Available online at www.sciencedirect.com
ScienceDirect
Optical Materials 31 (2009) 490–495
OPTICAL Materials
www.elsevier.com/locate/optmat

Nanoparticles doped with TM and RE ions for applications in optoelectronics

M. Godlewski [a,b,*], S. Yatsunenko [a], A. Nadolska [b], A. Opalińska [c], W. Łojkowski [c], K. Drozdowicz-Tomsia [d], E.M. Goldys [d]

[a] Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland
[b] Department of Mathematics and Natural Science College of Sciences, Card. S. Wyszyński University, Warsaw, Poland
[c] Institute of High Pressure Physics, Polish Academy of Sciences, Sokołowska 29/37, 01-142 Warsaw, Poland
[d] Division of Information and Communication Sciences, Macquarie University, Sydney, Australia

Received 15 July 2007; accepted 14 October 2007
Available online 8 February 2008

Abstract

Nanoparticles of wide band gap compounds, when doped with rare earth or transition metal ions, are perspective candidates for efficient phosphors in a new generation of light sources for an overhead illumination, i.e., in compact fluorescence lamps and in semiconductor-based white light emitting diodes. Mechanisms of emission enhancement in doped nanoparticles are discussed based on the relevant experimental results. Mechanisms observed are due to carrier confinement, n-type co-doping, due to surface plasmons generation and super radiance.

PACS: 78.67.Bf; 78.67.Hc; 71.55.Gs; 71.55.Ht; 71.45.−d; 78.55.Et; 78.55.Hx

Keywords: Nanoparticles; Radiative recombination processes; Transition metal ions; Rare earth ions

1. Introduction

In a series of recent papers we reported that intra-shell transitions of transition metal (TM) and rare earth (RE) ions in nanoparticles result in bright emissions and show fast photoluminescence (PL) decay [1–5]. PL decay is in most of the cases shorter than those observed for auto-fluorescence of living cells. These properties of doped nanoparticles open chances for their use for multi-labelling, for time-resolved separation of label and cell emission, and also for a better depth penetration, when a multi-photon excitation is used. However, these applications of doped nanoparticles will not be discussed in the present paper.

New more efficient phosphors are required also in the case of modern light sources. In particular, new phosphors are needed in white light emitting diodes (w-LEDs). There a phosphor emission is excited by blue/violet emission of GaN-based LED (see Ref. [6] and references given there). White emission is obtained via mixing (so-called hybrid diodes) of phosphor emission (excited by LED) and LED emission (peaked at about 400 nm), i.e., phosphor should be optimised for about 400 nm excitation.

2. Why we need new phosphors?

At present it is estimated that about 9 billions of traditional light bulbs (incandescent lamps) are used all over the world for an overhead illumination. Their efficiency is very low, since only about 3–5% of electrical energy is converted to visible light, resulting in 12–24 lm/W efficiency. This is why these lamps will soon be totally replaced by

* Corresponding author. Address: Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland. Tel.: +48 22 843 6861; fax: +48 22 843 0926.
E-mail address: godlew@ifpan.edu.pl (M. Godlewski).

0925-3467/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.optmat.2007.10.020

either compact fluorescence lamps (CF lamps) or by semiconductor-based white LEDs. Such replacement will result in a huge energy (money) saving, since one incandescent lamp uses more electricity than a CF lamp, resulting in about 9 USD higher costs per lamp each year. The money saving will approach 100 billions USD per year or even more, if the present day CF lamps and w-LEDs are improved.

Most of the available highly efficient light conversion phosphors were developed for use in fluorescence lamps, i.e., for down-conversion of emission of mercury vapours, which emit in UV (55% at 254 nm, 9% at 185 nm) and only 5% at visible and near UV spectral region. These phosphors are not optimised for 400 nm excitation. In commercial LEDs, blue/violet emission from InGaN-based LEDs (about 400 nm) is mixed with yellow emission of YAG:Ce phosphor to get a white colour impression, i.e., the availability of efficient phosphors excited at about 400 nm is crucial for improvement of these new white light sources.

3. New ideas

3.1. Photon cutting

Luminophors used presently in fluorescence lamps, such as: Y_2O_3:Eu for red colour, $LaPO_4$:Ce,Tb for green colour, and $BaMgAl_{10}O_{17}$:Eu or $BaMgAl_{10}O_{17}$:Eu,Mn for blue colour, fairly efficiently convert UV photon emitted by Hg vapours to visible photons with ratios close to 1:1. Even though efficiency of a light conversion approaches 100% (1 UV photon excites 1 visible photon), this efficiency is much lower when we calculate energy of photons. For example, it is below 50% for green phosphor, for which 254 nm photon emitted by Hg vapours results in 542 nm emission of the phosphor.

