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Fabrication, Assessment, and Application of Confined Structures in Photonic Glasses

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ABSTRACT

Sol-gel route is employed to prepare three nanostructured systems, namely core-shell Er³⁺-activated silica particles, Er³⁺-activated silica inverse opal; and spherical microresonators coated by Er³⁺-activated silica-hafnia film. Fabrication protocol, morphology, and spectroscopic assessment are presented. All the structures exhibit high compositional homogeneity leading to a significant ⁴I_{13/2} luminescence quantum yield. In the case of inverse opals a quantum efficiency of about 90% was estimated by lifetime measurements. The spherical microresonators was considered for whispering gallery mode analysis showing that the fluorescence spectra are quasi independent on the thermal effect linked to injected power.

Keywords: silica micro-nano spheres, microresonators, inverse opals, sol-gel, erbium, quantum efficiency.

1. INTRODUCTION

Silica-based glasses take up a consolidated place as photonic materials [1]. The fruitful exploitation of silicate glasses is not restricted only 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 optimising chemical composition and developing innovative fabrication processes and structures, in order to reduce the costs, increase the performances, and discover new functionalities. In this context, a significant role is played by confined structures such as amorphous and transparent glass-ceramic waveguides [2], spherical microresonators [3], colloidal-based system [4], and photonic crystals [5]. Aim of this lecture is to highlights recent results obtained in some of the above-mentioned systems.

2. NANO SCALE PHOTONIC STRUCTURES

The research on nano-scale structures can find application in different fields such as bioimaging, biosensing and photonic. One of the promising system for application in the above mentioned areas are the Er³⁺-activated core-shell like structures. Typically, monosize silica particles are synthesized via base-catalyzed hydrolysis of TEOS. However, the incorporation of rare earth ions, into the silica spheres, by dissolving a rare earth salt in ethanol fails for the base-catalyzed reaction because the rare earth ion immediately forms an insoluble rare earth hydroxide. Incorporation of lanthanide ions during the growth of silica particles is possible using an acid catalysis. On the other hand acid-catalyzed hydrolysis of TEOS results in particles with broad size distribution. Using a seeded growth method on the previously fabricated monosize silica spheres it is possible to grow monosize larger particles and incorporate Er³⁺ ions into the shell, obtaining a core-shell-like Er³⁺-activated structure [6]. Core-shell-like Er³⁺-activated silica spheres, where the core is the silica sphere and the shell is an Er₂O₃-SiO₂ coating, were prepared using the following protocol. 150 mg of silica spheres of 270 nm, obtained by Stober method, were added to a solution with the molar ratio TEOS:CH₃COOH:H₂O of 1:8:8, plus 0.2 wt% ErCl₃. The mixture was agitated for 45 min using a magnetic stirrer. After synthesis, the SiO₂ particles were separated from the solution by centrifuging at 1000 rpm and washed at least twice with pure ethanol. Subsequently core-shell-like Er³⁺-activated silica spheres were annealed at 950 °C for 30 min. Figure 1 shows a SEM image of the core-shell-like Er³⁺-activated silica spheres after annealing at 950 °C for 30 min. From Fig. 1 it is evident that seeded growth in the Erbium solution occurs on individual particles without clustering.

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The photoluminescence in the 1.5 μm region of core-shell-like Er^{3+} -activated silica spheres, were measured using the 514.5 line of an Ar^+ laser as excitation source. The shape of the emission band is typical of Er^{3+} -activated silicate glasses and the spectral bandwidth, measured at 3 dB from the maximum intensity, is 27 ± 2 nm [7]. The decay curve exhibits a single-exponential behaviour with a measured lifetime (τ_{meas}) of 12.8 ± 0.1 ms. We can compare this result with the lifetime of 18 ± 3 ms reported by Dood *et al.* [8], which can be considered close to the radiative lifetime (τ_{rad}) for erbium in silica. From the ratio: $\eta = \tau_{\text{meas}} / \tau_{\text{rad}}$ we estimate a quantum efficiency of 71% for the sol-gel-based core-shell silica spheres.

