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Photoluminescence from Tb-doped photonic crystal microcavity for white light generation

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Abstract. Terbium-doped one-dimensional triple microcavities have been prepared by sol-gel processing. The photoluminescence (PL) of Tb³⁺ ions outside a microcavity structure, when excited by blue laser light at 488 nm, consisted of three distinct peaks at 542 nm, 587 nm and 619 nm. When embedded in the microcavities, the three Tb³⁺ PL peaks were enhanced, balanced and broadened by the photonic crystal structure and combined into a continuous broad band. An analysis in the CIE colour space showed that white light can be obtained by mixing the modified Tb³⁺ PL with the blue exciting light, while this is impossible with the original PL profile. This novel technique may improve white light generation by enhancing and modifying the spontaneous emission of current phosphors. It may also lead to the development of new rare earth phosphor materials based on 4f-4f transitions, able to generate white light more efficiently, via simpler and cheaper alternatives to the current phosphor compositions. A novel configuration to combine this kind of structure with a white light-emitting-diode (LED) is also proposed.

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1. Introduction

Fluorescent materials enable a key technology for white light generation since, whether fluorescent or LED lamps are used, the excitation of a phosphor by ultraviolet (UV) or blue light to generate white light output is always an important technique [1-5]. For the current white LED lamps, Cerium(III)-doped yttrium aluminium garnet (Ce:YAG) and the various Europium(II)-doped ceramics are the most popular types of phosphors. Ce:YAG phosphors are usually combined with blue light excitation, whereas the Eu(II)-doped ceramics are excited in the near-UV [3-5]. The transitions from 4f^{N-1}5d¹ to 4f^N states of the Ce³⁺ or Eu²⁺ ions (N, the number of electrons in the ground state 4f shell, is 1 for Ce³⁺ and 7 for Eu²⁺) cause PL emission. The peak wavelengths of the emitted light range from blue to red and can be mixed with each other, or with the blue exciting light, in order to generate the white appearance.

The transitions between the 4f and 5d states are electric-dipole allowed [3, 6]. That is why the Ce³⁺ and Eu²⁺ ions have strong absorption and emission cross sections. The 5d electrons are strongly affected by the environment surrounding these ions, including the ligand field, chemical environment, temperature, etc.. This causes the 4f-5d absorption and emission bands to be broad. The broad band emission and high PL intensity are the advantages of the current phosphors. But the sensitivity of the 5d states is also the reason why almost all these phosphors

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must be lightly doped (~ 0.1 at.%), single-phase ceramic powders. They must have high chemical purity and have to be fabricated and stored carefully to guarantee their fluorescent quality. These factors limit the development of new phosphors, decrease their working lifetime and increase their cost.

On the other hand, rare-earth (RE) ions are also known to have extremely rich $4f^N$ ($N = 1-14$, from Ce^{3+} to Yb^{3+}) electronic energy configurations [7]. Many transitions between the $4f^N$ states are located in the visible range. And one outstanding advantage of the $4f-4f$ transitions is that they are little influenced by the environment since the $4f$ orbits are shielded by the completely filled $5s$ and $5p$ electronic sub-shells [3, 6]. That means that these active RE ions do not need to be located in a specific crystal lattice position, as in the case of $4f-5d$ transitions. They can heavily dope ceramics, glasses, amorphous or organic materials freely and still keep their fluorescence properties without too much change. This is an obvious advantage for the development of new types of phosphors, which may decrease the fabrication costs as well. However, the $4f-4f$ transitions of the RE ions are not utilized in the current white LED techniques because they also have two significant shortcomings.

