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Photonic properties and applications of glass micro- and nanospheres

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Fabrication, morphological and spectroscopic assessment of micro- and nano-spheres are reported. Spheres with size ranging from few hundreds of nm to few hundreds of μm have been prepared by different methods, i.e. sol–gel, melting and core-shell techniques. Pure and rare-earth-doped spheres find their major applications as microsensors and microlasers, respectively. We refer here to Erbium-activated systems only: (i) coated micro spheres where the silica core, obtained by telecom fiber melting, is coated with an Er^{3+}–$70SiO_2$–$30HfO_2$ film; (ii) Er^{3+}-activated microspheres obtained from silicate-modified glasses and phosphate glasses using a plasma torch; (iii) sol–gel Er^{3+}-doped silica micro- and nano-spheres. The whispering gallery mode spectra were analysed as a function of sphere diameter, thickness of coating (if any) and Erbium content. Photoluminescence spectra of different systems gave interesting indications on the potential of some activated microspheres for lasing applications. For instance, sol–gel Er^{3+}-activated core-shell-like structures exhibited a lifetime of 12.8 ms, leading to a quantum efficiency (QE) of 71%. Even higher QE (~76%) was estimated in sol–gel Er^{3+}-silica spheres.

1 Introduction The recent developments of optically confined structures constituted by micro- and nano-spherical resonators, which can also be activated by rare-earth ions, have opened new possibilities in both basic and applied physics, in a large area covering information communication technologies, health and biology, structural engineering, and environment monitoring systems. Spherical microresonators are optical microcavities where light can be guided through the so called whispering-gallery-modes (WGMs) with an unique combination of strong temporal and spatial confinement leading to high quality factor [1–3]. This kind of resonator, in the 40 μm to 400 μm diameter range, has been considered for a large number of applications including compact laser sources and biological sensing [4]. On a smaller scale, monodisperse colloidal spheres have proved to be suitable for the implementation of opal photonic crystal structures [5], which are expected to be a key component for future large-scale-integrated optical circuits.

If activated with a controllable concentration of rare-earth ions like Er^{3+}, these nanospheres have significant potential for use as integrated optics structures, luminescent markers or nanosensors, and active photonic bandgap materials [6, 7].

In this paper we have focused only on Er^{3+}-activated glass micro- and nanospheres prepared by different techniques. Particular attention has been devoted to the measurement of WGM emission spectra as well as of the spectroscopic properties of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions.

2 Erbium activated silica-hafnia coated microspheres Silica microspheres serving as a base resonator structure were made by melting the end of a stripped standard telecommunication fiber [8]. 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 [9]. 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.

Room temperature photoluminescence (PL) measurements in the region of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ 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 PL spectra as well as the decay curves obtained for MS1 and MS2 microspheres exhibit the typical spectroscopic features already observed for planar waveguides of same composition [9], namely: (i) 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; (ii) single exponential decay with a lifetime of 4.4 ms and 6.2 ms for the microsphere 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 MS1 microsphere, 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 [9], where a detailed discussion regarding concentration quenching effect is reported. On the basis of these results, only the MS2 microsphere was considered for WGM analysis.

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(Er).

microsphere labelling	D (±5 μm)	t (±0.05 μm)	C(Er) (mol%)
MS1	250	0.8	1
MS2	430	1.1	0.1

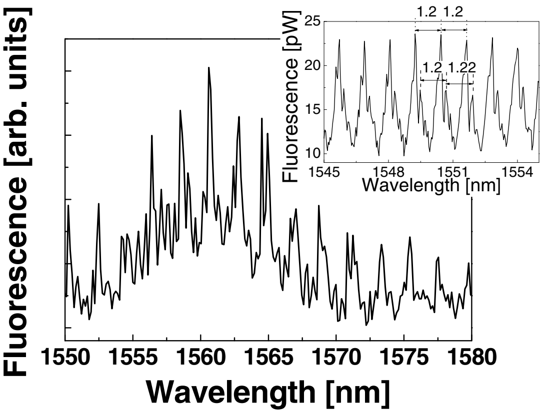

Figure 1 Fluorescence spectrum of the MS2 coated silica sphere obtained upon 1480 nm excitation through a tapered fiber. The inset gives the FSR of the resonator.

