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Glass photonic structures fabricated by sol–gel route

R. Tomala^a, A. Lukowiak^a, B. Borak^b, A. Chiappini^c, W. Blanc^d, M. Ferrari^{c,e}, A. Bouajaj^f,
D. Ristic^g, S. Taccheo^h, W. Strek^a

^a*Institute of Low Temperature and Structure Research, PAS, Wroclaw, Poland;* ^b*Department of Mechanics, Materials Science and Engineering, Wroclaw University of Science and Technology, Wroclaw, Poland;* ^c*IFN–CNR CSMFO Lab. & FBK Photonics Unit, Povo, Trento, Italy;* ^d*Institut de Physique de Nice, Université Côte d'Azur, CNRS UMR7010, Nice, France;* ^e*Museo Storico della Fisica e Centro di Studi e Ricerche Enrico Fermi, Roma, Italy;* ^f*Laboratory of Innovative Technologies, LTI, ENSA–Tangier, University Abdelmalek Essaâdi, Tangier, Morocco;* ^g*Ruder Boskovic Institute, Division of Materials Physics, Laboratory for Molecular Physics, Zagreb, Croatia;* ^h*Laser and Photonics Group, College of Engineering, Swansea University, Bay Campus, Swansea, UK*

ABSTRACT

To emphasize the scientific and technological interest in the silica-based glassy systems and the versatility of the sol–gel route, nano and micrometer scale structures are discussed focusing the attention mainly on the rare-earth-activated materials and their spectroscopic characterization. We have demonstrated that various SiO₂-based binary systems can be successfully employed for the fabrication of amorphous planar waveguides, glass–ceramic waveguides, and tapered rib waveguide laser. Different technological processes allowed to realize Er³⁺-activated microspheres that can be exploited as microresonator and it has been evidenced that through specific coating it is possible to modify modal free spectral range and/or modal dispersion of the microresonator and achieve laser action. In the case of rare-earth-doped 3-D colloidal crystals in different configurations (direct and inverse one), it has been shown that the relaxation dynamics of the electronic states can be engineered.

Keywords: nanostructure, silica, lanthanides, photoluminescence, planar waveguide, photonic crystal, microresonator

1. INTRODUCTION

Silica-based glasses take up a consolidated place as photonic materials¹. The fruitful exploitation of silicate glasses is not only restricted to the ICT area. Many other photonic devices, with a large spectrum of applications covering Health and Biology, Structural Engineering, and Environment Monitoring Systems, have been developed during the last years. Even if several of these devices are actually available on the market, at the state of the art the research is focused on further optimization of the chemical composition and development of innovative fabrication processes and structures, in order to reduce the costs, increase the performances, and enable new functionalities.

In this context, a significant role is played by confined structures that can be prepared using different fabrication techniques. Among them, the sol–gel processing has been recently successfully applied for various materials due to the advantages in terms of design, form, composition, structure, and optical properties of the fabricated materials. Silica-based glasses have already had a wide range of utility in optical applications^{2–4} but many other systems can be exploited by the sol–gel route as well. Particularly interesting are transparent glass-ceramic waveguides, spherical microresonators, colloidal systems, and photonic crystals. Among these materials, rare earth (RE) doped materials glasses are particularly worth of investigations because they can be used as not only as active building blocks of integrated optics components but also as (bio)active nanostructures in medicine⁵.

To emphasize the scientific and technological interest in the aforementioned topic and the versatility of the sol–gel route, the glass-based nano and micrometer scale range systems are here discussed, *i.e.* (a) planar waveguides, (b) microresonators, (c) colloidal crystals and (d) nanosized glass particles (see Figure 1).

Figure 1. Scheme (a) and pictures (b-e) of different forms of sol-gel-derived materials and photonic structures.

