Novel Sr_2LuF_7-SiO_2 nano-glass-ceramics: structure and up-conversion luminescence

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Keywords: nano-glass-ceramics, rare-earth ions, sol-gel technique, energy transfer, up-conversion.

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1.   Introduction

Rare earth (RE)-doped up-conversion (UC) materials are a very important class of materials since they present a broad range of applications, such as infrared quantum counters detectors, temperature sensors, compact solid-state lasers, lighting and displays, solar cells, labelling, biomedical imaging and so on [1-11]. Among the up-converters RE ions, Tm^{3+}, Er^{3+} and Ho^{3+} have been extensively used due to their ladder-like energy levels structures, which introduce abundant energy levels into the gap of lattice host enabling photon absorption and subsequent energy transfer (ET) steps, giving rise to efficient UV, VIS and NIR emissions under low pump-power densities. Moreover, in order to further enhance the UC efficiency, these ions are often co-doped with Yb^{3+} ions, due to their large absorption cross-section in the 900-1100 nm NIR region, corresponding to the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition, and a very efficient ET to these ions when they are very close in the host lattice. Additionally, compared to the co-doped RE ions, Yb^{3+} exhibit a reduced tendency for concentration-dependent quenching. Thus, very high Yb^{3+} concentrations can be used in order to increase their excitation probabilities.

Among RE-doped UC materials, RE-doped transparent oxyfluoride nano-glass-ceramics (nGCs) take advantage of the mechanical, thermal and chemical properties of oxide glass and the low phonon energy of fluoride environments that prevents non-radiative multiphoton relaxations. In this regard, RE doped-nGCs containing Y, La and Gd based-nanocrystals (NCs) have been extensively investigated [12-21], due to the facile incorporation of RE ions into the fluoride nanocrystalline phase (Y^{3+}, La^{3+} and Gd^{3+} ions can be easily substituted by RE^{3+} ions), which enhances the UC efficiency.   On the other hand, RE-doped Lu-based fluorides, which present interest owing to their applications as scintillators, related to their high absorption cross-section for any kind of radiation [22-26], have received less attention. In particular, it should be noticed that there is only one report on RE doped-Sr_2LuF_7 systems which was ascribed to cubic structure [27]. Moreover, there are only few reports about Lu-based nGCs, which have been prepared by melt-quenching method. Thus, Guo et al. studied the luminescent properties of nGCs containing $BaLuF_5$ doped with Eu^{3+} [28] or Er^{3+} [29] ions, $NaLuF_4$ co-doped with Yb^{3+}-Tb^{3+} ions [30] and KLu_2F_7 doped with Er^{3+} [31].

Additionally, Chen et al. analysed the distribution of RE ions and the UC luminescence in nGCs containing Eu^{3+} doped-LuF_3 [32] and Yb^{3+}-(Er^{3+}/Tm^{3+}) co-doped $NaLuF_4$ NCs [33], respectively. Therefore, in spite of the expensive lutetium raw materials and tough preparation [28-30], there is a growing interest in Lu-based nGCs as potential materials for scintillators [34] and also because they present excellent properties as up-conversion host matrix [26, 31, 33, 35]. In this respect, an alternative preparation procedure to obtain nGCs is through thermal treatment of precursor glasses obtained by sol-gel method. Besides its low cost, this method presents advantages such as its simplicity and precise control of the final composition [36] in comparison with conventional melting methods. Moreover, starting materials, in particular RE-dopant ions, can be mixed in the sol-gel method at molecular level, which improves the luminescence.

In this work we present for the first time RE doped nGCs containing Sr_2LuF_7 NCs, obtained from the sol-gel glasses. A complete structural analysis has been carried out, leading to the assignment of the Sr_2LuF_7 nanocrystalline phase as cubic. In order to analyse the incorporation grade of the RE dopant ions in the NCs, the Eu^{3+} ions were used as structural optical probes taken advantage of the hypersensitive character of the $^5D_0 \rightarrow {^7F_2}$ transition, allowing us to discern between crystalline and glassy environments for RE ions. For nGCs co-doped with Yb^{3+}-Tm^{3+}, Yb^{3+}-Er^{3+} and Yb^{3+}-Ho^{3+} ions, intense UV, VIS and NIR UC emissions under 980 nm excitation were observed, and their corresponding ET mechanisms were described.

