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► **To cite this version:**

Giancarlo C. Righini, Christina Armellini, Alessandro Chiasera, Yoann Jestin, Maurizio Ferrari, et al.. Er³⁺-activated sol-gel silica derived spherical Microresonators. *Glass Technology*, 2007, 48 (4), pp.200-203. hal-00275674

HAL Id: hal-00275674

<https://hal.science/hal-00275674>

Submitted on 27 Apr 2022

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Er³⁺-activated sol-gel silica derived spherical microresonators

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Details of the synthesis, spectroscopic, optical, morphological and structural characterisation of silica microspheres activated by Er³⁺ ions produced by the sol-gel route are presented. Acetic acid is used to catalyse the hydrolysis and condensation of tetraethyl orthosilicate in the presence of ErCl₃. SEM and TEM images are used to determine the dimension of the spheres and demonstrate the high quality of their surfaces. Photoluminescence measurements, both on single spheres and on pressed KBr pellets, containing 5% Er³⁺-doped silica spheres, confirm the incorporation of Er³⁺ ions into the silica matrix. The measured lifetime is 13.7 ms, relative to the ⁴I_{13/2} metastable state corresponding to a system quantum efficiency of 76%.

1. Introduction

The sol-gel technique provides an inexpensive and excellent approach for the preparation of organic-inorganic materials, and offers the possibility of preparing tailored materials with attractive physical and chemical properties.⁽¹⁻³⁾ It is well known that silica microspheres are important in both basic and applied physics since they can be employed in a wide range of areas covering information and communication technologies, health and biological applications, structural engineering, and environmental monitoring.⁽⁴⁾ In particular, silica spheres, arranged in close packed structures,⁽⁵⁾ can be used to form passive optical devices such as switches, mirrors, filters and

superprisms.⁽⁶⁾ Silica spheres of predictable size and shape, activated with a controllable concentration of rare earth (RE) ions, such as Er³⁺ or Eu³⁺, have significant potential for use in optical applications such as integrated optics structures, active photonic band gap materials,⁽⁷⁾ luminescent markers,⁽⁸⁾ nanosensors and microlasers.⁽⁹⁻¹¹⁾

Larger microspheres, tens of microns in diameter, activated with Er³⁺ ions can be used to fabricate whispering gallery mode lasers operating at 1.5 μm. These dielectric spheres activated with RE ions have the property to confine and guide the light in a thin ring through whispering gallery modes and behave as an optical amplifier in a cavity with high quality factor, offering ideal conditions for lasing action.⁽¹⁰⁾ As a consequence of these unique properties there is

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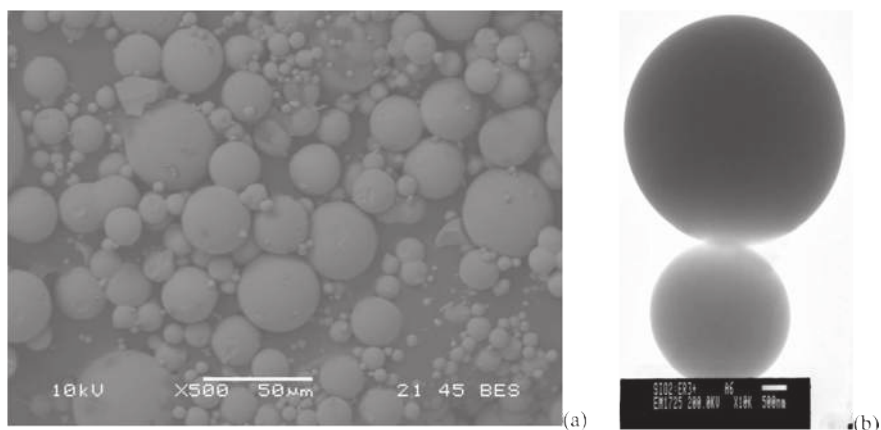


Figure 1. (a) SEM image of Er^{3+} silica spheres obtained by the acid catalysed sol-gel route; (b) TEM image of the spheres, which demonstrates the high surface quality of the spheres

an increasing activity devoted to the fabrication of lasing dielectric microspheres.^(9,11) Significant results have been obtained with phosphate, tellurite, and silicate microspheres, mostly fabricated by melting the precursor glass.⁽¹⁰⁾

In this work we report on Er^{3+} -activated microspheres fabricated by a different technique, namely an acid catalysed sol-gel route. Optical and spectroscopic assessment, as well as morphological and structural characterisation of the systems, are reported.

