text{MG}_3\text{-Cu}$ -doped and $\text{MG}_3\text{-Fe}$ -doped samples, respectively.

3.2. N_2 Sorption. Table 1 shows the textural properties of nine SiO_2 glasses: in this results, we can see that the porosity glasses is adequate for catalysis system, and these properties

FIGURE 13: TL glow curves of $\text{MG}_2\text{-Fe}$ at different doses in the interval 100–800 Gy.

FIGURE 14: TL glow curves of $\text{MG}_3\text{-Cu}$ obtained by exposing to beta irradiation for different doses: 100–800 Gy.

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_3 group. On the other hand, with the Fe-doped cation was decreased the pore sizes of the SiO_2 glasses.

The N_2 sorption isotherms and pore-size distributions (PSD) of three SiO_2 glasses one Cu-doped ($\text{MG}_1\text{-Cu}$) and two cation-undoped (MG_1 and MG_2), 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 $\text{MG}_3\text{-Fe}$ at different doses in the interval 100–800 Gy.

FIGURE 16: Excitation and emission spectra of $\text{MG}_2\text{-Fe}$, $\text{MG}_3\text{-Cu}$, and $\text{MG}_3\text{-Fe}$ taken at room temperature.

(NLDFT) 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 $\text{MG}_3\text{-Cu}$ -doped and $\text{MG}_3\text{-Fe}$ -doped samples, respectively.

3.3. Optical Measurement. The TL response induced by an irradiation dose of 400 Gy in SiO_2 glasses with impurities: $\text{MG}_2\text{-Fe}$, $\text{MG}_3\text{-Cu}$, and $\text{MG}_3\text{-Fe}$, 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 $\text{MG}_3\text{-Cu}$ 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 $\text{MG}_2\text{-Fe}$ irradiated 5 times is $\pm 2\%$ 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 $\text{MG}_2\text{-Fe}$, $\text{MG}_3\text{-Cu}$, and $\text{MG}_3\text{-Fe}$ taken at room temperature without annealing. Silica glasses MG_3 excitation band is centered at 314 nm, and the emission is centered at 525 nm, while the MG_2 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.

TABLE 1: Textural properties of porous glasses.

Sample	MG ₁	MG ₁ -Fe	MG ₁ -Cu	MG ₂	MG ₂ -Fe	MG ₂ -Cu	MG ₃	MG ₃ -Fe	MG ₃ -Cu
$A_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$	449	352	680	766	134	711	298	970	629
$V^{\text{P}}/\text{mm}^3 \text{ g}^{-1}$	440	322	609	706	181	605	3630	1908	1749
$\overline{W}_{\text{DBC}}/\text{nm}$	4.7	3.4	6.0	4.8	3.5	3.7	4.8	6.0	6.8

A_{BET} $\equiv$ BET area; V^{P} $\equiv$ pore volume; $\overline{W}_{\text{DBC}}$ $\equiv$ DBC mean pore widths.

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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