



Photonic crystal assisted up-converter based on Tb^{3+} / Yb^{3+} - Doped aluminosilicate glass

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ABSTRACT

Great efforts have been made in the last few years to increase the energy efficiency of solar cells. Among several factors which influence their performance, the light harvesting efficiency is the most relevant factor. In order to reduce the transparency losses of sub-bandgap solar photons, especially for wide gap solar cell materials, the development of up-conversion (UC) coatings to transform near infrared (NIR) light into short-wavelength visible photons is clearly a suitable approach. In spite of recent advances, the development of UC materials involves techniques which are generally not cost effective. This work will primarily focus on the evaluation of UC luminescence in aluminosilicate glass phosphors co-doped with the Tb^{3+}/Yb^{3+} ion pair and synthesized by sol-gel (SG), a technique which is especially adequate to the deposition of films. The optimization of dopant concentrations has also been investigated, together with the structural, morphological and UC emission study of the coatings obtained. Lastly, a potential demonstrator has been developed in the form of a 1-D photonic crystal (PC) microcavity, in order to integrate the spectral conversion function into a more complex but more efficient structure.

1. Introduction

The solar energy market has been growing quickly in the last decades due to the technological improvements and the new policies that support renewable energy sources to meet energy demand. It is known that conventional energy sources have drawbacks in terms of environmental pollution and limited availability. One of the challenges which remain for solar energy is to increase the efficiency of photovoltaic (PV) technologies. To address this issue, different paths have been followed, either based on new materials and techniques, or aimed at matching the solar spectrum with the spectral efficiency of PV cells. In the latter case, UC [1,2] as well as down-conversion [3,4] processes in lanthanide-doped photonic materials, can be used to manage the solar spectrum. UC is a promising route to solve the transmission loss problems of sub-bandgap photons, especially in the case of wide gap semiconductor solar cell materials. In the presence of UC material, transmitted sub-bandgap photons are converted into above-bandgap light which is then absorbed by the cell material. To date, Ho^{3+}/Yb^{3+} , Er^{3+}/Yb^{3+} and Tm^{3+}/Yb^{3+} emitter/absorber pairs have been widely employed as up-converters with 980 nm laser excitation [5–9]. It is important to match the energy levels between Yb^{3+} and the emitting ions for an efficient UC emission, based on the judicious choice of a suitable pair. Tb^{3+} is another good candidate for emitter given its ultraviolet, violet, blue,

green, yellow and red light emissions and much longer luminescence lifetimes compared to Ho^{3+} , Er^{3+} and Tm^{3+} [10]. Although Tb^{3+} does not have intermediate levels which can receive energy from Yb^{3+} ions, it can efficiently be excited by a cooperative energy transfer process in which two excited Yb^{3+} ions simultaneously transfer their energy to a Tb^{3+} ion. Therefore, the Tb^{3+}/Yb^{3+} pair is a potential choice for UC applications.

UC emission based on the Tb^{3+}/Yb^{3+} pair has been studied in different host matrices, mainly based on fluoride compounds due to their low phonon energies. For example, cooperative UC was observed in oxyfluoride glasses ca. 2 mm thick prepared by conventional melt/quenching [11]. Cooperative energy transfer was found to be the dominant mechanism responsible for the UC emission observed in $BaMgF_4:Tb^{3+}/Yb^{3+}$ spherical agglomerated particles with an average diameter in the range 2–3 μm , annealed at 800 °C [12]. Moreover, $NaGdF_4:Yb, Tb$ nanoparticles have been synthesized by a modified thermolysis method, with very high Tb^{3+} and Yb^{3+} optimum concentrations of 10% and 80%, respectively [13]. Concerning silica-based hosts, cooperative resonant energy transfer has been demonstrated in Tb^{3+}/Yb^{3+} co-doped SG silica samples with 0.5 mol% Tb^{3+} and 4 mol % Yb^{3+} [14]. Tb^{3+}/Yb^{3+} co-doped glassy, glass-ceramic and (fully) ceramic aluminosilicate materials were also prepared by the SG technique, but only the ceramic particles, densely packed with some micro

