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Down-conversion in Tb^{3+}/Yb^{3+} doped SiO_2-HfO_2 glass ceramics thin films for enhanced silicon solar cell performance

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***Abstract*— The thermalisation of charge carriers in the UV-blue range, generated by the absorption of high-energy photons, is one of the major loss in silicon-based solar cells. The method investigated in this work for reducing these energy losses is via down-conversion (DC) layers doped rare earths ions placed on the front side of the silicon solar cells, allowing an efficient conversion from UV-blue photons to near-IR photons. This paper examines the Tb^{3+}/Yb^{3+} energy transfer efficiency in a $70SiO_2$–$30HfO_2$ glass-ceramics waveguides. The evaluation of the transfer efficiency between Tb^{3+} and Yb^{3+} is obtained by comparing the luminescence decay of Tb with and without Yb co-doping ions. A transfer efficiency of 25 % was obtained with the sample doped with a highest concentration of rare earth (5%).**

***Keywords*— solar cells, rare earth, down conversion, transfer efficiency, glass-ceramic**

I. INTRODUCTION

Recent years have seen considerable research on renewable energies, especially photovoltaic. Indeed, the improvement of the efficiency of the solar cells is today an important ecological issue. The efficiency of solar cells is strongly reduced by several factors. On one hand, a fraction of the solar spectrum (about 18%) is not exploitable by photovoltaic cells since the corresponding photons have lower energy that the band gap of Si. On the other hand, 30% of the solar spectrum consisting of very high-energy ultraviolet photons are absorbed but the excess of energy is lost as heat.

The down-conversion process, by which one high energy photon is converted into two low energy photons, is extremely promising [1]. Up-conversion involves the addition of photons via sequential absorption and energy transfer between ions in an excited state, with subsequent emission of photons with higher energy [2]. The motivation for using rare-earths for down and up coversion process is that this family of elements luminesce over a wide range, from the near-infrared, through the visible to the ultraviolet. Their optical transitions involve 4f orbitals, which are well shielded from their local environment by the outer completely-filled $5s^2$ and $5p^6$ orbitals [3].

In this paper we focus on down conversion process using a cooperative energy between one Tb^{3+} and two Yb^{3+} ions permits to cut high energy photon at wavelength shorter than 488 nm into two low energy photons around 980 nm [3] (figure 1).

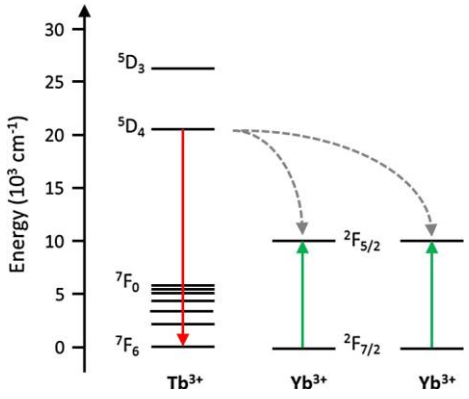

Fig. 1 The Tb^{3+}:$^5D_4$ energy level corresponds to about twice the energy of the Yb^{3+}:$^2F_{5/2}$ energy level. The cooperative energy transfer between a Tb^{3+} ion and two Yb^{3+} ions can generate two NIR photons, emitted by Yb^{3+} ions, after the absorption of a single photon by a Tb^{3+} ion.

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The choice of the matrix is a crucial point to obtain an efficient down-conversion process. The materials need to be chosen to minimize non-radiative transition process from the rare-earth ions to the host matrix [4,5]. Recently, some studies have demonstrated that the transparent glass ceramics may be a valid system to support an effective quantum cutting process [6,7]. Sol gel-derived silica-hafnia is a reliable and flexible system that has proved to be suitable for rare earth doping and fabrication of glass ceramic planar waveguides with excellent optical and spectroscopic properties for photonic applications [9]. In particular, previous works on silica-hafnia glass ceramic using X-ray absorption fine structure (EXAFS) and X-ray photoelectron spectroscopy (XPS) confirmed that Er3+ ions remain incorporated in HfO_2 nanocrystals due to substitution of Hf^{4+} by Er^{3+} in the crystalline lattice [9,10].

