Appl Phys B (2009) 97: 665–669
DOI 10.1007/s00340-009-3603-z

Applied Physics B
Lasers and Optics

Core-shell LaF_3:Er,Yb nanocrystal doped sol–gel materials as waveguide amplifiers

S.H. Bo · J. Hu · Z. Chen · Q. Wang · G.M. Xu ·
X.H. Liu · Z. Zhen

Received: 10 March 2009 / Revised version: 19 May 2009 / Published online: 17 June 2009
© Springer-Verlag 2009

Abstract The oleic acid (OA)-modified LaF_3:Er,Yb and LaF_3:Er,Yb–LaF_3 core-shell nanocrystals are synthesized. The lifetime values could be further improved by incorporating core-shell nanocrystals. A kind of sol–gel derived organic–inorganic hybrid material (SGHM) allows for 50 wt.% or even more of both the two nanocrystals in the matrix, and we give the explanation from scattering analysis. It's precisely because we use the erbium nanocrystals rather than erbium organic complexes, and avoid the undesirable luminescence quenching by Er–Er clustering with a high Er^{3+} concentration. LaF_3:Er,Yb–LaF_3/SGHM transparent films and optical waveguides are also fabricated. The nanocomposite films show strong 1550 nm luminescence intensity under the excitation of 980 nm after heat treatment below 150 °C and the full-width-at-half-maximum is about 51 nm. The loss and optical gain of the waveguide are measured. A relative gain of about 3.5 dB is measured at 1550 nm in a 1.7 cm long waveguide.

PACS 42.70.-a · 42.82.Et · 81.20.Fw

1 Introduction

Erbium-doped fiber amplifier (EDFA) has been applied to optical communication in the low loss telecommunication windows at 1535 nm wavelength. Compared with the EDFA, the erbium-doped waveguide amplifier (EDWA) has attracted more and more attention recently due to high optical gain in a much smaller size in photonic integrated circuits [1]. Usually, inorganic host materials, such as glasses and crystals, are used to fabricate EDWA. Compared to inorganic hosts, polymers can also be used for fabricate EDWA. They have many advantages, such as simple processing, low cost, and good thermal stability. Recently, species containing high-energy oscillators, such as O–H bonds have hampered the development of low-temperature processed Er^{3+} ions doped polymer waveguide amplifiers at 1550 nm. So the protection of Er^{3+} ions from quenching becomes very important. The first method is using Er-doped organic polydentate cage complexes. The ligands can protect and sensitize the Er^{3+} ions to increase the pump efficiency. Because of many C–H groups around Er^{3+} ions, the lifetime of these materials is very short (below 10 μs) [2–4]. Besides, the lack of the pump source and the Er–Er concentration quenching also restrict the development of these materials [3, 4]. The second method is that the Er^{3+} ions are shielded in inorganic nanostructures, such as Si nanocrystals [5], $LaPO_4$ nanocrystals [6, 7], LaF_3 nanocrystals [8], and CaF_2 nanocrystals [9]. The nanocrystals appear to be a very promising approach because of fairly long emission lifetime and appropriate pump power. However, the inorganic nanocrystals are hard to embed in the common polymer in large amounts (below 10 wt.%) [9, 10], and there are few reports on the optical gain of the nanocrystals-doped polymer materials at 1550 nm [11]. In this study, we prepared

---

S.H. Bo · J. Hu · Z. Chen · Q. Wang · G.M. Xu · X.H. Liu ·
Z. Zhen (✉)
Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, 100190, People's Republic of China
e-mail: zhenz@mail.ipc.ac.cn
Fax: +86-01-62554670

