H. Schäfer and M. Haase

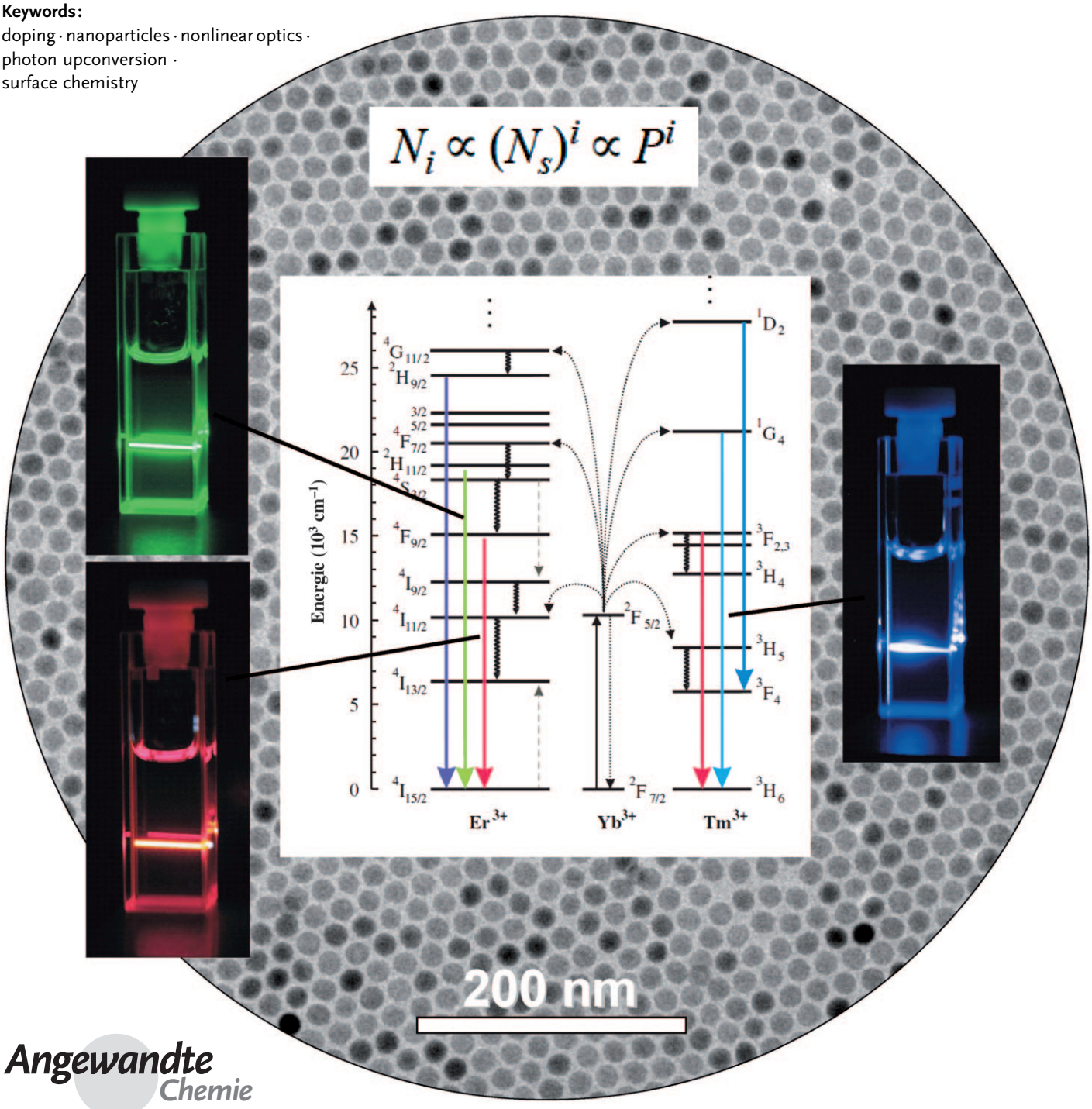
DOI: 10.1002/anie.201005159

Upconversion

Upconverting Nanoparticles

*Markus Haase and Helmut Schäfer**

Keywords:
doping · nanoparticles · nonlinear optics · photon upconversion · surface chemistry



Upconversion (UC) refers to nonlinear optical processes in which the sequential absorption of two or more photons leads to the emission of light at shorter wavelength than the excitation wavelength (anti-Stokes type emission). In contrast to other emission processes based on multiphoton absorption, upconversion can be efficiently excited even at low excitation densities. The most efficient UC mechanisms are present in solid-state materials doped with rare-earth ions. The development of nanocrystal research has evoked increasing interest in the development of synthesis routes which allow the synthesis of highly efficient, small UC particles with narrow size distribution able to form transparent solutions in a wide range of solvents. Meanwhile, high-quality UC nanocrystals can be routinely synthesized and their solubility, particle size, crystallographic phase, optical properties and shape can be controlled. In recent years, these particles have been discussed as promising alternatives to organic fluorophosphors and quantum dots in the field of medical imaging.

From the Contents

1. Introduction

In linear optics it is assumed that optical properties are independent of the intensity of the incident light. The expression "nonlinear optics" is usually used to describe all other phenomena for which the optical properties of the material depend on the radiant flux density of the exciting light. Nonlinear optics, an integral part of contemporary optics, is based on a number of nonlinear phenomena and processes. Photon upconversion (UC) is one such phenomenon and is characterized by the conversion of long-wavelength radiation, for instance infrared or near infrared (NIR) radiation, to short-wavelength radiation, usually in the visible range. The upconversion process proceeds by different mechanisms, which are summarized and discussed in detail in several review articles[1–3] and can be roughly divided into three classes: APTE effect (for addition de photon par transferts d'energie), later also named ETU for energy-transfer upconversion,[4,5] excited-state absorption (ESA), and photon avalanche (PA). It is worth mentioning that the expression "upconversion" is sometimes used to describe the consequence of these mechanisms, that is, the conversion from long-wavelength to short-wavelength radiation, and sometimes for a specific mechanism itself.

All three mechanisms are based on the sequential absorption of two or more photons by metastable, long-lived energy states. This sequential absorption leads to the population of a highly excited state from which upconversion emission occurs. In the case of ESA, the emitting ions sequentially absorb at least two photons of suitable energy to reach the emitting level (Figure 1). In ETU, one photon is absorbed by the ion, but subsequent energy transfer from neighboring ions results in the population of a highly excited state of the emitting ion (Figure 1). Energy-transfer steps between two ions, both in excited states, leading to emission lines at short wavelength were first mentioned by Auzel in 1966.[6,7]

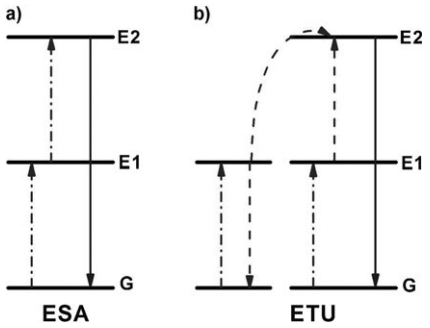


Figure 1. UC processes for lanthanide-doped crystals: a) excited-state absorption, b) energy-transfer upconversion. –•–•–: photon excitation, - - - - -: energy transfer, ——: emission. Reproduced from reference [47] by permission of The Royal Society of Chemistry.

ETU and ESA should not be confused with two other nonlinear optical processes, simultaneous two-photon absorption (STPA)[1,8–10] and second-harmonic generation (SHG), which is efficient if coherent excitation sources with sufficiently high power are used.[11–14] Several early reviews focused on the synthesis and application of upconversion phosphors.[4,5,15,16]

Important requirements for photon upconversion, such as long lifetimes of the excited states and a ladder-like arrangement of the energy levels with similar spacings, are realized for certain ions of the d and f elements. A large number of suitable hosts doped with transition-metal ions (3d, 4d, 5d) have been reported to show upconversion, for example Ti^{2+}-,[17,18] Ni^{2+}-,[19–22] Mo^{3+}-,[23,24] Re^{4+}-,[23,25,26] or Os^{4+}-doped solids.[27–30] Actinide-doped materials have also been inves-

[*] Prof. Dr. M. Haase, Dr. H. Schäfer
Inorganic Chemistry I, University of Osnabrück
Barbarastrasse 7, 49069 Osnabrück (Deutschland)
E-mail: helmut.schaefer@uos.de

tigated with respect to upconversion.[31,32] These systems require low temperatures, show poor optical properties, and are therefore at present mainly a subject of basic research.

High upconversion efficiencies even at room temperature, however, are observed for lanthanide-doped solids. The most efficient UC phosphor to date, Yb^{3+}- and Er^{3+}-doped $NaYF_4$, was introduced by Menyuk et al. in 1972[33] and Kano et al. in 1973[34] Owing to their outstanding properties, UC materials have been proposed for several applications, such as lasers,[11,35–37] solar cells,[38] wave guides,[39,40] and display devices.[41]

The availability of cheap semiconductor lasers together with the rise of nanoscience increased interest in the design of suitable synthesis procedures for nanocrystalline upconversion materials. In analogy to semiconductor nanocrystals (quantum dots), the aim was to synthesize small UC nanocrystals with high luminescence efficiency that form transparent solutions in a wide range of solvents. In comparison with bulk luminescent material, small luminescent particles show a classical drawback, namely poor luminescent efficiency. Core–shell architectures helped to overcome this problem (see Section 3.4). Dispersible upconverting nanophosphors show only low cytotoxicity,[42–46] and since excitation with NIR-light causes only a very low autofluorescence background of the biological materials, they seem to be a promising alternative for organic dyes or quantum dots in biological tagging experiments.

As the development and investigation of UC nanophosphors has become an essential part of materials science, several reviews have already been published.[47–49,460] This Review presents the current state of affairs in the area of lanthanide-doped UC nanocrystals, with emphasis on the synthesis and investigation of lanthanide-doped nanoparticles (NPs). Despite the fact that the number of published articles related to this field has increased dramatically and therefore interferes with the clarity, one aim of this account is to give an almost complete general survey with respect to the relevant literature.

2. Selection of Suitable Dopants and Host Materials

An inorganic upconversion phosphor consists of a crystalline host and a dopant (usually lanthanide ions) added in low concentrations. The dopant provides luminescent centers, and the host lattice with its crystal structure provides a matrix to bring these centers into optimal position.[50–52] The ion-to-ion distance and spatial arrangement is especially important in the case of so-called sensitized luminescence, as will be discussed in detail in Section 2.2.2 (ETU mechanism).[53] Many lanthanide-doped host materials are able to emit visible light under NIR excitation, but highly efficient upconversion requires a good tuning between host lattice, dopant ions, and dopant concentration.

2.1. Choice of Host Lattice

The choice of the host lattice determines the distance between the dopant ions, their relative spatial position, their coordination numbers, and the type of anions surrounding the dopant. The properties of the host lattice and its interaction with the dopant ions therefore have a strong influence on the upconversion process. With regard to the ETU mechanism (Figure 2), Er^{3+} is excited into the $^4F_{7/2}$ state in two steps. The $^2H_{11/2}$ and the $^4S_{3/2}$ states are populated by nonradiative multiphonon relaxation steps. From these levels, the ion may either return directly to the $^4I_{15/2}$ ground state or may first populate the $^4F_{9/2}$ state by an additional nonradiative multiphonon relaxation step. In the first case green light is emitted, in the second case red light. To achieve efficient excitation of the $^2H_{11/2}$ state and, hence, intense upconversion emission, the $^4I_{11/2}$ state must be strongly populated. In other words, an efficient upconversion process benefits from a long $^4I_{11/2}$ lifetime.[2,54] In fluoride materials, long lifetimes of the excited states are commonly observed because of the low phonon energies (ca. 350 cm^{-1})[69] of the crystal lattice (Table 1). However, lattice impurities may increase the multiphonon relaxation rates between the metastable states, thereby reducing the overall visible emission intensity.[55] Small nonradiative losses are also observed for lattices containing heavy halogenides, but these materials suffer from low chemical stability. Metal oxides present the desired chemical stability,

Markus Haase received his PhD in 1989 with Prof. A. Henglein from the Technical University in Berlin. After postdoctoral research at UC Berkeley with Prof. A. P. Alivisatos, he moved to the Philips Research Laboratories in Aachen, Germany. In 1996, he joined the group of Prof. H. Weller at the University of Hamburg, where he finished his Habilitation in 2001. He received the Nernst–Haber–Bodenstein Prize of the Deutsche Bunsengesellschaft for Physical Chemistry in 2002. Since 2004 he has been professor at the University of Osnabrück. His research interests include the synthesis and application of inorganic nanoparticles and luminescent materials.

Helmut Schäfer studied chemistry at the Carl von Ossietzky University of Oldenburg and received his PhD in 2001 with Prof. M. Weidenbruch for his work on organogermanium compounds. As a postdoctoral fellow, he moved to the Institute of Material Science (IWT) Bremen, German Aerospace Center Cologne, and to the University of Osnabrück. Since 2004 he has been a researcher in the group of Prof. Markus Haase. His research interests are closely connected with materials science and include the investigation of alternative synthesis routes to known compounds as well as the synthesis of novel inorganic compounds with particular characteristics.

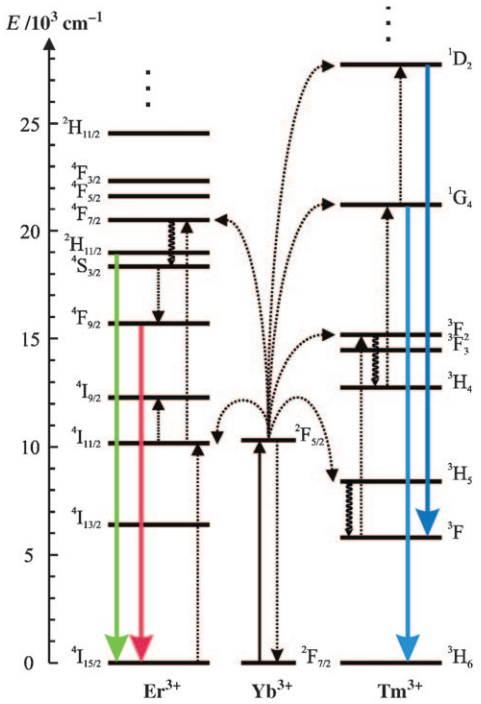


Figure 2. Energy-level diagram, upconversion excitation, and visible emission schemes for the Yb^{3+}-sensitized Er^{3+} and Tm^{3+} systems. Arrows indicate radiative and nonradiative energy transfer and multiphonon relaxation processes. Reproduced from reference [59] Copyright Wiley-VCH 2004.

Table 1: Highest phonon lattice energy of commonly used matrices for rare-earth ions. Reproduced with permission from reference [56]. Copyright Wiley-VCH 2007.

Material	Highest Phonon Energy [cm^{-1}]
phosphate glass	1200
silica glass	1100
fluoride glass	550
chalcogenide glass	400
$LaPO_4$	1050
YAG[a]	860
YVO_4	600
LaF_3	300
$LaCl_3$	240

[a] YAG: yttrium aluminum garnet.

but conventional oxygen-based systems often exhibit large phonon energies above 500 cm^{-1}[56] (Table 1).

Host lattices based on cations like Na^+, Ca^{2+} and Y^{3+} with ionic radii close to those of the lanthanide dopant ions prevent the formation of crystal defects and lattice stress, and therefore generally Na^+ and Ca^{2+} fluorides are superior host materials for upconversion phosphors.[57–62] The upconversion efficiency of, for instance, $NaYF_4$:Yb^{3+},Er^{3+} is 20 times higher than that of La_2O_3:Yb^{3+},Er^{3+} and 6 times higher than that of $La_2(MoO_4)_3$:Yb^{3+},Er^{3+}.[63] Nevertheless, Yb^{3+},Er^{3+} doped phosphors based on oxide type matrices are also commercially available[65] and were used, for instance, by Kuningas et al.[66,67]

Among the fluoride hosts, hexagonal $NaYF_4$ (β-$NaYF_4$) is the most efficient host material for green and blue upconversion phosphors known to date.[1,11,51,68–79] The UC efficiency of the green emission in hexagonal-phase $NaYF_4$:Yb^{3+}/Er^{3+} is approximately 10 times stronger than that in cubic $NaYF_4$:Yb^{3+}/Er^{3+}.[50] The question why it is superior to all other host materials in terms of upconversion luminescence efficiency was thoroughly investigated, particularly by Güdel et al.[51] It could be shown that the generally high emission intensities of this phosphor originate from the interaction of dopant ions located on two different lattice sites.[51]

Especially in the case of small particles, we must take additional effects into consideration. Since additional nonradiative pathways exists for ions at or near the surface and even for ions in the core of the particles,[80,81] quenching is possible even when pure fluoride matrices are used.[461]

2.2. Dopant Systems Available for Upconversion

2.2.1. Single Doping

Owing to the long lifetime of the excited states, an excited lanthanide ion may sequentially absorb a second photon of suitable energy at comparatively low excitation densities and reach an ever-higher excited state. If within one ion energy gaps between three or more subsequent energy levels are very similar, sequential excitation to a highly excited state is possible with a single monochromatic light source, since each absorption step requires the same photon energy. Lanthanide ions with an energy-level structure suitable for this type of excitation include Er^{3+}, Tm^{3+}, and Ho^{3+}, which are currently the most common emitters (activators) in upconversion phosphors.[47] The efficiency of the upconversion process is particularly high for Er^{3+}, where a similar energy gap of about 10350 cm^{-1} exists between two subsequent pairs of energy levels, namely between the $^4I_{11/2}$ and $^4I_{15/2}$ states and between the $^4I_{11/2}$ and the $^4F_{7/2}$ states (Figure 2, left). In addition, the energy difference between $^4F_{9/2}$ and $^4I_{13/2}$ states is in the same region, and hence at least three different transitions in Er^{3+} ions are induced by IR photons of the same energy, thus leading to emission of green and red light (Figure 2, left, and Figure 3a–c) after the sequential absorption of two photons.

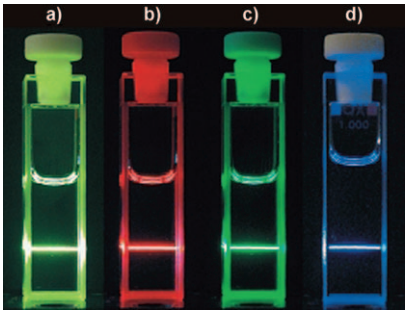


Figure 3. Photographs of the upconversion luminescence in 1 wt% colloidal solutions of nanocrystals excited with 973 nm light. a) Total upconversion luminescence of the $NaYF_4$:20% Yb^{3+},2% Er^{3+}. b,c) The same luminescence through red (b) and green (c) color filters. d) Total upconversion luminescence of the Yb^{3+},Tm^{3+}-doped sample. Reproduced from reference[59]. Copyright Wiley-VCH 2004.

Blue emission is observed in systems doped with Tm^{3+} after the absorption of four photons (Figure 2, right, and Figure 3d). Several reports are focused on the synthesis and investigation of (single) rare-earth-ion-doped nanomaterials.[69,74,82–174]

Since 4f–4f transitions are Laporte-forbidden, inefficient absorption of the exciting light can be a serious problem, especially in the case of thin samples of lanthanide doped materials. In principle, the absorption can be improved by increasing the concentration of the lanthanide dopant in the material. But radiationless deactivation can occur, and the process of cross-relaxation severely limits the range of useful dopant concentrations. The upper limit of concentration depends on the exact distance of the lattice sites occupied by lanthanide ions, but in most upconversion materials the concentration of Er^{3+} does not exceed 3% and of Tm^{3+} not about 0.5%. At these concentrations, however, the absorption of light is insufficient, which hinders the practical use of these materials as phosphors.[47] To increase the absorption of lanthanide-doped phosphors, the materials are often additionally doped with strongly absorbing ions called sensitizers, which should also ensure efficient energy transfer to the activator.