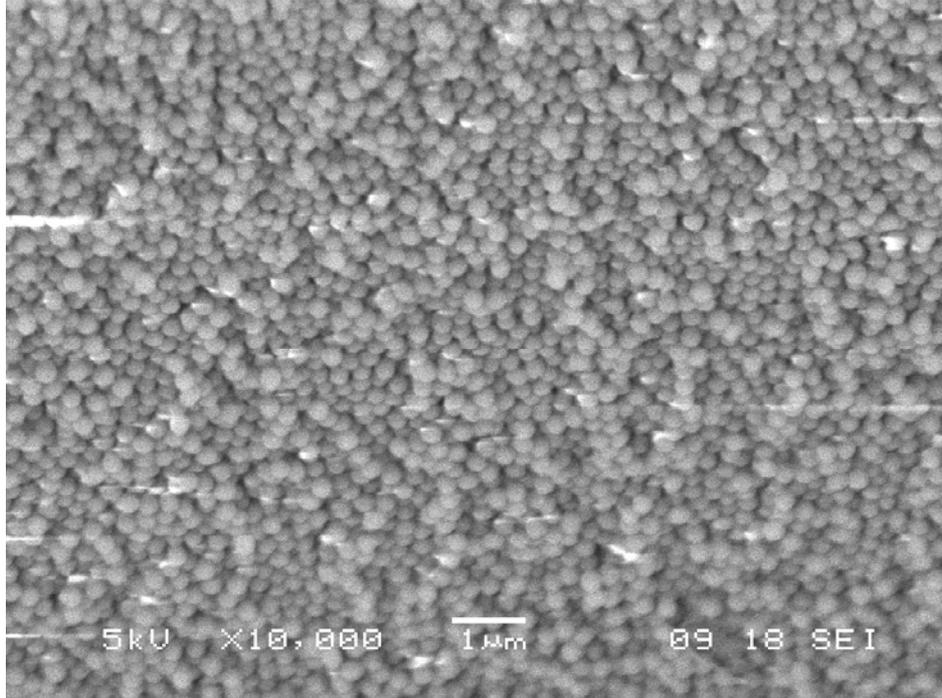


Figure 1. SEM images of core-shell Er^{3+} -activated silica particles prepared by seeded growth procedure.

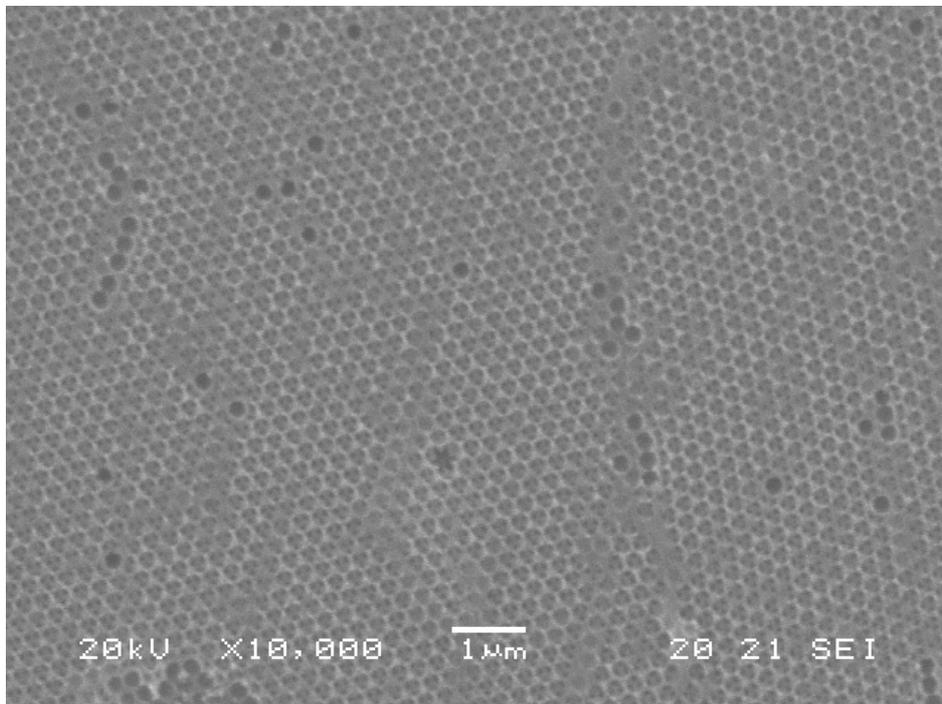


Figure 2. Scanning Electron Microscopy Image related to (111) facet of Er^{3+} -activated silica inverse opal.

