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Synthesis of YAG:Ce/TiO_2 nanocomposite films

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ABSTRACT

Our work is devoted to the development of YAG:Ce^{3+} phosphor nanoparticle-based converter layer for white LEDs. To avoid losses due to scattering effects, the strategy is to control separately the down-conversion and the extraction of light instead of using micron-sized luminescent particles acting simultaneously as both converter and scatterer. YAG:Ce nanoparticles were synthesized by a glycothermal method in autoclave at low temperature (300 °C). $Y_3Al_5O_{12}$ garnet phase with a crystallite size of 25 nm was obtained, as verified by X-ray diffraction and electron microscopy. The quantum yield of nanoparticles is 55%. The colloidal nanoparticles are finally incorporated into a sol–gel matrix of TiO_2. The small difference in refractive index between particles and matrix and the nanosize of the particles contribute to the transparency of the converter films. The surface of these layers can be periodically patterned by soft nano-imprint lithography. The diffraction due to the obtained photonic crystal at the surface may offer the opportunity to compensate the absence of scattering to extract the converted light.

1. Introduction

Yttrium aluminium garnet ($Y_3Al_5O_{12}$) doped with Ce^{3+} ions (YAG:Ce) is a well-known phosphor, commonly used as light converter in commercial white LEDs. Indeed, its capacity to efficiently absorb blue light and emit in the yellow range (thanks to the 4f–5d transitions of Ce^{3+}) allows generation of white light from blue InGaN LED chips.

Traditionally, YAG:Ce particles, produced by solid state reaction at high temperature ($\geqslant$1400°), are incorporated into epoxy bulbs and deposited on LEDs as shown in Fig. 1a. Because of their synthesis route, these particles are in the micrometer size range, and thus present strong light scattering effects. This drastically affects absorption, dissipation and extraction properties of the converter layer. This scattering can be beneficial because it contributes to the extraction of light out from the converter layer. But it also induces losses such as the absorption of backscattered light into the p–n junction, thus decreasing the external yield of the device.

In this work, we investigate a strategy that aims at controlling separately the down-conversion and the light extraction instead of using micron-sized particles simultaneously acting as converter and scatterer. For this purpose, the strategy can consist in forming YAG:Ce thin films onto blue LEDs. The luminescent thin films should be transparent (i.e. non diffusive) and present a high quantum yield. Due to the absence of loss by scattering, these films are also very good waveguides. Thus, for white LEDs applications, the light has to be extracted from the top of the film. This could be controlled by photonic crystal diffraction at the surface of the film, thus allowing also some control of the light emission directionality (Fig. 1b) [1].

Few examples of synthesis of YAG:Ce thin films for light conversion are found in literature by sol–gel [2], rf magnetron sputtering [3], liquid phase epitaxy [4] or pulsed laser deposition [5]. The advantage of these techniques is that thin-film phosphors can be easily integrated onto LEDs arrays. However, it has several drawbacks:

(1) These films need to be further annealed (above 900 °C) after deposition so that the YAG phase crystallizes, meaning that the substrate needs to be resistant to high temperatures.
(2) The obtained films are polycrystalline, presenting grain boundaries, cracks and rough surface that induce light scattering.

To realize transparent down-conversion layer for white emitting devices, our strategy consists in synthesizing luminescent YAG:Ce particles with a nanometer size (limiting light scattering in the converting layer), then incorporating these already crystallized particles into a matrix and finally depositing the composite as a thin film onto a LED. The refractive index n of the surrounding matrix should be relatively high in order to limit the total

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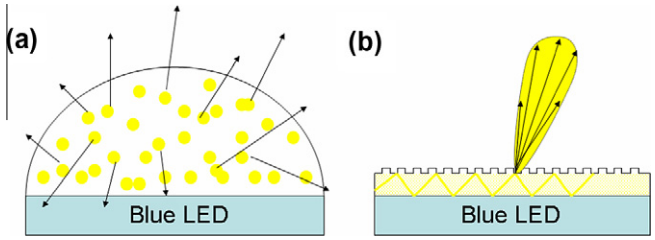

Fig. 1. Schematic of light propagation in (a) standard LEDs and (b) transparent thin-film based LEDs with light extraction by surface patterning. (a) In standard LEDs, micron-sized powders acting as scatterer and emitter are represented by yellow circles. Arrows materialize light scattering from particles. (b) Transparent converter film is represented in yellow on the blue LED. The yellow light is guided and directionally extracted from the layer by a periodic surface pattering.

reflection of the excitation blue light at the film/GaN substrate interface and thus allowing light extraction at the textured film/air interface. *n* should also be comparable to the YAG refractive index to avoid light losses due to *n* mismatch.

Recently, colloidal suspensions of YAG nanoparticles in ethanol were synthesized through a glycothermal route at relatively low temperature ($\leqslant$300 °C) [6]. This technique does not require any further thermal annealing for crystallization, leading to nanoparticles with an average size of 30 nm and dispersible in ethanol. When doped with cerium, these YAG: particles present a quantum yield between 21% and 56% depending on the experimental conditions [7,8].