2. SOL-GEL-DERIVED STRUCTURES

Planar waveguides

The advantages of the sol-gel technology are undoubtedly simplicity and versatility. Due to the synthesis route, where different precursors can be mixed in solution, it is possible to obtain various inorganic or organic-inorganic networks with different shapes. The oxide coatings obtained by spin-coating, dip-coating, spraying, and other techniques are probably the most common sol-gel-derived glass (or glass-ceramic) forms used in photonic structures. First of all, they are used as planar or strip (channel) waveguides. The advantages in their fabrication and glass properties, that one can mention here, are: different composition of the glassy network, easy and various procedures for substrate coating, transparency, chemical inertness, dense or porous (important for example, in sensing) structure, smooth surface, and easy way of doping. Particularly interesting is the possibility to modify the refractive index of a waveguide in a wide range through selecting proper composition of the glass.

The sol-gel-derived layer can act as a waveguide when some particular aspects are fulfilled, such as, proper refractive index and thickness, lack of porosity, film homogeneity, and smooth surface. Doping with some elements leads to the fabrication of optically active structures that can be used as parts of integrated optics and sensing systems.

SiO₂-TiO₂

One of the first binary systems tested for optical applications were silica-titania materials. Their ability to be a host for RE ions forming an active planar or strip waveguide was shown in 90s last century⁶⁻⁸. This matrix possesses high transparency, low optical losses, and demonstrate a possibility of formation of the photo induced optical second harmonic generation⁹. Choosing different molar ratio of oxides changes the refractive index of glass in a wide range whereas, good properties were obtained with optimum titania concentration of 20 mol% (or even lower, between 7% and 12%¹⁰) that allowed to minimize phase separation and improve dissolution of RE ions¹¹. To ensure lack of photoluminescence quenching (for example, for Er³⁺ ions at 1.5 μm), the film porosity should be removed, *i.e.* fully densified samples must be prepared. To avoid non-radiative de-excitation involving OH groups, special synthesis protocols and waveguides storage should be provided as well¹².

For some applications, planar structures must fulfill also other particular requirements. For instance, if erbium doped planar waveguide would like to be used as erbium doped waveguide amplifier in the same way as in the erbium doped fiber amplifier, its relatively small dimension exacts much higher concentration of Er³⁺ ions than in the case of the fiber system. Unfortunately, the silica-based systems suffer RE ions clustering and reduced amplifier efficiency due to the energy transfer between the ions. The desired properties can be achieved in the glass-ceramic matrices where the active ions are located in the crystalline phase. On the other hand, phosphorus or aluminum doping of silicate glass was shown to increase

RE ions solubility^{8,13}. These co-dopants dissolve clustering rare earth ions, such as Nd^{3+} , and disperse them homogeneously in the glass matrix. Their appropriately high concentration can make fluorescence sufficiently intense for lasing¹³. Aluminum and phosphorous doping was useful also in the case of $\text{SiO}_2\text{--TiO}_2$ waveguides¹⁴. For example, with the addition of 5 mol% of P_2O_5 , the Nd^{3+} (1 mol%) luminescence lifetime increased from 45 μs to 200 μs ⁷. Although, it was also noticed that the presence of aluminum oxide in the ternary glass induced a lower chemical stability that made the stripe waveguide formation by photolithography followed by wet etching unsuitable¹⁵. Research in such systems lead to the realization of the first grating coupled monolithic solid state optical amplifier based on a Nd^{3+} doped sol-gel tapered rib waveguide derived in a matrix with a composition of $50\text{SiO}_2:50\text{TiO}_2:10\text{AlO}_{1.5}$ ¹⁶.

Silica-titania films may be used also as waveguide layers for application in planar evanescent wave sensors. Sensors based on entrapped organic and inorganic dyes, enzymes, and other biomolecules have been reported. Their response is usually based on optical or electrical measurements, for example, pH or humidity sensor when the matrix is doped with pH indicators^{17,18}) or cerium ions¹⁹, respectively. Other than planar structures can be useful as well, such as reported by Biswas *et al.*²⁰ the application of over coupled long period fiber gratings coated with $\text{SiO}_2\text{--TiO}_2$ thin film for detecting changes in the surrounding refractive index and for bio-sensing.