Er^{3+} -activated silica inverse opals are another example of nano-scale structures. The opal templates were assembled using a commercially available monodispersed polystyrene (PS) microsphere colloidal suspension

(Duke Company - 1%wt) with an average diameter of 270 nm. The PS template was prepared using a vertical deposition technique. The silicon substrate was placed in a vial with deionized water containing 0.036 wt % PS in suspension. The water was then slowly evaporated at 50 °C in an oven. The silica sol activated by erbium ions (SsEi) was obtained after stirring a solution of the following precursors for 2 h at room temperature: 0.428cc Tetraethyl Orthosilicate (TEOS), 0.001cc HCl, 3.6cc Ethanol, 0.069cc H₂O and 1.68mg ErCl₃. The SsEi was filtered using a syringe filter with a 0.2 μm pore size. The void spaces of the opal template were then infiltrated by dropping ~10 μl of SsEi over the samples and were left to dry at room temperature. The template was removed by heat-treatment: the samples were slowly heated to 450 °C (at 0.1 °C/min) and then left at this temperature for 30 min. Furthermore a rapid thermal annealing at 900 °C for 10 min was carried out in order to promote a more complete condensation densification of the structure and elimination of adsorbed water. An SEM image of Er³⁺-activated silica (ErSiO₂) inverse opals is shown in Figure 2. Figure 2 reveals that the hollow regions of the air spheres are well ordered in a triangular lattice corresponding to the (111) planes of a fcc crystalline structure. The average dimension of the air-hollows is ~210 nm. This value is smaller than the diameter of the latex spheres (270 nm) used to form the template, which demonstrates that shrinkage occurs during the sintering process. This fact is not surprising given that the latex spheres are mesoporous and, in the early stages of calcination, probably decrease in size as water vapour is released from the pores. The ErSiO₂ inverse opal sample exhibited violet regions, and the reflected light was easily observed by the naked eye, because the bright colour resulted from optical Bragg diffraction from the crystal planes. Figure 3 shows the normalized reflectance spectra obtained at different angles of ErSiO₂ inverse opals measured along the normal of the (111) plane of ErSiO₂ inverse opals.

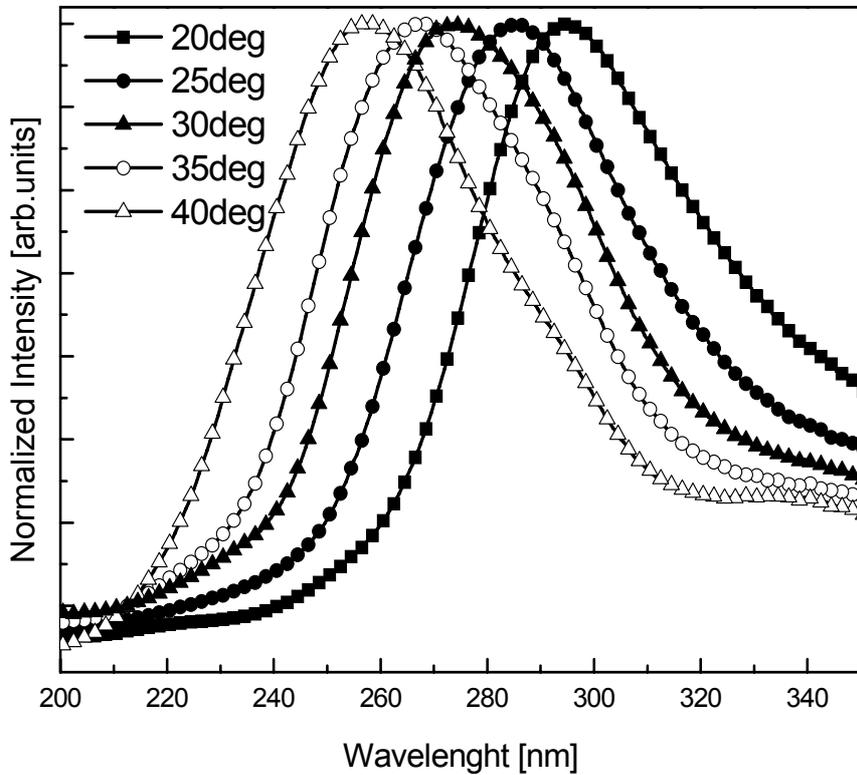


Figure 3. Reflectance spectra at different incidence angles performed on the of Er³⁺-activated silica inverse opal along the normal of the (111) plane of the sample.

