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Visible to NIR downconversion process in Tb^{3+}-Yb^{3+} codoped silica-hafnia glass and glass-ceramic sol-gel waveguides for solar cells

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ABSTRACT

The efficiency of photovoltaic solar cells is strongly related to the spectral absorption and photo-conversion properties of the cell's active material, which does not exploit the whole broadband solar spectrum. This mismatch between the spectrum of the solar light and the wavelength dependent cell's response can be partially overcome by using luminescent conversion layers in front or in the back of the solar cell. In this paper, the investigation of Tb^{3+}-Yb^{3+} co-doped SiO_2-HfO_2 glass and glass-ceramic waveguides is presented. Due to a down-conversion process based on cooperative energy transfer between one Tb^{3+} ion and two Yb^{3+} ions, a blue photon at 488 nm can be divided in two NIR photons at 980 nm. Films with different molar concentrations of rare earths, up to a total amount of [Tb + Yb] = 15%, were prepared by a sol-gel route, using dip-coating deposition on SiO_2 substrates. For all the films, the molar ratio [Yb]/[Tb] was taken equal to 4. The comparison of the energy-transfer efficiency between Tb^{3+} and Yb^{3+} ions in the glass and in the glass-ceramic materials demonstrated the higher performance of the glass-ceramic, with a maximum quantum transfer efficiency of 179% for the highest rare earth doping concentration. Moreover, experimental results and comparison with proper rate equations modelling showed a linear dependence of the photoluminescence emission intensity for the Yb^{3+} ions $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition at 980 nm on the excitation power, indicating a direct transfer process from Tb^{3+} to Yb^{3+} ions. The reported waveguides could find applications not only as downconverting filters in transmission but also as efficient solar concentrators in the near-IR spectral region.

1. Introduction

Nowadays, photovoltaics (PV) has become a solid technology, which is still in further progression and gaining larger portions of the electricity market. While the total renewable power capacity (in GW) increased by 18% from 2014 to 2015, the solar PV capacity increased by more than 28% [1]. The evolution of PV technology is driven by the constant reduction of the cost per watt of the solar modules, and this can be achieved by increasing the conversion efficiency per unit area at affordable costs, with the theoretical possibility to approach the thermodynamic limit up to 93% [2].

One of the major limitations to the efficiency of photovoltaic solar cells is the spectral mismatch between the limited absorption and photo-conversion properties of the cell's active material and the broadband spectrum of the incoming solar radiation. Indeed, the absorption of radiation and its electrical conversion in PV solar cells is spectrally controlled by the bandgap of the semiconductor material. This corresponds, for instance, to 1127 nm for c-Si (E_g = 1.1 eV) and to 690 nm for amorphous silicon (a-Si, E_g = 1.8 eV). Radiation with energy lower than the bandgap is not able to generate electron-hole pairs and it is lost. Radiation with energy much higher than the gap is also not efficient because most of the energy is lost in thermalization processes [3]. These two phenomena are the main sources of losses in PV solar cells, accounting respectively for a loss in power of 24% by the non-absorption of low energy photons and 32% by thermalization [4], which also increases the temperature of the cell, further reducing its efficiency [5]. Therefore, improving the match between the solar spectrum and the band gap of the semiconductor would result in a

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significant increase of the cell's efficiency [2]. This could be achieved, for example, by using a series of different bandgap semiconductors (as in multi-junction solar cells), each able to absorb a different part of the solar spectrum, but increasing significantly the technology complexity and finally the overall cost of the PV module. A different approach consists in using luminescent materials for downconverting and upconverting solar radiation [6–9], to transfer as much of the solar spectrum close to the energy gap of the semiconductor, where absorption and efficiency of the cell are maximum. Indeed, theoretical calculations indicate that it could be possible to increase the cell's efficiency to about 80% by concentrating the 300–1500 nm solar spectrum into a single narrow emission at the semiconductor bandgap [10].

Thus, the present work is focused on the development of rare earth doped waveguides for spectral downconversion. A detailed review of materials and methods for obtaining optical downconversion in solar cells applications was recently reported by de la Mora and co-workers [11]. In particular, rare earth ions are good candidates for spectral modification, thanks to their wide variety of electronic levels [12,13]. Examples of downconverting lanthanides materials are Pr^{3+}-Yb^{3+} codoped KY_3F crystals [14], Nd:SrTiO thin films [15], $LiGdF_4$:Eu^{3+} and $LiGdF_4$:Er^{3+}, Tb^{3+} [16], Tb^{3+}-Eu^{3+} codoped CaF2 nanocrystals [17]. Among rare earths, the combination of Tb^{3+} and Yb^{3+} ions can allow the occurrence of a quantum cutting process. Tb^{3+}-Yb^{3+} couple has been used in (Y,Yb) PO_4:Tb^{3+} [18], $GdAl_3(BO_3)_4$ [19], $GdBO_3$ [20], Y_2O_3 [21], CaF_2 nanocrystals [22], lanthanum borogermanate glasses [23], nanostructured glass-ceramic materials [24–31].