2. Experimental

Er^{3+} -activated silica microspheres were realised by using an acid catalysed sol-gel route. Tetraethyl orthosilicate (TEOS, Aldrich, >99%), glacial acetic acid (Carlo-Erba, 99.9%), distilled water (resistivity >15 MΩ/cm) and erbium (III) chloride (ErCl_3 , Aldrich, 99%) were used as reagents. A solution with molar ratio $\text{TEOS}:\text{CH}_3\text{COOH}:\text{H}_2\text{O}$ of 1:4:4, plus 1 wt% ErCl_3 , was stirred for 30 min at room temperature. After synthesis, the SiO_2 particles were separated from the solution by centrifuging and then washed with pure ethanol. Finally, the particles were dried at 80°C overnight and subsequently heat treated at 950°C for 30 min and at 1100°C for 30 min. Particle sizes were determined by scanning electron microscopy (SEM; JEOL-JSM 6300) and the surface quality was studied using transmission electron microscopy (TEM; JEOL 2010).

Micro-Raman spectra for a single sphere were obtained using the 457 nm line of an Ar^+ ion laser as excitation source. The spectra were collected with a multichannel spectrometer using a single monochromator configuration with notch rejection filter, and a cooled CCD detector for high sensitivity.

Photoluminescence spectroscopy (PL), in the region of the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition of Er^{3+} ions was performed using the 514.5 nm line of an Ar^+ ion laser and the 980 nm line of a Ti:Sapphire laser as excitation sources. The luminescence was dispersed by a 320

mm single grating monochromator with a resolution of 1 nm. The light was detected using a NIR photo multiplier tube and standard lock-in technique.

PL spectra were obtained both on the single sphere and on a large quantity of spheres (referred to as the 'LaS' system in the present paper) in pressed KBr pellets; each pellet contained 5% doped silica spheres. For both single spheres and 'LaS', decay curves were obtained by recording the signal by a digital oscilloscope.

2. Results and discussion

Figure 1(a) shows that particles of different diameters have been produced, ranging from hundred nanometres to approximately 100 μm. Figure 1(b) demonstrates the high surface quality of the spheres. The silica spheres can be separated and selected based on their size and Figure 2 shows a photo of a single Er^{3+} -activated silica sphere of about 100 μm diameter stuck onto a tapered silica fibre by means an optically transparent adhesive component.

Figure 3 shows two Raman spectra obtained on the single sphere heat treated (a) at 950°C and (b) at 1100°C. The Raman bands at about 440, 490, 600, 800, and 1060 cm^{-1} are characteristic of the silica network.⁽¹²⁾

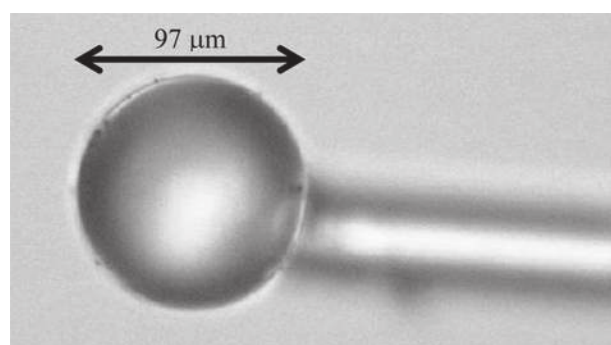


Figure 2. Optical micrograph of a single Er^{3+} -activated silica sphere of about 100 μm stuck onto a tapered silica tapered by means a transparent optical component adhesive

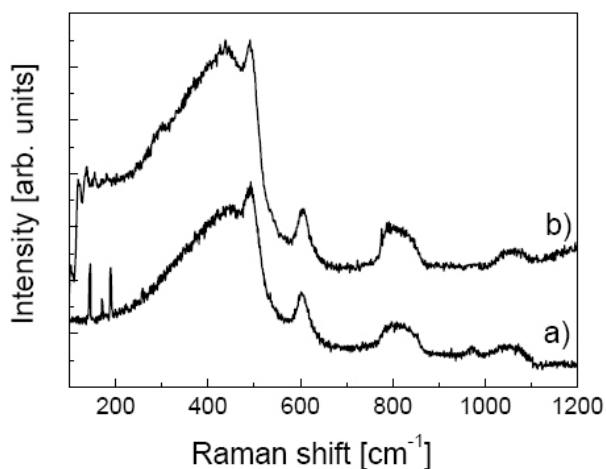


Figure 3. Raman spectra obtained on a single sphere heat treated at 950 (a) and 1100°C (b)