2.2.2. Codoping: Systems with Activators and Sensitizers

In the case of upconversion phosphors based on Er^{3+} or Tm^{3+}, the most widely used sensitizer for 980 nm light is the Yb^{3+} ion. The energy separation of the $^2F_{7/2}$ ground state of Yb^{3+} and its $^2F_{5/2}$ excited state matches well the transition energy between the $^4I_{11/2}$ and $^4I_{15/2}$ states and also the $^4F_{7/2}$ and $^4I_{11/2}$ states of Er^{3+}, thus allowing for efficient (quasi-)resonant energy transfer between the two ions. Usually, Yb^{3+} is codoped into the lattice in high concentrations (18–20%). Yb^{3+} is also the standard sensitizer for Tm^{3+}-doped upconversion materials, in which the energy of four 980 nm photons is transferred from the Yb^{3+} ions to one Tm^{3+} ion (Figure 2). Both ion couples (Er^{3+}/Yb^{3+} and Tm^{3+}/Yb^{3+}) show the highest upconversion efficiency when doped into hexagonal-phase $NaYF_4$ (β-$NaYF_4$). Apart from high upconversion efficiencies, the emission of Yb^{3+},Er^{3+} codoped phosphors saturates only at high excitation densities. Saturation is found at 100 $W cm^{-2}$ for $NaYF_4$:Yb^{3+},Er^{3+}.[175] Many reports on Yb^{3+},Er^{3+}- and Yb^{3+},Tm^{3+}-doped nanocrystalline[43,44,46,52,55,57–62,64,71–73,75,77–79,87,90,91,93,102,176–262] and macrocrystalline[33,50,65,66,68–70,120,166,204,208,263–292] upconversion phosphors have been published. Yb^{3+} is a common sensitizer not only for Er^{3+},Tm^{3+} systems but also for Ho^{3+}[293] and Pr^{3+}[294] ions. The activator–sensitizer concept can also be applied to transition-metal ions. For instance, Cs_2NaYCl_6:Os^{4+},Er^{3+} or $Cs_2NaYbCl_6$:Mo^{3+} showing energy transfer between Er^{3+} and Os^{4+} and between Mo^{3+} and Yb^{3+}, respectively, were investigated by Güdel and co-workers.[2,295]

3. Synthesis, Growth, and Properties of Rare-Earth-Doped Nanocrystals

3.1. Nanocrystals Based on Oxidic Materials

There have been numerous reports on the properties of nanocrystalline upconversion materials that are based on lanthanide-doped oxide hosts.[54,56,57,64,65,71,82,84,85,87–92,94–96,98,105,127,128,167,180,181,190,197–199,202,205,209,219,220,256,262,278,296–332] Several classes of materials have been investigated, such as binary oxide host lattices,[82,94,167,180,181,197,199,305] ternary oxide host lattices,[85,198] phosphates,[64] vanadates,[84] molybdates,[278] titanates,[88] zirconates,[314] silicates,[56,312] hydroxides[57,333] and oxysulfides.[197,333,334]

In 2003 we reported the first observation of photon upconversion in transparent colloids.[64] The green and red emission bands as well as the absorption spectrum can be taken from Figure 4. The Er^{3+}-doped $LuPO_4$ and $YbPO_4$ nanoparticles were prepared by coprecipitation in a method analogous to that used to prepare $LaPO_4$:Ce^{3+},Tb^{3+} and $CePO_4$:Tb^{3+} nanocrystals.[335,336] Bulk $LaPO_4$:Ce^{3+},Tb^{3+} is a commercially applied lamp phosphor.[337,338] Redispersible Er^{3+}-doped YVO_4 nanocrystals were synthesized in a hydrothermal process by Kong and co-workers.[84] Surface modification of rare-earth-doped Y_2O_3 nanoparticles leads to water-redispersible NPs.[315] Despite their comparatively low upconversion efficiency, this type of NP is still in the focus of scientific investigation[300,315] and has already been used for applications in bioimaging[180,315] (see also Section 5).

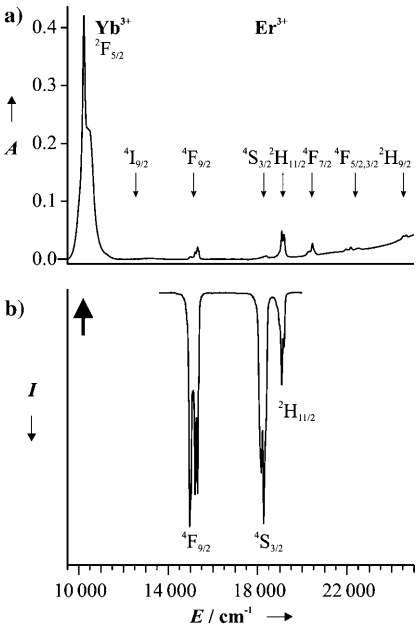


Figure 4. a) Absorption spectrum and assignments of the $YbPO_4$:5%Er^{3+} colloid. b) Upconversion luminescence spectrum and assignments after excitation at 10230 cm^{-1} (see arrow) with a laser power of 300 mW. Reproduced from reference [64]. Copyright Wiley-VCH 2003.

3.2. Nanocrystals Based on Fluorides

Fluorides as host lattices for upconversion fluorescent particles benefit from many properties (see also Section 2.1), and the most frequently synthesized and investigated upconversion fluorescent NPs consist of fluoride sublattices.

3.2.1. Rare-Earth-Doped LnF_3 Nanoparticles

The optical properties of bulk LaF_3:Yb^{3+},Er^{3+}[339–341] and bulk YF_3:Yb^{3+},Er^{3+}[272,341,342] were already investigated in the late 1960s and early 1970s, respectively. Depending on the ionic radius of the lanthanide ion,[343] the lanthanide trifluorides crystallize either in a trigonal (tysonite LaF_3 type, space group $P\bar{3}c1$) or an orthorhombic structure (β-YF_3 type, space group *Pnma*).[344] At room temperature, the trifluorides of the lighter lanthanides (Ln = La–Nd) form the trigonal structure only,[345–348] whereas for the heavier lanthanides (Ln = Dy–Lu) and yttrium, the orthorhombic structure is observed.[349–352] From Ln = Sm–Tb, the LnF_3 system is dimorphic.[343]

The first synthesis procedures for LaF_3 nanoparticles were reported in 2001 by Dang and co-workers[353] and by Zhang et al.[354] One year later, redispersible LaF_3 nanocrystals doped with rare-earth ions such as Eu^{3+}, Er^{3+}, Nd^{3+}, and Ho^{3+} were synthesized by van Veggel and Stouwdam.[80] These nanoparticles display luminescence emission in the NIR region and are therefore of interest for optical telecommunication.[80] In the following years, an increasing number of papers on the synthesis of rare-earth-doped lanthanide trifluoride nanocrystals was published. The synthesis and the properties of YF_3 nanoparticles,[58,233,262,283,332,356–358] YbF_3 nanocrystals,[276] and LaF_3[178,182,193,200,217,253,262,355,359–369] and LuF_3 nanoparticles[370,371] have been intensively investigated.

Yan et al. achieved highly uniform, monodisperse LaF_3 nanoplatelets of about 16 nm in size by thermolysis of $La(CF_3COO)_3$ in a hot oleic acid/octadecene solution.[372] In one of the most cited articles of 2005, Li and Yan[58] described a two-step synthesis method for doped YF_3 nanoparticles. By doping these particles with the ion couple Yb^{3+}/Er^{3+}, red, green, and an unusually strong 411 nm blue upconversion emission band were obtained.[58] In double logarithmic plots of the emission intensity versus excitation intensity, straight lines with a slope of about two are obtained for the green and red emissions, thus indicating that two IR photons are absorbed per emitted photon (Figure 5a;[58] see also Güdel et al. and Yi et al.)[373,374] For the blue emission, a slope of three was observed, corresponding to a three-photon process (Figure 5b;[58] see also Güdel et al.)[373]

Chow and Yi investigated colloidal LaF_3:Yb^{3+},Er^{3+}; LaF_3:Yb^{3+},Ho^{3+}; and LaF_3:Yb^{3+},Tm^{3+} particles with a small particle size and a narrow size distribution.[362] Upconversion fluorescent trifluoride nanoparticles have not lost their popularity to date and therefore are still in the focus of investigation. In 2008 Hu et al. prepared hydrophobic as well as amphiphilic UC LaF_3:Yb^{3+},Er^{3+} and LaF_3:Yb^{3+},Ho^{3+} nanoparticles with an average particle size of 15 nm (Figure 6) in an oleic acid containing aqueous solution.[217]

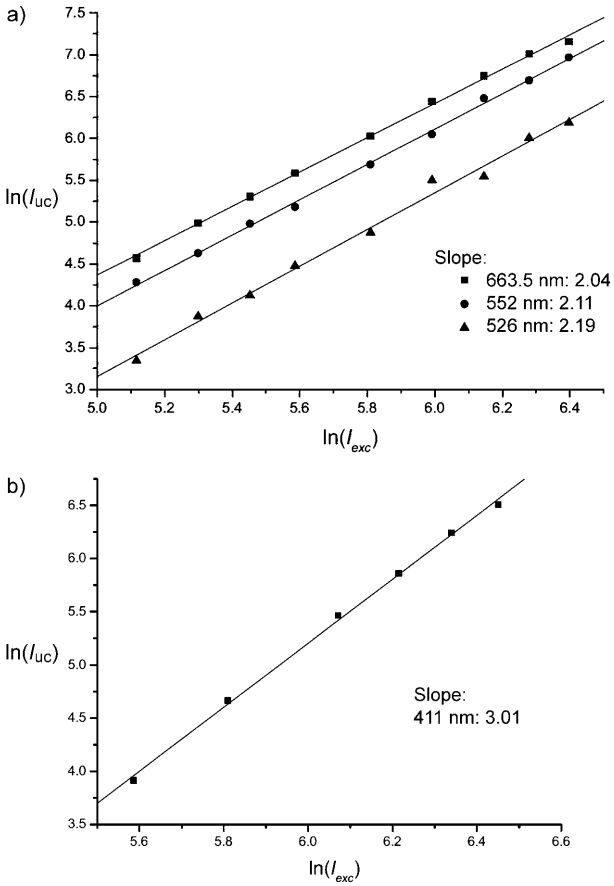


Figure 5. Power dependence of YF_3:Yb^{3+},Er^{3+} upconversion intensity shown by double logarithmic plots. a) Emission peaks at 663.5, 552, and 526 nm. b) 411 nm blue emission peak. Reproduced with permission from reference [58]. Copyright Wiley-VCH 2005.

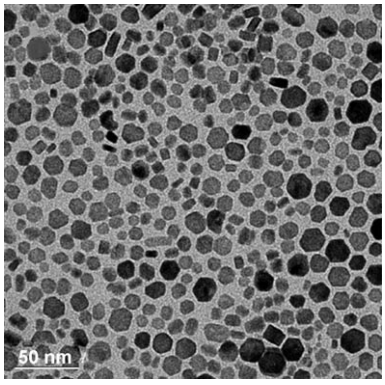


Figure 6. TEM images of upconversion LaF_3:Yb^{3+},Ho^{3+} nanocrystals. Reproduced with permission from reference [217]. Copyright American Chemical Society 2008.

They showed photographs of the upconversion luminescence of a colloidal solution of LaF_3:Yb^{3+},Ho^{3+} in water (Figure 7).

3.2.2. Lanthanide-Doped M(RE)F_4 Nanoparticles (M = Li, Na, K; RE = Rare Earth)

The phase equilibrium within the bulk fluoride host system $MF(RE)F_3$ has been intensively investigated and

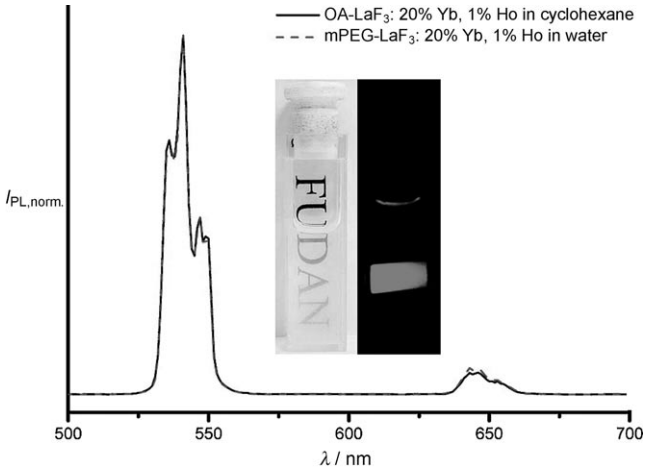


Figure 7. Room-temperature upconversion luminescence spectra of oleic acid treated LaF_3:Yb^{3+},Ho^{3+} nanocrystals (2 mg mL^{-1}) in cyclohexane and glycol monomethyl ether treated LaF_3:Yb^{3+},Ho^{3+} nanocrystals in water under CW excitation at 980 nm (power ca. 800 mW). CW = continous wave, mPEG = poly(ethylene glycol) monomethyl ether. Inset: a photograph of glycol monomethyl ether treated LaF_3:Yb^{3+},Ho^{3+} nanocrystals showing an almost pure green color. Reproduced with permission from reference [217]. Copyright American Chemical Society 2008.

discussed during the past six decades.[453–458] Upconversion phosphors based on bulk, microcrystalline, or sub-microcrystalline $NaYF_4$ have been intensively investigated, and the results are summarized in several reports.[33,34,50,375–378] Because of their outstanding properties, Yb^{3+},Er^{3+}- and Yb^{3+},Tm^{3+}-doped $NaYF_4$ are the most frequently investigated materials. Fewer reports discuss $M(RE)F_4$ host lattices other than $NaYF_4$, such as $NaGdF_4$, $LiGdF_4$, KYF_4, and $LiLuF_4$, or upconversion experiments using doping ions other than the classical couples Yb^{3+},Er^{3+} and Yb^{3+},Tm^{3+}.

Yb^{3+},Er^{3+}-doped and undoped $NaLuF_4$ microplates have been synthesized and investigated by Li et al.[379] Very recently not only the optical but also the magnetic properties of Yb^{3+},Er^{3+}-doped $NaGdF_4$ have been investigated by Hao et al.[380] Yb^{3+},Er^{3+}-doped $LiYF_4$ nanocrystals derived from trifluoroacetate precursors were reported by Yan et al.[381]

In $LiYF_4$:Nd^{3+} bulk material the avalanche effect, an effect also leading to upconversion phenomena,[382,383] has been observed below 60 K.[384] The spectroscopic properties of Gd^{3+}-doped KYF_4 and $LiYF_4$, Nd^{3+}-doped $LiYF_4$ have been investigated by Sytsma, Khaidukov, and Guyot et al.,[385–387] and Meijerink et al. investigated Er^{3+}-doped $LiYF_4$.[388] Pr^{3+}-doped KYF_4 and $LiLuF_4$ as possible white emitters were synthesized and discussed by Toncelli et al.[389] Bulk KYF_4:Ln (Ln = Pr^{3+}, Er^{3+}, Tm^{3+}, Ho^{3+}, Yb^{3+}, Nd^{3+}, Er^{3+}) are well known as upconversion-pumped solid-state lasers.[129,150,390–395] A very remarkable result was achieved by Meijerink: Visible quantum cutting could be shown in case of Eu^{3+}-doped $LiGdF_4$.[396]

In 2004 three research groups reported on the successful synthesis of small luminescing $NaYF_4$ nanocrystals that formed transparent colloidal solutions. The first synthesis developed by Haase, Güdel et al. was based on the coprecipitation of $NaYF_4$:Yb^{3+},Er^{3+} and $NaYF_4$:Yb^{3+},Tm^{3+} nanoparticles in the high-boiling solvent *N*-(2-hydroxyethyl)ethylenediamine (HEEDA).[59] The synthesis yielded transparent colloidal solutions of cubic-phase particles. The upconversion efficiency of such solutions was about eight orders of magnitude higher than those of the colloids of lanthanide-doped phosphate nanocrystals reported by the same groups.[59,64]

Photos displaying this emission as a beam of light in solution became a standard eye-catcher in papers dealing with upconversion nanoparticles later on (Figure 3). Although the synthesis procedure was a strong improvement compared to earlier routes, the method suffers from several drawbacks, such as a rather broad particle size distribution (5–30 nm) and the formation of the less efficient cubic α-phase of $NaYF_4$. In the same year, Yi, Chen et al. reported on the synthesis of Yb^{3+},Er^{3+}-doped cubic $NaYF_4$ particles by co-precipitation of the rare-earth chlorides with NaF in the presence of ethylenediamine tetraacetic acid (EDTA).[62] The spherical, as-prepared particles showed a narrow size distribution of 32–46 nm diameter. Annealing of dry powders of these particles at 400–600 °C led to larger particles with the hexagonal phase showing strong UC luminescence efficiency.

Also in 2004, the first small hexagonal-phase (β-phase) Yb^{3+},Er^{3+}-doped $NaYF_4$ particles with a mean size of 25 nm were synthesized in acetic acid solution by the Li group (Figure 8a).[73] The quality of the $NaYF_4$ nanocrystals improved significantly when the procedure developed by Yan et al. for the synthesis of uniform LaF_3 particles with well-defined size and shape was modified and applied to the preparation of $NaYF_4$ and other $NaLnF_4$ particles (Figure 8b).[372] The method, based on the thermal decomposition of trifluoroacetates in solvent mixtures of oleic acid and octadecene, was further refined by several groups and is now a common route to monodisperse and uniform $NaYF_4$ nanocrystals in the cubic and the hexagonal phase.[75,79,93,186,192,194,201,207] The synthesis procedure was transferred to the generation of $NaYF_4$ for the first time by Chow and Yi in 2006.[186] They reported on the formation of very small hexagonal $NaYF_4$:Yb^{3+},Er^{3+} nanoparticles when the decomposition reaction is performed in pure oleylamine at

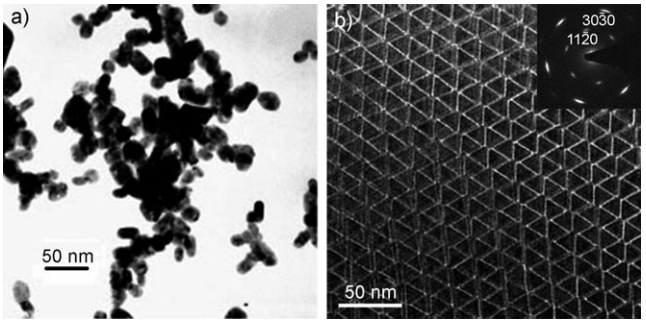


Figure 8. a) TEM image of $NaYF_4$:Yb^{3+},Er^{3+} nanocrystals prepared in acetic acid using EDTA. Reproduced with permission from reference [73]. Copyright Wiley-VCH 2005. b) TEM images of the edge-to-edge superlattices of LaF_3 nanoplates. Inset is the SAED pattern. (SAED = selected area electron diffraction) Reproduced with permission from reference [372]. Copyright American Chemical Society 2005.

330 °C. To our knowledge, this is the first example of a successful synthesis of β-$NaYF_4$ particles with a particle size in the range of 10 nm.[186] The particles could be dispersed in organic solvents, were uniform in shape, and showed a narrow size distribution ((10.5 ± 0.7) nm) as deduced from TEM and dynamic light scattering measurements (DLS, (11.1 ± 1.3) nm, Figure 9). Capobianco et al. generated cubic phase lanthanide-doped $NaYF_4$ nanoparticles, hexagonal in shape with an average size of 27.6 nm and a standard deviation of 1.6 nm (Figure 10).[79]

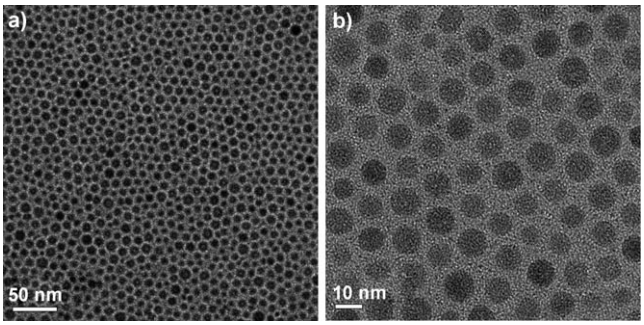


Figure 9. a) TEM image of $NaYF_4$:20%Yb^{3+},2%Er^{3+} nanocrystals at a magnification of 50000×. b) TEM image of $NaYF_4$:20%Yb^{3+},2%Er^{3+} nanocrystals at a higher magnification of 150000×. Reproduced with permission from reference [186]. Copyright Wiley-VCH 2006.

