Photoluminescence of silica monoliths prepared from cold sintering of nanometric aerosil precursors under high pressure

Jackeline Barbosa Brito [a], Tania Maria Haas Costa [a,b], Fabiano Severo Rodembusch [b], Naira Maria Balzaretti [a,*]

[a] Institute of Physics, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, Bairro Agronomia, Porto Alegre, RS CEP 91501-970, Brazil
[b] Institute of Chemisty, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, Bairro Agronomia, Porto Alegre, RS CEP 91501-970, Brazil

A B S T R A C T

Blue photoluminescent silica monoliths were obtained by cold sintering of nanosized precursors under high pressure. The samples were prepared from hydrophobic and hydrophilic fumed silica AEROSIL® precursors which were placed inside a soft capsule of hBN and pressed at 7.7 GPa. Practically no photoluminescence (PL) emission was observed for the nanometric powdered precursors while a relatively intense emission was measured for the sintered monoliths, which was dependent on the excitation wavelength (2.47–5.63 eV). The emission was observed in the range between 2.0 and 3.5 eV for all samples with the peak at ∼2.7 eV for excitation between 3.26–3.44 eV. The blue band is probably related to the defects produced during the cold sintering process related to plastic deformation and internal stress of the monolith. The intensity of PL spectra of the monoliths obtained from the hydrophilic precursor (A200) was higher than the intensity of the spectra observed for the monoliths obtained from hydrophobic precursors (R974, R816 and R812) probably due to the presence of the carbon groups at the surface of the hydrophobic precursors, hindering the cold sintering process.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The photo physical characterization of silica-based materials seems to be crucial to better predict its applications as high technological materials. Photoactive silica has attracted attention as emitting centers with potential application in optical devices and sensors [1–11]. Although silica glass is a wide band gap (∼11 eV) insulator, intrinsic structural defects are responsible for luminescent centers under UV excitation, such as non-bridging oxygen centers, oxygen vacancies, peroxy linkages and radicals, among others [3–7]. The effect of these defects is enhanced for nanosized SiO_2 particles, as should be expected due to the large surface/volume ratio [8]. It is well known that the non-bridging oxygen centers are one of the most important defects in silica, characterized by absorption bands at 2.0, 4.9 and 6.8 eV. They are responsible for the luminescence emission of silica at 1.95 eV and the electronic properties of these centers depend on the glass composition [8,9]. In addition, silica obtained by sol-gel shows blue emission when excited with UV light probably due to charge transfer between silicon and oxygen atoms [2]. According to Garcia et al., the remaining organic radicals from the sol-gel synthesis

would also play an important role in the luminescence properties [10]. Vaccaro et al. [11] observed a bright visible luminescence of silica nanoparticles associated with defects stabilized by oxygen chemisorption. According to them, a luminescence band at 2.27 eV, assigned to the silanone groups at the surface of the silica nanoparticles, disappeared when the sample was in contact with the atmosphere, while a luminescence band at 2.41 eV, related to dioxasilyrane groups, was not influenced by the exposition to the atmosphere.

Photoluminescence related to defects and impurities in silica has been extensively investigated [2,4,7,10,12–14]. In particular, the effect of solid phase reaction of fumed silica sintered under high temperature on the luminescence properties has been examined carefully in the last decade. Laurence et al. [15], for instance, observed that the intensity of the PL of fumed silica powder treated at 980 °C during 168 h was much lower than the PL intensity of a pellet of the same precursor, treated at the same conditions, suggesting that the PL was not related to impurities or contaminations, but to intrinsic defects produced during the solid state sintering process peculiar to the pellet samples. They proposed that the dehydroxylation reaction of fumed silica produces edge sharing tetrahedral units with relatively large energy strain. The thermal treatment would not be as much as necessary to promote the relaxation of this strained structural arrangement. According to them, the source of the PL would not be related to

any known point defect in silica but to this regions with a high density of defects. In fact, in a subsequent paper, they proposed that the spectral an temporal properties peculiar to the pellet samples would arise from a high density of defects at the surface of the silica grains (quasi-continuum photoluminescence process) [16]. Similar results were found by Yamada et al. [17], Spallino et al. [18] and Vaccaro et al. [19]. Uchino et al. [20] have shown that the formation of a metastable defect pair consisting of $=SiO_2$ and $=Si$: during the dehydroxylation reaction of fumed silica under high temperature should explain the PL band excited at 330–360 nm based on the good agreement between DFT calculations and experimental results.

Costa et al., on the other hand, prepared hard, dense and transparent silica monoliths by sintering of sol-gel silica powder under high pressure (4.5 GPa) at room temperature [21]. They observed that the reduction of the free space among the silica nanograins induced by cold-sintering process allowed the condensation of the silanol groups to form Si–O–Si bonds, producing free water that remained trapped in the closed porosity after high pressure sintering. The mild conditions of the sol-gel process also allow the incorporation of organic fluorophores, quantum dots, rare earth ions, gold nanoparticles and other nanostructured or molecular species inside the silica glass making the combination of sol-gel method and the high pressure technique very attractive to prepare potential photoactive devices [22,23]. More recently the versatility of the high pressure technique was confirmed when blue–green luminescent carbon nanodots entrapped in silica matrix were produced by the pyrolysis of methyl groups well dispersed on the edges of nanometric grains of silica (AEROSIL® R974) previously cold sintered under high pressure [24]. However the optical behavior of the silica monolith itself, produced by high-pressure compaction, was not previously investigated.