J. Hu · Z. Chen
The Graduate University of Chinese Academy of Sciences, Beijing, 100049, People's Republic of China

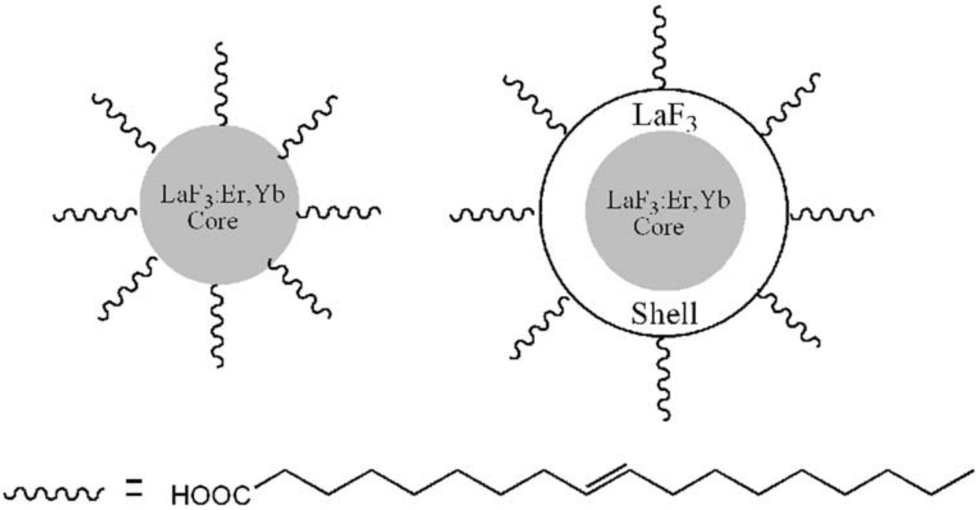

Fig. 1 Structure scheme of the oleic acid (OA)-modified LaF$_3$:Er,Yb and LaF$_3$:Er,Yb–LaF$_3$ core-shell nanocrystals

the selected SGHM as the polymer matrix using organic–inorganic composite material. The sol–gel materials containing organic and inorganic parts can easily bend with organic ligands modified inorganic nanocrystals. Furthermore, the thermal stability of the SGHM is better than other polymers because of the silicon networks. OA-modified LaF$_3$:Er,Yb and LaF$_3$:Er,Yb–LaF$_3$ core-shell nanocrystals can be easily produced in the water–ethanol system and can be more easily dispersible in the organic/inorganic materials at 50 wt.% or even larger concentration by a common organic solvent, retaining long luminescence lifetimes. We successfully fabricated the optical waveguides, and a relative optical gain of about 3.5 dB was measured at 1550 nm in a 1.7 cm long waveguide. This indicated the possibility of this system as a promising material for use in planar optical amplifier applications.

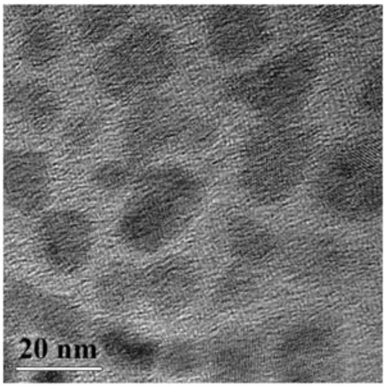

Fig. 2 The HRTEM image of oleic acid (OA)-modified LaF$_3$:Er,Yb–LaF$_3$ core-shell nanocrystals

2 Experiments

LaF$_3$:Er,Yb and LaF$_3$:Er,Yb–LaF$_3$ core-shell nanocrystals, stabilized with oleic acid ligand, were prepared by the coprecipitation technique in aqueous/ethanol solution essentially the same as described in our previous publication [10] and in [12]. The structure scheme of the LaF$_3$:Er,Yb and LaF$_3$:Er,Yb–LaF$_3$ core-shell nanocrystals are shown in Fig. 1. The size distribution for LaF$_3$:Er,Yb nanocrystals measured by the TEM technique is 7–10 nm. In Fig. 2, LaF$_3$:Er,Yb–LaF$_3$ core-shell nanocrystals are well-separated with diameters of about 12–15 nm. When the two kinds of nanocrystals are incorporated in the polymer matrix, these particles are so small that the Rayleigh scattering may nearly be neglected. We prepared the selected SGHM using 3-methacryloxypropyltrimethoxysilane (MAPTMS) as precursor and zirconium tetra-n-butoxide (ZBO) as a refractive-index modifier [11, 13–15]. First of all, MAPTMS was hydrolyzed with equivalent molar H_2O in the presence of 0.1 M HCl as a catalyst at room temperature for 1 h. At the same time, ZBO reacted with MAA at room temperature for 1 h in a molar ratio of 1:1. After that, ZBO solution was added dropwise to the prehydrolyzed MAPTMS solution under vigorous stirring and then the mixed solution was kept stirred for 1 h to advance hydrolysis and condensation. The mixed solution reacted with added water for 15 h. Then the resulting solution was dissolved with toluene. The solvent was removed, and then a clear polymer resin was obtained. The refractive indices of the SGHM films were adjusted by altering the Zr/Si ratio in the sol–gel hybrid matrices. When the Zr/Si = 0.5 (molar ratio), the refractive index of the film is 1.516 at 1315 nm, and the quality of the SGHM films is the best.