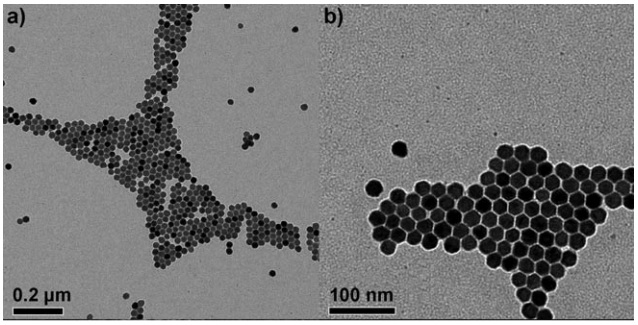


Figure 10. TEM images of spherical $NaYF_4$:2%Er^{3+},20%Yb^{3+} nanocrystals. a) Low magnification; b) high magnification. Reproduced with permission from reference [79]. Copyright American Chemical Society 2007.

One advantage of the use of trifluoroacetates is the rapid formation of reactive fluoride compounds at elevated temperatures. Drawbacks mentioned in the literature are the emission of toxic gases, the requirement of high reaction temperatures, and the rather narrow temperature window of the decomposition (less than 10 °C), which leads to difficulties with respect to the reproducibility.[245] Therefore, efforts were made in the development of alternative synthesis routes that also allow an exact control of the phase, shape, and size of the particles.

In 2008 Li and Zhang reported on different methods for the synthesis of pure hexagonal-phase $NaYF_4$ nanocrystals in solvent mixtures of oleic acid and octadecene at 300 °C.[61] In their procedure the metal trifluoroacetates are replaced by in situ generated rare-earth oleates, NaOH, and NH_4F.[61] Alternatively, stearic acid and trioctylphosphine oxide (TOPO) were used instead of oleic acid, and an eicosene/trioctylamine mixture replaced octadecene as high-boiling solvent.[215] The particles were of outstanding quality in terms of size distribution (average size 21 nm) and shape uniformity (nanospheres and hexagonal plates depending on the amount of oleic acid (Figure 11).[215] Using a synthesis route with NaF

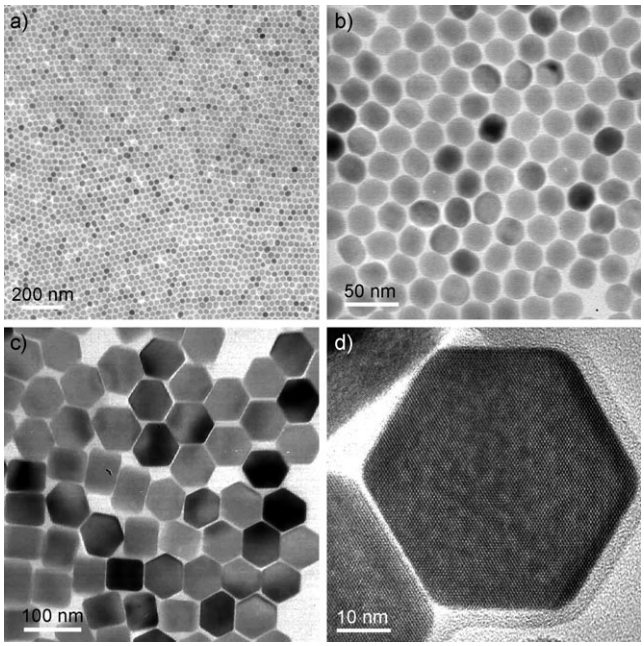


Figure 11. TEM images of $NaYF_4$:Er^{3+},Yb^{3+} nanospheres (a, b) and nanoplates (c, d) at different magnifications. Reproduced with permission from reference [215]. Copyright IOP Publishing 2008.

and rare-earth oleates as precursors, Chen and co-workers published a method yielding doped β-$NaYF_4$ NPs with high size uniformity and an extremely narrow size distribution of (28.25 ± 0.76) nm in 2009.[245] Impregnating nanocrystals of α-$NaYF_4$ doped with Er^{3+} and Yb^{3+} into a porous, anodized aluminum oxide (AAO) membrane led to nanotubes composed of close-packed uniform nanocrystals[285] (Figure 12).

Doping of cubic or hexagonal $NaYF_4$ nanocrystals with Yb^{3+},Er^{3+} and Yb^{3+},Tm^{3+} ions leads to emission bands in the green or red and blue spectral regions, respectively (Figure 3). In several papers, strategies to expand the range of emission colors were investigated. In 2008, Nann et al. showed that a large number of emission colors can be realized by simply mixing colloids of upconversion nanoparticles containing different dopant ions. Colloids of $NaYbF_4$:Er^{3+}, $NaYbF_4$:Tm^{3+}, $NaYF_4$:Yb^{3+}, and $NaYbF_4$:Ho^{3+} with emission bands in the green and red ($NaYbF_4$:Er^{3+} and $NaYbF_4$:Ho^{3+}); mainly blue and IR ($NaYF_4$:Yb^{3+}); and blue and IR ($NaYbF_4$:Tm^{3+}) regions were synthesized and combined in different concentrations.[211] By doping the same $NaYF_4$ host with all three ions Yb^{3+}, Tm^{3+}, and Er^{3+} and adjusting their concentrations, Wang and Liu obtained colloids with bluish to whitish ($NaYF_4$:Yb^{3+},Tm^{3+},Er^{3+}) and greenish-yellowish to redish ($NaYF_4$:Yb^{3+},Er^{3+}) overall color output (Figure 13).[60]

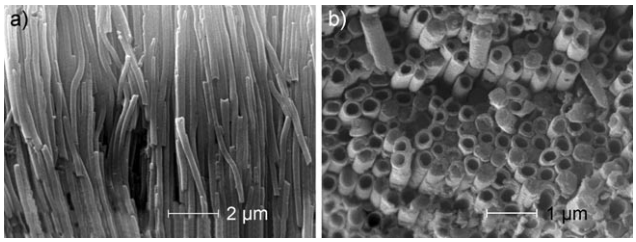


Figure 12. a) Magnified cross-sectional SEM image of rare-earth fluoride nanotube arrays after removing the AAO template. b) Bottom-view SEM image showing rare-earth fluoride nanotubes oriented in a perpendicular fashion on the substrate. Reproduced with permission from reference [285]. Copyright Springer 2009.

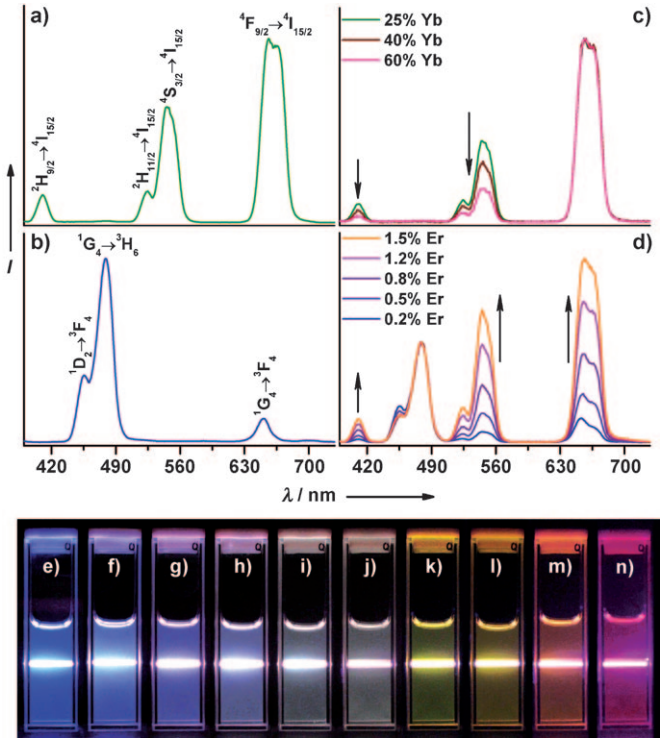


Figure 13. Room-temperature upconversion emission spectra of a) $NaYF_4$:Yb^{3+},Er^{3+} (18 and 2 mol%), b) $NaYF_4$:Yb^{3+},Tm^{3+} (20 and 0.2 mol%), c) $NaYF_4$:Yb^{3+},Er^{3+} (25–60 and 2 mol%), and d) $NaYF_4$:Yb^{3+},Tm^{3+},Er^{3+} (20, 0.2, and 0.2–1.5 mol%) particles in ethanol. Compiled luminescent photos showing corresponding colloidal solutions of e) $NaYF_4$:Yb^{3+},Tm^{3+} (20 and 0.2 mol%), f–j) $NaYF_4$:Yb^{3+},Tm^{3+},Er^{3+} (20, 0.2, and 0.2–1.5 mol%), and k–n) $NaYF_4$:Yb^{3+},Er^{3+} (18–60 and 2 mol%). The samples were excited at 980 nm with a 600 mW diode laser. Reproduced with permission from reference [60]. Copyright American Chemical Society 2008.

Advantages of the oleate-based synthesis are the narrow particle size distribution, the high luminescence efficiency, and the high phase purity of the particles. Although the hexagonal bulk phase is thermodynamically preferred at low temperatures,[407] the cubic α-phase is obtained when the synthesis is performed at lower temperatures (below 300 °C), thus indicating that the reaction in oleic acid is controlled by kinetics. In contrast, we could show that the simple solid-state reaction between NH_4F, Na_2CO_3, and the rare-earth carbonates yields nanocrystalline β-phase $NaYF_4$ even at room temperature.[228] If the same reaction is performed in oleylamine or in a mixture of oleylamine and oleic acid, hexagonal-phase $NaYF_4$ nanocrystals are obtained that display a broad particle size distribution from 4 to 10 nm.

A powerful tool for phase and size control is additional doping with Gd^{3+} ions.[399] Gd^{3+} ions were incorporated by Wang et al. into upconverting $NaYF_4$:Yb^{3+},Er^{3+} nanocrystals at different doping levels, leading to a ternary doped $NaYF_4$:Yb^{3+},Er^{3+},Gd^{3+} system.[399] Without additional Gd^{3+} ions a mixture of cubic and hexagonal phases was found under the chosen reaction conditions. With increased Gd^{3+} concentrations the transformation from cubic to hexagonal structure becomes more and more noticeable, and the size of the corresponding particles decreases. Doping of binary doped $NaYF_4$:Yb^{3+},Er^{3+} or ternary doped $NaYF_4$:Yb^{3+},Er^{3+},Tm^{3+} with Gd^{3+}, leading to the corresponding ternary or quaternary doped lanthanide species, was used for fine tuning of the visible color of the upconverting nanocrystals.[399]

There are now a large number of reports dealing with the synthesis and investigation of high quality lanthanide doped cubic[44,46,55,59–63,71,72,75,78,79,93,117,177,186,187,189,194,196,200,201,204,208,212,213,222,224,226,261,262,275,283,397–404] and hexagonal $NaYF_4$ particles.[46,62,72,73,78,93,117,176,177,183,186,191,192,194–196,201,203,204,207,215,216,221,225,399–401,405,462] Especially the development of a suitable synthesis that is able to form small hexagonal nanoparticles faced problems because of the tendency toward regular-shaped nanoplates or rods in the micrometer and sub-micrometer range.[93]

In 2008 we investigated nanosized Yb^{3+},Er^{3+}-doped cubic KYF_4 particles about 13 nm in size synthesized by the HEEDA route.[214] The nanocrystals showed only poor luminescence efficiency, which could be improved significantly by coating with undoped material (see Section 3.4.1).

Finally, chelating ligands and donor ligands such as EDTA, citrate, TOPO, trioctylphosphine (TOP), and poly(vinyl pyrrolidone) (PVP) have been employed in addition to the amphiphilic surfactant to reduce the particle size and to prevent the particles from agglomeration.[61,62,187,201,408]

3.2.3. Ln-Doped Fluoride Nanocrystals with Other Stoichiometries: MF_2, MYF_5, MY_2F_7

Most of the work on upconversion nanocrystals is focused on fluoride materials with $M(RE)F_4$ stoichiometry. However, there are some examples of upconversion nanocrystals with compositions other than $M(RE)F_4$ or $(RE)F_3$ discussed in Section 3.2.1. and 3.2.2.

The structure of cubic $NaYF_4$ (space group $Fm\bar{3}m$, no. 225) is isomorphic with CaF_2. In the NaF–MF_3 system the charge on the lanthanide ions is balanced by an appropriate number of sodium ions, and this is the case not only for the fluorite-type structure but also for the nonstoichiometric phases with varying compositions given by $Na_{0.5-x}M_{0.5+x}F_{2+2x}$, where $0 \leq x \leq 1/7$.[409] Several groups investigated the doping of alkaline-earth fluoride nanocrystals with lanthanide ions. Efficient upconversion emission is reported for some of these systems. Li et al. reported in 2009 on the successful hydrothermal synthesis of high-quality monodisperse

CaF_2:Yb^{3+},Er^{3+} nanocrystals about 10 nm in size (Figure 14) in a water/ethanol solvent mixture.[77] They found that the upconversion efficiency of the CaF_2 particles is even slightly

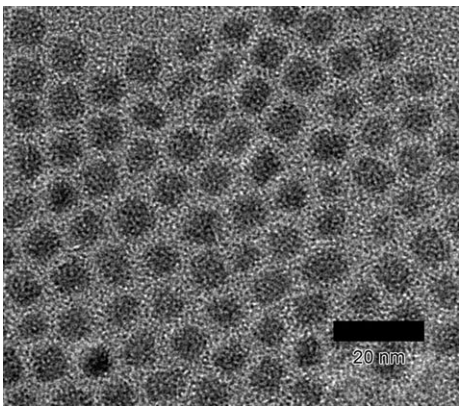


Figure 14. TEM image of CaF_2:Yb^{3+},Er^{3+} nanocrystals. Reproduced with permission from reference [77]. Copyright American Chemical Society 2009.

stronger than cubic Yb^{3+},Er^{3+}-doped $NaYF_4$ particles of the same size. In this so-called liquid–solid–solution (LSS) process developed by Wang, Li et al., a general phase transfer between the interfaces takes place.[262] Yan's group modified the trifluoroacetate method for $NaYF_4$ nanocrystals for the synthesis of alkaline-earth-metal difluorides. Uniform alkaline-earth-metal fluoride MF_2 (M = Mg, Ca, Sr) particles with various shapes (3D nanoneedle networks of tetragonal MgF_2, nanoplates and nanopolyhedra of cubic CaF_2, nanoplates and nanowires of cubic SrF_2) were synthesized by the thermolysis of alkaline-earth-metal trifluoroacetates ($M(CF_3COO)_2$) in hot surfactant solutions. The best upconversion properties were found in the case of Yb^{3+},Er^{3+}-doped SrF_2 after modification of the surface.[223] The obtained particle sizes were 13 nm × (80–170 nm) (MgF_2), 33 nm × 45 nm (CaF_2), 36 nm × 25 nm (SrF_2, Figure 15) and 1000 nm for BaF_2. Kumar et al. reported on the optical properties of CaF_2:Er^{3+} nanocrystals doped into a hexafluoroisopropylidene (6F)-based polymer composite.[99,410] Using the Langmuir–Blodgett (LB) technique, Yan et al. prepared films of CaF_2 nanoparticles 9.5 nm × 2 nm in size.[239]

Small Yb^{3+},Tm^{3+}-doped $BaYF_5$ particles (15 nm × 5 nm in size) were obtained by the Capobianco group by the thermal decomposition of rare-earth trifluoroacetates in solvent mixtures of oleic acid and octadecene containing barium acetylacetonate.[227] The particles displayed intense blue light from the $^1G_4 \rightarrow {}^3H_6$ Tm^{3+} transition under excitation in the NIR region in transparent solution.

We reported on the synthesis and optical properties of Yb^{3+},Er^{3+} doped RbY_2F_7 and CsY_2F_7 nanoparticles.[259,411] Two synthesis routes were described, which led to particles with broad size distributions in the range of 6 to 60 nm for the rubidium compound and 8–50 nm for the cesium compound. The structural and optical properties of colloidal Ln^{3+},Yb^{3+}-doped KY_3F_{10} nanocrystals were reported by Capobianco and co-workers.[412]

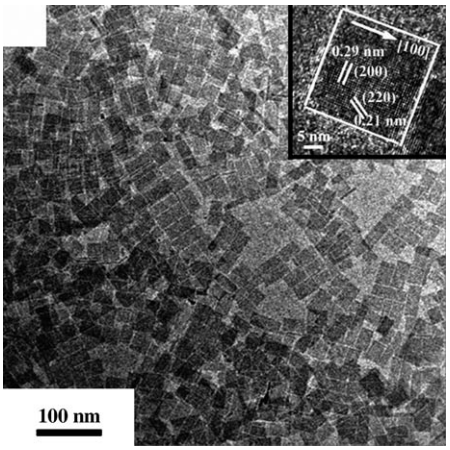


Figure 15. TEM and high-resolution (HR) TEM (inset) images of SrF_2 nanoplates. Reproduced with permission from reference [223]. Copyright American Chemical Society 2009.

Finally, there have been several reports on nanoscale glass–ceramics in which, for example, rare-earth-doped PbF_2 nanoparticles are considered to be responsible for the emission of visible light under NIR excitation[102,123,124,413,414].

3.3. Investigation of Single Upconversion Nanocrystals

Luminescing nanoparticles are usually characterized by ensemble-averaged measurements of their optical properties. Characterization of the upconversion luminescence on the single-particle level was performed by the groups of Wua and Nann in 2008 and 2009, respectively.[234,415] Individual $NaYF_4$:Yb^{3+},Er^{3+} particles deposited on a silicon nitride membrane[234] or attached to a gold nanosphere[415] were spectroscopically investigated and found to be nonblinking and photostable (Figure 16).[234]

3.4. The Core–Shell Concept

The luminescence efficiency of nanoparticles is usually smaller than that of the corresponding bulk materials, owing to the large surface-to-volume ratio of nanoparticles. In the case of lanthanide-based upconversion materials, the presence of surface ligands with high-energy vibrational modes such as OH or NH_2 groups can lead to quenching of the excited lanthanide states by multiphonon relaxation processes. If the concentration of a dopant in the host lattice is high, as in the case of Yb^{3+}, energy transfer from the center of the particle to the surface through adjacent dopant ions may further decrease the efficiency. The standard strategy to reduce energy losses on the nanoparticle surface is to coat the particle with an appropriate shell material. In the case of lanthanide-doped nanomaterials, this shell material should not allow any kind of energy transfer from the core of the particle to its outer surface. It should be kept in mind, however, that the luminescence or upconversion efficiency is significantly increased only if the interface between the

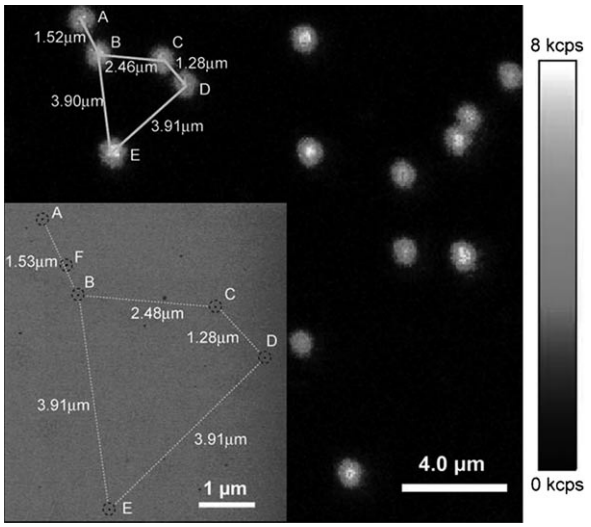


Figure 16. Individual UCNPs on a silicon nitride membrane. Confocal upconverted luminescent image of individual UCNPs. The TM-SEM image (inset) taken at the upper left corner region of the optical image shows that the individual diffraction-limited luminescent spots are emitted from individual UCNPs. Reproduced with permission from reference [234]. Copyright National Academy of Science (USA) 2009.

particle core and the shell is of high quality, that is, if the interface contains a much smaller number of quenching sites than the surface of the core particle before coating.