From Figure 5 we can observe that with an increase of the incident angle, the stop band position shifts to shorter wavelengths. This behaviour can be express by the modified form of the Bragg's law:

$$\lambda = 2 \cdot 0.816 \cdot d \cdot \sqrt{n_{eff}^2 - (\sin \theta)^2}, \quad (1)$$

where λ is the free-space wavelength of light, d is the dimension size of the hollow spheres, n_{eff} is the effective refractive index and θ is the angle measured from the normal to the planes. Moreover by using equation (1) and taking in count the following formula [7]:

$$n_{eff}^2 = n_{air}^2 \cdot f + n_{silica}^2 \cdot (1 - f). \quad (2)$$

It is possible to estimate the volume fraction of ErSiO_2 in the inverse opal sample. In fact, assuming an effective refractive index of $n_{\text{eff}} = 1.1268$ (obtained, by fitting formula (1) with the incidence angles θ versus the stop band positions (free-space wavelength) λ) and considering the following values $n_{\text{silica}} = 1.4742$ and $n_{\text{air}} = 1$, we can calculate a volume fraction of about 23%, that it's very close to a maximal infiltration fraction for a inverse opal structure (26%). These results confirm the very good quality of the inverse structure obtained.

As far as concerns spectroscopic assessment the photoluminescence of ErSiO_2 inverse opal exhibits a main emission peak at 1540 nm. The spectral width of the emission band measured at 3 dB from the maximum of the intensity is 21 ± 1 nm, and the Stark structures at 1490, 1567 and 1617 nm appear well defined. The decay curve exhibit a single exponential profile with a lifetime $\tau_{1/e}$ of 16.8 ± 0.1 ms, leading to a quantum efficiency of about 90%.

3. SPHERICAL MICRORESONATORS

Dielectric microspheres are an important scientific and technological tool for manipulation of light on micrometric and sub-micrometric scale. The following example focuses onto the spectroscopic properties of Er^{3+} -activated silica spheres. Silica microspheres serving as a base resonator structure were made by melting the end of a stripped standard telecommunication fiber [9]. Typical diameters were in the range 125 μm (the fiber diameter) to 450 μm . In order to functionalise the surface, a thin film of Er^{3+} -activated 70SiO_2 - 30HfO_2 was sol-gel deposited by dip coating technique [10]. Before further coating, each layer was annealed in air for 50 s at 900 °C. Final films, resulting from 30 to 40 coatings, were stabilized by a last treatment for 5 min in air at 900 °C. As a result of this procedure, crack-free films surrounding the microspheres were obtained. The main characteristics of two microspheres are summarized in Table 1.

Table 1. Diameter D of the silica spheres coated by Er^{3+} -activated 70SiO_2 - 30HfO_2 film of thickness t and erbium concentration $C(\text{Er})$.

Microsphere labelling	$D [\pm 5 \mu\text{m}]$	$T [\pm 0.05 \mu\text{m}]$	$C(\text{Er}) [\text{mol}\%]$
SP1	250	0.8	1
SP2	430	1.1	0.1

Room temperature photoluminescence measurements in the region of the ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ transition of the Er^{3+} ions were performed using a 980 nm diode laser as excitation source, detecting the scattered light from the microsphere in free space configuration and dispersing the luminescence light with a 320 mm single grating. The light was detected using a InGaAs photodiode and a lock-in technique. Decay curves were obtained by chopping the CW exciting beam with a mechanical chopper and by recording the signal with a digital oscilloscope. The photoluminescence spectra as well as the decay curves obtained for SP1 and SP2 microspheres exhibit the typical spectroscopic features already observed for planar waveguides of same composition [11]. In particular a main emission peak at 1.53 μm with a shoulder at about 1.55 μm and a spectral bandwidth of about 48 nm for both Er^{3+} concentrations, are observed. The ${}^4\text{I}_{13/2}$ decay exhibits a single exponential profile with a lifetime of 4.4 ms and 6.2 ms for the microspheres doped with 1 mol% and 0.1 mol%, respectively. The decrease of the lifetime with the increase of the erbium concentration indicates that energy transfer processes, including cross-relaxation and up-conversion, are effective. In fact, in the case of the 1 mol% doped SP1 microspheres, an intense infrared-to-green up-conversion luminescence was observed upon 980 nm excitation. These lifetimes values are in perfect agreement with those obtained in [11,12], where a detailed discussion regarding concentration quenching effect is reported. On the basis of these results only the SP2 microsphere was considered for whispering gallery mode (WGM) analysis. To excite WGMs, light was launched by a tapered single-mode fiber. The pumping wavelength was chosen at 1480 nm in order to obtain a good overlap between the pump and laser mode volumes in the micro-sphere, and to have efficient microsphere in/out coupling for both pump and laser signals. The tapered fiber was obtained by heating and stretching a standard telecommunication fiber, single mode at 1.55 μm . Further details on the fiber coupling experimental setup can be found in [3]. Figure 4 shows the fluorescence spectrum of the microsphere SP2 after excitation of the WGMs; the free spectral range (FSR) of 1.22 nm is highlighted in the inset. The spectrum shown in the inset also makes evident the presence of the two TE and TM polarizations and a degenerating effect on the azimuthal index finding his origin in the ellipticity of the sphere. Indeed, these spheres present an average ellipticity of 0.12%, due to inhomogeneities in the thickness of the coating. This fact is responsible of losses which reduce the quality factor and hamper laser action. A positive outcome of this analysis, however, is that these microspheres exhibit a behaviour of the fluorescence spectra which is quasi independent on the thermal effect linked to injected power. This result indicates that the silica-hafnia coating strongly reduces the typical red-shift observed in spherical microresonators fabricated by other glass systems [10]