In the current paper we present the result obtained after characterization of a serie of 70SiO2–30HfO2 samples activated by different molar concentrations of rare earths [Tb + Yb]/[Si + Hf] = 1%, 3%, 5%, prepared by sol–gel route using the dip-coating technique.

II. Experimental

A series of glass ceramic $70SiO_2$–$30HfO_2$ planar waveguides samples co-doped by fixed different concentration of rare earth, ([Tb+Yb]= 1mol%,3 mol%, 5 mol%) were prepared by sol–gel route using the dip-coating technique and keeping constant the molar ration between Tb and Yb ([Yb]/[Tb]=4).

The starting solution, obtained by mixing tetraethylorthosilicate (TEOS), ethanol, deionized water and hydrochloric acid as a catalyst, was pre-hydrolyzed for 1 h at 65 °C. The molar ratio of TEOS:HCl:H_2O was 1:0.01:2. An ethanolic colloidal suspension was prepared using as a precursor HfOCl2 and then added to the TEOS solutions, with a Si/Hf molar ratio of 70/30. The quantity of ethanol was adjusted for each solution in order to obtain a final total [Si+Hf] concentration of 0.448 mol/l. Terbium and ytterbium were added as $Tb(NO_3)3;5H_2O$ and $Yb(NO_3)3;5H_2O$. The final mixture was left at room temperature under stirring for 16 h. The obtained sol was filtered with a 0.2 μm Millipore filter. Silica–hafnia films were deposited on cleaned pure SiO_2 substrates by dip-coating, with a dipping rate of 40 mm/min. Before further coating, each layer was annealed in air for 50 s at 900 °C. After a 10 dipping cycle, the film was heated for 2 min at 900 °C. Final films, obtained after 30 dips, were stabilized by a treatment for 5 min in air at 900 °C. As a result of the procedure, transparent and crack-free films were obtained. An additional heat treatment was performed in air at a temperature of 1000 °C for 30 min in order to nucleate nanocrystals inside the film $70SiO_2$–$30HfO_2$ glass ceramic planar waveguides doped with rare earth ions were thus produced. Table 1 gives the compositional and optical parameters of the obtained silica-hafnia planar waveguides.

TABLE 1: COMPOSITIONAL AND OPTICAL PARAMETERS OF THE PREPARED SAMPLES

Sample label	[Tb^{3+}] mol%	[Yb^{3+}] mol%	n@543, 5 nm	n@683 nm	Thikness
AR1	0,2	0	1,623	1,617	1,1
A1	0,2	0,8	1,604	1,608	0,9
AR2	0,6	0	1,624	1,620	1,1
A2	0,6	2,4	1,630	1,625	1,2
AR3	1	0	1,626	1,621	1,2
A3	1	4	1,638	1,633	1,1

The thickness of the waveguides and the refractive index at 632.8 and 543.5 nm were obtained by a m-lines apparatus (Metricon, mod2010) based on the prism coupling technique, using a Gadolinium Gallium Garnet (GGG) prism, with the setup reported in [11].

The luminescence spectrum in the region of the transition $^2F_{5/2}\rightarrow{}^{11}F_{7/2}$ of Yb^{3+} ion was analyzed by a single grating monochromator with a resolution of 2 nm and detected using a Si/InGaAs two-color photodiode and standard lock-in technique.

Luminescence decay measurements of the $^5D_4$ state of Tb^{3+} ion were performed after excitation with the third harmonic of a pulsed Nd-YAG laser. The visible emission was collected by a double monochromator with a resolution of 5 cm^{-1} and the signal was analyzed by a photon-counting system. Decay curves were obtained recording the signal by a multichannel analyzer Stanford SR430. More information about the experimental setups can be found in [12].