In Tb^{3+}-Yb^{3+} codoped systems, the relaxation $^2F_{5/2} \rightarrow {}^2F_{7/2}$ between the excited state and the fundamental level of Yb^{3+} ions produces a near infrared (NIR) photon at 980 nm, which is close to the edge of the silicon band gap. Tb^{3+} is used as sensitizer, with absorption in the blue at 488 nm through the $^7F_6 \rightarrow {}^5D_4$ energy levels and cooperative transfer to Yb^{3+} ions. The result of this process is the conversion of one high-energy blue photon at 488 nm in two lower-energy NIR photons at 980 nm. The choice of the matrix is also of paramount importance. Glass-ceramic materials can combine the advantages of the glass with the better spectroscopic properties of the crystals [24–26]. Based on previous experiments [27–31], the binary oxide composition 70% SiO_2 – 30% HfO_2 was chosen. Sol-gel derived silica-hafnia is a reliable and flexible system suitable for rare earth doping and fabrication of planar waveguides. It was demonstrated by XRD and EXAFS studies that in silica-hafnia glass ceramics the rare-earth ions are embedded in the ceramic HfO_2 nanocrystals [27], which have a high refractive index, excellent transparency and low phonon cutoff frequency of about 700 cm^{-1}. The presence of hafnia nanocrystals, therefore, provides a strong reduction of the non-radiative transition processes, making the silica-hafnia glass-ceramic a suitable matrix to produce rare-earth activated films for downconversion. As an additional feature, glass-ceramic waveguides allow to obtain high radiation confinement, opening new possibilities for integrating downconversion processes and light concentration.

Previous studies on 70% SiO_2 – 30% HfO_2 downconverting waveguides [28–30] codoped with Tb^{3+} and Yb^{3+} ions showed that, for a given concentration of donors (Tb^{3+}), the increase of the number of acceptors (Yb^{3+}) located close to the Tb^{3+} ions can have detrimental effects, due to concentration quenching. The optimal concentration rate resulted to be [Yb]/[Tb] = 4. On the other hand, the transfer efficiency increases with the total rare earth concentration and it is much higher in glass-ceramics than in glasses [30]. A maximum transfer efficiency value of about 55% was reported for glass-ceramic films activated by 1.8% of terbium and 7.2% of ytterbium ([Yb + Tb] = 9%), compared with only 26% for the glass counterpart with the same composition. It is worth observing that the transition from glass (G) to glass-ceramic (GC) is obtained by only changing the final annealing treatment: at 900 °C for the glass and 1000 °C for the glass-ceramics.

In the current paper, we focus on the energy-transfer process between the two rare earth ions in different structural environments (G and GC materials) at increasing values of rare earths' molar concentrations up to [Tb + Yb]/[Si + Hf] = 15%, still keeping the optimal rate [Yb]/[Tb] = 4. We also aim at obtaining a deeper understanding of the mechanisms involved in the process, in particular for the GC samples, which exhibit a higher performance.

2. Energy-transfer considerations

Although numerous studies on Tb^{3+}-Yb^{3+} co-doped materials for downconversion have been reported in the literature, the full understanding of the mechanisms underlying the energy transfer process is still debated, and different solutions have been used to explain different systems [28–38]. Most of the papers deal with the comparison of the lifetime of the $^5D_4$ excited state of Tb^{3+} ions with and without Yb^{3+} acceptor ions, to evaluate the transfer efficiency, assuming the absence of non-radiative processes.

The energy transfer efficiency η can be obtained experimentally by dividing the integrated intensity of the decay curves of the Tb^{3+}-Yb^{3+} co-doped systems by the integrated intensity of the Tb^{3+} single doped curve [28–30]:

$$\eta_{Tb-Yb} = 1 - \frac{\int I_{Tb-Yb}\,dt}{\int I_{Tb}\,dt} \tag{1}$$

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 downconversion 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:

$$\eta_{EQE} = \eta_{Tb-r}(1-\eta_{Tb-Yb}) + 2\eta_{Tb-Yb} \approx 1 + \eta_{Tb-Yb} \tag{2}$$

where the quantum efficiency for Tb^{3+} ions, η_{Tb-r}, is set equal to 1.

It must be noted that the previous expressions lead to an overestimation of the efficiency value, and some authors are critical on this approach, finding that for some oxyfluoride glasses the absolute measurement of the total efficiency could be much lower than what is estimated through the lifetime analysis [32].

A different approach to investigate the transfer process can be obtained by focusing on the power law dependence of the downconversion emission versus the excitation intensity. According to some researchers, this dependence should be linear [3,7,33,34]; for others, on the contrary, a nonlinear downconversion process would be responsible for the cooperative quantum cutting, and the slope n of the power dependence curve of Yb^{3+} emission was reported to be 0.5 [35] or between 0.5 and 1 [36,37]. In addition, it is interesting to note that Strek et al. [38] have observed a temperature dependence for the slope, with n = 0.5 at room temperature and n = 1 at lower temperatures (77 K), indicating the non-resonant nature of the quantum cutting energy transfer process.

In Fig. 1a a comprehensive energy level scheme for the two ions is reported. In a general description, after the absorption of one 488 nm blue photon, the excited Tb^{3+} ion in the $^5D_4$ energy level can transfer his energy to two Yb^{3+} ions in the ground state, resulting in the emission of two 980 nm photons. The energy transfer mechanism between these ions can be described either by a direct process or by the involvement of an intermediate virtual state (v). As reported in [37], if one considers only the Tb^{3+} system, the rate equations can be written as follows:

$$\frac{dN_1}{dt} = \sigma\phi N_0 - A_{Tb}N_1 - W_1N_1N_0 + W_2N_v^2 \tag{3}$$

$$\frac{dN_v}{dt} = 2W_1N_1N_0 - 2W_2N_v^2 \tag{4}$$

In the previous equations, N_0, N_1, N_v are the populations of the