In recent years authors have begun to quantify the effectiveness of the light conversion that occurs in the designed UC phosphors and UC nanoparticles.[59,69,175,214,228,259,411,416] We used bulk hexagonal $NaYF_4$:18% Yb^{3+},2% Er^{3+} reference material and determined the visible-light output of different UC nanoparticles in comparison with this bulk sample.[59,214,259,411] The efficiency ratios between the reference sample and the UC nanoparticles strongly depend on the laser power, the constitution, and the size of the NPs and are in the range of 100 to 150000.[59,214,259,411] In 2009 we compared the emitted light intensity of hexagonal Yb^{3+},Er^{3+}-doped $NaYF_4$ NPs (7 nm in size) with cubic NPs of the same constitution (28 nm in size). At 1.78 W laser power, the efficiency ratio was approximately 10.[228] In terms of the determination of the absolute quantum yield (QY) of bulk UC phosphors, Page et al. did the pioneering work.[175] For the green emission of Yb^{3+},Er^{3+}-doped hexagonal $NaYF_4$, the QY was 4%. Based on the setup used by Page et al., very recently also the absolute quantum yield of colloidal hexagonal $NaYF_4$:Yb^{3+},Er^{3+} nanoparticles was determined by Boyer and van Veggel.[416] They found values in the range of 0.005 to 0.3, depending on the particle size.[416]

3.4.1. *Particles with a Passivating Shell of Undoped Material*

If the excitation energy is mainly transferred to the particle surface through neighboring dopant ions, the most straightforward choice for the shell material is the pure (i.e., undoped) host material of the core particle. The formation of core–shell particles with small lattice mismatch between the core and the shell material has been intensively investigated for semiconductor nanoparticles as well as for some doped nanomaterials with large bandgaps.[336,367,417] More recently, synthesis procedures for core–shell particles of lanthanide fluoride material have been developed. The formation of passivating shells on rare-earth-doped LaF_3,[178] $NaYF_4$,[61,72,192,221,224,463] KYF_4,[214] and $NaGdF_4$[418] and on undoped YF_3[419] and $NaYF_4$[420] particles have been published by several authors. An individual case is reported by Yang and co-workers, who investigated particles consisting of an undoped core with Yb^{3+},Er^{3+}-doped $NaYF_4$ on the periphery of the particle.[421]

A significant enhancement of the upconversion fluorescence by depositing undoped core material on the surface of rare-earth-doped $NaYF_4$ core particles was demonstrated for the first time by Yi and Chow (Figure 17).[192] A luminescent enhancement of nearly 30 times was achieved by a 1.5 nm thick shell of undoped β-phase $NaYF_4$. The article is one of the most cited in the field.

$NaYF_4$:Yb^{3+},Er^{3+}//$NaYF_4$core–shell nanoparticles with different crystallographic phases of the core and the shell were discussed by Mai et al. in their 2007report.[72] A synthesis procedure for β-$NaYF_4$:Yb^{3+},Er^{3+}//α-$NaYF_4$ core–shell particles with a size of about 30 nm is given, but a hard proof for the existence of both crystallographic phases within one particle remains to be shown.

Usually, the successful deposition of undoped material on the surface of the core particles is deduced from an increase of the average particle size in combination with an enhancement of the luminescence efficiency.[192,214] Site-selective spectroscopy was also used to identify dopant sites on the particle surface and to show that these sites are converted into bulk sites when undoped material is deposited onto the core particle.[422] If the core and the shell consist of materials displaying different image contrasts in electron microscopy, like in the case of $NaYF_4$//SiO_2 core–shell particles, the core–shell structure and the uniformity of the shell thickness can be visualized directly (Figure 18). The quality of the core–shell structure can also be investigated by X-ray photoelectron spectroscopic (XPS) measurements.[423–426] Ideally, a synchrotron radiation source is used, which allows tuning of the photon energy of the X-rays exciting the sample. At low photon energies, only electrons of elements located in the outmost layers of the particle can reach the detector, whereas at high photon energies electrons from the core can also escape the particle, and the composition of the whole core–shell particle is probed.[336,427] Recently, van Veggel and co-workers used this technique in combination with energy-dispersive X-ray spectroscopy (EDX) to demonstrate the existence of the core–shell structure of β-$NaYF_4$//β-$NaGdF_4$ nanocrystals.[420]

3.4.2. *Particles with Shells Containing Dopants*

In the majority of cases published, the shell is inert and its sole role is to increase the luminescence efficiency of the core (see Section 3.4.1). Starting in 2008, different groups reported on core–shell nanoparticles in which the shell also contains optically active centers.[209,221,251,428] These efforts were related

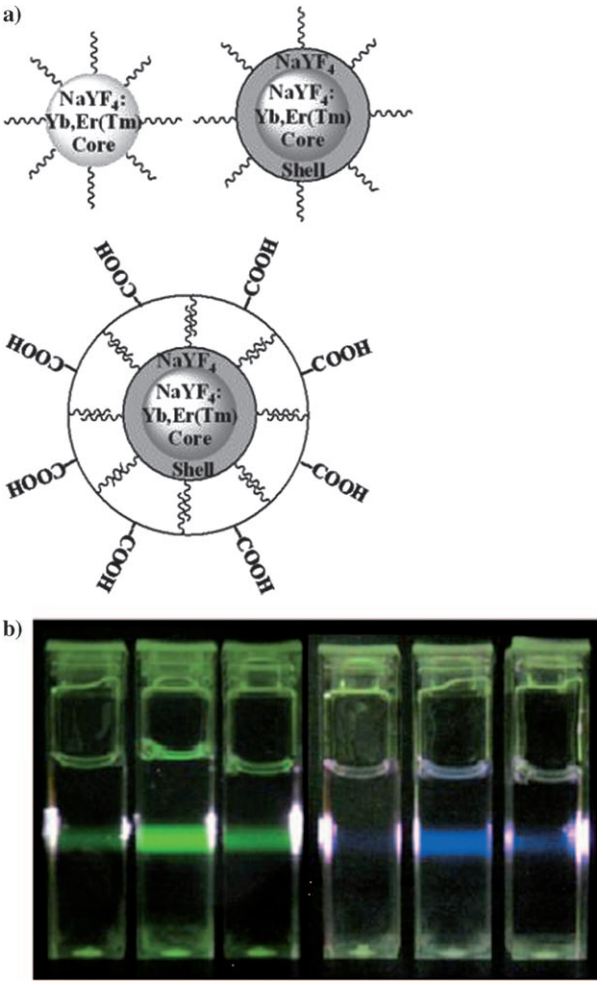


Figure 17. a) Structure of upconversion nanoparticles. b) Photographs of the upconversion luminescence: green from $NaYF_4$:Yb^{3+},Er^{3+} and blue from $NaYF_4$:Yb^{3+},Tm^{3+} nanoparticles in solution. Reproduced with permission from reference [192]. Copyright American Chemical Society 2007.

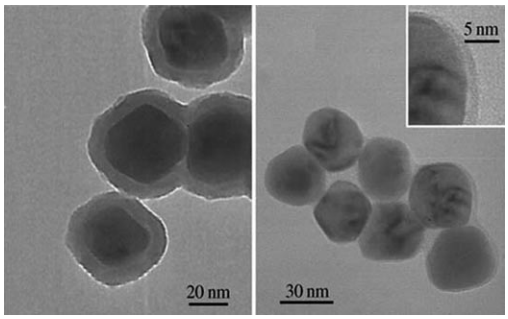


Figure 18. TEM images of silica-coated poly(vinyl pyrrolidone)/$NaYF_4$:Yb^{3+},Er^{3+} nanocrystals. Left: thickness of the layer approximately 10 nm. Right: with a very thin silica layer. Reproduced with permission from reference [179]. Copyright Wiley-VCH 2006.

to different aims, such as enhancement of the luminescence or the tunability of the upconversion fluorescence.

By doping the particle core with Tm^{3+} and the shell with Er^{3+} nanoparticles, tunable multicolor fluorescence was obtained which displayed no quenching of the Tm^{3+} emission. J. Zhang et al. reported on hexagonal-phase core-shell-structured $NaYF_4$:Yb^{3+},Tm^{3+}//β-$NaYF_4$:Yb^{3+}, Er^{3+} (AB)[251] and on core–shell–shell β-$NaYF_4$:Yb^{3+},Tm^{3+}//β-$NaYF_4$:Yb^{3+},Er^{3+}//β-$NaYF_4$:Yb^{3+},Tm^{3+} (ABA) nanocrystals.[251] The sandwich ABA nanocrystals showed a remarkable enhancement of the Er^{3+} fluorescence.

Capobianco and co-workers showed a strong enhancement of the green and red emission bands of $NaGdF_4$:Yb^{3+},Er^{3+} particles by growing a shell of Yb^{3+}-doped $NaGdF_4$ on the surface of the cores.[428] Additional energy transfer from excited Yb^{3+} ions in the shell to the Er^{3+} ions in the core increases the overall efficiency of the particles (Figure 19). The emission of the active core–active shell particles is more intense by a factor of approximately three (green) and ten (red) compared to standard core–shell particles composed of a doped core and an inert shell.

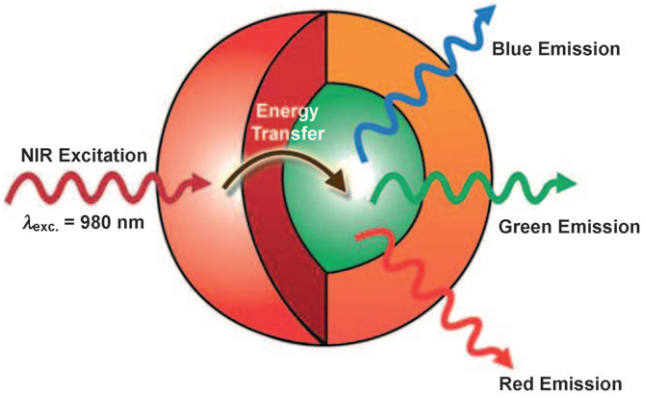


Figure 19. Schematic illustration of the active core–active shell nanoparticle architecture showing the absorption of NIR light by the Yb^{3+}-rich shell (red) and subsequent energy transfer to the Er^{3+},Yb^{3+}-doped core (green), which leads to upconverted blue, green, and red emissions. Reproduced with permission from reference [428]. Copyright Wiley-VCH 2009.

3.4.3. Particles with Silica Shells

A large number of different colloidal nanomaterials have been coated with shells of amorphous silica. These shells are usually generated by Stöber type reactions based on the controlled hydrolysis of tetraalkoxy silanes. Silica as shell material benefits from many advantages. Silica is chemically inert, optically transparent, and there are a large number of procedures for coupling functional molecules to the surface of SiO_2. Thus, the biofunctionalization of nanoparticles is possible by anchoring suitable molecules to the SiO_2 surface of core–shell particles,[45] and protocols for the conjugation of biomolecules to a silica surface are well-established.[429–431]

In 2005 Nann and Darbandi transferred the technique to fluoride nanoparticles in order to functionalize the surface of YF_3.[419] The surface modification of rare-earth-doped $NaYF_4$ nanoparticles was reported by Zhang and Li one year later.[61] They succeeded in growing a silica shell with adjustable thickness in the range of 2–10 nm on the surface of PVP-

stabilized Yb^{3+},Er^{3+}- and Yb^{3+},Tm^{3+}-doped cubic $NaYF_4$ nanocrystals (Figure 18).

By incorporating tetramethylrhodamine isothiocyanate (TRITC), fluorescein isothiocyanate (FITC), or quantum dots into a silica shell grown on Yb^{3+},Er^{3+}-doped or Yb^{3+},Tm^{3+}-doped $NaYF_4$ NPs, Zhang and co-workers were able to tune the emission spectra of the upconversion particles.[221] The new feature of their approach is the observed fluorescence resonance energy transfer (FRET) between the excited dopant ions and the organic dyes or quantum dots encapsulated in the silica shell. The FRET therefore leads to luminescence emission of the dyes or quantum dots upon excitation of the core–shell particle in the NIR region.

4. Surface Functionalization by Modification of the Ligand Shell and the Particle Surface

Rapid advances in the diagnostics and monitoring of infectious and genetic diseases are one of the driving forces behind the development of more sensitive and efficient markers for labeling experiments. The ability of upconversion nanoparticles (UCNPs) to emit visible light upon excitation with low-intensity NIR light should significantly reduce the autofluorescence background of the biological material in biolabeling experiments. To be suitable for biotagging applications, however, the particles must be compatible with biological substrates, should show only specific binding to the biological target, and must be soluble (dispersible) in aqueous media.

Without post-synthesis treatment, UCNPs are not dispersible in polar media.[432,433] The desired properties are obtained either by exchanging or manipulating the organic ligands coordinated to the surface, by addition of amphiphilic polymers interacting with the apolar groups of the surface ligands, or by surface silanization. These methods have already been reviewed in the reports by Wang and Liu and by Capobianco and Vetrone.[47,48] Therefore, only some very recent results are listed here.

The most popular method to obtain water dispersibility is coating of the $NaYF_4$ NPs with a shell of SiO_2 prepared by a sol–gel process.[42,45,62,201,221,246,464] To link these particles to biomolecules, reactive functional moieties such as amino or carboxylic acid groups are required. In the case of SiO_2-coated particles, biofunctional amine group can be introduced by treating the SiO_2 surface with 3-aminopropyltrimethoxysilane, as shown by Shan and Ju,[201] or with *N*-[3-(trimethoxysilyl)propyl]ethylenediamine (AEAPTMS), as shown by Jiang et al.[246] Carboxylic acid functionalized $NaYF_4$ nanophosphors were synthesized by direct oxidation of the oleic acid ligands using the Lemieux–von Rudloff reagent.[206] The presence of carboxylic acid groups on the one hand confers solubility of the particles in water and on the other hand ensures that streptavidin can easily be linked through covalent bonds (Figure 20). The replacement of the ligands that are attached to the particle surface after the synthesis by ligands bearing polar groups is another technique to render the particles water-soluble. We found that 1-hydroxyethane-

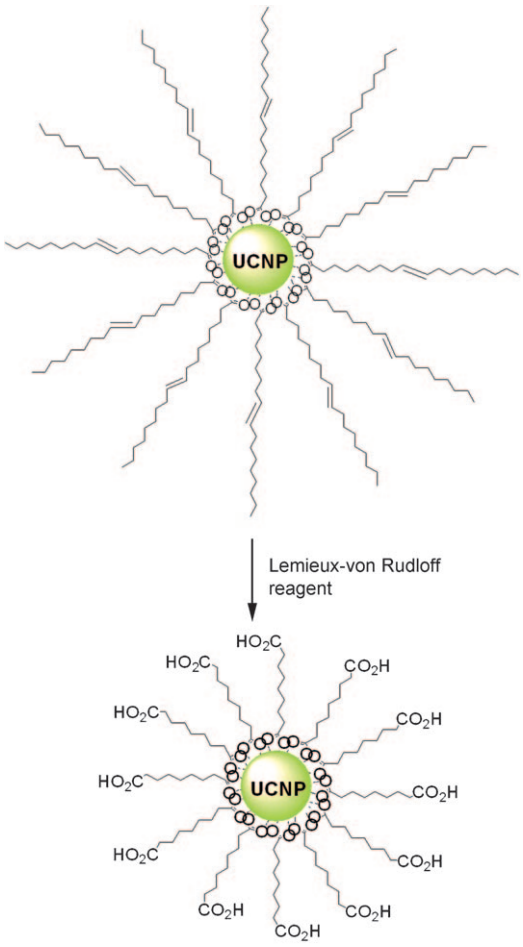


Figure 20. Mechanism of the generation of carboxylic acid functionalized upconversion nanoparticles from oleic acid capped precursors. Reproduced with permission from reference [206]. Copyright American Chemical Society 2008.

1,1-diphosphonic acid (HEDP) strongly binds to the surface of $NaYF_4$:Yb^{3+},Er^{3+} nanocrystals, resulting in high colloidal solubility of the particles in water.[55] Van Veggel and co-workers report on the exchange of oleate ligands coordinated to Yb^{3+},Tm^{3+}- and Yb^{3+},Er^{3+}-doped $NaYF_4$ particles with a polyethylene glycol phosphate ligand.[406]

5. Application of Upconversion Nanocrystals

5.1. Application in Biology and Diagnostics

Many diagnostic techniques imply the specific binding of reagents, so-called reporter molecules, to target molecules. Today, a variety of such reporter molecules exist, including, for instance, radioisotopes, enzymes, and fluorescent markers. High-quality upconversion NPs linked to biological macromolecules are investigated as fluorescent markers for imaging biological processes as well, as they benefit from a narrow particle size distribution, high photostability, narrow emission bandwidths, good biocompatibility, and a high signal-to-noise ratio owing to the weak autofluorescence background gen-

erated by NIR excitation.[460] Moreover, the penetration depth into biological tissue is high for NIR radiation. Biological applications of upconverting NPs range from the simple introduction of luminescing NPs into biological systems to the specific detection of biomolecules using different techniques, for instance, FRET-based chemosensing. Depending on the nature of the investigated biomaterial, the detection of biomolecules can be divided into in vitro and in vivo detection. Biological applications of UCNPs were recently reviewed by Lui et al.[460] and Wolfbeis et al.[465]

5.1.1. *In Vitro Detection*

The first demonstration of the potential of upconversion materials in diagnostics, in this case of rare-earth-doped yttrium oxysulfide, was reported about 10 years ago by Tanke et al. and by Hampl et al..[297,434–436] At that time, the size of upconversion particles was in the range of hundreds of nanometers, and only surface labeling could be shown.[434] Moreover, the level of nonspecific binding between reagents and markers was high, thus reducing the detection sensitivity. Nevertheless, the signal-to-noise ratio could be dramatically improved compared to conventional reporters. By using similar 400 nm UC particles, Hampl et al. achieved a detection limit of 10 pg human chorionic gonadotropin in a 100 μL sample, a tenfold improvement over conventional reporter systems like colloidal gold.[436] To use upconversion particles analogous to luminescent molecular dyes, however, small (less than 30 nm) upconversion nanoparticles with narrow size distribution and high luminescence efficiency are required, which were not available at that time. In fact, it took several years until smaller particles suitable for this purpose became available.

The strong interaction of biotin and avidin (or streptavidin) is widely used in bioanalytical applications.[437–442] For instance, bioconjugation of silica-coated LaF_3:Ln^{3+} NPs to fluorescein isothiocyanate (FITC) was shown.[178] The FITC is excited by direct 480 nm irradiation.[178] Successful bioconjugation of the biotinylated LaF_3//SiO_2 upconversion core–shell particles to FITC–avidin (Figure 21) was shown by a significant 25-fold increase of the FITC fluorescence compared to the same system where the particles were not biotinylated.[178] In a parallel report, the same group showed that the optical properties of the biotinylated inorganic NPs were nearly identical to the unfunctionalized NPs, which is a prerequisite for designing a UCNP-based biosensor.[443]

A different upconversion biosensor based on the FRET between bioconjugated UCNPs and gold NPs was developed in Li's group.[184] To our knowledge it is the first example of using the FRET technique for a bioassay based on UCNPs. In this case, the FRET system consists of biotinylated 50 nm $NaYF_4$:Yb^{3+},Er^{3+} NPs and biotinylated 7 nm Au NPs. The emission band of the UCNPs at 520 nm exactly fits the plasmon absorption band of the gold NPs. Quenching therefore occurs in the case of close proximity of both particles. This requirement is fulfilled when avidin is added, which works as a coupling (i.e., network-forming) compound between the particles owing to the sensitive and selective interaction between avidin and biotin. The luminescence of the system when excited by NIR light was gradually quenched with increasing amounts of avidin added to the system, and so trace amounts of avidin could be detected.