$\text{SiO}_2\text{--HfO}_2$

Sol-gel-derived silica-hafnia ($\text{SiO}_2\text{--HfO}_2$) layers, when doped with REs, have been proved to work well as active waveguiding structures^{21–23}. High transparency, refractive index higher than for silica, and lower phonon energy are the most important advantages of this binary oxide matrix. When doped with Er^{3+} ions, due to the light emission, it can be used in broad area of integrated optics covering application in sensing, biomedical diagnostic, energy conversion, telecommunication, lighting, and photon management. The fully densified glass layers are obtained after annealing the gel at 900 °C for 5 min²¹. The system can be easily transformed to glass-ceramic when the films are heat treated at 1000 °C for 30 min leading to the formation of HfO_2 nanocrystals in the amorphous silica network (see Figure 2a). The modified spectroscopic properties of the partially crystallized material, in comparison to the glass, are interesting, among others, due to the possibility of introducing higher concentration of erbium ions avoiding concentration quenching²³. Proper experiments were performed also in the case of $\text{HfO}_2\text{--SiO}_2$ glass where the influence of P_2O_5 addition (5 mol%) on Er^{3+} photoluminescence was studied²⁴. In comparison to the $70\text{SiO}_2\text{--}30\text{HfO}_2$ sample, the luminescence lifetime of Er^{3+} was slightly higher (5.7 ms at 1.5 μm) and the layer of a ternary glass was still transparent (Figure 2b), but the optical losses increased up to 3.5 dB/cm (at 632.8 nm).

Figure 2. a) HRTEM image of the $70\text{SiO}_2\text{--}30\text{HfO}_2$ sample annealed at 1000 °C for 30 min, showing HfO_2 nanocrystals homogeneously dispersed in the amorphous matrix²³. b) Transmission spectrum of the $65\text{SiO}_2\text{--}30\text{HfO}_2\text{--}5\text{P}_2\text{O}_5$ planar waveguide doped by 0.5 mol% Er^{3+} ions (inset: planar structure guiding red light)²⁴.

$\text{SiO}_2\text{--SnO}_2$

$\text{SiO}_2\text{--SnO}_2$ binary system, in glass-ceramic form, can be considered promising material since it combines the properties of glass-ceramic materials (high absorption-emission cross section and transparency) and the feature concerning photorefractivity of tin oxide²⁵.

When doped with Eu^{3+} ions it has been proved that SnO_2 nanocrystals produced a beneficial effect on the Eu^{3+} luminescence where an increase of 5 times has been observed²⁶ (see Figure 3). Moreover, it has been demonstrated that the capability to control the size of the nanocrystals permits to realize planar waveguides with an attenuation coefficient of 0.8 ± 0.2 dB/cm (at 632.8nm).

At the same time focusing the attention on the photorefractive properties, Lukowiak *et al.*²⁷ have discussed the change of refractive index induced by laser irradiation of glass-ceramics. They have observed a high photosensitivity of $25\text{SnO}_2:75\text{SiO}_2$ glass-ceramic waveguide with the UV-induced refractive index change $\Delta n \sim -1.6 \cdot 10^{-3}$ (see Figure 4). These result enables the direct writing of both channel waveguides and Bragg gratings, making this material a promising system for the low-cost development of efficient and multifunctional circuits for smart optical applications.

Figure 3. Room temperature excitation spectra of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission at 613 nm of 1 mol% Eu^{3+} -doped $(100-x)\text{SiO}_2-x\text{SnO}_2$ samples: (a) $x=25$ mol% sample after various heat treatments in air; (b) $x=8, 16, 25$ mol% samples heat treated at 1100 °C for 30 min. Reprinted with permission from ref.²⁶, AIP Publishing LCC .

Figure 4. The effective refractive index change of the $25\text{SnO}_2-75\text{SiO}_2$ film at 1550 nm (squares) and at 635 nm (circles), measured on a slab waveguide after UV irradiation at 248 nm, as a function of cumulative dose²⁷.