The SGHM were diluted in toluene. Then LaF$_3$:Er,Yb–LaF$_3$ was dissolved in the sol as LaF$_3$:Er,Yb–LaF$_3$/SGHM = 50 wt.% and 3 wt.% of the photoinitiator IHT-PI-TPO was added into the above solution, and it was dissolved at room temperature by ultrasonic treatment for 20 min. The films were prepared from the composite sols on silicon wafers

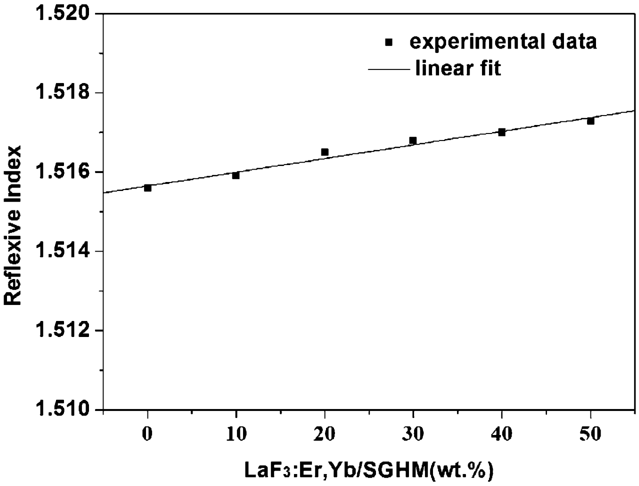

Fig. 3 Concentration effect for refractive index of the LaF_3:Er,Yb nanocrystals doped into the SGHM (Zr/Si = 0.5) films at 1315 nm

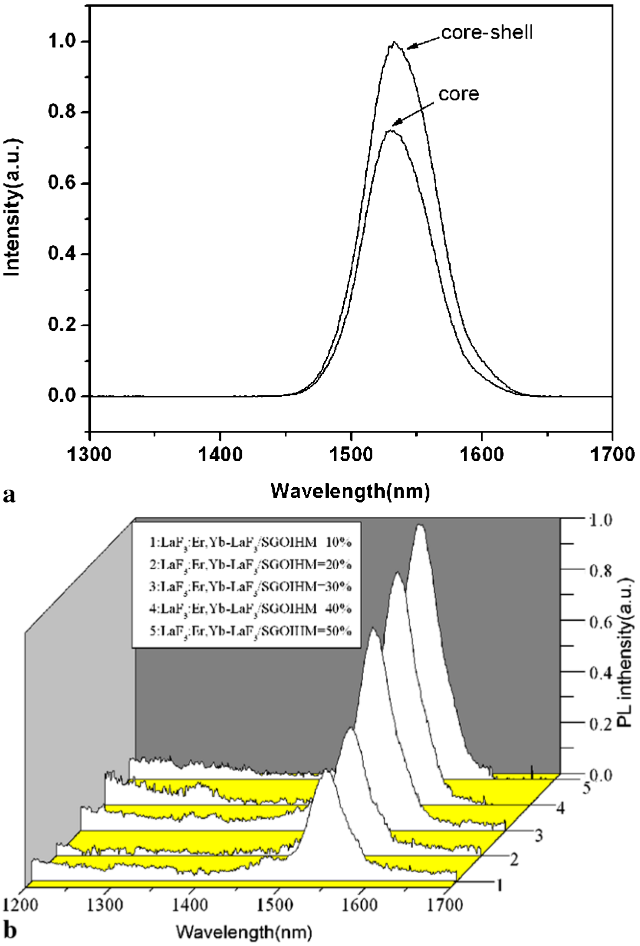

Fig. 4 (**a**): Emission spectra for LaF_3:Er,Yb and LaF_3:Er,Yb–LaF_3 nanocrystals. (**b**): Room temperature PL spectra under excitation of 980 nm of the LaF_3:Er,Yb–LaF_3 doped SGHM films. The films were measured after being treated by pre-baking (80 °C, 4 min), UV-radiation (at 365 nm, 3 min), and post-baked (150 °C, 3 h)

by spin-coating at 1500 rpm for 30 s after filtration with 0.2 µm syringe filter. The complete films were pre-baked at 80 °C for 4 min, UV-radiation (300 W, 365 nm) for 10 min, and post-baked at 150 °C for 3 h in air. Then transparent, crack-free over 4 µm thick films which can satisfy the device requirement were prepared by a single-step spin-coating process.