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pores, showed UC emission from Tb^{3+} upon 976 nm excitation, with the best results being obtained with 2.5 mol% Yb^{3+} and 1 mol% Tb^{3+} [15]. According to the literature, most efforts have been focused on particle synthesis. However, micro or nanoparticles cannot be easily coupled with deposition of films and multilayered structures. Besides, applications in solar cells, solid state lasers or microelectronics often require the use of materials in thin film form. To the best of our knowledge, only a few reports have appeared in the literature dealing with the preparation and characterization of Er/Yb activated thin films [1,16–18]. Recently, we have reported efficient down-conversion emission in aluminosilicate phosphors co-doped with $\text{Tb}^{3+}/\text{Yb}^{3+}$ [4], showing NIR emission from Yb^{3+} under 484 nm excitation for different concentrations of Tb^{3+} . To follow up, we planned to study the UC properties of this material.

In the present investigation, we report for the first time the synthesis of $\text{Tb}^{3+}/\text{Yb}^{3+}$ co-doped aluminosilicate glass-based microcavity (a 1-D PC) by SG, in order to integrate the UC function into a more complex but more efficient structure. PCs are periodic dielectric structures which can manipulate the spontaneous emission (SE) of light from active ions such as lanthanides embedded in those structures [19]. A Fabry-Perot Microcavity (MC) consists of two parallel distributed Bragg reflectors (DBRs), or Bragg mirrors, separated by a defect layer. The controlled defect layer creates a pass band within the stop band of high reflectivity characteristic of the Bragg mirrors. Previous work has proved that a 1-D MC can effectively change the SE properties of lanthanide ions, in particular increasing the emitted light intensity [19,20]. In this work, this technique has been extended to UC coatings, with a $\text{Tb}^{3+}/\text{Yb}^{3+}$ co-doped MC being prepared to demonstrate the enhancement the photoluminescence (PL) intensity.

2. Methods

2.1. Materials

Aluminosilicate glass films were synthesized by SG method. The precursors used for the preparation of the aluminosilicate sol were TEOS (tetraethyl orthosilicate, Alfa Aesar, 98%) and $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ (Aluminum nitrate nonahydrate, Alfa Aesar, 98.0–102.0%), with Ethanol (Merck, 99.5%) and distilled water used as solvents and HCl as a catalyst (Sigma Aldrich, 37%). Terbium and ytterbium nitrates were added in the required amounts for the doped solutions. The samples prepared had the nominal composition (in mol %): $(90-x-y) \text{SiO}_2 \cdot 10 \text{AlO}_{1.5} - x \text{TbO}_{1.5} - y \text{YbO}_{1.5}$ ($x = 0, 1, 3, 5$ and $y = 0, 5, 10, 15$). Henceforth, all compositions in this paper are expressed in mol%.

2.2. Synthesis

The preparation of the solution labelled “A” involves the hydrolysis of TEOS. This was initiated by preparing a solution composed of TEOS, water (in a molar ratio water/TEOS = 4) and ethanol (Merck, 99.9%, the volume being chosen according to the desired thickness). HCl was added to achieve pH = 2. After mixing, solution “A” was stirred and heated at $\sim 70^\circ\text{C}$ during 1 h. A separate solution (labelled “B”) was prepared by dissolving the required amount of aluminum nitrate in ethanol, which was added slowly to solution “A” while stirring. This mixed solution (labelled “C”) was then stirred for 10 min at $\sim 70^\circ\text{C}$. For doped solutions, terbium and ytterbium nitrates were dissolved in the stoichiometric proportions in ethanol (solution “D”) and this was finally added to solution “C” and stirred for an additional 10 min at 70°C . The final solution was aged for 24 h at room temperature.

