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Energy transfer from Tb^{3+} to Yb^{3+} in silica hafinia glass ceramic for photovoltaic applications

S. Belmokhtar[1*], A. Bouajaj[1], M. Britel[1], S. Normani[2], C. Armellini[2], B. Boulard[3], F. Enrichi[4], F. Belluomo[5], A. Di Stefano[5], M. Ferrari[2]

[1]*Laboratory of innovative technologies, LTI, ENSA–Tangier, University Abdelmalek Essaâdi, Tangier, Morocco.*
[2]*CNR-IFN, Istituto di Fotonica e Nanotecnologie, CSMFO Lab. Via allaCascata 56/C, Povo, 38123 Trento, Italy*
[3]*Institut des Molécules et Matériaux du Mans, UMR 6283, Equipe Fluorures, Université du Maine, Av. Olivier Messiaen, 72085 Le Mans cedex 09, France.*
[4]*Veneto Nanotech, Laboratorio LANN, C.so Stati Uniti 4, 35127 Padova, Italy*
[5]*Meridionale Impianti SpA, Via Senatore Simonetta 26/D, 20867 Caponago (MB), Italy*

[*]*E-mail: belmoukhtar@ensat.ac.ma; Tel: (+212651386772)*

Abstract
The aim of this paper is to study the possibility to improve the efficiency of solar cells by using downconversion of high energy photons into low energy ones thanks to the Tb^{3+}/Yb^{3+} energy transfert mechanism in $70SiO_2$-$30HfO_2$ glass-ceramic waveguides. The preparation of the waveguides by a sol-gel method is first presented. Then results of compositional and optical (Photoluminescence) characterization are given. The result found is that the transfer efficiency is about 38% for the sample with the highest concentration of rare earths (5%).

Keywords: Quantum cutting; Down-conversion; Rare earths; Glass-ceramic; Energy transfer; photovoltaic solar cells

Introduction
Recent years have seen the development of large research on renewable energy and in particular photovoltaic. Indeed,improving the efficiency of solar cells is an ecological challenge.
One of the keyst o improve the efficiency of photovoltaic solar cells is the match between solar spectrum and semiconductor band gap. The trackf ollowed in this work is to modify the solar spectrum to adapt it to the cell [1].
In this work we focus on a down-conversion mechanism which can reduce thermal losses. The down conversion, also called quantum cutting, permits to generate more than one low energy photon exploiting the energy of one incident high energy photon [2,3]. Therefore, we investigated the Tb^{3+}/Yb^{3+} energy transfer efficiency in a $70SiO_2$-$30HfO_2$ glass-ceramic waveguide.
In silica-hafnia glass-ceramic the rare earth ions are embedded in hafnia nanocrystals which have a cut off frequency of about 700 cm^{-1} [4,5]. The presence of hafnia nanocrystal produces a strong reduction of the non-radiative transition process reflected by a lengthening of the measured emission lifetime [6,7].
The energy transfer from Tb^{3+} to $Yb^{3+}$was proved by the excitation and emission spectra. Yb^{3+} emission in the wavelength range of 950- 1100 nm ($^2F_{5/2}\rightarrow{}^2F_{7/2}$) was observed upon the excitation of $^5D_4$ energy level of Tb^{3+} at 484 nm in the Tb^{3+}-Yb^{3+} co-doped glass-ceramics, and the estimation of transfer efficiencies were performed using the decay curves of the $^5D_4$ state after excitation at 355nm.

2. Materials and methods
A series of glass ceramic $70SiO_2$–$30HfO_2$ planar waveguides samples co-doped by different concentration of Tb^{3+} and Yb^{3+} were prepared by sol–gel route using the dip-coating technique.

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 arth ions were thus produced. Table 1 gives the compositional and optical parameters of the obtained silica-hafnia planar waveguides.

Table 1. Rare earth concentration, relative index and layer thickness of the sample

Sample label	Terbiumconcentration in mol%	YtterbiumConcentration in mol%	n@543.5 nmTE polarization[± 0.001]	n@632.8 nmTE polarization[± 0.001]	Layerthickness[±0.2μm]
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 [8].
Photoluminescence spectroscopy was performed by farfield excitation using the 476 nm line of an Ar+ ion laser as excitation source. The luminescence spectrum in the region of the transition $^2F_{5/2} \rightarrow {}^2F_{7/2}$ 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 [9].

3. Results and discussion

The prepared samples are thin layers of 70 SiO_2 - 30 HfO_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, AR 2, and AR 3, respectively.
Fig. 1 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. 2. 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+}: $^2F_{5/2}$.