3 Results and discussion

The refractive indices of SGHM films containing the LaF_3:Er,Yb nanocrystals at 1315 nm are shown in Fig. 3. When we used the LaF_3:Er,Yb–LaF_3 core-shell nanocrystals, similar results were obtained. As shown in Fig. 3, the refractive indices of the nanocomposite films change only a little with increasing LaF_3:Er,Yb nanocrystals. This indicates that the refractive index of the oleic acid (OA)-modified LaF_3:Er,Yb is similar to that of the SGHM when Zr/Si (molar ratio) is 0.5. The refractive index of oleic acid is 1.4582, and hence oleic acid (OA)-modified LaF_3 nanocrystal has lower refractive index than LaF_3 crystal (the refractive index is 1.58 at 1540 nm). For the same particle size, the greater is the difference in the refractive index between the polymer and the doping, the greater scattering loss exists. Because of the low index mismatch between the nanocrystals and the polymer matrix and/or the small dispersed particle size, a lot of LaF_3 nanocrystals can be doped in the SGHM materials, and the nanocomposite films have excellent transmissions (low losses) [16].

The photoluminescence (PL) measurements of the films were recorded by a liquid-nitrogen-cooled near-infrared photomultiplier tube (NIR PMT) detector under the excitation of a 980-nm continuous-wave (cw) laser diode delivering an output power ranging from 0 to 1.5 W. The fluorescence lifetime test of the nanocrystals at room temperature in the infrared region was performed on a Fluorolog FL3-11 spectrofluorometer equipped with a SPEX 1934D phosphorimeter by monitoring the decay of the luminescence intensity excited at 980 nm. The luminescence lifetime (τ) was measured to be 60 µs for LaF_3:Er,Yb and 90 µs for LaF_3:Er,Yb–LaF_3 nanocrystals using a single exponential decay fit. This indicated that the LaF_3 shell can better protect the Er^{3+} ions in LaF_3. Figure 4(a) presents the emission spectra for the LaF_3:Er,Yb and LaF_3:Er,Yb–LaF_3 nanocrystals. The transition is at the right position for telecommunication applications. The photoluminescence measurements of LaF_3:Er,Yb–LaF_3 core-shell nanocrystals doped SGHM films (LaF_3:Er,Yb–LaF_3/SGHM = 10, 20, 30, 40, and 50%) were recorded under the excitation of 980 nm CW laser diode (the intensity is about 25 mW) and they are shown in Fig. 4(b). Emission spectra peaking at 1540 nm are assigned to the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ translation of Er^{3+} ions with a band full-width-at-half-maximum of 51 nm. The composite

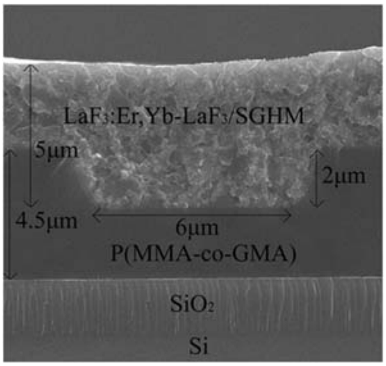

Fig. 5 The SEM image of the waveguide cross-section

Fig. 6 Output near-field profile from a 1.7 cm long waveguide at 1550 nm. The input signal power is 0.05 mW