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 microsphere, 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 [10].

Figure 1 shows the fluorescence spectrum of the MS2 microsphere 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 [10]. 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, 11].

3 Er^{3+}-activated microspheres obtained by silicate-modified glasses and phosphate glasses In this section we report on microspheres fabricated from glass powders by using a microwave plasma torch, following the protocol reported in [12, 13]. Two different kinds of glasses were employed: an experimental modified-silica glasses, doped with 0.5 at% of Er^{3+} (Baccarat glass), and a commercial Er^{3+}/Yb^{3+} co-doped phosphate glass (Schott IOG2), which contains 2 wt% of Er_2O_3 and 3 wt% of Yb_2O_3.

The diameter of the spheres obtained by plasma torch depends essentially on the powder size, and typically may

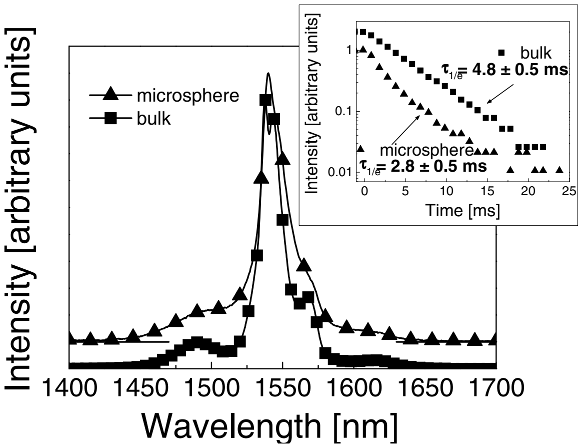

Figure 2 Room temperature photoluminescence spectra of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ion for the bulk sample (square) and the microsphere (triangle) Baccarat glass. In the inset the luminescence decay curves from the $^4I_{13/2}$ state of Er^{3+} ion are reported for the bulk sample (square) and the microsphere (triangle).

vary from 10 μm to 200 μm [13]. A sorting procedure is then necessary to select the spheres with the desired size. In the present case microspheres with a diameter ranging from 50 μm to 100 μm were selected, and then glued to the tip of an optical fiber for easier handling. Photoluminescence spectroscopy, in the region of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ion, was performed with the same apparatus employed for the spectroscopic assessment of Er^{3+}-activated silica-hafnia coated micro-spheres.

The photoluminescence spectra of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ion are reported in Fig. 2 for the Baccarat glass bulk sample and the corresponding microsphere. The inset of Fig. 2 shows the related luminescence decay curves obtained after pumping at 980.8 nm with an excitation power of 450 mW. A doubling of the effective bandwidth and almost an halving of the lifetime is measured on the microsphere as compared to the precursor Baccarat glass. In the case of Schott IOG2 glass, on the contrary, no significant broadening of the bandwidth was observed while the lifetime slightly decreased from about 7 ms to about 6 ms when passing from precursor to the microsphere. The observed spectral differences as well as the different lifetimes measured in the bulk glass and in the microspheres may be attributed to the difficulty of controlling the fabrication process parameters, including the plasma torch temperature; though the difference can also be due to photon trapping effects as discussed recently by Koughia and Kasap [14]. A discussion concerning the inhomogeneous changes in the local environment of Er^{3+} ion induced by the microsphere fabrication process is given in Refs. [12, 15].

Figures 3 and 4 show the WGMs emission spectra obtained for Baccarat glass and Schott IOG2 microspheres, respectively. The diameter of the spheres is 85 μm for the silicate-modified glass and 70 μm for the IOG2 glass. Experimental setup for coupling was the same employed in the case of coated microspheres with excitation at 1480 nm.