The first problem is that the $4f-4f$ transitions are electric-dipole forbidden [8]. They can only happen through magnetic-dipole or electric-quadrupole mechanisms, but mainly through electric-dipole transitions induced by crystal field effects. This forbidden character makes the $4f-4f$ transitions much weaker than the $4f-5d$ ones. But this is still not fatal, since the weak absorption and emission intensities of $4f-4f$ transitions may be compensated by additional active ions through heavy doping. The other problem stems from the fact that the $4f$ electrons are well shielded. This makes the $4f-4f$ transition peaks quite narrow, so that the spontaneous emission (SE) from any of the $4f^N$ levels of the RE ion always manifests itself as one or more distinct peaks, according to their fluorescence branching ratios. It is difficult to generate a continuous white light spectrum based on distinct peaks with different intensities.

In the present paper, a technique using one-dimensional (1-D) photonic bandgap (PBG) structures is firstly introduced for white light generation. It is demonstrated that this novel technique may also be a way to improve the application of $4f-4f$ transitions for white light generation. PBG structures, also known as photonic crystals, are periodic dielectric structures which can manipulate the SE of fluorescent materials embedded inside them, by changing the optical mode density which surrounds the active ions [9, 10]. It has been proved in our previous work that a 1-D PBG structure can effectively change the SE properties of RE doping ions, namely broadening their PL bandwidth and simultaneously enhancing the emitted light intensity [11]. In the present work, this technique has been extended to white light generation and a 1-D terbium-doped triple coupled microcavity was prepared as a demonstration of this novel idea. When pumped by blue light at 488 nm, the PL from Tb^{3+} ions outside a PBG structure includes three distinct peaks. But when a triple microcavity structure is doped with terbium, these three peaks are enhanced, balanced and broadened, combining into a continuous fluorescence band ranging from green to red. This result supports a new method to explore the white light generation phenomenon through an increased member of RE-containing materials. A possible scheme to apply this technique to white LED illumination is also discussed.

2. Experiments

The multilayer microcavity samples were prepared by sol-gel processing. Silicate glass and titania films were alternately deposited on single crystal silicon substrates. The silicate sol was prepared by mixing 3 ml of tetraethylorthosilicate (TEOS), 6 ml of isopropanol and 0.48 ml of 0.01N HCl, with continuous stirring at 70 °C for 3 hours; then, an additional 16 ml of isopropanol, 0.5 g of $Al(NO_3)_3$ and 0.3 g of $Tb(NO_3)_3$ were added, corresponding to a dopant concentration of 5 mol% Tb^{3+} ions (on a cation basis). The titania sol was prepared by mixing 2.5 ml of titanium isopropoxide with 3 ml glacial acetic acid, followed by stirring for 1 hour; then, 16 ml of ethanol and 0.21 g of $Tb(NO_3)_3$ were added, leading to a dopant concentration of 5 mol% Tb^{3+} ions (Tb/Ti ratio of 5:100). The additional 16 ml of isopropanol and the 16 ml of ethanol were volumes empirically determined to adjust the single layer silicate and titania film thickness to the designed values. All sols were aged for 24 hours, before the multilayer spin-coating deposition process. Each individual layer was heat treated at 1050 °C for 30 s. More

details about the fabrication technique can be found in [12]. A reference sample with the structure of $H_{10}L_{14}$, having the same number of silicate glass and titania layers, but without the PBG structure, was also prepared, in order to determine the effects which originated specifically from the triple microcavity structure.

The SEM cross section micrograph of one sample was taken with a FEG-SEM JEOL JSM-7001F, in the back-scattered electron mode. The reflection spectra of all samples and their PL spectra from green to red were recorded by two standard setups.

Figure 1. Experimental setup for the measurement of reflection spectra.

A top view of the reflection measurement setup is sketched in figure 1. White light from a tungsten lamp (Cuda products corporation, I-150) was focused by a lens. It went through an iris and a beam splitter and then irradiated the surface of the sample, which was held on a rotation stage. The diameter of the light spot on the sample was about 5 mm. The iris could control the brightness of the light spot and it helped to confirm that the sample was in the perpendicular direction, by turning the rotation stage until the reflected light spot coincided with the iris hole. A piece of borosilicate glass was used as the splitter and the ~ 4 % of light it reflected entered a 10X microscope objective and was then coupled into a multimode optical fiber with a core diameter of 600 μm . The collected light was sent to a spectrometer consisting of a 0.85 m double monochromator (Spex 1403) and a photomultiplier tube (PMT, Hamamatsu, R928). The spectrum of the light reflected by an aluminium mirror was recorded as the 100 % reflectivity reference; the reflection spectra of other unknown samples were obtained by rationing their reflection and the reference spectra.