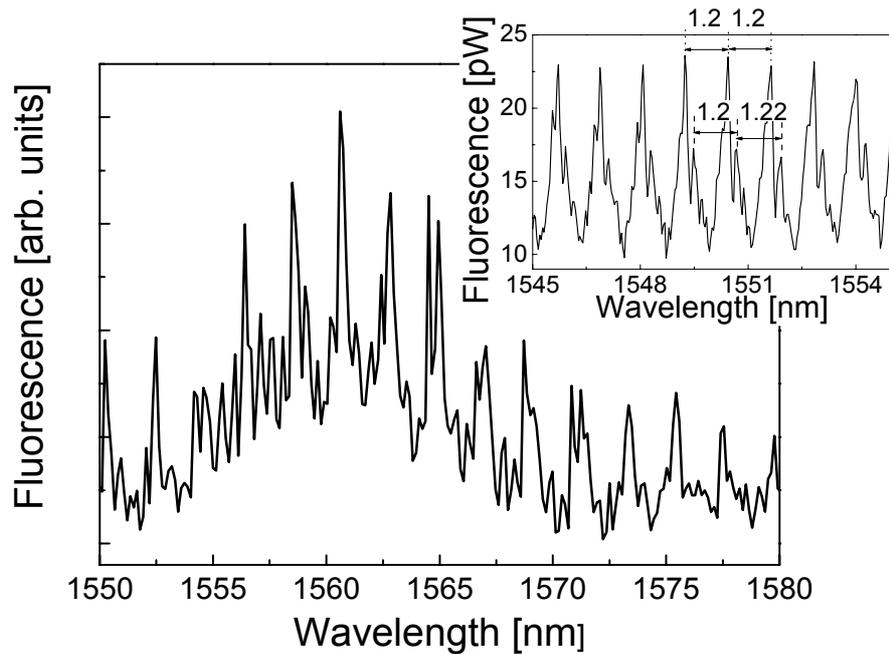


Figure 4. Fluorescence spectrum of the SP2 coated silica sphere obtained upon 1480 nm excitation through a tapered fiber. The inset gives the FSR of the resonator.

4. CONCLUSIONS

Three examples of confined structures are discussed: i) core-shell Er^{3+} -activated silica particles; ii) Er^{3+} -activated silica inverse opal; iii) spherical microresonators coated by Er^{3+} -activated silica-hafnia film. Core-shell-like Er^{3+} -activated silica spheres, where the core is a 270 nm silica sphere and the shell is an Er_2O_3 - SiO_2 coating, exhibit quantum efficiency of 71%. Large dimension and well ordered Er^{3+} -activated silica inverse opals were fabricated using colloidal route. Reflectance measurements showed the presence a pseudo photonic stop band in the visible region. Inverse opal exhibits a main emission peak at 1540 nm, with a spectral width of 21 ± 1 nm, and a $^4\text{I}_{13/2}$ lifetime of 16.8 ± 0.1 ms corresponding to a very high quantum efficiency of the system. The coated microspheres have exhibited a WGM fluorescence behaviour quasi independent on the thermal effects related to the injected power. This result confirms the suitability of these microspheres as microlasers, once the inhomogeneity in the thickness of the coating is reduced. It is also confirmed that sol-gel coating is compatible with functionalization or chemical modification of the microsphere surface without significant decrease of the resonator's quality factor: this characteristic is important for the use of microspheres as potentially high-sensitivity biosensors. The possibility to develop appropriate protocols for fabrication of optimized confined structures in photonic glasses on nano-scale domain represents a breakthrough to higher performance and low cost products as well as to innovative physics.

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