III. RESULTS AND DISCUSSION

The prepared samples are thin layers of $70SiO_2$-$30HfO_2$ doped rare earth ions with different concentrations. The total amounts of the samples A1, A2 and A3, are 1mol%, 3mol% and 5mol%, respectively. For each composition a reference sample without Yb^{3+} ions was prepared; these samples are labeled AR1, AR2, and AR3, respectively. Fig. 2 shows the down-conversion luminescence from silica-hafnia glass ceramic containing Tb^{3+} and Yb^{3+} ions. The emission of the $^2F_{5/2}\rightarrow{}^2F_{7/2}$ transition of the Yb^{3+} ion upon excitation at 476 nm, indicating that Tb-Yb energy transfer is effective. The decay curves of the $^5D_4$ state are reported in Fig. 3. Luminescence decay measurements were performed after excitation with the third harmonic of a pulsed Nd-YAG laser, at 355 nm; recording the signal by a multichannel analyzer .Nearly Single exponential luminescence decays are observed. The shortening of the luminescence decay observed for the co-doped samples is due to the energy transfer from the Tb^{3+}: $^5D_4$ to the Yb^{3+}: $^2F_{5/2}$.

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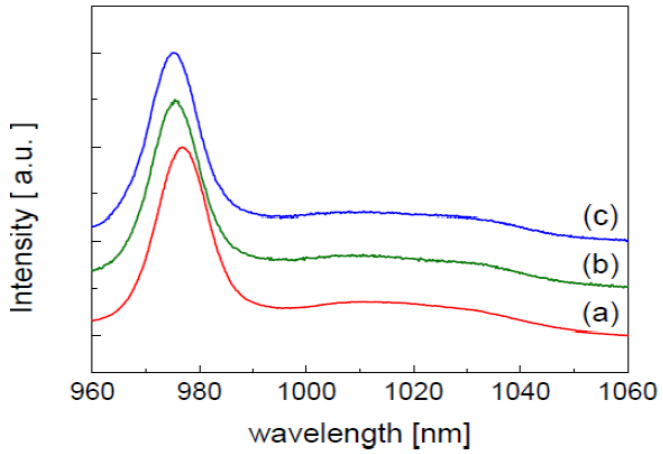

Fig.2 Room temperature photoluminescence spectra of the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+} ions after excitation at 476 nm for the three samples: (a) A1; (b) A2; (c) A3.

The effective quantum efficiency is defined by the ratio between the number of emitted photons and the number of photons absorbed by the material. In our case, a perfect down-conversion system would have an effective quantum efficiency value of 200%, corresponding to the emission of two photons for one absorbed. The relation between the transfer efficiency and the effective quantum efficiency is linear and is defined as:

$$\eta_{EQE} = \eta_{RE}\text{-}r(1\text{-}\eta_{RE\text{-}Yb})+2\eta_{RE}\text{-}Yb$$

where the quantum efficiency for the donor ion , $\eta_{RE\text{-}r}$, is set equal to 1. The evaluated values of energy transfer efficiency and effective quantum efficiency are reported in Table 2.

