

Up-conversion in sol-gel derived nano-glass-ceramics comprising NaYF₄ nano-crystals doped with Yb³⁺, Ho³⁺ and Tm³⁺

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ABSTRACT

NaYF₄ is an excellent host material for rare-earth ions presenting very high efficiencies in up-conversion processes. Thus, nano-glass-ceramics containing NaYF₄ nano-crystals emerge as promising candidates for general lighting appliances and integrated optical devices. Here we report highly transparent sol-gel derived nano-glass-ceramics comprising Yb³⁺-Ho³⁺ and Yb³⁺-Ho³⁺-Tm³⁺ co-doped NaYF₄ nano-crystals. A structural analysis by means of X-ray diffraction measurements confirmed the formation of NaYF₄ nano-crystals during thermal treatment. Luminescence features have been related to the crystallinity degree of the samples. Violet, blue, green and red up-conversion emissions were obtained under infrared excitation at 980 nm and corresponding mechanisms involved have been analysed. Additionally, the total visible up-conversion emission has been quantified in terms of the standard chromaticity coordinates. In particular, an overall colour emission, very close to the standard equal energy white-light illumination point of the chromaticity diagram, was obtained in the Yb³⁺-Ho³⁺-Tm³⁺ triply-doped samples.

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1. Introduction

Rare-earth (RE) doped nano-structured materials have attracted a great interest in recent years due to luminescent properties induced by their nano-scale size with potential applications in the field of solid state luminescence [1–5]. In this way, emission efficiency can be enhanced significantly with an appropriate choice of the host matrix. In particular, oxyfluoride nano-glass-ceramics present very high quantum efficiency due to low phonon energy of fluoride crystals, reducing the non-radiative decay rates, combined with mechanical and chemical stabilities of the glassy matrix. Moreover, the shortening of distances among RE ions in nano-crystals favours energy transfer processes [6,7]. Thus, there is an increasing interest due to their applications in fields such as solid state lasers, displays, phosphors, medical imaging, communications and solar cells [1–3,8–10].

NaYF₄ is known to be a very efficient host material showing high intensity for near-infrared to UV-visible up-conversion emissions of RE ions due to low energy phonon modes (300–400 cm⁻¹) [11–13], specially with suitable doping concentrations. In this respect, multi-phonon relaxation is reduced, increasing the probability of radiative transitions [14,15].

The development of highly transparent nano-glass-ceramics is desirable in order to reduce light scattering and consequent loss

of luminescence efficiency. In this sense, sol-gel technique [16] permits to develop nano-glass-ceramics by an adequate heat-treatment of the precursor bulk glasses, with the advantage of homogeneous doping, predetermined RE ions concentration and controlled nano-crystal sizes. In addition, this low cost method is characterized by its simplicity, opposite to technical requirements and difficulties of conventional melt-quenching techniques at high temperatures [17].

In previous works, we have successfully obtained highly transparent nano-structured Eu³⁺ and Er³⁺ doped silica glass-ceramics by sol-gel technique, with SnO₂ [3,4] and LaF₃ [18,19] nano-crystals, respectively. Glassy and nano-crystalline environments for RE ions were distinguished by means of site selective and time resolved measurements [4]. Moreover, we have also developed sol-gel derived nano-glass-ceramics comprising RE-doped NaYF₄ nano-crystals for up-conversion luminescence applications [20].

Luminescence properties of Yb³⁺-Ho³⁺ co-doped glasses can be found in the literature, prepared by the melt-quenching method in a fluorindate glass matrix [21] and nano-glass-ceramics by the sol-gel method comprising LaF₃ nano-crystals [22]. Ho³⁺ ions embedded into the nano-crystals in small concentrations have been found to be an efficient source of visible emission due to energy transfer from excited Yb³⁺ ions by stepwise up-conversion mechanisms [21,22].

In this work, we report Yb³⁺-Ho³⁺ and Yb³⁺-Ho³⁺-Tm³⁺ doped NaYF₄-based nano-glass-ceramics prepared by an adequate heat-treatment of precursor glasses synthesized by the sol-gel technique. A structural analysis has been carried out by means of

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XRD patterns analysing the crystallization degree of nano-glass-ceramics as function of the heat-treatment temperature of the sample. Up-conversion spectra under infrared laser excitation at 980 nm for different thermal treatments and pump powers have been obtained and corresponding mechanisms have been discussed. The total up-conversion emission, seen by the naked eye, has been quantified by means of standard chromaticity diagram (CIE) formalism. A comparison between co-doped and tri-doped samples reveals that the introduction of Tm^{3+} ions, with an appropriate heat-treatment and doping levels, results in the addition of a blue up-conversion emission, which along with the green and red ones, gives rise to an efficient white light generation seen by the naked eye.