The measurement setup for PL was similar to the reflection one. The differences were: the removal of the iris, the splitter and the microscope objective; the replacement of the white light beam with the 488 nm line of an Ar^+ ion laser (Spectra-Physics mod. 2017) with a power of 200 mW; and a rotation of the sample, pumping it at a large incidence angle ($\sim 45^\circ$), while collecting the PL directly by the multimode optical fiber in the perpendicular direction.

3. Results

The PL of Tb^{3+} ions ranges from green to red outside a PBG structure and it includes three distinct peaks at 542 nm, 587 nm and 619 nm, respectively. The idea is to enhance, balance and broaden these three PL peaks by means of a PBG structure and make them combine into an appropriate continuous fluorescence band. For this purpose, a triple coupled microcavity with the structure $(\text{LH})_3\text{L}_2\text{HLHL}_2\text{HLHL}_2(\text{HL})_3$ was designed, where L and H represent low and high refractive index quarter-wave films. The reflection spectrum of this structure can be simulated by the transfer matrix method (TMM) [11, 13]. Generally, this reflection profile contains three defect peaks (or “pass bands”) located inside the stop band. The wavelength range covered by the stop band and the position of the defect peaks can both be tuned through the refractive index and thickness of each layer. In the present work, the proposed structures were prepared by the sol-gel method and the low and high refractive index materials were sol-gel derived silicate glass and titania films, respectively. Based on the refractive indices of these two materials, ~ 1.45 for silicate glass and ~ 2.2 for titania in the visible range, when the thickness of the silicate layers is ~ 110 nm and that of the titania layers is ~ 50 nm, the stop band of the proposed structure will cover the visible range and the three defect peaks will closely match the three PL peaks of Tb^{3+} .

Figure 2. FEG-SEM cross section micrographs of (a) sample #1 and (b) the reference sample, in the back-scattered electron mode. The bright strips are titania layers and the dark strips are silicate glass. The estimated thickness of each silicate layer in sample #1 is 114 ± 8 nm and that of each titania layer is 52 ± 6 nm. The three layers labelled D1-D3 in (a) are the cavity defect layers.

The two best results obtained in the present work are reported in this paper. One of the samples was labelled sample #1 and the other sample #2. The SEM cross section micrographs of sample #1 and the reference sample are shown in figure 2. The reflection spectrum of sample #1 is plotted in figure 3 (solid line on top). The PL of the Tb^{3+} ions outside a microcavity is also drawn at the bottom of figure 3, measured on the reference sample. The PL spectra of both PBG samples are plotted in figure 4 (solid lines at bottom), together with their reflection spectra (solid lines on top) and the reference PL spectrum (dashed lines). Figure 4 (a) refers to sample #1 and figure 4 (b) to sample #2. Since the reference sample was prepared with the same sols and processing methods of sample #1, the PL intensities of both can be compared directly in figure 4 (a). Generally, the PL was enhanced near the resonance wavelengths and changed very little outside the defect peaks. According to that, the PL spectrum of sample #2 in figure 4 (b) was normalized to the reference spectrum by the PL intensity emitted outside the resonance wavelengths (around 542 nm and 587 nm). Compared to the reference PL, it is clear that the PL near the resonance wavelengths of each microcavity spectrum was enhanced and the three distinct PL peaks of Tb^{3+} ions were broadened and combined into a continuous fluorescence band.

Figure 3. Simulated (dashed line) and measured (solid line) reflection spectra of sample #1. The structure of this triple coupled microcavity is illustrated at the top-left: the light blocks represent silicate glass layers and the dark blocks represent titania layers; all layers are doped with 5 mol % Tb. The Tb^{3+} PL without microcavity, for a reference sample pumped by the 488 nm Ar^+

laser line, is plotted as a solid line at the bottom of the figure. The Tb^{3+} ion transitions for each PL peak are also indicated.