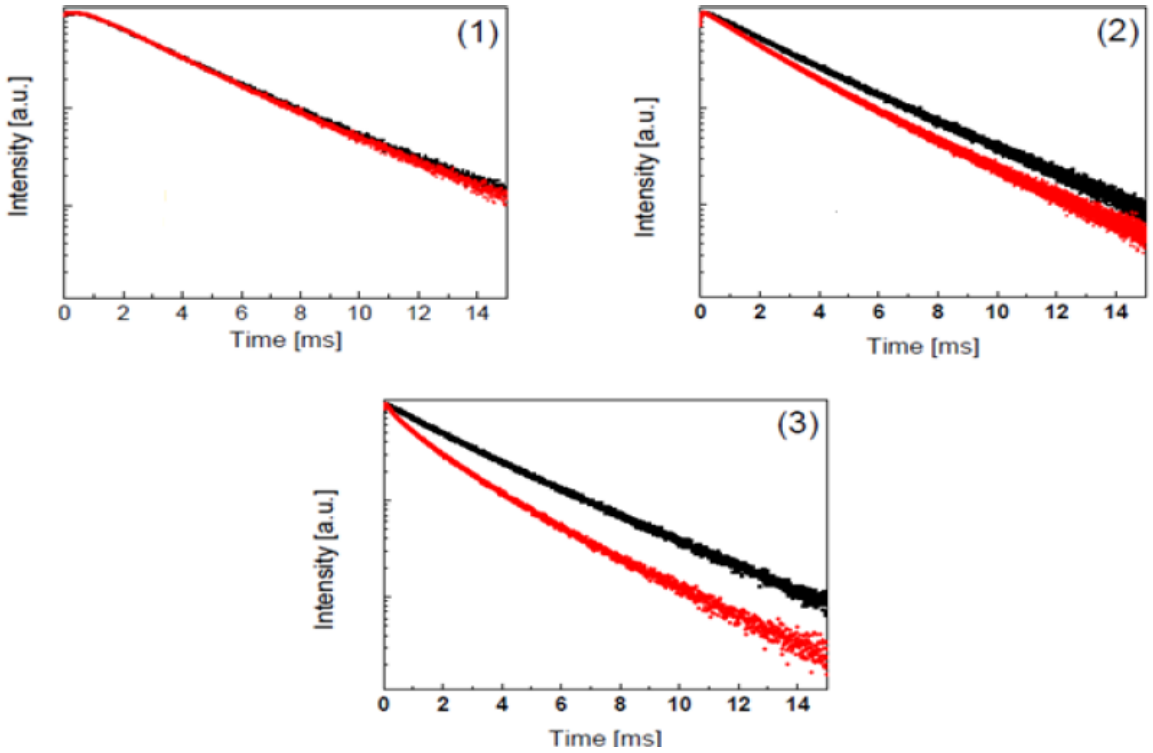

Fig. 3 Decay curves of the luminescence from the $^5D_4$ metastable state of Tb^{3+} ions upon excitation at 355nm. (1) Luminescence decay for the samples AR1 (black curve) and A1 (red curve); (2) Luminescence decay for the samples AR2 (black curve) and A2 (red curve); (3) Luminescence decay for the samples AR3 (black curve) and A3 (red curve).

The energy transfer efficiency $\eta_{RE\text{-}Yb}$, where RE indicates the donor ion, can be obtained experimentally by dividing the integrated intensity of the decay curves of the RE^{3+}-Yb^{3+} co-doped systems by the integrated intensity of the RE^{3+} single doped curve [13]:

$$\eta_{RE-Yb} = 1 - \frac{\int I_{ER-Yb}\,dt}{\int I_{ER}\,dt}$$

TABLE 2: TRANSFER EFFICIENCY AND EFFECTIVE QUANTUM EFFICIENCY AS FUNCTION OF (YB3++TB3+) MOLAR CONCENTRATION FOR SAMPLES WITH CONSTANT MOLAR RATIO YB/TB=4

Composition (Tb+Yb Concentration In Mol%)	1%	3%	5%
Transfer Efficiency	1%	18%	38%
Effective Quantium Efficiency	101%	118%	138%

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It is observed that the transfer efficiency for A1 and A2 samples, equal to 1% and 18%, respectively, and the highest transfer efficiency, equal to 38%, has been achieved in $70SiO_2$-$30HfO_2$ glass ceramic films activated by 1% of terbium and 4% of ytterbium (sample A3)

IV. Conclusions

In summary, efficient quantum cutting in Tb^{3+}:Yb^{3+} co-doped $70SiO_2$–$30HfO_2$ glass–ceramic waveguides deposited by a sol–gel route is reported in this paper. A fixed concentration rate [Yb]/[Tb] = 4 and increasing rare earths total amounts [Tb + Yb] = 1%, 3%, 5% have been studied. A clear NIR photoluminescence emission around 980 nm is detected, due to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+} ions. The energy transfer efficiency, estimated from the PL decay curves of the $^5D_4 \rightarrow {}^7F_5$ transition at 543.5 nm of Tb^{3+} ions, increases when increasing the total [Tb + Yb] concentration. The best performance is almost 38% and it is obtained for the most doped glass–ceramic sample.

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