In this context, the aim of this work was to investigate the luminescence properties of fumed silica sintered under high pressure at room temperature, where the strain in the local atomic arrangements due to the dehydroxylation process at the interfacial region should be enhanced compared to the sintering under high temperature. Silica monoliths were produced by cold sintering at 7.7 GPa of commercial nanosized hydrophilic and hydrophobic fumed silica nanograins. The hydrophobic samples consisted of silica grains containing well dispersed carbon groups at the surface (1–3 wt%). The discussion of the results was based on the effect of controlled carbon contamination and of the large density of defects induced by the cold sintering under high pressure.

2. Materials and methods

Table 1 summarizes the properties of the precursor powders used as raw material to produce the silica monoliths by cold sintering under high pressure. Fig. 1 shows the schematic representation of these samples.

The silica precursor powders were pre-compacted in a piston-cylinder type die at ~0.25 GPa into cylinders of 3.0 mm diameter

Table 1
Properties of the precursor AEROSIL® powders from Evonik, Inc.

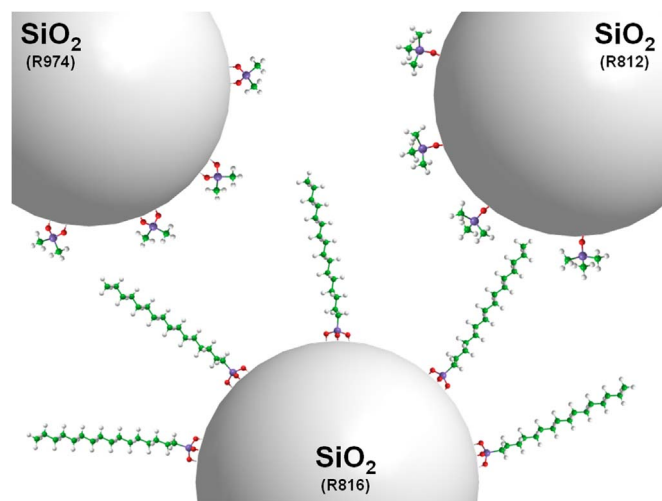| Sample	Average particle size (nm)	Specific surface area (BET) (m²/g)	Carbon content (wt %)	Carbon groups
A200	12	175–225	–	–
R974	12	200	0.7–1.3	Dimethyl
R816	12	200	0.9–1.8	Hexadecyl
R812	7	200	2.0–3.0	Trimethyl

Fig. 1. Schematic representation of the AEROSIL® precursors used to prepare the luminescent silica monoliths.

and 2.6 mm height. The cylinders were, then, individually placed inside a soft capsule made of hBN surrounded by a graphite cylinder and a ceramic gasket and, then, pressed at 7.7 GPa at 25 °C during 2 min using a toroidal high pressure apparatus [25].

A Bomem MB 100 FTIR spectrometer with a resolution of $4 cm^{-1}$ (32 scans) was used to investigate the effect of high-pressure compaction on the infrared spectra of the hydrophobic and hydrophilic samples. The monoliths were crushed and dispersed in KBr pellets for the FTIR measurements. The PL emission spectra were measured with a Shimadzu RF5301PC spectrofluorometer with a solid sample holder with an angle designed to limit the reflected excitation beam from the emission monochromator. All measurements (monoliths and precursor powders) were obtained using excitation and emission slits of 5.0 nm/5.0 nm.

3. Results and discussion

Fig. 2 schematically presents the cold sintering process used to obtain the photoluminescent silica monoliths based on the previous work of Costa et al. [21], where silanol groups condense to form siloxane bonds. This mechanism would be responsible for the impressive consolidation of the monolith at room temperature. This scheme did not consider the effect of the small amount of hydrocarbon groups at the grain surfaces of the hydrophobic samples, which could hinder the condensation process [26].

3.1. Chemical characterization of the silica matrix

Dense monolithic samples were obtained after the high-pressure compaction from all silica precursors, as shown in Fig. 3.

The FTIR analysis of the AEROSIL® samples before and after cold sintering under high pressure are presented in Figs. 4 and 5. In order to better observe the vibrational bands, the original spectra were subtracted from a baseline using the software Origin© 8.0.

All the spectra, before and after compaction, present typical absorption bands of silica in the region between 400–1500 cm^{-1} (Fig. 4). The band around 1100 cm^{-1} arises from 3-fold degenerate stretching frequencies of the SiO_4 tetrahedral structural units [27]. The band around 800 cm^{-1} is due to Si–O–Si bending modes [27,28], while the band around 470 cm^{-1} is due to –O–Si–O bending [27]. A broad shoulder at ~950 cm^{-1}, related to stretching vibration of nonbridging silanol groups [24,29,30], appeared after cold sintering under high pressure for all samples,