Finally, it is worth mentioning other photopatternable hybrid materials, for instance, $\text{ZrO}_2/\text{ormosil}$ and $\text{GeO}_2-\text{SiO}_2$, that are useful in fabrication of micro-optical elements, such as lenses, phase holograms, and gratings. These examples show just some of the wide possible optical applications of the materials described in this chapter.

Microresonators

Optical microresonators have recently attracted much interest in the scientific community since they are a very promising system for many different applications such as sensing, lasing and non-linear optics including frequency comb generation and stimulated Raman scattering²⁸. Among them, a particular class of optical resonators is constituted by spherical dielectric structures where optical rays are totally internally reflected. Due to minimal reflection losses and potentially very low material absorption, these guides modes, known as whispering gallery modes (WGM), can confer the resonator an exceptionally high quality factor Q , leading to high energy density, narrow resonant wavelength lines, and a lengthy cavity ring down.

Concerning the different shapes (microdiscs, microtorroids, and microspheres), microsphere is probably the easiest microresonator to produce since it can be simply made by melting the tip of a standard optical fiber and using sol-gel technique to realize a coating with controlled thickness²⁹. Alternatively, RE-doped spheres with desired size³⁰ can be obtained by means of wet chemistry approach using a weak acid catalyst such as acetic acid. Nevertheless, the two previously mentioned approaches have pro and cons. The first one permits a precise control of the dopant concentration, thickness, and refractive index of the active medium however, the realization is quite time consuming. Conversely for the second one the synthesis of the microspheres takes only few hours, but it is very difficult to control the size of the final product. Moreover, the main advantage of the first method concerns the possibility to prepare tailored materials with an attractive improvement in their physical and chemical properties^{31,32}, such as selecting the radial order n of the 'active' WGM³³.

Sol-gel microresonators

From a spectroscopic and morphological point of view, it has been verified that typical Er^{3+} ions emission embedded in a silica matrix were observed for all the systems. The comparison of the PL spectra performed on the single sphere and on a large quantity of spheres indicates that Er^{3+} ions occupy sites with similar local environments in all the particles. The decay curve of the metastable level $^4\text{I}_{13/2}$ exhibited a single exponential profile with a lifetime τ_{meas} of 13.7 ms for the spheres heat treated at 1100 °C, and the estimated quantum efficiency of the system was 76%³⁰.

A complementary approach is based on the deposition of a thin film on a silica sphere. Initially a silica microsphere serving as a base resonator structure is made by melting the end of a stripped standard telecommunication fiber (SMF 28). After melting and solidification controlled by surface tension, a near-perfect spherical shape, with a radius of thousands of micrometers is achieved. The activation of the surface can be obtained depositing a thin film on the surface of the spheres by the sol-gel route. A specific deposition of the active coating can be achieved using the protocol developed for the fabrication of the silica-hafnia amorphous planar waveguides. As a result of this procedure, crack free films surrounding microspheres can be easily obtained. A typical WGM luminescence spectrum is shown in Figure 6a. The sharp peaks seen in the figure are attributed to the WGMs with a different value of the l number. The modes with different values of the m number are frequency degenerated so that they cannot be observed unless the sphere is slightly elliptical. The modes presented in Figure 6a can be attributed to the fundamental ($p=0$) mode since the internal ($p>0$) modes are more difficult to couple light in and/or out and therefore, are less likely to be visible. In Figure 6b is shown a lasing spectrum of a coated microsphere. If the coating is thick enough so that the number of erbium ions interacting with the electric field of the WGMs is high enough, the stimulated emission gain can become greater than the cavity round trip loss and the sphere will start to lase. Figure 6b presents the lasing spectrum of a WGM with the peak power of 280 nW. To calculate the mode volume of the WGMs in Figures 6a and 6b we first need to consider the m values of the modes. For the studied system we can calculate the effective refractive index of the fundamental ($l=m$) mode around 1560 μm ($l=430$) which is around 1.53. Since the effective index of a body of a 3 μm taper is about 1.4, we can conclude that the taper is phase matched to the WGM with $m=l \cdot 1.4/1.53=394$. Thus we can conclude that the azimuthal mode distension is about $R\pi(1-m)/l=18 \mu\text{m}$. Since the radial distension for the $p=0$ mode is about 1 μm and the polar distension is just the circumference of the sphere, we conclude that the mode volume is around 8000 μm^3 .