Before deposition by spin-coating, the solution was filtered through a $0.2 \mu\text{m}$ PTFE syringe filter to prevent particulate contamination. The films were spun at 2000 rpm for 30 s on single-side polished Si (100) wafers. The coated substrate was then heat-treated in a muffle furnace at 1100°C for 30 s, in air, to yield a $\sim 90 \text{ nm}$ thin film. To obtain a higher film thickness, the number of layers was increased by repeating

the whole process.

The multilayer MC samples were also prepared by SG processing. Doped aluminosilicate and pure titania films were alternately deposited on silicon substrates. The aluminosilicate sol was prepared following the method described previously. For the preparation of titania sol, 2.5 mL of TPOT were mixed with 3 mL of glacial acetic acid and stirred for 1 h at room temperature, after which ethanol was added (the volume being chosen according to the desired thickness), while stirring for 1 h. The final solution was aged for 5 h in a closed recipient. Spin-coating of the titania sol was performed in the same manner described for the aluminosilicate sol, to yield $\sim 60 \text{ nm}$ thin layers.

The 1-D PC structure consisted of a symmetric MC with a defect positioned at 542 nm, corresponding to the strongest PL peak of Tb^{3+} , with the structure $(\text{LH})_n \text{L}_2 (\text{HL})_n$, where L and H represent low (aluminosilicate glass) and high refractive index (titania) films, respectively, and the subscript n, the number of periods of the Bragg mirrors. The quarter-wave thickness of each layer, corresponding to the basic condition for constructive interference in the DBRs [19,20], was calculated as $(542 \text{ nm}/4 n_{\text{L,H}})$, where $n_{\text{L,H}}$ is the refractive index of the aluminosilicate glass or TiO_2 films, with values of ~ 1.500 (obtained by spectroscopic ellipsometry in this work) and ~ 2.199 [21], respectively, and 542 nm is the peak wavelength of the Tb^{3+} PL green emission. The defect of the Fabry-Perot MC consists of a double thickness low index layer. For each MC sample, a corresponding reference sample was also prepared from the same sols and by the same processing technique as the original sample, containing only the $\text{Tb}^{3+}/\text{Yb}^{3+}$ -doped aluminosilicate layers, $\text{L}_{1,2}$, in order to identify the specific effect of the MC structure.

2.3. Optical and microstructural characterization

To evaluate the thickness and refractive index of the spin-coated SG films, spectroscopic ellipsometry was carried out with a Uvisel Horiba Jobin Yvon phase-modulated ellipsometer, at 70° incidence angle, in the wavelength range of 200–1200 nm. A suitable modelling of the ellipsometric angles Ψ and Δ was employed, using a classical dispersion function, through the minimization of the mean square deviation between the calculated (modelled) and the experimental data, using the DeltaPsi2 software package of Jobin-Yvon.

A Nicolet 5700 Fourier transform infrared (FTIR) spectrometer (Thermo Electron Corporation) was used to record visible spectra at a resolution of 4 cm^{-1} . The reflectance spectra were measured with the same FTIR spectrometer, together with a SPECAC variable angle reflectance attachment.

Surface view and cross section scanning electron micrographs of the films were taken with a JEOL JSM-7001F Field Emission Gun-Scanning Electron Microscope (FEG-SEM) in the backscattered electron mode. The samples were covered with a thin layer of Au to enhance the surface conductivity. The microscope was coupled to a INCA energy dispersive X-ray spectrometer (EDS, Oxford Instruments) used for chemical analysis.

2.4. Luminescence characterization

UC PL spectra were recorded between 400 and 750 nm. A 975 nm laser diode (Lumics LU0975T080-D605N12A Laser Module) at 2 W power, or from 1 to 4 W, for power dependent emission studies, was used for excitation. The laser was focused on the samples by a $10\times$ micro-objective (NA = 0.28) and the generated UC PL was collected by a multimode fibre (core diameter of $600 \mu\text{m}$) and guided into a grating spectrometer (0.85 m double monochromator, Spex 1403) and a photomultiplier tube detector (Hamamatsu, R928).

3. Results & discussion

In order to evaluate the performance of the aluminosilicate

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