2. Experimental

Silica glasses with composition $95\text{SiO}_2-5\text{NaYF}_4$ co-doped with 0.3Yb^{3+} and 0.1Ho^{3+} (mol%) and tri-doped with $0.3\text{Yb}^{3+}-x\text{Ho}^{3+}-0.1\text{Tm}^{3+}$ with $x = 0.1, 0.05$ and 0.025 (mol%) were obtained by sol-gel method as described in Refs. [17,20] hydrolyzing tetraethoxysilane (TEOS) with a mixed solution of ethanol and H_2O , using acetic acid as a catalyst. The molar ratio of TEOS:ethanol: H_2O : CH_3COOH was 1:4:10:0.5. The required quantity of $\text{Y}(\text{CH}_3\text{COO})_3 \cdot x\text{H}_2\text{O}$, NaCH_3COO , $\text{Yb}(\text{CH}_3\text{COO})_3 \cdot x\text{H}_2\text{O}$, $\text{Ho}(\text{CH}_3\text{COO})_3 \cdot x\text{H}_2\text{O}$ and $\text{Tm}(\text{CH}_3\text{COO})_3 \cdot x\text{H}_2\text{O}$, were dissolved in CF_3COOH and H_2O solution, to ensure an homogeneous dispersion, which was slowly mixed with the initial solution. The molar ratio of metal ions to CF_3COOH was 1:4. After gelation, precursor glasses were obtained by slow solvent evaporation. Finally, these sol-gel glasses were heat-treated in air at different temperatures ranging from 500 to 650 °C, optimum temperatures in order to achieve controlled precipitation of nano-crystallites, giving rise to transparent nano-glass-ceramics.

X-ray diffraction patterns (XRD) were carried out by using a Cu anode ($\text{Cu K}\alpha_{1,2}$ in the 10–90 2-Theta range. Measurements were corrected by using LaB_6 .

Luminescence measurements were obtained by exciting the samples with light from a 300 W Xe arc lamp, passed through a 0.25 m double-monochromator and detecting with a 0.25 m monochromator equipped with a photomultiplier. Up-conversion emission spectra were obtained under 980 nm laser excitation with a pump power up to 200 mW, focused with a microscope objective of 3 mm focal length. All spectra were collected at room temperature and corrected by the instrumental response.

3. Results and discussion

3.1. Structural characterization

X-ray diffraction measurements, carried out in the $95\text{SiO}_2-5\text{NaYF}_4: 0.3\text{Yb}^{3+}$ and 0.1Ho^{3+} (mol%) transparent nano-glass-ceramics heat-treated from 500 to 650 °C, show peaks with increasing intensity and sharper structure when increasing the heat-treatment temperature, see Fig. 1. In this respect, these peaks indicate the segregation of cubic NaYF_4 nano-crystals (JCPDS No. 06-0342) into the sample, with no second crystalline phase. It is remarkable that for lower treatment temperatures, i.e. 500 and 550 °C, diffraction peaks were hardly detected showing a low degree of crystallization. Nano-crystals sizes were calculated from the width and the position of the XRD peaks by using Scherrer's equation, $D = K\lambda/\beta \cos \theta$, where D is the crystal size, λ the X-ray wavelength, θ the diffraction angle, β the full-width at half-maximum (FWHM) of the diffraction peak and K a constant determined by the instrument. The corresponding radii obtained, 6.3 and 9.7 nm under 600 and 650 °C thermal treatment of the $\text{Yb}^{3+}-\text{Ho}^{3+}$