Efficiency of fluorescence phosphors can be improved if one UV photon emitted by Hg can excite two visible photons (200% efficiency, i.e., 1 UV photon induces 2 visible photons). Such situation was found in some Pr^{3+} doped phosphors, such as YF_3 and LaF_3 [7], $SrAlF_5:Pr^{3+}$ [8], and many other (see e.g. [9–12]).

Energy structure of 3+ Praseodymium ion consists of ^3H, ^3F, ^1D, ^1G, ^3P, ^1I, ^1S multiplets split by the spin–orbit interaction [13], as shown in Fig. 1. In the photon cutting (photon cascade) process observed in [7] efficient $4f^2$–$4f^15d^1$ excitation is followed by a fast down-in-energy thermalization to the highest lying 4f state of Pr^{3+} ($^1S_0$). The radiative decay from the $^1S_0$ level of Pr^{3+} proceeds then via a cascade process, in which two or more photons are emitted (for example: $^1S_0$–$^3P_1$, $^1I_6$; $^3P_0$–$^3H_4$).

Such situation in YF_3 and LaF_3 is however not favourable, since the first step in the photon cascade results in a near UV emission. We thus looked for other systems, in which $4f^2$–$4f^15d^1$ excitation is shifted down in energy below $^1S_0$ state. This we observed for ZrO_2 nanoparticles doped with Pr^{3+} ions (with 0.5% concentration). Their description can be found elsewhere [14]. For ZrO_2 a broad excitation band (due to an overlap of $4f^2$–$4f^15d^1$ or charge transfer (CT) transition with band-to-band host excitation) is moved down in energy as compared to its position in above mentioned fluorite hosts and overlaps with the $^1S_0$ state. This is why emission from the latter state we could only excite using two photon excitation (Fig. 2a).

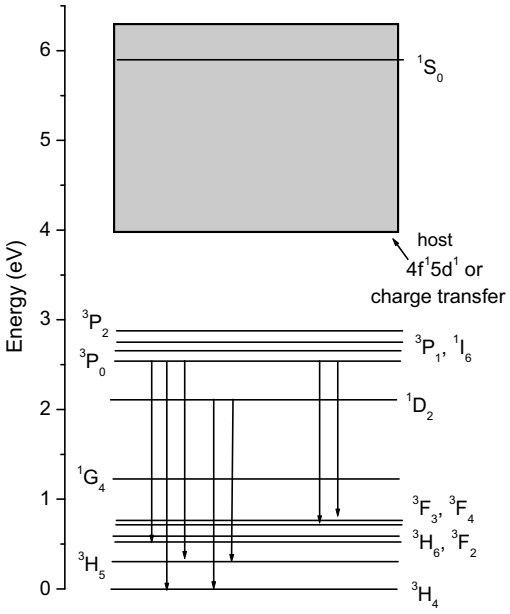

Fig. 1. Energy structure of Pr^{3+} ion in ZrO_2 nanoparticles with the observed 4f–4f transitions.

What was observed in PL depended on post-growth thermal treatment of nanoparticles. For as-grown powders cascade emissions were very weak (hardly seen in Fig. 2) as compared to their intensity in post-growth annealed samples. Emission shown in Fig. 2c (for as grown sample) is dominated by the red $^1D_2$–$^3H_4$ Pr^{3+} 4f–4f transition. For annealed nanoparticles this transition was accompanied by strong blue–green 4f–4f transitions, with a dominant $^3P_0$–$^3H_4$ PL.

Fig. 2b and c show a complicated PL spectrum observed under 250 nm (host band-to-band excitation, which spectrally overlaps with the region of the most efficient Hg vapours emission) and under 296 nm excitation (resonant excitation due to either $4f^2$–$4f^15d^1$ or charge transfer transition), i.e., at the maximum of the strong and broad PL excitation (PLE) peak. In both cases Pr^{3+} PL is dominated by the $^1D_2$–$^3H_4$ transition. The relevant PLE spectrum, the one observed for the $^1D_2$–$^3H_4$ Pr^{3+} 4f–4f transition, is shown in Fig. 3. A very rich PL spectrum is observed upon 4f–4f, $4f^2$–$4f^15d^1$ or CT and host excitations, consisting of many 4f–4f transitions, and (see Fig. 2b) some broad, underlying host related bands. The latter are not observed when the resonant ($4f^2$–$4f^15d^1$ or CT) excitation is used (see Fig. 2c). The resulting 4f–4f transitions are shown in Fig. 1.

Unfortunately, even though UV excitation results in several transitions in a visible region of the spectrum, the most efficient excitation occurs at about 300 nm, which does not fit to the spectral regions of neither the Hg