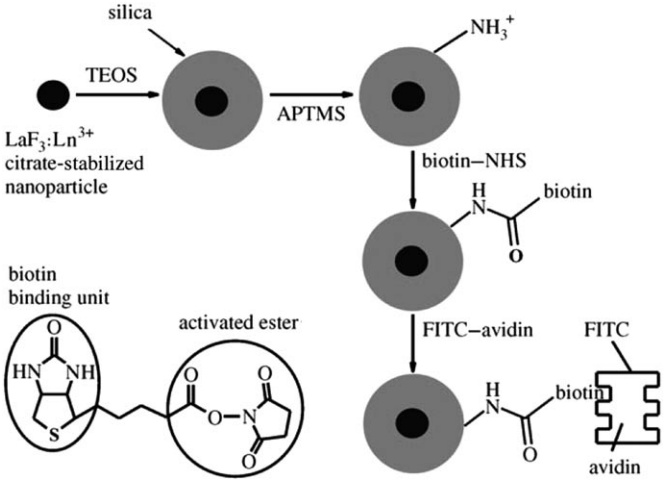


Figure 21. Preparation and bioconjugation strategy of silica-coated LaF_3:Ln^{3+} nanoparticles to FITC–avidin (not to scale). APTMS = $(CH_3O)_3Si(CH_2)_3NH_2$. TEOS = $(C_2H_5O)_4Si$, biotin-NHS = biotin *N*-hydroxysuccinimide activated ester (see lower left corner). Reproduced with permission from reference [178]. Copyright Wiley-VCH 2006.

5.1.2. *In Vivo Detection*

The simplest in vivo application of upconverting nanocrystals is their introduction into living organisms and the detection of the distribution of nanoparticles inside the organism. Nanoparticles of Yb^{3+},Er^{3+}-doped yttria, for instance, are found to present good biocompatibility when inoculated in worms, and upon excitation in the NIR, agglomerates of the particles can clearly be detected.[180] In larger organisms such as mice, UCNPs could be detected even in depths of around 10 mm.[43]

RNA interference (RNAi) is a powerful gentechnological method for the specific suppression of genes and has broad applications ranging from functional gene analysis to target-based therapy.[444–446] The method is based on small interference RNA (siRNA), that is, short pieces of double-strand RNA 21–23 nucleotides in length. Imaging of siRNA can be performed with a special FRET system based on a siRNA-staining acceptor dye. This acceptor dye is usually combined with an organic donor dye, but the latter can be replaced with quantum dots, as shown by Gao et al.[447] But especially for in vivo applications, quantum dots suffer from their potential toxicity and strong autofluorescence background.[184,448,449] In a recent report Zhang and Jiang used rare-earth codoped $NaYF_4$ UCNPs for the intracellular investigation of siRNA in live cells.[450] The UCNPs, which display an emission band at 540 nm, work as the FRET donor, and the siRNA intercalating dye BOBO-3, with a broad absorption band at 550 nm, served as the FRET acceptor. If the distance between the BOBO-3 stained siRNA and the biomodified UCNPs is short, energy transfer from the NIR-excited nanoparticle to BOBO-3 is efficient and leads to an emission at 600 nm (Figure 22).

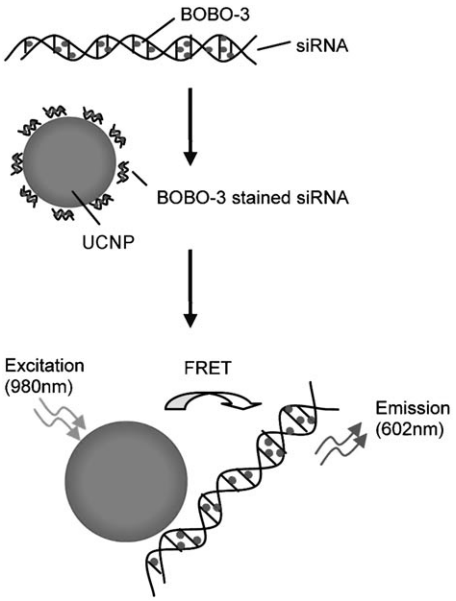


Figure 22. FRET-based UCNP/siRNA-BOBO3 complex system. Energy is transferred from the donor (UCNP) to the acceptor (BOBO-3) upon excitation of the nanoparticles at 980 nm. Reproduced with permission from reference [450]. Copyright Wiley-VCH 2006.

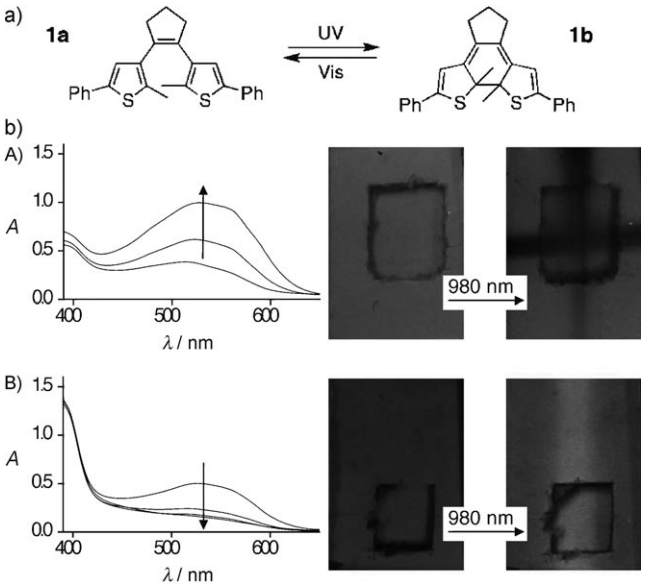


Figure 23. a) Photoswitching realized by transition between electronically and structurally different isomers of DTE. b) Reactions A) **1a** + $NaYF_4$:Tm^{3+},Yb^{3+}→**1b** and B) **1b** + $NaYF_4$:Er^{3+},Yb^{3+}→**1a** upon irradiation by NIR light (980 nm). The light beams to the right (A) and (B) correspond to the direction of the laser beam. The irradiation in (A) was carried out twice with perpendicular orientations. The small squares in all images are the cutout holes in the sample holder, through which the absorbance was measured. Reproduced with permission from reference [238]. Copyright American Chemical Society 2009.

5.2. Other Applications

Apart from the biological application, UCNPs are discussed for some other devices.[466,467] In recent reports, a combination of UCNPs and dithienylethene (DTE) is discussed for optical memory applications and remote-control photoswitching.[238,363,459] DTE photoswitches are based on ring-closing and ring-opening reactions induced by ultraviolet and visible light, respectively. To sensitize the system to NIR light, Branda et al. developed composite films consisting of DTE and either $NaYF_4$:Yb^{3+},Er^{3+} or $NaYF_4$:Yb^{3+},Tm^{3+} nanoparticles[238]. When the UCNPs are excited in the NIR, the emitted energy, either visible or UV radiation depending on the doping, is transferred to the DTE molecule, thus resulting in a ring-opening or ring-closing reaction (Figure 23a). The switching between the two states of the system is accompanied by a color change of the composite material along the path of the IR light (Figure 23b). Photopatterns on the basis of upconversion nanoparticles useful for potential applications in the field of security were designed by Kim et al.[451]

6. Conclusions and Outlook

Regarding various applications, upconverting nanoparticles benefit from their unique properties as they show 1) high sensitivity of detection because of the lack of autofluorescence background, 2) less toxic components than quantum dots (QDs), and 3) high penetration depths in combination with photostability and optical tunability. Many different dopant–host compositions have been developed and intensively investigated. Most scientists concur that in terms of biomedical applications, hexagonal-structured lanthanide-doped $NaYF_4$ is currently the most promising candidate.

Meanwhile, there is a large number of reports dealing with the successful generation of high-quality lanthanide-doped hexagonal $NaYF_4$ NPs showing narrow size distribution and high luminescence efficiency. Although there is a large body of literature describing various different synthesis procedures for hexagonal $NaYF_4$ particles in substance, only two different synthesis routes can be extracted from the current literature that lead to particles which fulfill the requirements. In the most known cases, the particles were prepared either by the trifluoroacetate route (transferred to $NaYF_4$ by Chow and Yi) or by the oleate route (by Zhang and Li).[186,215] Apart from further improvement of the synthesis procedures for generating lanthanide-doped β-$NaYF_4$ nanoparticles to obtain desired optical properties, size, and size distribution of the particles, and to make the synthesis more user-friendly, the discovery of new upconversion ions, combinations of ions, and host materials will remain areas of intense research.

The use of upconverting nanocrystals in nucleic acid assays and immunoassays in in vitro und in vivo imaging has been demonstrated over the past five years. Very often, applications are still limited to the simple introduction of luminescing NPs into biological systems and detection of the particles themselves. For the replacement of molecular fluorescent markers (molecular weight ca. 300 $g\,mol^{-1}$),[452] which allow estimation of the position of single molecules within cellular structures with nanometer precision, particles with sizes in the region of 20 nm are still too large.

Therefore, for most advanced imaging applications in the field of biomedicine, for example the specific imaging of molecular and cellular events in the case of molecular neuroimaging, the overall quality of current upconversion NPs is still insufficient. In general, many methods still suffer from low reproducibility, mainly relevant to overall surface conditions that impair the colloidal stability and the luminescence efficiency.

So we dare to claim that despite the good progress, essential challenges still remain to be faced before these particles can fully reach their potential regarding the practical application in clinical settings by ultimate consumers.

The authors thank the colleagues involved in the peer review for the helpful comments.

Received: August 17, 2010
Revised: January 21, 2011
Published online: May 30, 2011

[1] F. Auzel, *Chem. Rev.* **2004**, *104*, 139.
[2] H. U. Güdel in *Topics in Current Chemistry*, *Vol. 214* (Ed.: H. Yersin), Springer, New York, **2001**, p. 1.
[3] D. R. Gamelin, H. U. Güdel, *Acc. Chem. Res.* **2000**, *33*, 235.
[4] F. Auzel, *Proc. IEEE* **1973**, *61*, 758.
[5] J. Wright in *Topics in Applied Physics*, *Vol. 15* (Ed.: D. J. Diestler, F. K. Fong, K. F. Freed, R. Kopelman, J. C. Wright), Springer, New York, **1976**, p. 239.
[6] F. Auzel, *C. R. Acad. Sci.* **1966**, *262*, 1016.
[7] F. Auzel, *C. R. Acad. Sci.* **1966**, *263*, 819.
[8] K. König, *J. Microsc.* **2000**, *200*, 83.
[9] W. M. McClain, R. E. Harris in *Excited States* (Ed.: E. C. Lim), Academic Press, New York, **1978**, S. 1.
[10] Y. Dong, J. Xu, G. Zhou, G. Zhao, M. Jie, L. Y. Yang, L. Su, J. Qiu, W. Feng, L. Lin, *Opt. Express* **2006**, *14*, 1899.
[11] R. Scheps, *Prog. Quantum Electron.* **1996**, *20*, 271.
[12] N. Bloembergen, *Phys. Rev.* **1962**, *127*, 1918.
[13] L. R. Dalton, *Chem. Mater.* **1995**, *7*, 1060.
[14] W. R. Zipfel, R. M. Williams, R. Christie, A. Yu Nikitin, B. T. Hyman, W. W. Webb, *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 12, 7075.
[15] Y. Mita, E. Nagasawa, *NEC Res. Dev.* **1974**, *33*, 61.
[16] G. F. Garlick, *J. Contemp. Phys.* **1976**, *17*, 127.
[17] O. S. Wenger, H. U. Güdel, *Inorg. Chem.* **2001**, *40*, 5747.
[18] S. M. Jacobsen, H. U. Güdel, *J. Lumin.* **1989**, *43*, 125.
[19] R. Moncorge, F. Auzel, J. M. Breteau, *Philos. Mag. B* **1985**, *51*, 489.
[20] O. S. Wenger, H. U. Güdel, R. Valiente, *High-Pressure Res.* **2002**, *22*, 57.
[21] O. S. Wenger, H. U. Güdel, *Inorg. Chem.* **2001**, *40*, 157.
[22] O. S. Wenger, H. U. Güdel, R. Valiente, *Phys. Rev. B* **2001**, *64*, 235116.
[23] D. R. Gamelin, H. U. Güdel, *J. Am. Chem. Soc.* **1998**, *120*, 12143.
[24] D. R. Gamelin, H. U. Güdel, *J. Phys. Chem. B* **2000**, *104*, 10222.
[25] D. R. Gamelin, H. U. Güdel, *Inorg. Chem.* **1999**, *38*, 5154.
[26] M. Wermuth, H. U. Güdel, *J. Phys. Condens. Matter* **2001**, *13*, 9583.
[27] M. Wermuth, H. U. Güdel, *Chem. Phys. Lett.* **1997**, *281*, 81.
[28] M. Wermuth, H. U. Güdel, *J. Lumin.* **2000**, *87–89*, 1014.
[29] M. Wermuth, H. U. Güdel, *J. Am. Chem. Soc.* **1999**, *121*, 10102.
[30] M. Wermuth, H. U. Güdel, *J. Chem. Phys.* **2001**, *114*, 1393.
[31] N. A. Stump, G. M. Murray, G. D. Delcul, R. G. Haire, J. R. Peterson, *Radiochim. Acta* **1993**, *61*, 129.
[32] P. J. Deren, W. Strek, E. Zych, J. Drozdzynski, *Chem. Phys. Lett.* **2000**, *332*, 308.
[33] N. Menyuk, K. Dwight, J. W. Pierce, *Appl. Phys. Lett.* **1972**, *21*, 4, 159.
[34] T. Kano, T. Suzuki, A. Suzuki, S. Minagawa, *J. Electrochem. Soc.* **1973**, *120*, C87.
[35] W. Lenth, R. M. Macfarlane, *Opt. Photon. News* **1992**, *3*, 8.
[36] W. Lenth, R. M. Macfarlane, *J. Lumin.* **1990**, *45*, 346.
[37] M. F. Joubert, *Phys. Rev. B* **1993**, *48*, 10031.
[38] A. Shalav, B. S. Richards, T. Trupke, K. W. Kramer, H. U. Güdel, *Appl. Phys. Lett.* **2005**, *86*, 13503.
[39] C. Strohhofer, A. Polman, *J. Appl. Phys.* **2001**, *90*, 4314.
[40] P. G. Kik, A. Polman, *J. Appl. Phys.* **2003**, *93*, 5008.
[41] E. Downing, L. Hesselink, J. Ralston, R. M. Macfarlane, *Science* **1996**, *273*, 1185.
[42] A. R. Jalil, Y. Zhang, *Biomaterials* **2008**, *29*, 4122.
[43] D. K. Chatterjee, A. J. Rufaihah, Y. Zhang, *Biomaterials* **2008**, *29*, 937.
[44] M. Nyk, R. Kumar, T. Y. Ohulchanskyy, E. J. Bergey, P. N. Prasad, *Nano Lett.* **2008**, *8*, 3834.
[45] J. Shan, J. Chen, J. Meng, J. Collins, W. Soboyejo, J. S. Friedberg, Y. Ju, *J. Appl. Phys.* **2008**, *104*, 094308.
[46] F. Wang, D. K. Chatterjee, Z. Li, Y. Zhang, X. Fan, M. Wang, *Nanotechnology* **2006**, *17*, 5786.
[47] F. Wang, X. Liu, *Chem. Soc. Rev.* **2009**, *38*, 976.
[48] F. Vetrone, J. A. Capobianco, *Int. J. Nanotechnol.* **2008**, *5*, 1306.
[49] P. Rahman, M. Green, *Nanoscale* **2009**, *1*, 214.
[50] K. W. Kramer, D. Biner, G. Frei, H. U. Güdel, M. P. Hehlen, S. R. Luthi, *Chem. Mater.* **2004**, *16*, 1244.
[51] A. Aebischer, M. Hostettler, J. Hauser, K. Krämer, T. Weber, H.-U. Güdel, H.-B. Bürgi, *Angew. Chem.* **2006**, *118*, 2869; *Angew. Chem. Int. Ed.* **2006**, *45*, 2802.
[52] A. Aebischer, S. Heer, D. Biner, K. Krämer, M. Haase, H. U. Güdel, *Chem. Phys. Lett.* **2005**, *407*, 124.
[53] M. P. Hehlen, M. L. F. Phillips, N. J. Cockroft, H. U. Güdel in *Encyclopedia of Materials: Science and Technology, Vol. 10* (Ed.: E. J. Kramer), Pergamon/Elsevier, Oxford, **2001**, p. 9456.
[54] X. Chen, E. Ma, G. Liu, *J. Phys. Chem. C* **2007**, *111*, 10404.
[55] H. Schäfer, P. Ptacek, K. Kömpe, M. Haase, *Chem. Mater.* **2007**, *19*, 1396.
[56] R. Diamente, M. Raudsepp, F. C. J. M. van Veggel, *Adv. Funct. Mater.* **2007**, *17*, 363.
[57] Z. Xu, C. Li, P. Yang, C. Zhang, S. Huang, J. Lin, *Cryst. Growth Des.* **2009**, *9*, 4752.
[58] R. Yan, Y. Li, *Adv. Funct. Mater.* **2005**, *15*, 5, 763.
[59] S. Heer, K. Kömpe, M. Haase, H. U. Güdel, *Adv. Mater.* **2004**, *16*, 2102.
[60] F. Wang, X. Liu, *J. Am. Chem. Soc.* **2008**, *130*, 5642.
[61] Z. Li, Y. Zhang, *Angew. Chem.* **2006**, *118*, 7896; *Angew. Chem. Int. Ed.* **2006**, *45*, 7732.
[62] G. Yi, H. Lu, S. Zhao, Y. Ge, W. Yang, D. Chen, L.-H. Gu, *Nano Lett.* **2004**, *4*, 2191.
[63] G. Blasse, B. C. Grabmaier, *Luminescent Materials*, 1st ed., Springer, Berlin, **1994**, p. 1.
[64] S. Heer, O. Lehmann, M. Haase, H. U. Güdel, *Angew. Chem.* **2003**, *115*, 3288; *Angew. Chem. Int. Ed.* **2003**, *42*, 3179.
[65] T. Soukka, K. Kuningas, T. Rantanen, V. Haaslahti, T. Lovgren, *J. Fluoresc.* **2005**, *15*, 513.
[66] K. Kuningas, T. Rantanen, T. Ukonaho, T. Lölvgren, T. Soukka, *Anal. Chem.* **2005**, *77*, 7348.
[67] K. Kuningas, T. Ukonaho, H. Päkkilä, T. Rantanen, J. Rosenberg, T. Lövgren, T. Soukka, *Anal. Chem.* **2006**, *78*, 4690.
[68] J. F. Suyver, J. Grimm, K. W. Kramer, H. U. Güdel, *J. Lumin.* **2005**, *114*, 53.
[69] J. F. Suyver, J. Grimm, M. K. van Veen, D. Biner, K. W. Krämer, H. U. Güdel, *J. Lumin.* **2006**, *117*, 1.