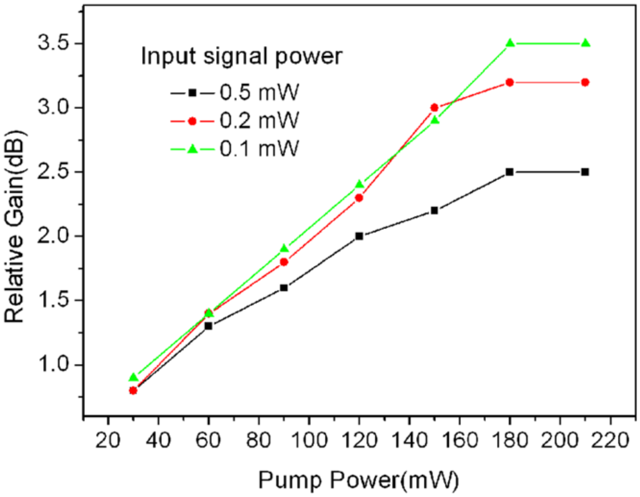

Fig. 7 Dependence of relative gain on pump powers with different input signal powers for a 1.7 cm long LaF$_3$:Er,Yb–LaF$_3$ nanocrystals-doped SGHM waveguide. The wavelength of signal is 1550 nm

films heat treated at below 150 °C exhibited a high PL intensity, and the peak intensities are increased by increasing the content of the LaF$_3$:Er,Yb–LaF$_3$ nanocrystals. The 4f → 4f transitions of erbium ions are actually forbidden transitions by parity selection rule, but can be allowed to some extent by the crystal field of lattice [17–20]. In the nanocrystals system, because Er^{3+} and Yb^{3+} ions substituted La^{3+} ions in LaF$_3$ crystal lattice, Er^{3+} ions can be well protected by the inorganic lattice and only a small part of lanthanide ions contact with the oleic acid or O–H groups. Besides, the Er^{3+} ions can be better isolated from O–H groups in core-shell structure. In that case, the O–H and C–H groups present directly around Er^{3+} ions can be minimized, getting high PL intensity after low temperature heat treatment.

The substrate was first fabricated using silicon wafer. Prior to use, 2 µm SiO$_2$ film as buffer layer was deposited on the silicon wafers. The optical amplifier multiplexer was fabricated using spin-coating. P(MMA-co-GMA) (polymethyl-methacrylate-co-glyciclyl-methacrylate) was used as a cladding and SGHM films doped 50 wt.% LaF$_3$:Er,Yb–LaF$_3$ core-shell nanocrystals as a core. It is suitable that the refractive index of the core is 1.517 and the cladding is 1.483 at 1315 nm. On the P(MMA-co-GMA) layer, a waveguide pattern was formed by reactive ion etching (RIE) using oxygen. Figure 5 shows the scanning electron microscopy image of the waveguide cross-section (without the up cladding). The active polymeric waveguide with a 6 µm × 2 µm is fabricated. Figure 6 is the output near-field profile from a 1.7 cm long waveguide at 1550 nm wavelength. The input signal power is 0.05 mW. A 975 nm laser diode was used as the pump source and a 1550 nm laser diode (Model: ELD-1-1550) was used for the signal.

Propagation loss was measured using the cutback method. We roughly estimated the propagation loss value of 3.1 dB/cm at 1550 nm. The propagation loss mainly comes from the waveguide scattering and polymer absorption [11]. The relative gain is determined from the ratio of the output signal observed on the optical spectrum analyzer (OSA, Ando AQ-6317B) when both the pump and signal beams are coupled to the polymer waveguide to the signal power without the pump. Figure 7 shows the measured relative gain as a function of pump power with different input signal powers in a 1.7 cm long reverse-mesa ridge waveguide. The relative gain gradually enhances with the increase of pump power. As the pump power was increased to 180 mW, a maximum gain was obtained from the reverse-mesa ridge waveguide. The smaller input signal power is used, the bigger gain can be obtained for the fixed pump power. At 150 mW pump power, the relative gain increases from about 2.2 to 3 dB when the signal power is from 0.5 to 0.1 mW. When the pump power is 180 mW and the input signal power is 0.1 mW, the maximum gain of about 3.5 dB (2.06 dB/cm) at 1550 nm was obtained. Large relative gain can be expected by optimizing the waveguide and minishing the loss. Compared with the optical gain (1.77 dB/cm) for EDWA using 70 wt.% LaF$_3$:Er,Yb/SGHM, we obtain a bigger optical gain of 2.06 dB/cm for EDWA using 50 wt.% LaF$_3$:Er,Yb–LaF$_3$/SGHM. This shows that the improved fluorescence lifetime is very important for the EDWA.

At present, the main difficulty in developing an EDWA lies in providing suitably high gain in a small size device, which requires high Er^{3+} doping without concentration-dependent effects. In this article, we reported that the OA-modified nanocrystals can be easily dispersible at a concentration of 50 wt.% or even more in the sol–gel polymer. A relative optical gain of about 3.5 dB was measured at 1550 nm in a 1.7 cm long waveguide.