2. Experimental

Silica glasses have been prepared by sol-gel method, as described in ref. [20], with the following compositions: $95SiO_2$-$5Sr_2LuF_7$ doped with $0.1Eu^{3+}$ and co-doped with $1.0Yb^{3+}$-$0.1Tm^{3+}$, $1.0Yb^{3+}$-$0.1Er^{3+}$ and $1.0Yb^{3+}$-$0.1Ho^{3+}$. Tetraethoxysilane (TEOS) $Si(OCH_2CH_3)_4$, used as a source of SiO_2, was hydrolysed for 1 h at room temperature with a mixed solution of ethanol and deionised H_2O, using acetic acid as a catalyst. The molar ratio of TEOS:ethanol:H_2O:CH_3COOH was 1:4:10:0.5. $Sr(CH_3COO)_2$ and $Lu(CH_3COO)_3 \cdot xH_2O$ were used as sources of Sr and Lu, respectively. The required quantities of $Sr(CH_3COO)_2$, $Lu(CH_3COO)_3 \cdot xH_2O$, $Eu(CH_3COO)_3 \cdot xH_2O$, $Yb(CH_3COO)_3 \cdot xH_2O$, $Tm(CH_3COO)_3 \cdot xH_2O$, $Er(CH_3COO)_3 \cdot xH_2O$ and $Ho(CH_3COO)_3 \cdot xH_2O$ were dissolved in a CF_3COOH and H_2O solution and slowly mixed with the initial solution. The molar ratio of Sr^{2+}, RE (Lu^{3+}, Eu^{3+}, Yb^{3+}, Tm^{3+}, Er^{3+}, Ho^{3+}) ions to CF_3COOH was 2:1:7. In order to make the solution homogeneous it was stirred vigorously for 1 h at room temperature. A highly transparent gel was obtained by leaving the resultant homogeneous solution in a sealed container at 35 ºC for a week. The gels were then dried by slow evaporation for approximately four weeks to remove residual water and solvents. Finally, these sol-gel glasses were heat-treated in an air atmosphere up to 700 °C in order to achieve the controlled precipitation of Sr_2LuF_7 nanocrystals required to produce transparent nGCs.

Powder X-ray diffraction (XRD) patterns of the samples were recorded with a Philips Panalytical X'Pert Pro diffractometer equipped with a primary monochromator, a Cu $K_{\alpha 1,2}$ radiation source, and an X'Celerator detector. The XRD patterns were collected with a step of 0.016º in the 2θ angular range from 15-90º and an acquisition time of 2 h. Furthermore, the diffraction pattern of LaB_6 was used as an internal standard to calibrate the parameters of the instrumental profile. Transmission electron microscopy (TEM-HRTEM) images were obtained using a JEOL 2010F microscope operating at 200 kV, equipped with a Field Emission Gun, which allowed us to achieve a point-to-point resolution of 0.19 nm. Samples were prepared by dispersing fine powder, obtained by grinding the samples, in acetone and dropping them onto carbon-coated copper grids. Selected areas of the HRTEM images were mathematically filtered by means of Fast Fourier Transform (FFT) analysis resulting in Power Spectra patterns,

corresponding to the eigen-frequencies of the observed NCs. Furthermore, the relevant frequencies were selected to filter the noise in the zoomed areas of the HRTEM images and to produce higher contrast images of the atomic planes of the observed NCs.

Transmittance of nGCs was measured by means of a Perkin-Elmer Lambda 9 ultraviolet-visible-infrared (UV-VIS-IR) spectrophotometer with a resolution of 0.5 nm in the wavelength range of 320-850 nm.

Luminescence measurements were obtained by exciting the samples with light from a 75 W Xe arc lamp whose beam was directed through a 0.2 m monochromator (PTI spectrometer controlled by Felix32 software) and detected with a 0.2 m monochromator with a R928 photomultiplier. The time resolved photoluminescence measurements were carried out using a PTI spectrometer, where a 75 W Xenon flash lamp acts as excitation source. Moreover, UC measurements were carried out with a laser diode at 980 nm with a pump power up to 200 mW and a beam diameter of 2 mm, focused with a 50 mm lens and detected through a 0.2 m monochromator equipped with a photomultiplier. All spectra were collected at room temperature and corrected for the instrumental response. CCD digital camera was used to take colour pictures of UC luminescence emitted by the nGCs.