[70] J. F. Suyver, A. Aebischer, S. García-Revilla, P. Gerner, H. U. Güdel, *Phys. Rev. B* **2005**, *71*, 125123.
[71] J. F. Suyver, A. Aebischer, D. Biner, P. Gerner, J. Grimm, S. Heer, K. W. Krämer, C. Reinhard, H. U. Gudel, *Opt. Mater.* **2005**, *27*, 1111.
[72] H.-X. Mai, Y.-W. Zhang, L.-D. Sun, C.-H. Yan, *J. Phys. Chem. C* **2007**, *111*, 13721.
[73] J. H. Zeng, J. Su, Z.-H. Li, R.-X. Yan, Y.-D. Li, *Adv. Mater.* **2005**, *17*, 2119.
[74] P. Boutinaud, R. Mahiou, N. Martin, M. Malinowski, *J. Lumin.* **1997**, *72–74*, 809.
[75] J.-C. Boyer, F. Vetrone, L. A. Cuccia, J. A. Capobianco, *J. Am. Chem. Soc.* **2006**, *128*, 7444.
[76] R. Kumar, M. Nyk, T. Y. Ohulchanskyy, C. A. Flask, P. N. Prasad, *Adv. Funct. Mater.* **2009**, *19*, 853.
[77] G. Wang, Q. Peng, Y. Li, *J. Am. Chem. Soc.* **2009**, *131*, 14200.
[78] L. Wang, Y. Li, *Chem. Mater.* **2007**, *19*, 727.
[79] J.-C. Boyer, L. A. Cuccia, J. A. Capobianco, *Nano Lett.* **2007**, *7*, 847.
[80] J. W. Stouwdam, F. C. J. M. van Veggel, *Nano Lett.* **2002**, *2*, 733.
[81] B. M. Tissue, *Chem. Mater.* **1998**, *10*, 2837.
[82] S. Polizzi, S. Bucella, A. Speghini, F. Vetrone, R. Naccache, J. C. Boyer, J. A. Capobianco, *Chem. Mater.* **2004**, *16*, 1330.
[83] H. Lai, B. Chen, W. Xu, X. Wang, Y. Yang, Q. Meng, *J. Alloys Compd.* **2005**, *395*, 181.
[84] Y. Sun, H. Liu, X. Wang, X. Kong, H. Zhang, *Chem. Mater.* **2006**, *18*, 2726.
[85] F. Vetrone, J.-C. Boyer, J. A. Capobianco, A. Speghini, M. Bettinelli, *J. Phys. Chem. B* **2003**, *107*, 10747.
[86] Z. Xu, X. Kang, C. Li, Z. Hou, C. Zhang, D. Yang, G. Li, J. Lin, *Inorg. Chem.* **2010**, *49*, 6706.
[87] H. Guo, N. Dong, M. Yin, W. Zhang, L. Lou, S. Xia, *J. Phys. Chem. B* **2004**, *108*, 19205.
[88] A. Patra, C. S. Friend, R. Kapoor, P. N. Prasad, *Chem. Mater.* **2003**, *15*, 3650.
[89] A. Patra, P. Ghosh, P. S. Chowdhury, M. A. R. C. Alencar, W. Lozano, B. N. Rakov, G. S. Maciel, *J. Phys. Chem. B* **2005**, *109*, 10142.
[90] A. Patra, C. S. Friend, R. Kapoor, P. N. Prasad, *J. Phys. Chem. B* **2002**, *106*, 1909.
[91] G. Chen, G. Somesfalean, Y. Liu, Z. Zhang, Q. Sun, F. Wang, *Phys. Rev. B* **2007**, *75*, 195204.
[92] X. Wang, X. Kong, Y. Yu, Y. Sun, H. Zhang, *J. Phys. Chem. C* **2007**, *111*, 15119.
[93] H.-X. Mai, Y.-W. Zhang, R. Si, Z.-G. Yan, L.-D. Sun, L.-P. You, C.-H. Yan, *J. Am. Chem. Soc.* **2006**, *128*, 6426.
[94] F. Vetrone, J.-C. Boyer, J. A Capobianco, A. Speghini, M. Bettinelli, *Nanotechnology* **2004**, *15*, 75.
[95] K. Soga, A. Okada, Y. Saito, Y. Kameyama, T. Konishi, *J. Photopolym. Sci. Technol.* **2007**, *20*, 7.
[96] Y. Suna, Y. Chena, L. Tian, Y. Yub, X. Kong, Q. Zengb, Y. Zhang, H. Zhang, *J. Lumin.* **2008**, *128*, 15.
[97] G. A. Kumar, C. W. Chen, R. E. Riman, *Appl. Phys. Lett.* **2007**, *90*, 093123.
[98] Y. Bai, K. Yang, Y. Wang, X. Zhang, Y. Song, *Opt. Commun.* **2008**, *281*, 2930.
[99] G. A. Kumar, C. W. Chen, J. Ballato, R. E. Riman, *Chem. Mater.* **2007**, *19*, 1523.
[100] R. Naccache, F. Vetrone, A. Speghini, M. Bettinelli, J. A. Capobianco, *J. Phys. Chem. C* **2008**, *112*, 7750.
[101] M. Yu, J. Lin, Z. Wang, J. Fu, S. Wang, H. J. Zhang, Y. C. Han, *Chem. Mater.* **2002**, *14*, 2224.
[102] V. K. Tikhomirov, M. Mortier, P. Gredin, G. Patriarche, C. Görller-Walrand, V. V. Moshchalkov, *Opt. Express* **2008**, *16*, 19, 14544.
[103] Y. Mao, T. Tran, X. Guo, J. Y. Huang, C. K. Shih, K. L. Wang, J. P. Chang, *Adv. Funct. Mater.* **2009**, *19*, 748.
[104] P. Zhang, S. Rogelj, K. Nguyen, D. Wheeler, *J. Am. Chem. Soc.* **2006**, *128*, 12410.
[105] J. A. Capobianco, F. Vetrone, T. D. Alesio, G. Tessari, A. Speghini, M. Bettinelli, *Phys. Chem. Chem. Phys.* **2000**, *2*, 3203.
[106] S. Q. Man, E. Y. B. Pun, P. S. Chung, *Appl. Phys. Lett.* **2000**, *77*, 483.
[107] I.-I. Oprea, H. Hesse, K. Betzler, *Phys. Status Solidi B* **2005**, *242*, 12, R109.
[108] A. S. Oliveira, M. T. de Araujo, A. S. Gouveia-Neto, J. A. Medeiros Neto, A. S. B. Sombra, Y. Messaddeq, *Appl. Phys. Lett.* **1998**, *72*, 753.
[109] C. B. de Araujo, L. S. Menezes, G. S. Maciel, L. H. Acioli, A. S. L. Gomes, Y. Messaddeq, A. Florez, M. A. Aegerter, *Appl. Phys. Lett.* **1996**, *68*, 602.
[110] M. Shojiya, M. Takahashi, R. Kanno, Y. Kawamoto, K. Kadono, *Appl. Phys. Lett.* **1995**, *67*, 2453.
[111] A. Remillieux, B. Jacquier, *J. Lumin.* **1996**, *68*, 279.
[112] J. Fernandez, R. Balda, M. Sanz, L. M. Lacha, A. Oleaga, J. L. Adam, *J. Lumin.* **2001**, *94–95*, 325.
[113] L. H. Acioli, J. T. Guo, C. B. de Araujo, T. Messaddeq, M. A. Aegerter, *J. Lumin.* **1997**, *72–74*, 68.
[114] R. Balda, M. Sanz, A. Mendorioz, J. Fernandez, L. S. Griscom, J. L. Adam, *Phys. Rev. B* **2001**, *64*, 144101.
[115] Jacquier, *J. Lumin.* **1994**, *60*, 175.
[116] Y. G. Choi, K. H. Kim, B. J. Lee, Y. B. Shin, Y. S. Kim, J. Heo, *J. Non-Cryst. Solids* **2000**, *278*, 137.
[117] F. Liu, E. Ma, D. Chen, Y. Yu, Y. Wang, *J. Phys. Chem. B* **2006**, *110*, 20843.
[118] X. Fan, J. Wang, X. Qiao, M. Wang, J.-L. Adam, X. Zhang, *J. Phys. Chem. B* **2006**, *110*, 5950.
[119] H. Yang, Z. Dai, J. Li, Y. Tian, *J. Non-Cryst. Solids* **2006**, *352*, 5469.
[120] Y. Kishi, S. Tanabe, *J. Alloys Compd.* **2006**, *408–412*, 842.
[121] Z. Pan, A. Ueda, R. Mu, S. H. Morgan, *J. Lumin.* **2007**, *126*, 251.
[122] N. Rakov, G. S. Maciel, M. L. Sundheimer, L. de S. Menezes, A. S. L. Gomes, Y. Messaddeq, F. C. Cassanjes, G. Poirier, S. J. L. Ribeiro, *J. Appl. Phys.* **2002**, *92*, 16337.
[123] V. D. Rodriguez, V. K. Tikhomirov, J. Mendez-Ramos, J. del-Castillo, C. Görller-Walrand, *J. Nanosci. Nanotechnol.* **2009**, *9*, 2072.
[124] J. Mendez-Ramos, V. K. Tikhomirov, V. D. Rodrıguez , D. Furniss, *J. Alloys Compd.* **2007**, *440*, 328.
[125] B. Henke, B. Ahrens, P. T. Miclea, C. Eisenschmidt, J. A. Johnson, S. Schweizer, *J. Non-Cryst. Solids* **2009**, *355*, 1916.
[126] M. Yin, V. N. Makhov, N. M. Khaidukov, J. C. Krupa, *J. Alloys Compd.* **2002**, *341*, 362.
[127] J. A. Capobianco, F. Vetrone, J. C. Boyer, *J. Phys. Chem. B* **2002**, *106*, 1181.
[128] F. Vetrone, J. C. Boyer, J. A. Capobianco, *J. Phys. Chem. B* **2002**, *106*, 5622.
[129] G. Huber, E. Heumann, T. Sandrock, K. Petermann, *J. Lumin.* **1997**, *72–74*, 1.
[130] T. Riedener, P. Egger, J. Hulliger, H. U. Güdel, *Phys. Rev. B* **1997**, *56*, 1800.
[131] J. Grimm, E. Beurer, P. Gerner, H. U. Güdel, *Chem. Eur. J.* **2007**, *13*, 1152.
[132] O. S. Wenger, C. Wickleder, K. W. Krämer, H. U. Güdel, *J. Lumin.* **2001**, *94–95*, 101.
[133] E. Beurer, J. Grimm, P. Gerner, H. U. Güdel, *J. Am. Chem. Soc.* **2006**, *128*, 3110.
[134] R. Balda, J. Fernandez, I. Saez de Ocariz, M. Voda, A. Garcia, *J. Phys. Rev. B* **1999**, *59*, 9972.
[135] J. J. Ju, J. H. Ro, M. Cha, *J. Lumin.* **2000**, *87–89*, 1045.
[136] M. Malinowski, M. F. Joubert, B. Jacquier, *Phys. Rev. B* **1994**, *50*, 12367.

[137] J. Fernandez, M. Sanz, A. Mendorioz, R. Balda, J. P. Chaminade, J. Ravez, L. M. Lacha, M. Voda, M. A. Arriandiaga, *J. Alloys Compd.* **2001**, *323–324*, 267.
[138] M. Malinovski, B. Jacquier, B. , M. Bouazaoui, M. F. Joubert, C. Linares, *Phys. Rev. B* **1990**, *41*, 31.
[139] K. Holliday, D. L. Russell, B. Henderson, *J. Lumin.* **1997**, *72*, 927.
[140] M. Wermuth, T. Riedener, H. U. Güdel, *Phys. Rev. B* **1998**, *57*, 4369.
[141] P. Müller, M. Wermuth, H. U. Güdel, *Chem. Phys. Lett.* **1998**, *290*, 105.
[142] R. Burlot-Loison, M. Pollnau, K. Krämer, P. Egger, J. Hulliger, H. U. Güdel, *J. Opt. Soc. Am. B* **2000**, *17*, 2055.
[143] T. Riedener, H. U. Güdel, *J. Chem. Phys.* **1997**, *107*, 2169.
[144] X. Li, Q. Li, J. Wang, L. Li, *J. Lumin.* **2007**, 124, 351.
[145] X. B. Chen, G. Y. Zhang, Y. H. Mao, Y. B. Hou, Y. Feng, Z. Hao, *J. Lumin.* **1996**, *69*, 151.
[146] A. S. L. Gomes, C. B. de Araujo, *J. Lumin.* **1991**, *48*, 876.
[147] Y. Wang, J. Ohwaki, *J. Appl. Phys.*. **1993**, *74*, 1272.
[148] Y. Wang, *Jpn. J. Appl. Phys.* **1994**, *33*, L334.
[149] R. M. Macfarlane, F. Tong, A. J. Silversmith, W. Lenth, *Appl. Phys. Lett.* **1988**, *52*, 1300.
[150] R. Brede, E. Heumann, J. Koetke, T. Danger, G. Huber, B. Chai, *Appl. Phys. Lett.* **1993**, *63*, 2030.
[151] J.-Y Allain, M. Monerie, H. Poignant, *Electron. Lett.* **1990**, *26*, 166.
[152] J.-Y Allain, M. Monerie, H. Poignant, *Electron. Lett.* **1990**, *26*, 261.
[153] M. Bresler, O. Gusev, E. Terukov, Y. Undalov, *Phys. Status Solidi B* **2005**, *242*, R82.
[154] R. Balda, J. Fernández, E. E. Nyein, U. Hömmerich, *Opt. Express* **2006**, *14*, 3993.
[155] P. Gerner, C. Reinhard, H. U. Güdel, *Chem. Eur. J.* **2004**, *10*, 4735.
[156] X. Wang, J. Song, H. Sun, Z. Xu, J. Qiu, *Opt. Express* **2007**, *15*, 1384.
[157] S. Chen, M. Wu, L. An, Y. Li, S. Wang, *J. Am. Ceram. Soc.* **2007**, *90*, 664.
[158] D. Dosev, I. M. Kennedy, M. Godlewski, I. Gryczynski, K. Tomsia, E. M. Goldys, *Appl. Phys. Lett.* **2006**, *88*, 011906.
[159] E. Beurer, J. Grimm, P. Gerner, H. U. Güdel, *Inorg. Chem.* **2006**, *45*, 9901.
[160] C. Reinhard, R. Valiente, H. U. Güdel, *J. Phys. Chem. B* **2002**, *106*, 10051.
[161] P. Gerner, O. S. Wenger, R. Valiente, H. U. Güdel, *Inorg. Chem.* **2001**, *40*, 4534.
[162] S. R. Lüthi, M. Pollnau, H. U. Güdel, *Phys. Rev. B* **1999**, *60*, 162.
[163] T. Riedener, K. Krämer, H. U. Güdel, *Inorg. Chem.* **1995**, *34*, 2745.
[164] M. P. Hehlen, G. Frei, H. U. Güdel, *Phys. Rev. B* **1994**, *50*, 16264.
[165] M. P. Hehlen, R. A. McFarlane, R. N. Schwarz, H. U. Güdel, *Phys. Rev. B* **1994**, *49*, 12475.
[166] P. Gerner, H. U. Güdel, *Chem. Phys. Lett.* **2005**, *413*, 105.
[167] F. Vetrone, J.-C. Boyer, J. A. Capobianco, A. Speghini, M. Bettinelli, R. Krsmanovic, S. Polizzic, *J. Electrochem. Soc.* **2005**, *152*, H19.
[168] M. Bouffard, T. Duvaut, J. P. Jouart, N. M. Khaidukov, M. F. Joubert, *J. Phys. Condens. Matter* **1999**, *11*, 4775.
[169] E. Sani, A. Toncelli, M. Tonelli, *J. Phys. Condens. Matter* **2006**, *18*, 2057.
[170] Y. Le Fur, N. M. Khaidukov, S. Aleonard, *Acta Crystallogr. C* **1992**, *48*, 2062.
[171] D. Wang, Y. Guo, G. Sun, J. Li, L. Zhao, G. Xu, *J. Alloys Compd.* **2008**, *451*, 122.
[172] X. Wang, S. Xiao, X. Yang, J. W. Ding, *J. Mater. Sci.* **2008**, *43*, 1354.
[173] C. Ma, P. A. Tanner, S. Xia, M. Yin, *Optical Materials* **2007**, *29*, 1620.
[174] N. M. Khaidukov, S. K. Lam, D. Lo, V. N. Makhov, N. V. Suetin, *Opt. Mater.* **2002**, *19*, 365.
[175] R. H. Page, K. I. Schaffers, P. A. Waide, J. B. Tassano, S. A. Payne, W. F. Krupke, W. K. Bischel, *J. Opt. Soc. Am. B* **1998**, *15*, 3, 996.
[176] L. Wang, Y. Li, *Nano Lett.* **2006**, *6*, 1645.
[177] Y. Wei, F. Lu, X. Zhang, D. Chen, *Chem. Mater.* **2006**, *18*, 5733.
[178] S. Sivakumar, P. R. Diamente, F. C. J. M. van Veggel, *Chem. Eur. J.* **2006**, *12*, 5878.
[179] F. Tao, F. Pan, Z. J. Wang, W. L. Cai, L. Z. Yao, *CrystEngComm* **2010**, *12*, 4263.
[180] S. F. Lim, R. Riehn, W. S. Ryu, N. Khanarian, C.-K. Tung, D. Tank, R. H. Austin, *Nano Lett.* **2006**, *6*, 169.
[181] F. Vetrone, J. C. Boyer, J. A. Capobianco, A. Speghini, M. Bettinelli, *J. Phys. Chem. B* **2003**, *107*, 1107.
[182] Y. Wei, F. Lu, X. Zhang, D. Chen, *Mater. Lett.* **2007**, *61*, 1337.
[183] Y. Wei, F. Lu, X. Zhang, D. Chen, *J. Alloys Compd.* **2007**, *427*, 333.
[184] L Wang, R. Yan, Z. Huo, L. Wang, J. Zeng, J. Bao, X. Wang, Q. Peng, Y. Li, *Angew. Chem.* **2005**, *117*, 6208; *Angew. Chem. Int. Ed.* **2005**, *44*, 6054.
[185] G.-S. Yi, G.-M. Chow, *Molecular Engineering of Biological and Chemical Systems (MEBCS)* **2006**, http://hdl.handle.net/1721.1/30391.
[186] G. S. Yi, G. M. Chow, *Adv. Funct. Mater.* **2006**, *16*, 2324.
[187] Y. Sun, Y. Chen, L. Tian, Y. Yu, X. Kong, J. Zhao, H. Zhang, *Nanotechnology* **2007**, *18*, 275609.
[188] Z. Duan, J. Zhang, W. Xiang, H. Sun, L. Hu, *Mater. Lett.* **2007**, *61*, 2200.
[189] X. Liang, X. Wang, J. Zhuang, Q. Peng, Y. Li, *Inorg. Chem.* **2007**, *46*, 6050.
[190] X. Bai, H. Song, G. Pan, Y. Lei, T. Wang, X. Ren, S. Lu, B. Dong, Q. Dai, L. Fan, *J. Phys. Chem. C* **2007**, *111*, 13611.
[191] C. Li, J. Yang, Z. Quan, P. Yang, D. Kong, J. Lin, *Chem. Mater.* **2007**, *19*, 4933.
[192] G.-S. Yi, G.-M. Chow, *Chem. Mater.* **2007**, *19*, 341.
[193] C. Liu, D. Chen, *J. Mater. Chem.* **2007**, *17*, 3875.
[194] H.-X. Mai, Y.-W. Zhang, L.-D. Sun, C.-H. Yan, *J. Phys. Chem. C* **2007**, *111*, 13730.
[195] C. Li, Z. Quan, J. Yang, P. Yang, J. Lin, *Inorg. Chem.* **2007**, *46*, 6329.
[196] J. Zhuang, L. Liang, H. H. Y. Sung, X. Yang, M. Wu, I. D. Williams, S. Feng, Q. Su, *Inorg. Chem.* **2007**, *46*, 5404.
[197] A. M. Pires, S. Heer, H. U. Güdel, O. A. Serra, *J. Fluoresc.* **2006**, *16*, 461.
[198] F. Pandozzi, F. Vetrone, J.-C. Boyer, R. Naccache, J. A. Capobianco, A. Speghini, M. Bettinelli, *J. Phys. Chem. B* **2005**, *109*, 17400.
[199] F. Vetrone, J.-C. Boyer, J. A. Capobianco, A. Speghini, M. Bettinelli, *J. Appl. Phys.* **2004**, *96*, 1, 661.
[200] Y. Wang, W. Qin, J. Zhang, C. Cao, J. Zhang, Y. Jin, P. Zhu, G. Wei, G. Wang, L. Wang, *Chem. Lett.* **2007**, *36*, 912.
[201] J. Shan, Y. Ju, *Appl. Phys. Lett.* **2007**, *91*, 123103.
[202] A. Bessiere, F. Pelle, C. Mathieu, B. Viana, P. Vermaut, *Mater. Sci. Forum* **2007**, *555*, 383.
[203] C.-J. Sun, Z. Xu, B. Hu, G. S. Yi, G. M. Chow, J. Shen, *Appl. Phys. Lett.* **2007**, *91*, 191113.
[204] F. Zhang, Y. Wan, T. Yu, F. Zhang, Y. Shi, S. Xie, Y. Li, L. Xu, B. Tu, D. Zhao, *Angew. Chem.* **2007**, *119*, 8122; *Angew. Chem. Int. Ed.* **2007**, *46*, 7976.
[205] G. Y. Chen, Y. Liu, Y. G. Zhang, G. Somesfalean, Z. G. Zhang, Q. Sun, F. P. Wang, *Appl. Phys. Lett.* **2007**, *91*, 133103.
[206] Z. Chen, H. Chen, H. Hu, M. Yu, F. Li, Q. Zhang, Z. Zhou, T. Yi, C. Huang, *J. Am. Chem. Soc.* **2008**, *130*, 3023.
[207] J. Shan, X. Qin, N. Yao, Y. Ju, *Nanotechnology* **2007**, *18*, 445607.