4 Conclusion

We have prepared the SGHM matrix via a sol–gel process and an excellent dopant OA-modified LaF_3:Er,Yb and LaF_3:Er,Yb–LaF_3 nanocrystals with good solubility in common organic solvents. 50 wt.% OA-modified LaF_3:Er,Yb–LaF_3 core-shell nanocrystals-doped SGHM-based transparent films and optical waveguides were fabricated. To our knowledge, 50 wt.% is the highest reported doped concentration in the polymer matrix. Strong 1550 nm infrared fluorescence was observed from the nanocomposite films when excited by 980 nm radiation after heat treatment below 150 °C. It was also demonstrated that erbium (III) NIR-luminescence could be detected in sol–gel materials without the need of using high drying temperatures in the preparation method. Loss and relative gain of the waveguide were measured. A relative optical gain of about 3.5 dB was measured at 1550 nm in a 1.7 cm long waveguide.

Acknowledgements We are grateful to the Directional Program of the Chinese Academy of Sciences (KJCX2.YW.H02) and the National Basic Research Program of China (973 Program, Grant No. 2006CB933000) for financial support.

References

1. P.G. Kik, A. Polman, MRS Bull. **23**, 48–54 (1998)
2. S.W. Magennis, A.J. Ferguson, T. Bryden, T.S. Jones, A. Beeby, I.D.W. Samuel, Synthetic Met. **138**(3), 463 (2003)
3. S.I. Klink, L. Grave, D.N. Reinhoudt, F.C.J.M. Van Veggel, M.H.V. Werts, F.A.J. Geurts, J.W. Hofstraat, J. Phys. Chem. A **104**, 5457 (2000)
4. G.A. Hebbink, D.N. Reinhoudt, F.C.J.M. Van Veggel, Eur. J. Org. Chem. **21**, 4101 (2001)
5. J.S. John, J.L. Coffer, Y. Chen, R.F. Pinizzotto, J. Am. Chem. Soc. **121**, 1888 (1999)
6. G.A. Hebbink, J.W. Stouwdam, D.N. Reinhoudt, F.C.J.M. Van Veggel, Adv. Mater. **14**, 1147 (2002)
7. O. Lehmann, M. Meyssamy, K. Kömpe, H. Schnablegger, M. Haase, J. Phys. Chem. B **107**, 7449 (2003)
8. J.W. Stouwdam, F.C.J.M. Van Veggel, Nano Lett. **2**, 733 (2002)
9. G.A. Kumar, C.W. Chen, R. Riman, S. Chen, D. Smith, J. Ballato, Appl. Phys. Lett. **86**, 241105 (2005)
10. J.S. Wang, J. Hu, X.H. Liu, Z. Zhen, J. Mater. Chem. **17**(16), 1597 (2007)
11. S.H. Bo, J.S. Wang, H. Zhao, H.H. Ren, Q. Wang, G.M. Xu, X.H. Liu, Z. Zhen, Appl. Phys B **91**, 79 (2008)
12. J.W. Stouwdam, F.C.J.M. Van Veggel, Langmuir **20**, 11763 (2004)
13. J.I. Jung, O.H. Park, B.S. Bae, J. Sol–Gel Sci. Technol. **26**, 897 (2003)
14. A. Farad, M. Andrews, G. Milova, A. Malek-Tabrizi, I. Najafi, Appl. Opt. **37**, 2429 (1998)
15. O.H. Park, J.I. Jung, B.S. Bae, J. Mater. Res. **16**, 2143 (2001)
16. G.A. Kumar, C.W. Chen, J. Ballato, R.E. Riman, Chem. Mater. **19**, 1523 (2007)
17. L.H. Slooff, A. Polman, S.I. Klink, G.A. Hebbink, L. Grave, F.C.J.M. Van Veggel, D.N. Reinhoudt, J.W. Hofstraat, Opt. Mater. **14**, 101 (2000)
18. G. Blasse, B.C. Grabmaier, *Luminescent Materials* (Springer, Berlin, 1994)
19. D.R. Vij, *Luminescence of Solids* (Plenum Press, New York, 1998)
20. J. Seokwoo, B. Paul, Chem. Mater. **15**, 1256 (2003)