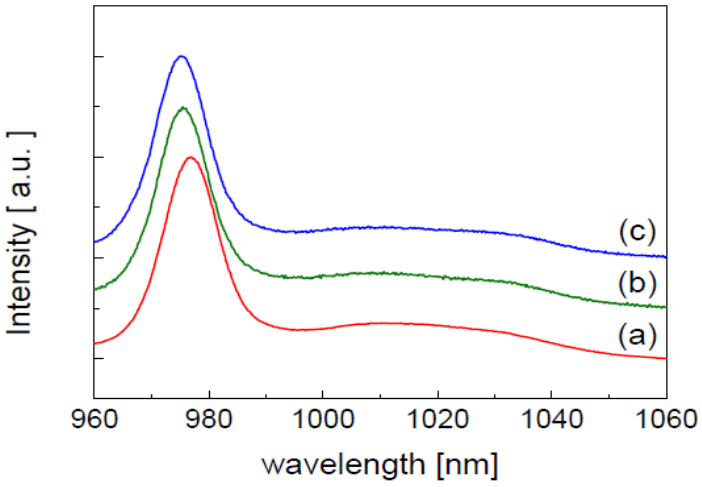

Figure 1: Room temperature photoluminescence spectra of the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+} ions after excitation at 476 nm for the three samples: (a) A1; (b) A2; (c) A3.

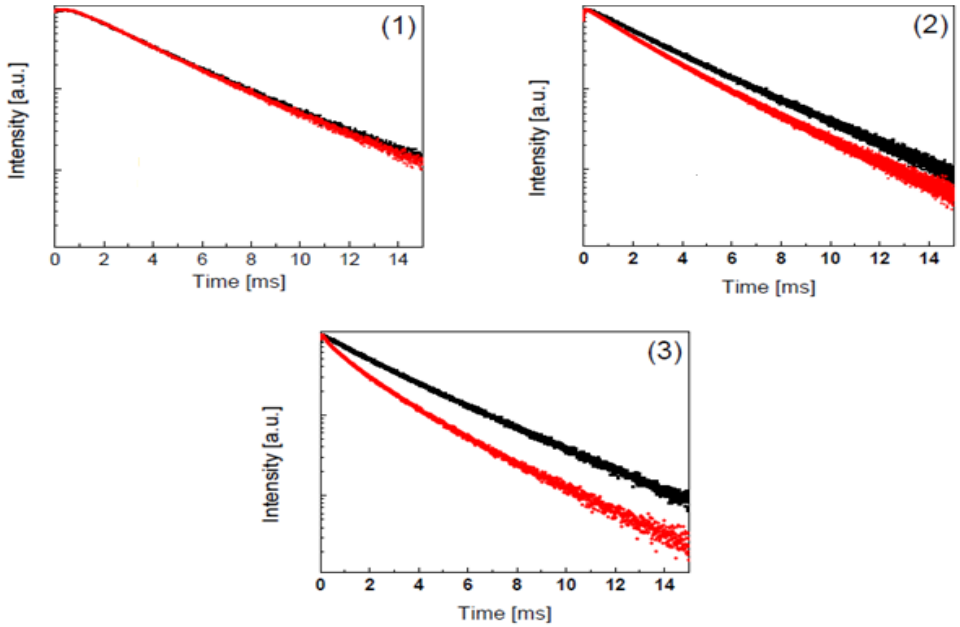

Figure 2: Decay curves of the luminescence from the $^5D_4$ metastable state of Tb^{3+} ions upon excitation at 355nm. (1) Luminescence decay for the samples AR1 (black curve) and A1 (red curve); (2) Luminescence decay for the samples AR2 (black curve) and A2 (red curve); (3) Luminescence decay for the 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 [10]:

$$\eta_{RE-Yb} = 1 - \frac{\int I_{RE-Yb} dt}{\int I_{RE} dt} \quad (1)$$

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:

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

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.

Table 2: Transfer efficiency and effective quantum efficiency as function of (Yb^{3+}+Tb^{3+}) molar concentration for B samples with constant molar ratio Yb/Tb=4

Composition (Tb+Yb concentration in mol %)	1%	3%	5%
Transfer efficiency	1%	18%	38%
Effective quantum efficiency	101%	118%	138%

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).

Conclusion

In summary, enhancement in the efficiencies of photovoltaic solar cells was realized by Silica-Hafnia ($70SiO_2$-$30HfO_2$) glass-ceramic waveguides containing Tb^{3+} and Yb^{3+} ions using sol gel method and dip-coating processing. Near-infrared emission at 980nm assigned to the $^2F_{5/2}\rightarrow {}^2F_{7/2}$ transition of the Yb^{3+} ions was observed upon excitation at 476 nm.
The energy transfer efficiencies were estimated from the decay curves of the $^5D_4$ metastable state of the Tb^{3+} ion, the transfer efficiency increased from 1% to 38% 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.

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