Figure 4. PL from terbium-doped triple coupled microcavity samples #1 (a) and #2 (b) (solid lines) and from the reference sample (dashed line), under the same pumping conditions at 488 nm. The PL of sample #2 in (b) has been normalized by the PL intensity emitted outside the resonance wavelengths. The reflection spectrum of each PBG sample is plotted as a solid line at the top of the figures.

4. Discussion

The top-left of figure 3 illustrates the designed triple coupled microcavity structure, in which the light blocks represent the silicate glass layers and the dark blocks represent the titania ones. Compared to this illustration, figure 2 shows that the proposed structure was prepared successfully. The bright thin strips in the SEM micrograph are titania layers and the darker thick strips are silicate glass. In the middle of the cross section, there are three silicate glass layers (D1-D3) whose thickness is double that of the other silicate layers and which correspond to the cavity defect layers. According to this picture, it can be estimated that the thickness of each silicate layer in sample #1 was 114 ± 8 nm and that of each titania layer was 52 ± 6 nm, close to the designed values of ~ 110 nm and ~ 50 nm, respectively.

The optical quality of the samples can be judged from their reflectivity spectra. The reflection spectrum of sample #1 is represented by the solid line at the top of figure 3, while the simulated reflection spectrum calculated by TMM is plotted as a dashed line. The refractive indices used in the TMM model were from our previous work [12] and the thickness of each layer was determined from the best fit of the simulated to the measured spectrum. The final fitting results were 110 nm for the silicate and 49.5 nm for the titania layers. These two values match the thicknesses obtained from the SEM micrograph (figure 2) very well, since 1 pixel in figure 2 represents ca. 4.5 nm. It is shown in figure 3 that the profile of the measured reflection spectrum coincided with the theoretical curve almost perfectly, including the stop band, the defect peaks and the fringes, demonstrating the high quality of sample #1. The conclusion was the same for sample #2, based on similar considerations. The three defect resonance wavelengths of sample #1 were 536 nm, 571 nm and 617 nm, respectively and the average Q factor ($\lambda/\Delta\lambda$) of these three defect peaks was 54. The three defect resonance wavelengths of sample #2 were 528 nm, 565 nm and 613 nm, respectively and their average Q factor was 49.

The Tb^{3+} PL outside the microcavity consists of three distinct peaks at 542 nm, 587 nm and 619 nm, with most of the PL energy concentrated on the green peak (542 nm). The three distinct PL peaks correspond to the 4f-4f transitions from the $^5\text{D}_4$ state of Tb^{3+} ions to their $^7\text{F}_5$, $^7\text{F}_4$ and $^7\text{F}_3$ states, respectively, as denoted in figure 3. The diagram of the eight lowest energy states of Tb^{3+} ion is given in figure 5 [14]. The relative intensity of all these transitions depends on the SE branching ratios.

Tb^{3+} ion is a typical example of the shortcomings of the 4f-4f transitions discussed in the introduction. It has strong absorption bands in the blue and UV and its $^5\text{D}_4$ level has very high

PL quantum efficiencies. In fact, Tb-doped phosphors are widely used in the current fluorescent lamps, but only for their green emission [1, 3]. Although the transitions of Tb³⁺ ions from the ⁵D₄ state to the ⁷F_J multiplets cover the visible range from blue to red, they cannot generate proper white light individually.

Figure 5. The lowest eight electronic energy states of Tb³⁺ ion. The right hand side shows a diagram with the Stark splittings of each state, drawn from data of Tb:YAG [14].