3. Results and Discussion

3.1 Structure and morphology

Structural characterization was carried out in terms of XRD patterns and TEM-HRTEM images. Fig. 1 shows the XRD curves of different nGCs with composition $95SiO_2$-$5Sr_2LuF_7$ RE^{3+}-doped, heat-treated from 250 to 700 ºC along with a precursor glass heat-treated at 200 ºC. In the sample treated at 200 ºC, only a broad diffraction band characteristic of SiO_2 in amorphous state is observed. However, in the samples treated from 250 ºC to 700 ºC, superposed to the broad amorphous band, diffraction peaks can be clearly distinguished at 27.0, 31.2, 44.9, 53.2, 55.7, 65.3, 72.0, 74.2 and 83.0º in the 2θ range from 15 to 90º, which correspond to the precipitation of Sr_2LuF_7 NCs in the cubic phase (fluorite structure, space group *Fm-3m*) [27]. It can be clearly seen that, when increasing the heat-treatment temperature, peaks become narrower and more intense, indicating a gradual growth and greater degree of crystallinity. Thus, by

using the Scherrer equation, from the width and position of diffraction peaks, mean NCs sizes of 4.5, 6.0, 7.8, 8.8 and 11.5 nm are obtained for heat treatments at 250, 275, 300, 500 and 700 ºC, respectively. These values are relatively smaller than those obtained by L. Gong et al. [27], around 12-19 nm. Importantly, all nGCs present a high degree of transparency due to the small NCs sizes, avoiding the scattering due to a mismatch of the refractive index (see inset in Fig. 1).

In addition, RE-doped nGCs containing Sr_2LuF_7 NCs, heat-treated at 700 ºC, were characterized in terms of TEM and HRTEM images (see Fig. 2). In that respect, Fig. 2a reveals well dispersed spherical NCs clearly distinguished over the gray background in the TEM image, corresponding to the crystalline and the glassy phase, respectively. The average nanoparticle size estimated from the TEM image is around 10 nm, in reasonably good agreement with the previous NC size calculated by the Scherrer equation. Moreover, HRTEM image shown in Fig. 2b presents the detailed lattice structure of a single precipitated Sr_2LuF_7 NC, which is indicative of a high degree of crystallinity. The power spectrum of the FFT pattern obtained from the selected NC and a higher contrasted image of this NC are also presented in the inset of Fig. 2b, obtained by filtering the direct image by using the frequencies determined from the FFT pattern. Lattice fringes can be clearly distinguished with an observed d-spacing of 2.1 Å, in good agreement with the expected lattice spacing value for the (220) plane of Sr_2LuF_7 cubic phase by using the Bragg equation.

In order to investigate the distribution of the RE dopant ions in the nGCs containing Sr_2LuF_7 NCs, the local environment of Eu^{3+} ions can be firstly analysed taking into account their luminescent features as structural optical probe ion. Thus, Fig. 3 shows the emission spectra of Eu^{3+} doped samples heat-treated at indicated temperatures, exciting at 392 nm, corresponding to the transition from the $^7F_0$ ground level to the $^5L_6$ excited level. It can be clearly seen that the relative intensities and spectral profiles strongly depend on the heat-treatment. For the sample heat-treated at 200 ºC, only broad emission peaks at 580, 593, 613, 653 and 700 nm are observed, related to transitions from $^5D_0$ to ^7F_J (J=0-4) levels respectively, according to the energy level diagram shown in the inset of Fig. 3. Moreover, the intensity ratio R of the $^5D_0 \rightarrow F_2$ transition to the $^5D_0 \rightarrow ^7F_1$ one [37], (very sensitive and insensitive to the local symmetry surrounding Eu^{3+} ions, respectively), presents an R value of 4.3. Thus, both results suggest that the Eu^{3+} ions should reside in a site with relatively high phonon energy and low symmetry, without inversion centre, which can be related with a glassy

environment for Eu^{3+} ions, according to the results obtained by XRD measurements. Similar spectral features are obtained for the sample heat-treated at 250 ºC, but with a smaller R value of 1.7 suggesting the incorporation of Eu^{3+} ions into the sites with inversion symmetry in the face-centered cubic Sr_2LuF_7 NCs (around 5 nm size), substituting the Lu^{3+} ions, with similar ionic radii and valence. For samples treated at higher temperatures, a significant reduction in R is observed (R $\approx$ 0.5), which is consistent with nGCs comprising larger NCs (around 8-11 nm). In addition, emissions coming mainly from upper energy level $^5D_1$ are also observed, showing higher intensities for the nGCs treated at higher temperatures, which also supports the progressive incorporation of Eu^{3+} ions into lower phonon energy environments of the precipitates Sr_2LuF_7 NCs.