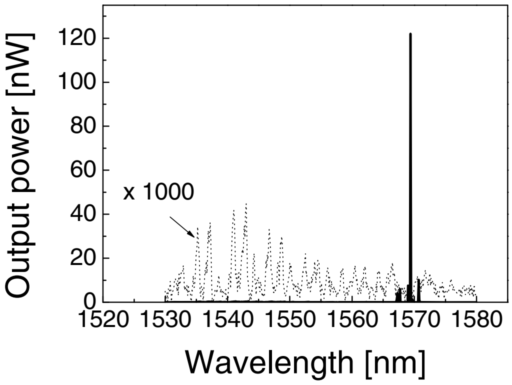

Figure 3 WGMs emission spectra from an 85 μm diameter Baccarat glass microsphere. The 1000 times magnified fluorescence spectrum below lasing threshold (dotted line) and the lasing spectrum (solid line) are shown.

The dotted lines show the fluorescence spectra with a series of peaks that are assigned to several families of WGMs [4]. When increasing the pump intensity above a threshold value which is around 2.5 mW, laser oscillation was obtained, as testified by the solid lines in both figures. Laser oscillation was achieved in the range from 1541.2 to 1569.3 nm and in the range from 1561.0 nm to 1601.8 nm for Baccarat and Schott IOG2 glasses, respectively [4, 12, 15]. Quality factor values in excess of 10^8 were obtained for the spheres prepared by plasma torch with resonance contrast around 80% [4].

4 Er^{3+}-doped sol–gel derived silica micro- and nanospheres

Sol–gel technique provides an excellent approach to rare-earth-activated glasses fabrication and can be successfully extended to the fabrication of micro and nanospheres.

4.1 Er^{3+}-activated SiO_2 microspheres prepared by acid catalysis

The first systems considered here concern Er^{3+}-activated SiO_2 microspheres prepared by acid ca-

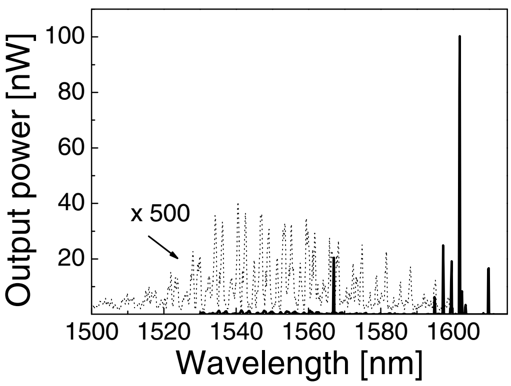

Figure 4 WGMs emission spectra from a 70 μm diameter Schott IOG2 microsphere. The 500 times magnified fluorescence spectrum below lasing threshold (dotted line) and the lasing spectrum (solid line) are shown.

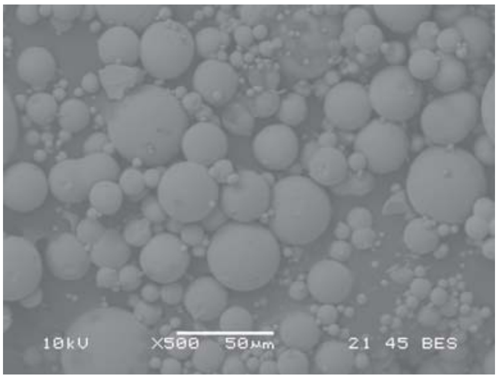

Figure 5 SEM image of Er^{3+} silica spheres obtained by sol–gel route in acid catalysis and heat treated at 1100 °C for 30 min.

talysis. The details of the fabrication protocol were reported in Ref. [16]. The spheres, obtained starting from a solution TEOS:CH_3COOH:H_2O of molar ratio 1:4:4 doped with 1 wt% $ErCl_3$, were heat treated at 1100 °C for 30 min in order to obtain complete densification. Acid catalysis does not allow obtaining spheres of controlled size distribution; in fact, the produced spheres had diameters ranging from hundred nanometers to approximately 100 µm, as shown in the SEM image of Fig. 5.

These silica spheres can be sorted as a function of the dimension and then stuck on the tip of a silica tapered fiber by means of an optically transparent adhesive component in order to easily handle them for spectroscopic measurements.

The most significant results concerning this kind of spheres regard the high surface quality of the spheres, proved by TEM analysis, and the efficient homogeneous dispersion of the Er^{3+} ion. In fact, photoluminescence spectra of a single sphere and of a large quantity of spheres pressed in KBr pellet exhibit the same shape, with a main emission peak at 1537 nm and a spectral bandwidth of about 27 nm, measured at 3 dB from the maximum intensity [16].