[208] Z. Wang, F. Tao, W. Cai, L. Yaob, X. Lib, *Solid State Commun.* **2007**, *144*, 255.
[209] P. Ghosh, J. Oliva, E. de la Rosa, K. Kanta Haldar, D. Solis, A. Patra, *J. Phys. Chem. C* **2008**, *112*, 9650.
[210] Z. Liu, G. Yi, H. Zhang, J. Ding, Y. Zhang, J. Xue, *Chem. Commun.* **2008**, 694.
[211] O. Ehlert, R. Thomann, M. Darbandi, T. Nann, *ACS Nano* **2008**, *2*, 120.
[212] Y. Wei, F. Lu, X. Zhang, D. Chen, *J. Alloys Compd.* **2008**, *455*, 376.
[213] J. Zhao, Y. Sun, X. Kong, L. Tian, Y. Wang, L. Tu, J. Zhao, H. Zhang, *J. Phys. Chem. B* **2008**, *112*, 15666.
[214] H. Schäfer, P. Ptacek, O. Zerzouf, M. Haase, *Adv. Funct. Mater.* **2008**, *18*, 2913.
[215] Z. Li, Y. Zhang, *Nanotechnology* **2008**, *19*, 345606.
[216] M. Wang, J.-L. Liu, Y.-X. Zhang, W. Hou, X.-L. Wu, S.-K. Xu, *Mater. Lett.* **2009**, *63*, 325.
[217] H. Hu, M. Yu, F. Li, Z. Chen, X. Gao, L. Xiong, C. Huang, *Chem. Mater.* **2008**, *20*, 7003.
[218] See Ref. [45].
[219] H. Liang, G. Chen, H. Liu, Z. Zhang, *J. Lumin.* **2009**, *129*, 197.
[220] G. Chen, H. Liu, H. Liang, G. Somesfalean, Z. Zhang, *J. Phys. Chem. C* **2008**, *112*, 12030.
[221] Z. Li, Y. Zhang, S. Jiang, *Adv. Mater.* **2008**, *20*, 4765.
[222] N. O. Nuñez, H. Míguez, M. Quintanilla, E. Cantelar, F. Cussó, M. Ocaña, *Eur. J. Inorg. Chem.* **2008**, 4517.
[223] Y.-P. Du, X. Sun, Y.-W. Zhang, Z.-G. Yan, L.-D. Sun, C.-H. Yan, *Cryst. Growth Des.* **2009**, *9*, 2013.
[224] H. Hu, L. Xiong, J. Zhou, F. Li, T. Cao, C. Huang, *Chem. Eur. J.* **2009**, *15*, 3577.
[225] Y. Wang, L. Tu, J. Zhao, Y. Sun, X. Kong, H. Zhang, *J. Phys. Chem. C* **2009**, *113*, 7164.
[226] J. H. Zeng, Z. H. Li, J. Su, L. Wang, R. Yan, Y. Li, *Nanotechnology* **2006**, *17*, 3549.
[227] F. Vetrone, V. Mahalingam, J. A. Capobianco, *Chem. Mater.* **2009**, *21*, 1847.
[228] H. Schäfer, P. Ptacek, H. Eickmeier, M. Haase, *Adv. Funct. Mater.* **2009**, *19*, 3091.
[229] V. K. Tikhomirov, K. Driesen, V. D. Rodriguez, P. Gredin , M. Mortier, V. V. Moshchalkov, *Opt. Express* **2009**, *17*, 11794.
[230] M. Wang, W. Hou, C.-C. Mi, W.-X. Wang, Z.-R. Xu, H.-H. Teng, C.-B. Mao, S.-K. Xu, *Anal. Chem.* **2009**, *81*, 8783.
[231] T. A. A. Assumpção, D. M. da Silva, L. R. P. Kassab, C. B. de Araújo, *J. Appl. Phys.* **2009**, *106*, 063522.
[232] Z. Li, Y. Zhang, B. Shuter, N. M. Idris, *Langmuir* **2009**, *25*, 12015.
[233] K. Tsujiuchi, A. Okada, D. Matsuura, K. Soga, *J. Photopolym. Sci. Technol.* **2009**, *22*, 541.
[234] S. Wua, G. Hana, D. J. Millirona, S. Alonia, V. Altoea, D. V. Talapin, B. E. Cohena, P. J. Schucka, *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 10917.
[235] S. Schietinger, L. de S. Menezes, B. Lauritzen, O. Benson, *Nano Lett.* **2009**, *9*, 2477.
[236] W. Feng, L.-D. Sun, Y.-W. Zhang, C.-H. Yan, *Small* **2009**, *5*, 2057.
[237] T. Rantanen, M.-L. Järvenpää, J. Vuojola, R. Arppe, K. Kuningas, T. Soukka, *Analyst* **2009**, *134*, 1713.
[238] C.-J. Carling, J.-C. Boyer, N. R. Branda, *J. Am. Chem. Soc.* **2009**, *131*, 10838.
[239] H.-P. Zhou, C. Zhang, C.-H. Yan, *Langmuir* **2009**, *25*, 12914.
[240] W. Feng, L.-D. Sun, C.-H. Yan, *Chem. Commun.* **2009**, 4393.
[241] J. Wu, Q. Tian, H. Hu, Q. Xia, Y. Zou, F. Li, T. Yi, C. Huang, *Chem. Commun.* **2009**, 4100.
[242] C. T. Xu, J. Axelsson, S. Andersson-Engels, *Appl. Phys. Lett.* **2009**, *94*, 251107.
[243] C. Lin, M. T. Berry, R. Anderson, S. Smith, P. S. May, *Chem. Mater.* **2009**, *21*, 3406.
[244] Y. Y. Zhang, L. W. Yang, H. L. Han, J. X. Zhong, *Opt. Commun.* **2009**, *282*, 2857.
[245] C. Liu, H. Wang, X. Li, D. Chen, *J. Mater. Chem.* **2009**, *19*, 3546.
[246] S. Jiang, Y. Zhang, K. M. Lim, E. K W Sim, L. Ye, *Nanotechnology* **2009**, *20*, 155101.
[247] J. C. Boyer, N. J. J. Johnson, F. C. J. M. van Veggel, *Chem. Mater.* **2009**, *21*, 2010.
[248] S.-Z. Zhang, L.-D. Sun, H. Tian, Y. Liu, J.-F. Wang, C.-H. Yan, *Chem. Commun.* **2009**, 2547.
[249] M. Yu, F. Li, Z. Chen, H. Hu, C. Zhan, H. Yang, C. Huang, *Anal. Chem.* **2009**, *81*, 930.
[250] C. T. Xu, N. Svensson, J. Axelsson, P. Svenmarker, G. Somesfalean, G. Chen, H. Liang, H. Liu, Z. Zhang, S. Andersson-Engels, *Appl. Phys. Lett.* **2008**, *93*, 171103.
[251] H.-S. Qian, Y. Zhang, *Langmuir* **2008**, *24*, 12123.
[252] Y. Guo, M. Kumar, P. Zhang, *Chem. Mater.* **2007**, *19*, 6071.
[253] S. Sivakumar, F. C. J. M van Veggel, P. S. May, *J. Am. Chem. Soc.* **2007**, *129*, 620.
[254] X. Liu, J. Zhao, Y. Sun, K. Song, Y. Yu, C. Du, X. Kong, H. Zhang, *Chem. Commun.* **2009**, 6628.
[255] Z.-X. Li, L.-L. Li, H.-P. Zhou, Q. Yuan, C. Chen, L.- D. Sun, C.-H. Yan, *Chem. Commun.* **2009**, 6616.
[256] S. F. Lim, R. Riehn, C.-k. Tung, W. S Ryu, R. Zhuo, J. Dalland, R. H Austin, *Nanotechnology* **2009**, *20*, 405701.
[257] J.-C. Boyer, M.-P. Manseau, J. I. Murray, F. C. J. M. van Veggel, *Langmuir* **2010**, *26*, 1157.
[258] F. Zhang, J. Li, J. Shan, L. Xu, D. Zhao, *Chem. Eur. J.* **2009**, *15*, 11010.
[259] H. Schäfer, P. Ptacek, H. Eickmeier, M. Haase, *J. Nanomat. Vol.* **2009**, Article ID 685624, 7 pages.
[260] V. Mahalingam, F. Vetrone, R. Naccache, A. Speghini, J. A. Capobianco, *Adv. Mater.* **2009**, *21*, 4025.
[261] H.-Q. Wang, T. Nann, *ACS Nano* **2009**, *3*, 3804.
[262] X. Wang, J. Zhuang, Q. Peng, Y. Li, *Nature* **2005**, *437*, 121.
[263] J. Silver, M. I. Martinez-Rubio, T. G. Ireland, G. R. Fern, R. Withnall, *J. Phys. Chem. B* **2001**, *105*, 948.
[264] X. X. Zhang, P. Hong, M. Bass, B. H. T. Chai, *Phys. Rev. B* **1995**, *51*, 9298.
[265] S. Xu, L. Zhang, S. Zhao, D. Fang, Z. Zhang, Z. Jiang, *J. Mater. Sci.* **2006**, *41*, 1839.
[266] M. Huang, F. Meng, *Luminescence* **2005**, *20*, 276.
[267] M. Liao, L. Wen, H. Zhao, Y. Fang, H. Sun, L. Hu, *Mater. Lett.* **2007**, *61*, 470.
[268] B. Dong, D. P. Liu, X. J. Wang, T. Yang, S. M. Miao, C. R. Li, *Appl. Phys. Lett.* **2007**, *90*, 181117.
[269] T. Kano, H. Yamamoto, Y. Otomo, *J. Electrochem. Soc.* **1972**, *119*, 1561.
[270] R. Liesiecki, W. Ryba-Romanowski, T. Lukasiewicz, *Appl. Phys. B* **2005**, *81*, 43.
[271] D. Zhong-Chao, Z. Jun-Jie, H. Dong-Bing, D. Shi-Xun, H. Li-Li, *Chin. Phys.* **2006**, *15*, 209.
[272] F. W. Ostermeier, J. P. van der Ziel, H. M. Marcos, L. G. Van Uitert, J. E. Geusic, *Phys. Rev. B* **1971**, *3*, 2698.
[273] W. Wang, M. Wu, C. K. Liu, *Spectrosc. Lett.* **2007**, *40*, 259.
[274] A. Braud, S. Girard, J. L. Doualan, M. Thuau, R. Moncorge, A. M. Tkachuk, *Phys. Rev. B* **2000**, *61*, 5280.
[275] B. Dong, H. Song, H. Yu, H. Zhang, R. Qin, X. Bai, G. Pan, S. Lu, F. Wang, L. Fan, Q. Dai, *J. Phys. Chem. C* **2008**, *112*, 1435.
[276] C. Li, Z. Quan, P. Yang, J. Yang, H. Liana, J. Lin, *J. Mater. Chem.* **2008**, *18*, 1353.
[277] P. D. Han, Z. L. Zhang, X. G. Huang, L. X. Wang, Q. T. Zhang, *Spectrosc. Spectral Anal.* **2010**, *30*, 2906.
[278] Z. Chen, W. Bu, N. Zhang, J. Shi, *J. Phys. Chem. C* **2008**, *112*, 4378.
[279] L. Han, F. Song, S.-Q. Chen, C.-G. Zou, X.-C. Yu, J.-G. Tian, J. Xu, X.-D. Xu, G.-J. Zhao, *Appl. Phys. Lett.* **2008**, *93*, 011110.

[280] G. Wang, W. Qin, L. Wang, G. Wei, P. Zhu, R. Kim, *Opt. Express* **2008**, *16*, 11907.
[281] Z. Yang, S. Xu, L. Hu, Z. Jiang, *J. Alloys Compd.* **2004**, *370*, 94.
[282] X. Chen, W. Wang, X. Chen, J. Bi, L. Wu, Z. Li, X. Fu, *Mater. Lett.* **2009**, *63*, 1023.
[283] R. Qin, H. Song, G. Pan, L. Hu, H. Yu, S. Li, X. Bai, L. Fan, Q. Dai, X. Ren, H. Zhao, T. Wang, *Mater. Res. Bull.* **2008**, *43*, 2130.
[284] T. R. Hinklin, S. C. Rand, R. M. Laine, *Adv. Mater.* **2008**, *20*, 1270.
[285] F. Zhang, D. Zhao, *Nano Res.* **2009**, *2*, 292.
[286] L.-N. Sun, H. Peng, M. I. J. Stich, D. Achatz, O. S. Wolfbeis, *Chem. Commun.* **2009**, 5000.
[287] J. Zhuang, J. Wang, X. Yang, I. D. Williams, W. Zhang, Q. Zhang, Z. Feng, Z. Yang, C. Liang, M. Wu, Q. Su, *Chem. Mater.* **2009**, *21*, 160.
[288] S. H. Lee, K. Teshima, N. Shikine, S. Oishi, *Cryst. Growth Des.* **2009**, *9*, 4078.
[289] A. Santana-Alonso, A. C. Yanes, J. Mendez-Ramos, J. del-Castillo, V. D. Rodrıguez, *Phys. Status Solidi A* **2009**, *206*, 2249.
[290] L. Gao, X. Ge, Z. Chai, G. Xu, X. Wang, C. Wang, *Nano Res.* **2009**, *2*, 565.
[291] S. J. Budijono, J. Shan, N. Yao, Y. Miura, T. Hoye, R. H. Austin, Y. Ju, R. K. Prud′homme, *Chem. Mater.* **2010**, *22*, 311.
[292] L. Wang, W. Qin, Y. Wang, G. Wang, C. Cao, G. Wei, R. Kim, D. Zhang, F. Ding, C. He, *J. Nanosci. Nanotechnol.* **2010**, *10*, 1825.
[293] R. K. Watts, H. J. Richter, *Phys. Rev. B* **1972**, *6*, 1584.
[294] B. Jaquier, C. Linares, R. Mahioou, J. L. Adam, E. Denoue, J. Lucas, *J. Lumin.* **1997**, *60*, 175.
[295] M. Wermuth, A. Schmitz, H. U. Güdel, *Phys. Rev. B* **2001**, *63*, 245118.
[296] T. Hirai, T. Orikoshi, I. Komasawa, *Chem. Mater.* **2002**, *14*, 3576.
[297] P. Corstjens, M. Zuiderwijk, A. Brink, S. Li, H. Feindt, R. S. Neidbala, H. Tanke, *Clin. Chem.* **2001**, *47*, 1885.
[298] X. Wang, X. Kong, G. Shan, Y. Yu, Y. Sun, L. Feng, K. Chao, S. Lu, Y. Li, *J. Phys. Chem. B* **2004**, *108*, 18408.
[299] H. Li, G. Zhu, H. Ren, Y. Li, I. J. Hewitt, S. Qiu, *Eur. J. Inorg. Chem.* **2008**, 2033.
[300] See Ref. [103].
[301] C. Salthouse, S. Hildebrand, R. Weissleder, U. Mahmood, *Opt. Express* **2008**, *16*, 21731.
[302] H. Guo, Y. M. Qiao, *Opt. Mater.* **2009**, *31*, 583.
[303] L. Yanhong, Z. Yongming, H. Guangyan, Y. Yingning, *J. Rare Earths* **2008**, *26*, 450.
[304] L. Qiang, Z. Lian-Cheng, G. Feng-Yun, L. Mei-Cheng, *Chin. Phys.* **2009**, *18*, 4030.
[305] F. Vetrone, J.-C. Boyer, J. A. Capobianco, A. Speghini, M. Bettinelli, *Chem. Mater.* **2003**, *15*, 2737.
[306] Q. Yanmin, G. Hai, *J. Rare Earths* **2009**, 27, 406.
[307] T. Anh, P. Benalloul, C. Barthou, L. K. Giang, N. Vu, L. Minh, *J. Nanomater.* **2007**, 48247.
[308] Q. Lü, A. Li, F. Guo, L. Sun, L. Zhao, *Nanotechnology* **2008**, *19*, 145701.
[309] J. Zhang, S. Wang, T. Rong, L. Chen, *J. Am. Ceram. Soc.* **2004**, *87*, 1072.
[310] D. Matsuura, T. Ikeuchia, K. Soga, *J. Lumin.* **2008**, *128*, 1267.
[311] I. Hyppänen, J. Hölsa, J. Kankare, M. Lastusaari, L. Pihlgren, *J. Nanomater.* **2007**, 16391.
[312] D. Hreniak, P. Gluchowski, W. Strek, M. Bettinelli, A. Kozlowska, M. Kozlowski, *Mater. Sci.-Pol.* **2006**, *24*, 405.
[313] L. An, J. Zhang, M. Liu, S. Wang, *J. Alloys Compd.* **2008**, *451*, 538.
[314] A. Patra, C. S. Friend, R. Kapoor, P. N. Prasad, *Appl. Phys. Lett.* **2003**, *83*, 284.
[315] S. A. Hilderbrand, F. Shao, C. Salthouse, U. Mahmood, R. Weissleder, *Chem. Commun.* **2009**, 4188.
[316] H. Eilers, *J. Alloys Compd.* **2009**, *474*, 569.
[317] T. Wang, J. Zhou, S. Shi, B. Li, R. Zong, *J. Electroceram.* **2008**, *21*, 765.
[318] O. Lehmann, H. Meyssamy, K. Kömpe, H. Schnablegger, M. Haase, *J. Phys. Chem. B* **2003**, *107*, 7449.
[319] L. Yang, S. Quan, Y. Yang, Z. Li, W. Wang, L. Guo, *Solid State Commun.* **2009**, *149*, 1814.
[320] G. Y. Chen, H. J. Liang, H. C. Liu, G. Somesfalean, Z. G. Zhang, *J. Appl. Phys.* **2009**, *105*, 114315.
[321] P. Ghosh, E. de La Rosa, J. Oliva, D. Solis, A. Kar, A. Patra, *J. Appl. Phys.* **2009**, *105*, 113532.
[322] J. Yang, C. Zhang, C. Peng, C. Li, L. Wang, R. Chai, J. Lin, *Chem. Eur. J.* **2009**, *15*, 4649.
[323] C. Joshi, K. Kumar, S. B. Rai, *J. Appl. Phys.* **2009**, *105*, 123103.
[324] C. Erk, S. M. Caba, H. Lange, S. Werner, C. Thomsen, M. Steinhart, A. Berger, S. Schlecht, *Phys. Chem. Chem. Phys.* **2009**, *11*, 3623.
[325] Y. Li, J. Zhang, X. Zhang, Y. Luo, X. Ren, H. Zhao, X. Wang, L. Sun, C. Yan, *J. Phys. Chem. C* **2009**, *113*, 4413.
[326] P. Ghosh, S. Sadhu, T. Sen, A. Patra, *Bull. Mater. Sci.* **2008**, *31*, 461.
[327] G. Feng, S. Liu, Z. Xiu, Y. Zhang, J. Yu, Y. Chen, P. Wang, X. Yu, *J. Phys. Chem. C* **2008**, *112*, 13692.
[328] Q. Lü, F. Y. Guo, L. Sun, A. Li, L. C. Zhao, *J. Appl. Phys.* **2008**, *103*, 123533.
[329] H. Liu, L. Wang, S. Chen, *Mater. Lett.* **2007**, *61*, 3629.
[330] G. De, W. Qin, J. Zhang, J. Zhang, Y. Wang, C. Cao, Y. Cui, *Solid State Commun.* **2006**, *137*, 483.
[331] R. Jia, W. Yang, Y. Bai, T. Li, *Opt. Mater.* **2006**, *28*, 246.
[332] S. Xiao, X. Yang, Z. Liu, X. H. Yan, *J. Appl. Phys.* **2004**, *96*, 1360.
[333] X. Wang, X. Sun, D. Yu, B. Zou, Y. Li, *Adv. Mater.* **2003**, *15*, 1442.
[334] X. Wang, Y. Li, *Chem. Eur. J.* **2003**, *9*, 5627.
[335] H. Meyssamy, K. Riwotzki, A. Kornowski, S. Naused, M. Haase, *Adv. Mater.* **1999**, *11*, 840.
[336] K. Kömpe, H. Borchert, J. Storz, A. Lobo, S. Adam, T. Möller, M. Haase, *Angew. Chem.* **2003**, *115*, 5672; *Angew. Chem. Int. Ed.* **2003**, *42*, 5513.
[337] J.-C. Bourcet, F. K. Fong, *J. Chem. Phys.* **1974**, *60*, 34.
[338] N. Hashimoto, Y. Takada, K. Sato, S. Ibuki, *J. Lumin.* **1991**, *48–49*, 893.
[339] R. A. Hewes, J. F. Sarver, *Bull. Am. Phys. Soc. Ser. II* **1968**, *13*, 687.
[340] R. A. Hewes, J. F. Sarver, *Phys. Rev.* **1969**, *182*, 427.
[341] F. Auzel, D. Pecile, *J. Lumin.* **1973**, *8*, 32.
[342] L. G. Van Uitert, L. Pictroski, W. H. Grodkiewics, *Mater. Res. Bull.* **1969**, *4*, 777.
[343] X. Sun, Y.-W. Zhan, Y.-P. Du, Z.-G. Yan, R. Si, L.-P. You, C.-H. Yan, *Chem. Eur. J.* **2007**, *13*, 2320.
[344] A. Zalkin, D. H. Templeton, *J. Am. Chem. Soc.* **1953**, *75*, 2453.
[345] M. Mansmann, *Z. Kristallogr.* **1965**, *122*, 375.
[346] B. A. Maksimov, M. I. Sirota, R. V. Galiulin, B. P. Sobolev, *Kristallografiya* **1985**, *30*, 284.
[347] I. P. Kondratyuk, A. A. Loshmanov, L. A. Muradyan, B. A. Maksimov, M. I. Sirota, E. A. Krivandina, B. P. Sobolev, *Kristallografiya* **1988**, *33*, 105.
[348] H. Müller-Bunz, Th. Schleid, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1377.
[349] K. Krämer, H. Romstedt, H. U. Güdel, P. Fischer, A. Murasik, M. T. Fernandez-Diaz, *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 273.
[350] B. V. Bukvetskii, L. S. Garashina, *Koord. Khim.* **1977**, *3*, 1024.
[351] M. Piotrowski, H. Ptasiewicz-Bak, A. Murasik, *Phys. Status Solidi A* **1979**, *55*, K163.
[352] V. F. Zinchenko, N. P. Efryushina, O. G. Eryomin, V. Ya. Markiv, N. M. Belyavina, O. V. Mozkova, M. I. Zakharenko, *J. Alloys Compd.* **2002**, *347*, 1.