Figure 5. a) The WGM luminescence of a coated microsphere b) WGMs laser spectra corresponding to the maximum (1560.4 nm) and minimum (1530.6 nm) wavelength peak values obtained from a 130 μm microsphere coated with 700 nm layer of 0.3 mol% Er^{3+} -doped $70\text{SiO}_2\text{--}30\text{HfO}_2$ ²⁸.

Moreover it is important to remind that coating a microresonator with high refractive index film can also be used to increase the applicability of the sphere for non-linear optics application³⁴. In fact, by coating a sphere with a proper thickness and refractive index mate it is possible to modify its modal free spectral range (FSR) and/or modal dispersion (ΔFSR – mode to mode change of the FSR). This “argument” is very important for all non-linear optics applications where small anomalous dispersion is crucial, in particular frequency comb generation using four wave mixing.

Ristic *et al.*³⁵ have demonstrated that depositing a coating of $\text{SiO}_2\text{--HfO}_2$ activated with 0.3 mol% of Er^{3+} produces very large normal and anomalous geometrical cavity dispersion and induces a splitting of the TE and TM free spectral ranges as evidenced in Figure 7.

Figure 6. a) WGM luminescence spectrum of a silica sphere, 140 μm in diameter, coated with a $70\text{SiO}_2\text{--}30\text{HfO}_2$ sol–gel layer. The lines at the top of the figure are for visual aid and indicate the position of the two visible families of modes. b) Linear fit of the modal eigenfrequencies used to determine the mean FSR (left) and second-order polynomial fit to the residual of the linear fit used to determine the modal dispersion (right) for the TM (upper) and TE (lower) modes. Reprinted with permission from ref³⁵, OSA Publishing.

Spherical glass particles

Nanoparticles can be easily obtained by the sol–gel method as well. One of the ways used for powders preparation is based on metal alkoxides hydrolysis and condensation reactions leading to many amorphous or crystalline oxides, *e.g.* SiO_2 ,

Al_2O_3 , TiO_2 , SnO_2 , ZnO , and ZrO_2 . Phosphors, energy converters, photocatalysts or layers building blocks could be given just as a few examples of their broad range of optical applications. Focusing the attention on monosize glass spheres, it is worth mentioning that if they are arranged in close packed structures²⁹, it may lead to the formation of optical passive devices such as switches, mirrors, filters, and superprisms^{36–38}. On the other hand, silica spheres of tailored size and shape, activated with defined concentration of RE ions, like Er^{3+} or Eu^{3+} , have significant potential use in optical devices such as integrated optics structures, active photonic band gap materials^{39,40}, luminescent markers⁴¹ or nanosensors⁴². Moreover, monosize spherical colloids represent a class of ideal building blocks that could be assembled into long range ordered lattices, such as opals, also called colloidal crystals.

SiO₂: monosize nano-spheres

Silica nanospheres can be synthesized through a modified protocol originally developed by Stoeber *et al.*⁴³. In particular, their final dimension can be predicted by the experimental expression proposed by Bogush *et al.*⁴⁴, that specifies the connection between d (average diameter of the spheres) and the reagents concentration expressed in mol/l. However, the Stoeber approach needs of appropriate conditions of temperature, pH, and reactants concentrations for the synthesis of monosize spheres with diameters ranging from 100 to 600 nm with a few percent standard deviation in diameter. The realization of SiO_2 nanoparticles of larger dimensions can be obtained using a strategy based on seeded growth (SG) technique. Figure 8 reports a typical SEM image of monosize SiO_2 spheres obtained using Stoeber method and SG technique.

