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Tb^{3+}/Yb^{3+} doped aluminosilicate phosphors for near infrared emission and efficient down-conversion

Rocío Estefanía Rojas-Hernandez*, Luís F. Santos, Rui M. Almeida

Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

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ABSTRACT

The spectral mismatch between incident solar photons and the bandgap of crystalline silicon in solar cells results in major energy losses. Photons with energies lower than the bandgap are lost due to transparency, while those with energies above the bandgap value will be absorbed, generating electron-hole pairs, but consuming only the energy E_g, with the excess being lost as heat through thermalization. Despite intensive research to obtain efficient down-conversion (DC) materials for frequency shifting layers in c-Si cells, their development so far involves techniques which are not cost effective. Taking this into account, aluminosilicate phosphors co-doped with the Tb^{3+}/Yb^{3+} ion pair have been synthesized by sol-gel (SG) processing, a low cost technique which allows scalability and is especially useful to obtain films. The molar composition 90 SiO_2-10 $AlO_{1.5}$ was chosen as host to investigate if DC based on the Tb^{3+}/Yb^{3+} pair leads to efficient quantum cutting in such material. We demonstrate the potential of this approach to obtain near infrared DC emission in aluminosilicate matrix with a conversion efficiency of up to 158%, with potential to improve the performance of low bandgap photovoltaic solar cells.

1. Introduction

Over the past few decades, researchers have been struggling for efficient and cost-effective conversion of solar energy into electricity through photovoltaic (PV) solar cells. With incorporation of quantum-cutting phosphors, the loss of energy due to thermalization of hot charge carriers, especially in low bandgap semiconductors like c-Si, can be minimized by the conversion of high-energy solar photons into lower energy but above bandgap photons through down-shifting and quantum cutting luminescent materials [1].

Recently, near infrared (NIR) quantum cutting has been achieved by means of lanthanide (Ln) ions [2–6], due to their rich energy level structure and high quantum efficiency of light emission. The properties of quantum-cutting luminescent materials are dependent on various factors such as the host matrix composition and structure, nature of dopant ions and their concentrations, etc. The host material, in particular, has an essential role in the luminescence properties. Effective control of the above parameters can enhance the quantum-cutting ability of the phosphor material. Crystalline Si is by far the most widely used material in PV solar cells. Therefore, it is necessary to find suitable doped luminescent layers to improve the efficiency of silicon based (low bandgap) solar cells. Among the Ln ions, the Tb^{3+}/Yb^{3+} pair represents an important sensitizer/acceptor combination for DC, due to the absorption of Tb^{3+} around 480 nm (near the maximum solar spectrum intensity) and its energy transfer to two acceptor Yb^{3+} ions which emit in the range of ~ 970 to 1100 nm, only slightly above the Si bandgap. Therefore, a promising system to study second-order energy transfer processes is the combination of one Tb^{3+} and two Yb^{3+} ions, where the former center, optimized for strong absorption, transfers its energy to the latter two, optimized for efficient emission, by a second-order co-operative, simultaneous quantum cutting process, rather than a first-order or sequential one. Quantum cutting emission from Tb^{3+}/Yb^{3+} pair has been studied in different host matrices. $Y_{0.74}Yb_{0.25}Tb_{0.01}PO_4$ powder, prepared by solid state reaction [7], lithium borate glass [8] (with a quantum efficiency of 137% when doped with 1 mol% Tb^{3+} and 5 mol% Yb^{3+}, under 266 and 355 nm excitation), lanthanum borogermanate glasses [9] (with quantum efficiency of 148% when doped with 0.1 mol% Tb and 0.5 mol% Yb), Tb^{3+}/Yb^{3+} co-doped transparent oxyfluoride glass ceramics containing CaF_2 nanocrystals, with molar composition $60SiO_2–20Al_2O_3–20CaF_2–0.3Tb^{3+}–xYb^{3+}$ (quantum efficiency of 155% for 0.3 mol% Tb and 26 mol% Yb) [10] and $50SiO_2-20Al_2O_3-27CaF_2-1Tb^{3+}–xYb^{3}$ glass (quantum efficiency of 120% with 5% Yb^{3+} doping), synthesized by conventional melting-quenching method [11]. However, these techniques require high temperatures. In contrast, soft chemical methods (co-precipitation and SG method) or combustion synthesis have the advantage of

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* Corresponding author.
E-mail address: rociorojas@tecnico.ulisboa.pt (R.E. Rojas-Hernandez).