In the first part of our work, we revisit this synthesis strategy to prepare colloidal solutions of YAG:Ce nanoparticles with controlled average size, size distribution and dispersion in ethanol. The second part concerns the incorporation of the luminescent YAG:Ce nanoparticles into transparent TiO_2 films deposited by spin-coating. TiO_2 is chosen because of its high refractive index, which approximately corresponds to the refractive index of the substrate and the particles. Moreover, our TiO_2 films are elaborated by sol–gel chemistry, starting from inorganic precursors soluble in ethanol. Considering that the previous YAG:Ce nanoparticles are well-dispersed in ethanol, TiO_2 films encapsulating YAG:Ce nanoparticles can be prepared without requiring any solvent exchange or surface functionalization, and the good dispersion of the particles is preserved.

After deposition of the converter layer, the last step is the surface patterning of the film to control the extraction of light out of the converter layer and to compensate the absence of scattering. Nano-imprint lithography, developed by Chou et al. [9] is well adapted for our system. This technique, more accessible than expensive and time-consuming techniques like electron beam lithography or reactive ion etching, allows sub-100 nm resolution onto large surface area. It is commonly used to pattern thermoplastics and UV curable resists but the sol–gel technique that we use also allows nano-imprint lithography. Last part of our work shows the successful application of this technique for the patterning of the surface of the composite layer, opening the way toward the careful study of the best structure adapted for the light extraction in our systems.

2. Experimental

2.1. YAG:Ce nanoparticles synthesis

The synthesis of YAG nanoparticles doped with 1% cerium was adapted from the one reported in [10]. Typically, 2.5 mmol of aluminium isopropoxide, 7.425 mmol of yttrium acetate hydrate and 0.075 mmol of cerium III acetate hydrate were mixed together in 20 mL of 1,4 butandiol (all products from Sigma Aldrich). When homogeneous, the mixture was poured in a 71 mL non-stirred autoclave (Parr, Series 4740 High Pressure Vessel) with 33 mL of solvent used to rinse the previous container. The vessel was placed in a ceramic heater at 300 °C for 3 h. The inner pressure reached 70 bars after 3 h. The synthesis was conducted with stirring by inserting a magnetic stirring bar in the vessel and placing a stirring plate underneath the heater.

After reaction, the obtained yellow solution was washed three times in ethanol by centrifugation at 11,000 rpm for 10 min, to retrieve a stable colloidal solution in ethanol.

The size of the particles in suspension was investigated by electron microscopy (Hitachi S4800 scanning electron microscope FEG-SEM and Philips CM30 transmission electron microscope TEM) and dynamic light scattering (DLS, Malvern Zetasizer). X-ray Diffraction (XRD, Philips X-Pert Cu Kα radiation) was performed on dry powder. The luminescent properties of solutions were measured with a fluorimeter (Xe lamp, HITACHI F-4500FL). The absolute fluorescence quantum yields of the powders were measured using an integrating sphere coated with Lambertian reflector as described by Greenham [11]. For this purpose, powders were mixed in epoxy resin and deposited on silica slide. These samples were inserted in the sphere and excited by an Ag laser. The light coming out from the sphere was measured by a calibrated silicon photodiode. Absorption and emission could be successively measured using proper filter between the sphere and the detector (UV and visible bandpass filter, respectively).

2.2. Incorporation of nanoparticles in TiO_2 and film deposition

The sol–gel method consists in depositing films from a liquid solution containing TiO_2 molecular precursors (called "sol") that can be converted into nanocrystalline TiO_2 after a thermal treatment. Titania sol was prepared by mixing 18 mL of Titanium (IV) butoxide with 9.8 mL of butanol during 10 min. Then, 27.3 mL of acetic acid was added and the mixture was heated at 50 °C. After 30 min, the solution was cooled to 0 °C with ice during 1 h. 8.9 mL of DI water and 37.6 mL of ethanol were mixed together and added drop by drop in the cold solution. The resulting mixture was heated at 50 °C for 1 h. The solution was stirred during all steps of the synthesis. Finally, the sol was filtered with a 45 μm porous membrane. Colloidal solution of nanoparticles in ethanol was added to titania sol. Then ethanol was evaporated from the mixture to condensate the solution. The less ethanol is remaining, the thicker will be the film. The films were deposited onto silicon substrates by spin-coating (2000 rpm, 30 s). The silicon wafers were previously cleaned by 20 min immersions in a fresh piranha solution (H_2O_2 (30%)/H_2SO_4 1:3 vol). This easy in-house elaboration technique gives access to various high refractive indices and film thicknesses depending on dilution of the sol and post-deposition thermal annealing. It is also suitable for low-cost fabrication.

2.3. YAG:Ce doped TiO_2 thin-film patterning and characterization

The architecture of a periodically patterned PDMS mold can be transferred to a TiO_2 sol–gel film by soft nano-imprint lithography [12,13]. A TiO_2 precursor solution was spin-coated onto the film. Before condensation of the gel, the anti-adhesive treated PDMS mold was deposited on it. The system was heated at 110 °C under pressure (20 PSI) during 5 min in a NXR2500 from Nanonex imprinter. During this step, the viscous sol fills the cavities of the mold and becomes solid because of the polymerization of the titania network induced by heat. After cooling, patterned film was separated from the stamp.