Moreover in the Figure 3(a) a band centred at about 970 cm^{-1} , attributed to the Si-OH vibration,⁽¹²⁾ can be seen. Comparison of the Raman spectra reveals a modification in the structural properties of the spheres as a function of the annealing temperature; in spectrum (b) the band centred at 970 cm^{-1} as well as the bands at 490 and at 600 cm^{-1} , attributed to the defect bands D1 and D2, respectively, are reduced in intensity. These observations confirm that by increasing the annealing temperature a more complete condensation of the surface and interior silanol groups is obtained along with an elimination of any adsorbed water, alcohol, or remaining acetate groups.⁽¹³⁾

Figure 4 shows the PL spectra obtained by excitation at 514.5 nm and at 980 nm of the 'LaS' heat treated at 1100°C (PL spectra obtained on an 'LaS' sample heat treated at 950°C exhibit the same behaviour). The shape of the emission band in Figure 4 is typical of Er^{3+} ions in silica glasses with a main emission peak at 1537 nm ^(5,14) and a spectral bandwidth, measured at 3 dB from the maximum intensity, of $27\pm 2\text{ nm}$.

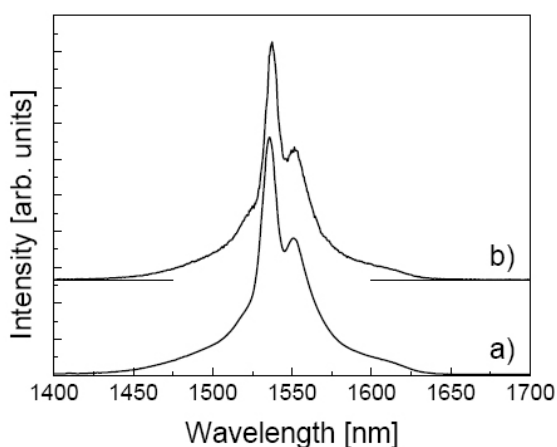


Figure 4. PL spectra obtained on a large quantity of spheres heat treated at 1100°C upon excitation (a) at 514.5 and (b) 980 nm

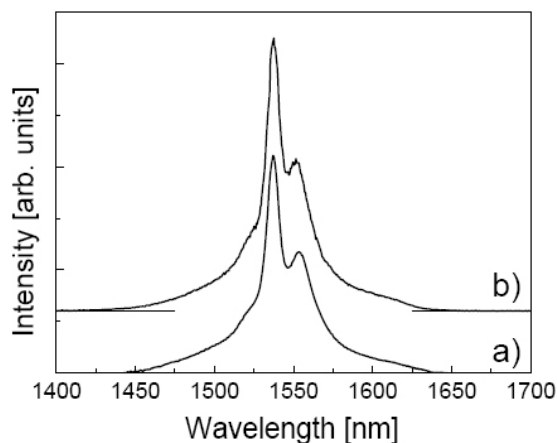


Figure 5. PL spectra obtained (a) from a single sphere and (b) on the 'LaS' sample upon excitation at 980 nm . The spheres were heat treated at 1100°C

Moreover the shape of the luminescence band is the same for excitation at 514.5 or 980 nm .

Figure 5 shows PL spectra obtained from a single sphere (Figure 5(a)) and on the 'LaS' sample (Figure 5(b)) upon excitation at 980 nm , after heat treatment at 1100°C . For the case of a single sphere the shape of the emission band is again typical of Er^{3+} ions in silica glasses with a main emission peak at 1537 nm ^(14,15) and a spectral bandwidth, measured at 3 dB from the maximum intensity, of $27\pm 2\text{ nm}$.

The PL spectra from both the single sphere and the 'LaS' sample have the same shape and this behaviour indicates that Er^{3+} ions occupy sites characterised by a similar local environment for all the spheres.