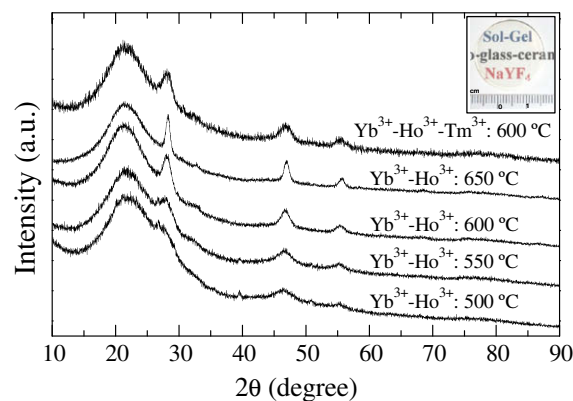


Fig. 1. XRD patterns of $95\text{SiO}_2-5\text{NaYF}_4: 0.3\text{Yb}^{3+}$ and 0.1Ho^{3+} (mol%) and $95\text{SiO}_2-5\text{NaYF}_4: 0.3\text{Yb}^{3+}, 0.025\text{Ho}^{3+}$ and 0.1Tm^{3+} (mol%) for indicated heat-treatment temperatures. Inset shows a photograph of a transparent sol-gel derived nano-glass-ceramics.

Table 1

Calculated average nano-crystals radii of $95\text{SiO}_2-5\text{NaYF}_4: 0.3\text{Yb}^{3+}$ and 0.1Ho^{3+} and $95\text{SiO}_2-5\text{NaYF}_4: 0.3\text{Yb}^{3+}, 0.025\text{Ho}^{3+}$ and 0.1Tm^{3+} (mol%) for indicated heat-treatment temperatures.

Heat-treatment (°C)	Radii (nm)
$\text{Yb}^{3+}-\text{Ho}^{3+}: 500$ °C	3.0
$\text{Yb}^{3+}-\text{Ho}^{3+}: 550$ °C	4.0
$\text{Yb}^{3+}-\text{Ho}^{3+}: 600$ °C	6.3
$\text{Yb}^{3+}-\text{Ho}^{3+}: 650$ °C	9.7
$\text{Yb}^{3+}-\text{Ho}^{3+}-\text{Tm}^{3+}: 600$ °C	6.7

co-doped sample respectively, see Table 1, point up similar results to those obtained in $\text{SiO}_2-\text{LaF}_3$ [22,23] and also in NaYF_4 nano-glass-ceramics [20]. By other side, XRD patterns for the 500 and 550 °C heat-treated $\text{Yb}^{3+}-\text{Ho}^{3+}$ co-doped samples, with calculated radii of 3.0 and 4.0 nm respectively, indicate a scarce degree of crystallinity and a predominant glassy environment revealing a lower partition of RE dopant ions into precipitated nano-crystals. Therefore, subsequent poor optical properties would be expected. Moreover, the XRD curve of the $\text{Yb}^{3+}-\text{Ho}^{3+}-\text{Tm}^{3+}$ tri-doped sample is also shown in Fig. 1. Corresponding nano-crystals radii around 6.7 nm were also calculated, see Table 1, comparable in size to $\text{Yb}^{3+}-\text{Ho}^{3+}$ co-doped samples.

3.2. Visible luminescence

Luminescence measurements of $95\text{SiO}_2-5\text{NaYF}_4: 0.3\text{Yb}^{3+}$ and 0.1Ho^{3+} (mol%) were obtained from the samples heat-treated at 600 and 650 °C, respectively. Emission and excitation bands have been assigned to transitions of Yb^{3+} and Ho^{3+} ions, according to energy level diagrams of Fig. 2.

Excitation spectra of $95\text{SiO}_2-5\text{NaYF}_4: 0.3\text{Yb}^{3+}$ and 0.1Ho^{3+} (mol%) detecting at 540 nm, corresponding to the $^5\text{S}_2, ^5\text{F}_4 \rightarrow ^5\text{I}_8$ transition, are presented in Fig. 3, for 600 and 650 °C heat-treatment temperatures, respectively. Non-radiative decays from upper-lying levels indicate a glassier environment due to a stronger multi-phonon relaxation rate. In this way, Fig. 3 shows relative lower intensity of the emission bands in the range 300–400 nm for the sample heat-treated at 650 °C, pointing out a higher degree of crystallinity at upper heat-treatment temperatures of the samples, as previously confirmed by XRD patterns.

Visible emission spectra are presented in Fig. 4 exciting at 415.5 nm ($^5\text{I}_8 \rightarrow ^5\text{G}_5$) and 540 nm ($^5\text{I}_8 \rightarrow ^5\text{S}_2, ^5\text{F}_4$) for two different heat-treatment temperatures of the $\text{Yb}^{3+}-\text{Ho}^{3+}$ co-doped samples, normalized at 640–660 nm emission band. Green emissions at

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