[353] J. Zhou, Z. Wu, Z. Zhang, W. Liu, H. Dang, *Wear* **2001**, *249*, 333.
[354] Z. F. Zhang, L. G. Yu, W. M. Liu, Q. J. Xue, *Tribol. Int.* **2001**, *34*, 83.
[355] J. W. Stouwdam, C. A. Hebbink, J. Huskens, F. C. J. M. van Veggel, *Chem. Mater.* **2003**, *15*, 4604.
[356] L. Wang, X. Xue, F. Shi, D. Zhao, D. Zhang, K. Zheng, G. Wang, C. He, R. Kim, W. Qin, *Opt. Lett.* **2009**, *34*, 2781.
[357] L. Wang, Y. Zhang, Y. Zhu, *Nano Res.* **2010**, *3*, 317.
[358] S. Zhong, Y. Lu, Z. Huang, S. Wang, J. Chen, *Opt. Mater.* **2010**, *32*, 966.
[359] G. De, W. Qin, J. Zhang, D. Zhao, J. Zhang, *Chem. Lett.* **2005**, *34*, 914.
[360] W. Yan, Q. Wei-Ping, D. Wei-Hua, Z. Ji-Sen, C. Chun-Yan, *Chin. Phys. B* **2008**, *17*, 9, 3300.
[361] A. Y. H. Lo, V. Sudarsan, S. Sivakumar, F. van Veggel, R. W. Schurko, *J. Am. Chem. Soc.* **2007**, *129*, 4687.
[362] G.-S. Yi, G.-M. Chow, *J. Mater. Chem.* **2005**, *15*, 4460.
[363] Z. Zhou, H. Hu, H. Yang, T. Yi, K. Huang, M. Yu, F. Li, C. Huang, *Chem. Commun.* **2008**, 4786.
[364] P. R. Diamente, F. C. J. M. van Veggel, *J. Fluoresc.* **2005**, *15*, 543.
[365] W. Yan, Q. Weiping, Z. Jisen, C. Chunyan, Z. Jishuang, J. Ye, *J. Rare. Earths* **2007**, *25*, 605.
[366] S. Sivakumar, F. C. J. M van Veggel, M. Raudsepp, *J. Am. Chem. Soc.* **2005**, *127*, 12464.
[367] J. W. Stouwdam, F. C. J. M. van Veggel, *Langmuir* **2004**, *20*, 11763.
[368] J. Pichaandi, F. C. J. M. van Veggel, M. Raudsepp, *ACS Appl. Mater. Interfaces* **2009**, *2*, 157.
[369] F. Wang, Y. Zhang, X. Fan, M. Wang, *J. Mater. Chem.* **2006**, *16*, 1031.
[370] C. Li, Z. Quan, P. Yang, S. Huang, H. Lian, J. Lin, *J. Phys. Chem. C* **2008**, *112*, 13395.
[371] X. Yang, S. Xiao, J. W. Ding, X. H. Yan, *J. Appl. Phys.* **2008**, *103*, 093101.
[372] Y.-W. Zhang, X. Sun, R. Si, L.-P. You, C.-H. Yan, *J. Am. Chem.Soc.* **2005**, *127*, 3260.
[373] M. Pollnau, D. R. Gamelin, S. R. Lüthi, M. P. Hehlen, H. U. Güdel, *Phys. Rev. B* **2000**, *61*, 3337.
[374] G. Yi, B. Sun, F. Yang, D. Chen, Y. Zhou, J. Cheng, *Chem. Mater.* **2002**, *14*, 2910.
[375] K. Zheng, L. Wang, D. Zhang, D. Zhao, W. Quin, *Opt. Express* **2010**, *18*, 2934.
[376] J. Zhao, X. Liu, D. Cui, Y. Sun, Y. Yu, Y. Yang, C. Du, Y. Wang, K. Song, K. Liu, S. Lu, X. Kong, H. Zhang, *Eur. J. Inorg. Chem.* **2010**, 1813.
[377] D. Ma, D. Yang, J. Jiang, P. Cai, S. Huang, *CrystEngComm* **2010**, *12*, 1650.
[378] F. Zhang, D. Zhao, *ACS Nano* **2009**, *3*, 159.
[379] C. Li, J. Yang, P. Yang, X. Zhang, H. Lian, J. Lin, *Cryst. Growth Des.* **2008**, *8*, 923.
[380] Z.-L. Wang, J. H. Hao, H. L. W. Chan, *J. Mater. Chem.* **2010**, *20*, 3178.
[381] Y.-P. Du, Y.-W. Zhang, L.-D. Sun, C.-H. Yan, *Dalton Trans.* **2009**, 8574.
[382] J. S. Chivian, W. E. Case, D. D. Eden, *Appl. Phys. Lett.* **1979**, *35*, 124.
[383] D. B. Gatch, W. M. Dennis, W. M. Yen, *Phys. Rev. B* **2000**, *62*, 10790.
[384] M. F. Joubert, S. Guy, C. Jacquier, C. Linares, *Opt. Mater.* **1994**, *4*, 43.
[385] J. Sytsma, S. J. Kroes, G. Blasse, N. M. Khaidukov, *J. Phys. Condens. Matter* **1991**, 8959.
[386] J. Sytsma, W. van Schaik, G. Blasse, *J. Phys. Chem. Solids* **1991**, *52*, 419.
[387] Y. Guyot, H. Manaa, J. Y. Rivoire, R. Moncorgé, N. Garnier, E. Descroix, M. Bon, P. Laporte, *Phys. Rev. B* **1995**, *51*, 784.
[388] R. T. Wegh, E. V. D. van Loef, G. W. Burdick, A. Meijerink, *Mol. Phys.* **2003**, *101*, 1047.
[389] A. Toncelli L. Bonelli, R. Faoro, D. Parisi, M. Tonelli, *Opt. Mater.* **2009**, 1205.
[390] G. Galzerano, E. Sani, A. Toncelli, G. Della Valle, S. Taccheo, M. Tonelli, P. Laporta, *Opt. Lett.* **2004**, *29*, 715.
[391] P. E. A. Mobert, A. Diening, E. Heumann, G. Huber, B. H. T. Chai, *Laser Phys.* **1998**, *8*, 210.
[392] X. X. Zhang, M. Bass, B. H. T. Chai, *Proc. SPIE* **1993**, *1863*, 123.
[393] E. Sani, A. Toncelli, M. Tonelli, N. Colucelli, G. Galzerano, P. Laporta, *Appl. Phys. B* **2005**, *81*, 847.
[394] S. Aleonard, Y. Le Fur, L. Pontonnier, N. F. Gorius, M. Th. Roux, *Ann. Chim. Fr.* **1978**, *3*, 417.
[395] M. A. Dubinskii, N. M. Khaidukov, I. G. Garipov, L. N. Dem′Yanets, A. K. Naumov, V. V. Semashko, V. A. Malyusov, *J. Mod. Opt.* **1990**, *37*, 1355.
[396] R. T. Wegh, H. Donker, K. D. Oskam, A. Meijerink, *Science* **1999**, *283*, 663.
[397] A. Patra, P. Gosh, *J. Phys. Chem. C* **2008**, *112*, 3223.
[398] J. Zhang, C. M. Shade, D. A. Chengelis, S. Petoud, *J. Am. Chem. Soc.* **2007**, *129*, 14834.
[399] F. Wang, Y. Han, C. S. Lim, Y. Lu, J. Wang, J. Xu, H. Chen, C. Zhang, M. Hong, X. Liu, *Nature* **2010**, *463*, 1061.
[400] X. Yu, M. Li, M. Xie, L. Chen, Y. Li, Q. Wang, *Nano Res.* **2010**, *3*, 51.
[401] Q. Wang, M. C. Tan, R. Zhuo, G. A. Kumar, R. E. Riman, *J. Nanosci. Nanotechnol.* **2010**, *10*, 1685.
[402] G. Chen, T. Y. Ohulchanskyy, R. Kumar, H. Ågren, P. N. Prasad, *ACS Nano* **2010**, *4*, 3163.
[403] W. Niu, S. Wu, S. Zhang, L. Li, *Chem. Commun.* **2010**, *46*, 3908.
[404] N. J. J. Johnson, N. M. Sangeetha, J.-C. Boyer, F. C. J. M. van Veggel, *Nanoscale* **2010**, *2*, 771.
[405] A. Yin, Y. Zhang, L. Sun, C. Yan, *Nanoscale* **2010**, *2*, 953.
[406] See Ref. [257].
[407] R. E. Thoma, G. M. Hebert, H. Insley, C. F. Weaver, *Inorg. Chem.* **1963**, *2*, 1005.
[408] R Qin, H. Song, G. Pan, H. Zhao, X. Ren, L. Liu, X. Bai, Q. Dai, X. Qu, *J. Cryst. Growth* **2009**, *311*, 1559.
[409] P. P. Fedorov, V. B. Aleksandrov, O. S. Bondareva, I. I. Buchinskaya, M. D. Val′kovski, B. P. Sobolev, *Crystallogr. Rep.* **2001**, *46*, 239.
[410] G. A. Kumar, C. W. Chen, R. Riman, S. Chen, D. Smith, J. Ballato, *Appl. Phys. Lett.* **2005**, *86*, 241105.
[411] H. Schäfer, P. Ptacek, H. Eickmeier, M. Haase, *Cryst. Growth Des.* **2010**, *10*, 2202.
[412] V. Mahalingam, F. Vetrone, R. Naccache, A. Speghini, J. A. Capobianco, *J. Mater. Chem.* **2009**, *19*, 3149.
[413] F. Zeng, G. Ren, X. Qiu, Q. Yang, J. Chen, *J. Non-Cryst. Solids* **2008**, *354*, 3428.
[414] A. S. Gouveia-Neto, E. B. da Costa, L. A. Bueno, S. J. L. Ribeiro, *J. Alloys Compd.* **2004**, *375*, 224.
[415] S. Schietinger, T. Aichele, H.-Q. Wang, T. Nann, O. Benson, *Nano Lett.* **2010**, *10*, 134.
[416] J.-C. Boyer, F. C. J. M. van Veggel, *Nanoscale* **2010**, *2*, 1417.
[417] M. M. Lezhnina, T. Jüstel, H. Kätker, D. U. Wiechert, U. H. Kynast, *Adv. Funct. Mater.* **2006**, *16*, 935.
[418] J.-C. Boyer, J. Gagnon, L. A. Guccia, J. A. Capobianco, *Chem. Mater.* **2007**, *19*, 3358.
[419] M. Darbandi, T. Nann, *Chem. Commun.* **2006**, 776.
[420] K. A. Abel, J.-C. Boyer, F. C. J. M. van Veggel, *J. Am. Chem. Soc.* **2009**, *131*, 14644.
[421] S. Gai, P. Yang, C. Li, W. Wang, Y. Dai, N. Niu, J. Lin, *Adv. Funct. Mater.* **2010**, *20*, 1166.
[422] O. Lehmann, K. Kömpe, M. Haase, *J. Am. Chem. Soc.* **2004**, *126*, 14935.

[423] J. Li, Y. A. Wang, W. Guo, J. C. Keay, T. D. Mishima, M. B. Johnson, X. Peng, *J. Am. Chem. Soc.* **2003**, *125*, 12567.
[424] D. S. Koktysh, X. Liang, B.-G. Yun, I. Pastoriza-Santos, R. L. Matts, M. Giersig, C. Serra-Rodriguez, L. M. Liz-Marzan, N. A. Kotov, *Adv. Funct. Mater.* **2002**, *12*, 255.
[425] M. A. Correa-Duarte, L. M. Liz-Marzán, I. Tunc, S. Suzer, *J. Phys. Chem. B* **2005**, *109*, 7597.
[426] H. Schäfer, P. Ptacek, K. Hickmann, M. Prinz, M. Neumann, M. Haase, *Russ. J. Inorg. Chem.* **2009**, *54*, 1914.
[427] C. McGinley, S. Al Moussalami, M. Riedler, M. Pflughoe, H. Borchert, M. Haase, A. R. B. de Castro, H. Weller, T. Möller, *Eur. Phys. J. D* **2001**, *16*, 225.
[428] F. Vetrone, R. Naccache, V. Mahalingam, C. G. Morgan, J. A. Capobianco, *Adv. Funct. Mater.* **2009**, *19*, 2924.
[429] T. Nann, P. Mulvaney, *Angew. Chem.* **2004**, *116*, 5511; *Angew. Chem. Int. Ed.* **2004**, *43*, 5393.
[430] D. K. Yi, S. T. Selvan, S. S. Lee, G. C. Papaefthymiou, D. Kundaliya, J. Y. Ying, *J. Am. Chem. Soc.* **2005**, *127*, 4990.
[431] T. J. Yoon, K. N. Yu, E. Kim, J. S. Kim, B. G. Kim, S. H. Yun, B. H. Sohn, M. H. Cho, J. K. Lee, S. B. Park, *Small* **2006**, *2*, 209.
[432] Y. Liu, W. Chen, S. Wang, A. G. Joly, S. Westcott, B. K. Woo, *J. Appl. Phys.* **2008**, *103*, 063105/1.
[433] F. Wang, Y. Zhang, Y. , X. Fan, M. Wang, *Nanotechnology* **2006**, *17*, 1527.
[434] H. J. M. A. A. Zijlmans, J. Bonnet, J. Burton, K. Kardos, T. Vail, R. S. Niedbala, H. J. Tanke, *Anal. Biochem.* **1999**, *267*, 30.
[435] F. van de Rijke, H. Zijlmans, S. Li, T. Vail, A. K. Raap, R. S. Niedbala, H. J. Tanke, *Nat. Biotechnol.* **2001**, *19*, 273.
[436] J. Hampl, M. Hall, N. A. Mufti, Y.-m. Yao, D. B. MacQueen, W. H. Wright, D. E. Cooper, *Anal. Biochem.* **2001**, *288*, 176.
[437] N. M. Green, *Adv. Protein Chem.* **1975**, *29*, 85.
[438] E. A. Bayer, M. Wilchek, *J. Chromatogr.* **1990**, *510*, 3.
[439] E. A. Bayer, M. Wilchek, *Methods Biochem. Anal.* **1980**, *26*, 1.
[440] M. Wilchek, E. A. Bayer, *Anal. Biochem.* **1988**, *171*, 1.
[441] E. P. Diamand, T. K. Christopoulos, *Clin. Chem.* **1991**, *37*, 625.
[442] G. A. Orr, *J. Biol. Chem.* **1981**, *256*, 761..
[443] P. R. Diamente, R. D. Burke, F. C. J. M. van Veggel, *Langmuir* **2006**, *22*, 1782.
[444] A. Fire, S. Q. Xu, M. K. Montgomery, S. A. Kostas, S. E. Driver, C. C. Mello, *Nature* **1998**, *391*, 806.
[445] G. Meister, T. Tuschl, *Nature* **2004**, *431*, 343.
[446] Y. Dorsett, T. Tuschl, *Nat. Rev. Drug Discovery* **2004**, *3*, 318.
[447] M. V. Yezhelyev, L. Qi, R. M. O'Regan, S. Nie, X. Gao, *J. Am. Chem. Soc.* **2008**, *130*, 9006.
[448] M. A. Walling, J. A. Novak, J. R. E. Shepard, *Int. J. Mol. Sci.* **2009**, *10*, 441.
[449] J. L. Pelley, A. Daar, M. A. Saner, *Toxicol. Sci.* **2009**, *112*, 276.
[450] S. Jiang, Y. Zhang, *Langmuir* **2010**, *26*, 6689.
[451] W. J. Kim, M. Nyk, P. N. Prasad, *Nanotechnology* **2009**, *20*, 185301.
[452] N. S. Badgujar, M. Pazicky, P. Traar, A. Terec, G. Uray, W. Stadlbauer, *Eur. J. Org. Chem.* **2006**, 2715.
[453] F. Hund, *Z. Anorg. Allg. Chem.* **1950**, *263*, 102.
[454] F. Hund, *Z. Anorg. Allg. Chem.* **1950**, *261*, 106.
[455] See Ref. [407].
[456] P. P. Fedorov, *Russ. J. Inorg. Chem.* **1999**, *44*, 1703.
[457] P. P. Fedorov, R. M. Sakaljukin, *Zh. Neorg. Khim.* **2000**, *45*, 1721.
[458] P. P. Fedorov, T. G. Filatova, *Zh. Neorg. Khim.* **2000**, *45*, 872.
[459] J.-C. Boyer, C.-J. Carling, B. D. Gates, N. R. Branda, *J. Am. Chem. Soc.* **2010**, *132*, 15766.
[460] F. Wang, D. Banerjee, Y. Liu, X. Chen, X. Liu, *Analyst* **2010**, *135*, 1839.
[461] F. Wang, J. Wang, X. Liu, *Angew. Chem.* **2010**, *122*, 7618; *Angew. Chem. Int. Ed.* **2010**, *49*, 7456.
[462] H.-Y. Si, D. Yuan, J.-S. Chen, G.-M. Chow, H.-Li Zhang, *J. Colloid Interface Sci.* **2011**, *353*, 569.
[463] L. P. Qian, L. H. Zhou, H.-P. Too, G.-M. Chow, *J. Nanopart. Res.* **2011**, 13, 499.
[464] H. S. Mader, M. Link, D. E. Achatz, K. Uhlmann, X. Li, O. S. Wolfbeis, *Chem. Eur. J.* **2010**, *16*, 5416.
[465] H. S. Mader, P. Kele, S. M. Saleh, O. S. Wolfbeis, *Curr. Opin. Chem. Biol.* **2010**, *14*, 582.
[466] H. S. Mader, O. S. Wolfbeis, *Anal. Chem.* **2010**, *82*, 5002.
[467] R. Ali, S. M. Saleh, R. J. Meier, H. A. Azab, I. I. Abdelgawad, O. S. Wolfbeis, *Sens. Actuators B* **2010**, *1*, 126.