The same behaviour is obtained for the decay curves of the metastable level $^4I_{13/2}$ in the case of single sphere and of the pellet containing 5 wt% of spheres. For both the systems a single exponential profile with a lifetime of 13.6 ± 2 ms was obtained. Figure 6 shows the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ photoluminescence spectra as well as the decay profile for the single and pellet-embedded Er^{3+}-activated silica spheres.

In order to give an estimation of the quantum efficiency η defined by the ratio $\eta = \tau_{meas}/\tau_{rad}$, the measured lifetime (τ_{meas}) must be compared with the radiative lifetime τ_{rad}. Recently, many investigations were performed on SiO_2 spherical colloids doped with Er^{3+} ions, and a radiative lifetime of 18 ± 3 ms for Er-doped SiO_2 was determined [17–20]. Assuming a τ_{rad} of 18 ms, a quantum efficiency η of ~76% was estimated for Er^{3+}-activated SiO_2 microspheres prepared by acid catalysis.

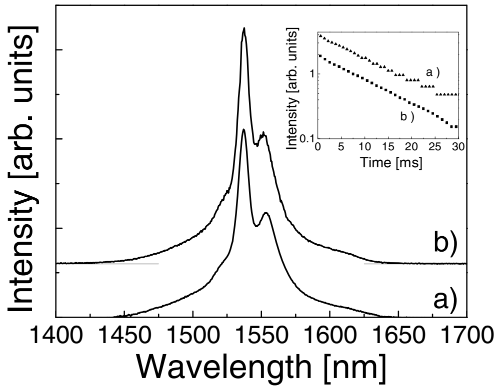

Figure 6 Photoluminescence spectra of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} silica spheres obtained by sol–gel route in acid catalysis and heat treated at 1100 °C for 30 min; a) single sphere, b) KBr pellet containing 5 wt% of spheres. The inset shows the decay curves for the two systems.

4.2 Er^{3+}-activated core-shell-like SiO_2 nanometric spheres The large size dispersion of spheres fabricated by sol–gel acid catalysis causes some drawbacks when a large number of single-size spheres is requested, for instance in synthetic opal fabrication [5]. It is known that monosized silica particles can be synthesized via base-catalyzed hydrolysis of TEOS following the Stober method [21]. 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 [15]. One effective solution is given by core-shell-like Er^{3+}-activated SiO_2 spheres where the core of pure silica is realized using the Stober method and the shell is an Er_2O_3–SiO_2 coating obtained by a seeded growth method staring from the acid catalysis [5, 22].

Figure 7 shows an SEM image of the core-shell-like Er^{3+}-activated silica spheres obtained as follows. Silica spheres of 270 nm, obtained by Stober method, were added to a solution with the molar ratio TEOS:CH_3COOH:H_2O of 1:8:8, plus 0.2 wt% $ErCl_3$. The mixture was agitated for

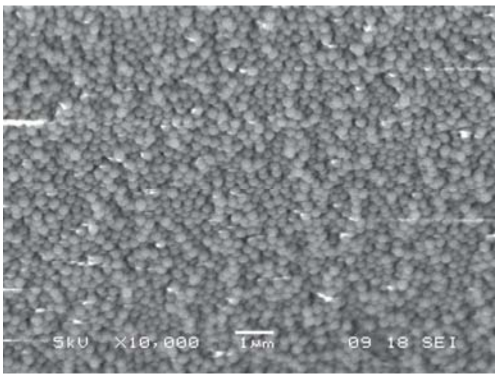

Figure 7 SEM image of core-shell-like Er^{3+}-activated silica spheres after annealing at 950 °C for 30 min. The spheres were prepared by seeded growth method using an acid-based reaction.