Figure 7. a) SEM image of the SiO_2 particles with a diameter of 250 nm. b) SEM image of particles after seeded growth using the acid-based reaction. Reprinted with permission from ref²⁹, Elsevier B.V..

These nanoparticles can be used to create 3-D photonic crystals based on opal structures built up from highly ordered monosized silica spheres. The periodic variation of the refractive index produces a band of photon frequencies which is not allowed to propagate within the ordered nanostructure, and its wavelength position can be ascribed using the modified Bragg Law: $\lambda = 2 \cdot d_{111} \cdot n_{\text{eff}}$, where d_{111} corresponds to the interplanar distance and n_{eff} is the effective refractive index. In particular, as evidenced by the Bragg Law, it is possible to tailor the properties of the system (*e.g.* the position of the stop band) just modifying its structural features such as dimension of the particles or effective refractive index.

Focusing the attention on activated opals, two main configurations can be exploited. It is possible to assembly Er^{3+} -doped silica particles in ordered structure to get the arrangement as evidenced in Figure 9a. Analyzing this picture, it is evident that the particles are well-ordered in a triangular lattice that can be associated to the $\langle 111 \rangle$ planes of a fcc crystalline structure. In the case of a second configuration, an inverse opal structure (see Figure 9b), that represents a negative replica of the direct one, can be obtained starting from a direct opal, infiltrating the air voids with a stable dielectric solution (*e.g.* activated with Er^{3+} ions), and then removing the polystyrene beads that constitute the colloidal crystal⁴⁵; in this case the direct opal is used only as a sacrificial template.

Figure 8. SEM image of (a) direct opal constituted by monosize silica particles³⁹ and (b) silica inverse opal both activated with Er³⁺ ions. Reprinted with permission from ref⁴⁵, Elsevier B.V.

The spectroscopic assessment of direct and inverse colloidal crystals was performed through investigating the photoluminescence associated to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of Er³⁺ ions, as well as estimating the quantum efficiency (QE) of the systems by measuring the luminescence lifetime. Photoluminescence measurements could verify that Er³⁺ ions occupy sites characterized by similar local environment so that inhomogeneous broadening is not so important with respect to the amount of the Stark splitting. The decay curve showed a single exponential behavior with a lifetime of 16.8 ± 0.1 ms. Considering the radiative lifetime τ_{rad} previously obtained⁴⁶ for different Er³⁺-silica systems (about 18 ms) and defining the quantum efficiency as: $QE = \frac{\tau_m}{\tau_{rad}}$, where τ_m is the measured lifetime, an extremely high quantum efficiency can be determined for this type of system.

3. CONCLUSIONS

The specific characteristics of the sol-gel technique allow to develop materials at nano- and micro scale that permit to progress in the conception, design, and realization of systems and devices with substantially improved performance and significant scientific results.

Initially it has been shown that different sol-gel-obtained binary systems allow fabricating planar waveguides. Of interest appears the possibility of introducing higher concentration of erbium ions avoiding concentration quenching. Moreover, it has been demonstrated that SnO₂ nanocrystals act as rare earth sensitizer and induce photorefractivity enabling fabrication of optical devices (channel waveguides, gratings and other structures).

Microresonators can be realized by the sol-gel technique as well in particular, two complementary approaches have been described: bulk microspheres and coatings. Referring to the later one, it has been demonstrated that it is possible to modify the modal free spectral range and/or modal dispersion of the microresonator choosing appropriate thickness and refractive index of the coating. It has been evidenced that coated silica microspheres with a high refractive index optically active layer can achieve laser action with a maximum output peak power of 600 nW.

Finally, spherical glassy particles were presented as building blocks for the realization of RE-doped 3-D colloidal crystals using two complementary configurations (direct and inverse one). Their tunability (changing the position of the stop band) is possible through the selection of particles size and their refractive index. From a spectroscopic point of view it has been evidenced that the relaxation dynamics of the electronic states can be engineered.

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