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decreased processing temperature. For example, $Y_{3-x-y}Tb_xYb_yGa_5O_{12}$ was prepared by solution combustion technique (with quantum efficiency of 128% for 0.01 mol% Tb^{3+} and 0.015 mol% Yb^{3+},under 379 nm excitation) [12] and Y_2O_3 powder samples were obtained by co-precipitation followed by an annealing process (the effective quantum efficiency was 137% [13] and 181% [14] with 0.01 mol% Tb^{3+}/0.2 mol% Yb^{3+} and 0.1 mol% Tb^{3+}/10 mol% Yb^{3+} doping, respectively, under 304 nm excitation). Regarding the luminescence measurements, these last two materials revealed enhanced properties, but the excitation was far from the maximum solar spectrum intensity (around ~ 500 nm). Glass ceramic films of molar composition 70 SiO_2 – 30 HfO_2 also appear to be a promising host obtained by SG dip-coating technique, with an effective quantum efficiency of 138% for 1 mol% Tb^{3+} and 4 mol% Yb^{3+} [15], when excited at 474 nm.

Among numerous luminescent materials for NIR emission, in this work we focus on an aluminosilicate phosphor doped with terbium and ytterbium, due to its good solubility for these ions, good chemical stability, sufficiently low phonon energies and easily synthesized at moderate temperature by SG processing, a low-cost technology that is versatile and scalable [16]. Moreover, the SG fabrication technique has the added advantage that it can easily be coupled with the deposition of films and multilayered structures in order to integrate the spectral conversion function into more complex but more efficient structures.

Although aluminosilicate materials have been studied intensively, the preparation by SG of homogeneous multicomponent samples based on the SiO_2 – Al_2O_3 matrix still presents challenges. And in spite of many works on the luminescent properties of doped SiO_2 – Al_2O_3 matrices, a correlation between their microstructures (which may include glassy and crystalline phases simultaneously in varying proportions) and photoluminescence (PL) emission characteristics is not yet clear at present. In this work, different Tb^{3+}/Yb^{3+} doped $SiO_2 - Al_2O_3$ mixtures were heat treated at 1100 °C, followed by a detailed investigation of the phases obtained and their contribution to the luminescence properties of the active ions. The PL behavior has been studied in detail as a function of the Tb and Yb concentrations.

2. Methods

2.1. Materials

For the preparation of the aluminosilicate sol, the precursors were TEOS (tetraethyl orthosilicate, Alfa Aesar, 98%) and $Al(NO_3)_3{\cdot}9H_2O$ (Aluminum nitrate nonahydrate, Alfa Aesar, 98.0–102.0%); Ethanol (Merck, 99.5%) and distilled water were used as solvents and HCl (Sigma Aldrich, 37%) was used as a catalyst. For the doped solutions, terbium and ytterbium nitrates were added in the required amounts. The samples prepared had the nominal composition (in mol%): (90-x-y) $SiO_2 - 10\ AlO_{1.5} - x\ TbO_{1.5} - y\ YbO_{1.5}$ ($x = 0, 1, 3, 5$ and $y = 0, 5, 10, 15$). Henceforth, all compositions in this paper are expressed in mol%.

2.2. Synthesis

As a first step, the hydrolysis of TEOS was initiated by preparing a solution composed of TEOS, water (in a molar ratio water/TEOS = 4), ethanol and HCl added in order to achieve pH = 2. After mixing, the solution was stirred and heated at approximately 70 °C during 1 h, labelled solution "A". A separate solution of Aluminum nitrate was prepared by dissolving the required amount of the nitrate in ethanol (labelled solution "B"), which was added slowly to solution "A" while stirring. This mixed solution (labelled "C") was then stirred for 10 min at 70 °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 several days and the bulk gels obtained were heat treated at 1100 °C for 30 min (with heating and cooling rates of about 5 °C/min), yielding samples in the form of powders.