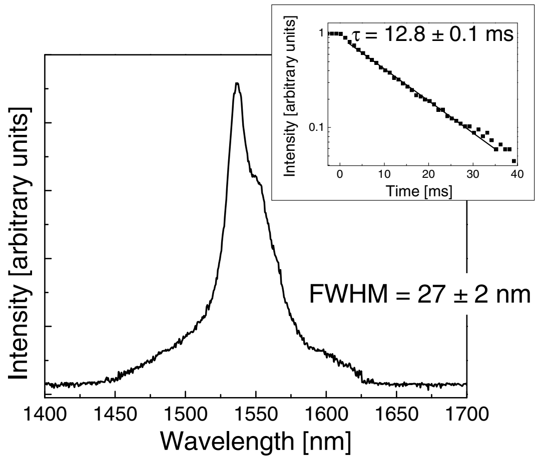

Figure 8 Room temperature photoluminescence spectrum of $^4I_{13/2} \rightarrow {^4I_{15/2}}$ transition of the Er^{3+} ions for the annealed silica core-shell-like structure, upon excitation at 514.5 nm. In the inset the luminescence decay curve from the $^4I_{13/2}$ state of Er^{3+} ions obtained in the same excitation conditions is reported.

45 min using a magnetic stirrer. After synthesis, the particles were separated from the solution by centrifuging at 1000 rpm and washed at least twice with pure ethanol [17]. Subsequently, the core-shell-like spheres were annealed at 950 °C for 30 min. The absence of any clustering of spheres is evident from Fig. 7, confirming that seeded growth in the erbium chloride solution occurs on individual particles.

The photoluminescence in the 1.5 μm region of annealed core-shell-like Er^{3+}-activated silica spheres was measured using the 514.5 line of an Ar^+ laser as excitation source. Figure 8 shows the room temperature photoluminescence spectrum of these core-shell-like spheres. The shape of the emission band is typical of Er^{3+}-doped silicate glasses, and the spectral bandwidth, measured at 3 dB from the maximum intensity, is 27 ± 2 nm [5], practically equal to the value measured for Er^{3+}-doped silica spheres obtained by sol–gel route in acid catalysis (see Section 4.1).

The inset in Fig. 8 shows the luminescence decay curve from the $^4I_{13/2}$ state of Er^{3+} ion in core-shell-like structure, still upon excitation at 514.5 nm. The decay curve exhibits a single-exponential behaviour with a lifetime of 12.8 ± 0.1 ms. Assuming a τ_{rad} of 18 ms, a quantum efficiency η of ~71% was estimated for these spheres. The slight difference in the shape of the $^4I_{13/2} \rightarrow {^4I_{15/2}}$ transition of the Er^{3+} ions and in the estimated quantum efficiency with respect to the Er^{3+}-activated SiO_2 microspheres prepared by acid catalysis is attributed to the different thermal annealing process (here 950 °C instead of 1100 °C).

5 Conclusion Dielectric micro- and nano-spheres are an important scientific and technological tool for manipulation of light on micrometric and sub-micrometric scale. A few examples are reported here, with focus onto the spectroscopic properties of Er^{3+}-activated dielectric spheres.

Two classes of microspheres have been considered, namely silica microspheres with a silica-hafnia coating, and glass microspheres. The former structures were obtained by melting the end of a telecom fiber and then coating it by sol–gel deposition; the latter ones were obtained by melting glass powders in a plasma torch. The latter spheres constitute tiny optical cavities where resonant modes exhibit high quality factor and low-threshold laser action. Spectroscopic measurements have shown that the plasma torch fabrication technique actually changes the local environment of the Er^{3+} ion in the microsphere with respect to the corresponding bulk glass. Further investigations on the influence of process parameters and on the necessary degree of control would be useful.

The coated microspheres, on the other side, 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.

Finally, Er^{3+}-activated sol–gel-derived micro- and nanospheres were prepared by acid catalysis and seeded-growth core-shell technique. For both the fabrication protocols a quantum efficiency higher than 70% was demonstrated, making these systems perspective candidates for efficient luminescent markers and nanosensors. The core-shell fabrication process, moreover, allowed us to obtain a large quantity of monosize Er^{3+}-doped spheres, perfectly suitable as building blocks of ordered structures such as active photonic crystals.