Figure 6 shows the decay curve of the metastable level $^4I_{13/2}$ of 'LaS' samples heat treated at 950 and 1100°C , as well as of a single sphere heat treated at 1100°C .

The decay curves of the metastable level $^4I_{13/2}$ for all

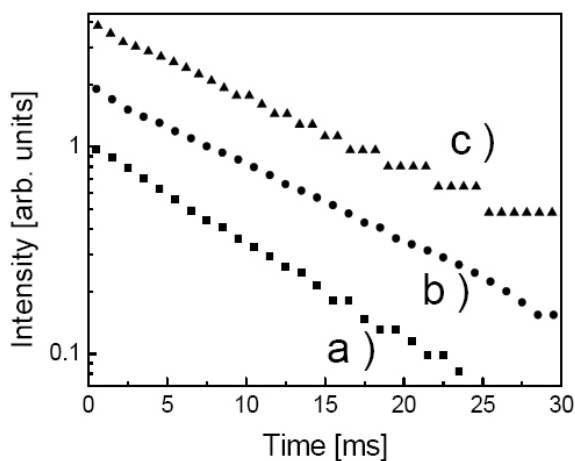


Figure 6. Room temperature luminescence decay curve from the $^4I_{13/2}$ state of Er^{3+} ions, obtained upon excitation at 980 nm , for: (a) 'LaS' heat treated at 950°C (■ points), (b) "LaS" sample heat treated at 1100°C (● points), and (c) a single sphere (Figure 2) heat treated at 1100°C (▲ points)

Table 1. Lifetime of the metastable state ${}^4I_{13/2}$ for the systems: A: 'LaS' sample heat treated at 950°C, B: 'LaS' sample heat treated at 1100°C, and C: a single sphere heat treated at 1100°C

Systems	A	B	C
Lifetime ${}^4I_{13/2}$ (ms)	9.7±0.2	13.7±0.2	13.6±0.2

the systems (a, b, and c) exhibit a single exponential profile and the lifetimes obtained upon excitation at 980 nm are given in Table 1.

Table 1 shows that there is a difference between the spheres heat treated at 950°C and the spheres heat treated at 1100°C. This difference, also shown by the micro Raman spectra, is essentially due to the presence of residual OH impurities that can quench excited Er^{3+} . In fact it is well known that two OH stretching vibrations are enough to bridge the gap of about 6500 cm^{-1} between the ground state ${}^4I_{15/2}$ and the first excited state ${}^4I_{13/2}$ of the Er^{3+} ions.⁽¹⁶⁾

In order to estimate the quantum efficiency η the measured lifetime (τ_{meas}) must be compared with the radiative lifetime τ_{rad} as $\eta = \tau_{meas} / \tau_{rad}$. Recently, many investigations have been performed on SiO_2 spherical colloids doped with Er^{3+} ions, in order to study the spontaneous emission of RE and to determine the local optical density (LOS) in these systems.^(16–18) In particular, Moroz *et al*^(16–18) determined a radiative lifetime of 18±3 ms that is larger than lifetime found in several other studies of Er-doped SiO_2 .^(14,19) Assuming a τ_{rad} of 18 ms a quantum efficiency, η , of 76% can be estimated for our spheres heat treated at 1100°C (systems B and C).

5. Conclusions

A simple and a cheap fabrication protocol has been developed to obtain Er^{3+} -activated microspheres by means of an acid catalysed sol-gel process. It has been demonstrated that it is possible to obtain Er^{3+} -activated microspheres of different sizes. SEM and TEM images reveal the high surface quality of the synthesised spheres. Micro-Raman spectra, obtained from a single sphere, revealed a modification in the structural properties as a function of the annealing temperature.

PL spectra typical of Er^{3+} ions embedded in a silica matrix were observed for all the systems and 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 spheres. The decay curve of the metastable level ${}^4I_{13/2}$ exhibits 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 is 76%.

The remarkable optical, morphological and spectroscopic properties of the fabricated erbium-

activated dielectric spheres show that this system can be used to develop a microlaser operating at 1.5 μm . Investigations on laser oscillations, obtained using a tapered fibre for coupling, are in progress.

Acknowledgements

Authors acknowledge the financial support of MIUR-FIRB RBNE012N3X, and CNR-CNRS 2006-2007. One of the authors (GRC) is now with Centro Fermi, Roma.

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