In figure 4 (a) and (b), the PL spectra from the Tb³⁺ ions embedded in the triple coupled microcavity structure of the two samples are plotted. By comparison with the spectrum of the reference sample, it is obvious that the PL near the resonance wavelengths has been enhanced by the PBG structure. This PL enhancement has modified the profiles of the three original distinct PL peaks of Tb³⁺ ions, causing them to broaden and overlap. The physical explanation of a similar phenomenon concerning the SE from an erbium-doped double microcavity has been discussed in great detail in a previous publication [11], where it was shown how the 1-D PBG structure can enhance and modify the SE of fluorescent materials. For the red PL at 619 nm, the corresponding pass bands of samples #1 and #2 were both located very close to this peak wavelength, which significantly enhanced the red PL. At the same time, the green pass bands of the two samples were both somewhat blue-shifted relatively to the green PL at 542 nm, thus not enhancing the green PL too much, but clearly broadening it on the blue side. The most interesting change was at the yellow pass band (571 nm for sample #1 and 565 nm for sample #2), whose defect peak was located between the green (542 nm) and yellow (587 nm) PL peaks of Tb³⁺. As a result, a new PL peak was generated at the resonance position, combining the green and yellow emissions of Tb³⁺ into a continuous PL band. These new PL peaks, as well as the new green PL peak at 528 nm for sample #2, can be explained by the Stark splitting of the 4f energy states, shown at the right hand side of figure 5.

In general, when RE ions are embedded in a solid, the crystal field interaction can split a free RE ion level with total angular momentum J into 2J+1 distinct sublevels, if J is an integer and into (J+1/2) sublevels, if J is a half-odd integer [15]. But the actual number of sublevels and their energy splitting are ultimately determined by the symmetry of the crystal field surrounding the RE ion. The diagram on the right hand side of figure 5 is an example of how the eight lowest energy levels of Tb³⁺ ions split into many sublevels, according to the PL data from Tb:YAG [14]. For the heavily doped silicate glass and titania films in the present case, the Tb³⁺ ions are located in environments of varying geometries and the crystal fields surrounding them are of much lower symmetry and much more random than those in YAG crystal, especially in the glassy matrix. So the actual Stark splitting of each state was much larger in samples #1 and #2 than in YAG crystal and the ⁷F_J states in these two samples became a quasi-continuous energy band. When outside the PBG structure, the excited ions are mainly located in the lowest sublevels of ⁵D₄ state, because of the Boltzmann distribution law and the transitions between each two sublevels still obey the SE branching ratios. That is why the reference PL spectrum included three distinct peaks and most of its energy was concentrated in the green peak. But once the Tb³⁺ ions were embedded into the triple coupled microcavity, the SE branching ratios

changed and the transitions between any two sublevels resonant with the defect peaks become strongly enhanced. This is where the “new” PL peaks come from. To the best of our knowledge, this kind of modification combining several distinct PL peaks into a continuous broad band by means of multiple coupled microcavities has not been reported before. For white light sources, a lamp possessing a continuous broadband spectrum will give higher colour rendering index (CRI) than those which have only several narrow bands.

The effective optical spectra of a 1-D PBG structure undergo blue-shifts when the propagating light deviates from the perpendicular direction. So the observed modified Tb^{3+} PL spectrum changes depending upon the detection angle. The final profile observed at different angles depends on the resulting enhancement at the effective resonant wavelengths for each propagation direction. However, both the theoretical simulations and the experimental results show that the blue-shift of the resonance wavelengths for deviations of up to 10° off-normal are less than 3 nm and the observed Tb^{3+} PL spectrum doesn't change too much. Such deviations correspond to a LED emitting with a 20° full viewing angle. For example, the blue-shift for a 15° deviation from the normal, corresponding to a 30° full viewing angle, is also still only 7 nm.

Figure 6. CIE coordinates for the PL of samples #1 and #2, plus the reference sample. The points corresponding to samples #1 and #2 overlap completely. The area covered between the two lines connecting the PL emission point and the exciting wavelengths represents the possible colours resulting from a mixture of the PL and the excitation lights. The E point at the centre of the diagram is the white colour point.