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References

[1] K. J. Vahala, Nature **424**, 839 (2003).
[2] A. B. Matsko, A. A. Savchenkov, N. Yu, and L. Maleki, J. Opt. Soc. Am. B **24**, 1324–1335 (2007).
[3] A. A. Savchenkov, A. B. Matsko, V. S. Ilchenko, N. Yu, and L. Maleki, J. Opt. Soc. Am. B **24**, 2988–2997 (2007).
[4] G. C. Righini, M. Brenci, A. Chiasera, P. Féron, M. Ferrari, G. Nunzi Conti, and S. Pelli, Proc. SPIE **6029**, 602903-1 (2005).
[5] A. Chiappini, C. Armellini, S. N. B. Bhaktha, A. Chiasera, M. Ferrari, Y. Jestin, M. Mattarelli, M. Montagna, E. Moser, G. Nunzi Conti, S. Pelli, G. C. Righini, and V. M. Sglavo, Proc. SPIE **6182**, 454 (2006).
[6] Special Isssue on Luminescent Nanomaterials (J. Nanomaterials, Volume 2007).

[7] H. Schniepp and V. Sandoghdar, Phys. Rev. Lett. **89**, 257403-1 (2002).
[8] G. C. Righini, M. Brenci, A. Chiasera, P. Feron, M. Ferrari, G. Nunzi Conti, and S. Pelli, Proc. SPIE **6029**, 19 (2006).
[9] R. R. Gonçalves, G. Carturan, L. Zampedri, M. Ferrari, M. Montagna, G. C. Righini, S. Pelli, S. J. L. Ribeiro, and Y. Messaddeq, Opt. Mater. **25**, 131 (2004).
[10] Y. Jestin, C. Armellini, A. Chiappini, A. Chiasera, Y. Dumeige, M. Ferrari, P. Féron, L.Ghisa, G. Nunzi Conti, S. Trebaol, and G. C. Righini, Proc. SPIE **6890**, 689008-1 (2008).
[11] Z. P. Cai, H. Y. Xu, G. Stéphan, P. Féron, and M. Mortier, Opt. Commun. **229**, 311 (2004).
[12] G. Nunzi Conti, A. Chiasera, L. Ghisa, S. Berneschi, M. Brenci, Y. Dumeige, S. Pelli, S. Sebastiani, P. Féron, M. Ferrari, and G. C. Righini, J. Non-Cryst. Solids **322**, 2360 (2006).
[13] P. Féron, Micro-optoelectronics: Materials, Devices and Integration, Quaderni di Ottica e Fotonica Vol. 8 (SIOF, Firenze, 2002), p. 117.
[14] C. Koughia and S. Kasap, Opt. Express **16**, 7709 (2008).
[15] G. C. Righini, C. Arnaud, S. Berneschi, M. Bettinelli, M. Brenci, A. Chiasera, P. Féron, M. Ferrari, M. Montagna, G. Nunzi-Conti, S. Pelli, H. Portales, C. Siligardi, A. Speghini, and L. Zampedri, Opt. Mater. **27**, 1711 (2005).
[16] G. C. Righini, C. Armellini, A. Chiasera, Y. Jestin, M. Ferrari, A. Chiappini, M. Montagna, C. Arfuso Duverger, P. Féron, S. Berneschi, M. Brenci, G. Nunzi Conti, S. Pelli, C. Gonçalves, and R. M. Almeida, Glass Technol.: Eur. J. Glass Sci. Technol. A **48**, 200 (2007).
[17] M. J. A. de Dood, B. Berkhout, C. M. van Kats, A. Polman, and A. van Blaaderen, Chem. Mater. **14**, 2849 (2002).
[18] M. J. A de Dood, L. H. Slooff, A. Polman, A. Moroz, and A. van Blaaderen, Appl. Phys. Lett. **79**, 3585 (2001).
[19] L. H. Slooff, M. J. A. de Dood, A. van Blaaderen, and A. Polman, Appl. Phys. Lett. **76**, 3682 (2000).
[20] M. J. A. de Dood, L. H. Slooff, A. Polman, A. Moroz, and A. van Blaaderen, Phys. Rev. A **64**, 0338071 (2001).
[21] W. Stober and A. Fink, J. Colloid Interf. Sci. **26**, 62 (1968).
[22] G. H. Bogush, M. A. Tracy, and C. F. Zukoski IV, J. Non-Cryst. Solids **104**, 95 (1988).