2.3. Structural and microstructural characterization

The presence of crystalline phases was characterized by X-ray diffraction, XRD (Philips PW 3020 diffractometer using CuKα radiation, $\lambda = 1.5406$ Å and operating at 40 mA and 30 W). Additional structural characterization was carried out by unpolarized Raman microscopy (Labram HR 800 Evolution micro-Raman spectrometer, Horiba JobinYvon, using a 532 nm diode laser for excitation and a 600 grove mm^{-1} grating); the laser power at the samples was 10 mW and the data were collected in the range of 100–1800 cm^{-1} at a resolution of 4 cm^{-1} at room temperature (RT), with a 100× objective lens.

2.4. Luminescence characterization

The luminescence properties of these materials were investigated by measuring emission and excitation spectra. The PL spectra of the phosphors were recorded with a spectrofluorimeter (Fluorolog®-3-22, HORIBA Jobin Yvon) at RT, working with a continuous wave 450 W Xe lamp; a R928 Hamamatsu detector was used for visible detection and a liquid-N_2-cooled DSS-IGA020L detector (Electro-Optical Systems, Inc.) for the NIR range. The emission spectra were measured over the visible wavelength range of 500–700 nm and in the NIR range of 925–1200 nm, with excitation at λ_{exc} = 484 nm. The experimental spectra were corrected for variations in lamp intensity over the spectral range, as well as for the excitation monochromator, emission monochromator and detector responses.

The PL decay profiles were also recorded with the same instrument, after the samples were exposed to monochromatic light of λ_{exc} = 484 nm. The signal was monitored by a Hamamatsu R928 photomultiplier tube. All PL measurements were collected at a right angle to the excitation beam.

3. Results and discussion

Fig. 1**(a–c)** show the XRD patterns of the samples with different dopant concentrations treated at 1100 °C during 30 min. While the sample with 1% Tb^{3+} is essentially amorphous, with no distinct diffraction peaks, an increase in the Tb concentration up to 3 or 5% causes a distinct diffraction peak to appear at 2θ ~ 21.87°, which can be assigned to cristobalite SiO_2. It is known that there are two polymorphs of cristobalite, the high-temperature β-phase (cubic symmetry) and the low temperature α-phase (tetragonal symmetry) [17]. The α-polymorph patterns are characterized by a peak at 2θ = 21.6° (JCPDS no. 04-0379), while the β-polymorph exhibits a main peak at 2θ = 21.98° (JCPDS no. 27-0605). The peak around 2θ = 36° could attributed to reflection from the (220) planes of β-cristobalite, corresponding to 2θ = 35.627°, or to the reflections from (200) and (112) planes of α-cristobalite, corresponding to 2θ = 36.056° and 36.373°, respectively. In addition, cristobalite also appeared in the samples doped with 1 or 3% Tb^{3+} and co-doped with 5% and 10% Yb^{3+}. On the other hand, the samples with 1% and 3% Tb^{3+} plus 15% Yb^{3+} show diffraction peaks related to β-$Yb_2Si_2O_7$ (JCPDS card 00-030-1440), while samples with 5% Tb^{3+} plus 5, 10 or 15% Yb^{3+} have diffraction peaks assigned to β-$Yb_2Si_2O_7$, but not to cristobalite. Therefore, the formation of β-$Yb_2Si_2O_7$ is favored at high [Yb^{3+}] = 15%, or even by Yb^{3+} contents < 15% (5 or 10%), if the [Tb^{3+}] = 5%.

Ln silicate systems have great interest for laser materials and phosphors. Despite the similar radii of Y^{3+} and Yb^{3+} ions, while there are seven different polymorphs reported for $Y_2Si_2O_7$, namely α, β, γ, δ, ε, ζ and η, there is only a β-polymorph known for $Yb_2Si_2O_7$ [14]. Although we have not been able to assess what are the fractions of the crystalline and amorphous phases present in each case, the absence of an amorphous halo at ~ 22° suggests that the co-doped samples with 15% Yb^{3+}, or those with 5% Tb^{3+} and 5 or 10% Yb^{3+}, are formed