The profile modification in figure 4 has balanced the green and red proportions of the Tb^{3+} PL to a good extent. The CIE colour coordinates of the reference PL spectrum and those of samples #1 and #2 PL have all been plotted in figure 6. The latter two points totally overlapped each other and they obviously moved to a “redder” position compared to the reference PL. The centre excitation wavelength of the current blue-excited white LED is ca. 465 ± 15 nm, but sometimes may even be located at 420 nm [4, 16]. The area covered between the two lines connecting the sample coordinate and the exciting wavelengths represents the possible colours that result from the sample PL and the excitation light. The white point E is shown at the centre of the CIE diagram. It is clear from figure 6 that, from the Tb^{3+} PL outside PBG structure, it is impossible to obtain white light simply by mixing blue light into it. However, the E point can be reached, in theory, by using the PL from the triple coupled microcavity.

Besides the profile modification, the absolute PL intensity of the PBG samples was enhanced as well. The total PL energy from sample #1 was ~ 1.7 times larger than that from the reference sample under similar pumping conditions. The normalized PL energy from sample #2 was ~ 1.9 times larger, similar to the result from sample #1. This SE energy enhancement can be attributed

to an increase in the emission rate of Tb^{3+} ions embedded in the triple microcavity, similarly to the explanation given in ref. [11].

Figure 7. Proposed scheme for the application of the PBG structure to a white light LED. The block connected with two wires is the light emitting semiconductor chip and the block on top of it is a proposed phosphor patch whose architecture is sketched on the right hand side.

Finally, a possible scheme to apply the 1-D PBG structure to a white LED is proposed in figure 7. It is similar to the typical architecture of a common white LED [3]. The base block connected with two wires is the semiconductor chip emitting the blue or UV excitation light. For the current white LED, this chip is buried under phosphor powders to down-convert the exciting light to a hybrid light having a white appearance. The present new scheme replaces the phosphor powders with a phosphor patch pasted onto the semiconductor chip directly. The configuration of the phosphor patch is sketched on the right hand side of figure 7. It consists of a very thin transparent glass substrate; a short-pass filter is deposited on its bottom side to let the exciting light pass, but to reflect all the other light of longer wavelength emitted by the phosphor. On the top side, a fluorescent PBG structure is deposited to convert the exciting light into a white one. Because the novel, PBG-assisted white light generation technique introduced in the present paper depends on an optical structure and not on a specific fluorescent material or a fabrication technique, any phosphors, from the traditional Ce:YAG to other possible fluorescent materials working based on 4f-4f transitions, can be applied in this scheme, as long as they can be incorporated into the PBG structure. Obviously, this will considerably improve the development of novel materials for white light generation. The current phosphors may also benefit from the enhancement and modification effects provided by the PBG structure. An added advantage of this scheme is that it will avoid most of the light scattering from the phosphor powders, which may be beneficial to the LED thermal management and energy efficiency [17].

5. Conclusion

In summary, terbium-doped triple coupled microcavities were prepared by sol-gel processing in the present work. The three pass bands of the triple microcavities were designed to match the three visible PL peaks of Tb^{3+} ions. The PL of Tb^{3+} ions outside a microcavity consisted of three distinct peaks. Once embedded into the microcavities, the three Tb^{3+} PL peaks were enhanced, balanced and broadened by the PBG structure and combined into a continuous broad band. The CIE coordinates of the original and the modified Tb^{3+} PL profile were calculated and compared. It was shown that white light can be obtained by mixing the modified PL emission with the blue exciting light, while this is impossible for the original PL profile. While the results obtained do not mean that the present terbium-doped PBG structure can immediately be used in a white LED, they clearly highlight the functions and potential of this novel PBG-assisted technique, which may improve white light generation by enhancing and modifying the SE of current phosphors. It may also significantly help the development of new RE phosphor materials based on 4f-4f transitions. These new improvements may be able to generate white light more

efficiently, allowing simpler and cheaper alternatives to the current phosphor compositions. A novel configuration to apply the PBG structure to a white LED has also been proposed.

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