Furthermore, Fig. 4 shows the excitation and emission spectra of the Eu^{3+} doped Sr_2LuF_7 nGCs heat-treated at 700 ºC, by detecting and exciting at the indicated wavelengths. The excitation spectra, by detecting at 592 and 616 nm, show the characteristic excitation peaks of Eu^{3+} ions related with transitions from $^7F_0$ ground level to the excited levels labelled in the figure (see energy level diagram in the inset of Fig. 3). Although both excitation spectra seem to be very similar, when one looks closer, it appears that the spectrum obtained by detecting the emission at 592 nm (insensitive to the crystal field environment for the Eu^{3+} ions) presents narrower and more resolved Stark components than those obtained by detecting at 616 nm (hypersensitive to the crystal field and forbidden in the centrosymmetric environments). This fact shows that an important fraction of the Eu^{3+} ions should be located into well ordered Sr_2LuF_7 nanocrystalline environments. This assumption can be further supported by the corresponding emission spectra. Thus, by site-selective excitation at 463 nm, a hypersensitive transition to the local structure around Eu^{3+} ions and therefore forbidden in the centrosymmetric environments, the relative intensity of all emissions is reduced when compared to those observed under excitation at 392 nm and, in particular the emissions coming from upper-lying $^5D_{1-2}$ levels almost disappear. This can be related to the remaining Eu^{3+} ions in the glassy phase and to those located at the interface of the NCs, presenting higher phonon energies that prevent these emissions from upper-lying levels. On the other hand, an R value of 0.5 was obtained when exciting at 392 nm, which confirms that the environment of Eu^{3+} ions gets closer to a centrosymmetric site, related to their distribution into the Sr_2LuF_7 NCs. As it is well-known, the 392 nm excitation is not selective and equally excites all Eu^{3+} ions, so the R

value obtained is averaged over all sites and corresponds to a dominant contribution from the volume NCs sites. On the contrary, by exciting at 463 nm, an R value of 1.6 is obtained. This value is lower than the one obtained for the sample treated at 200 ºC (R = 4.3) and those obtained, under the same excitation wavelength, for Eu^{3+} doped nGCs previously studied by authors comprising KYF_4 (R= 3.3) [13] and YF_3 (R=4) [12] NCs respectively. Accordingly, non-centrosymmetric environments for Eu^{3+} ions remaining in the glassy phase and near the surface sites are assigned in this case.

In order to confirm the presence of an important fraction of Eu^{3+} ions inside the Sr_2LuF_7 NCs, the photoluminescence decay curve of the $^5D_0$ level, exciting at 392 nm and detecting the 593 nm emission was obtained, see inset in Fig. 4. The decay curve shows a single exponential behaviour with a lifetime value of 9.3 ms, comparable to the previously obtained values for the authors in similar nGCs systems [12,13,38], while the short decay component ascribed to Eu^{3+} ions in the glassy phase was not observed, showing that Eu^{3+} ions were distributed dominantly into the Sr_2LuF_7 NCs.

3.2 Up-conversion luminescence

Next, in order to take advantage of these new nGCs based on low phonon energy Sr_2LuF_7 NCs, nGCs co-doped with Yb^{3+}-Tm^{3+}, Yb^{3+}-Er^{3+} and Yb^{3+}-Ho^{3+} ions, were prepared and their UV, visible and NIR UC emissions under 980 nm excitation, were studied.

Fig. 5 shows UC emission spectra of $1.0Yb^{3+}$-$0.1Tm^{3+}$ (mol %) co-doped nGCs, heat-treated at 700 ºC, under 980 nm IR excitation and pump powers up to 200 mW. An intense blue emission, visible to the naked eye, is observed even for pump power as low as 25 mW. The visible UC spectra show the dominant blue emission, centered at 451 and 477 nm, along with a weaker red one, at around 650 nm, assigned to the $^1D_2 \rightarrow ^3F_4$, $^1G_4 \rightarrow ^3H_6$ and $^1G_4 \rightarrow ^3F_4$ transitions of Tm^{3+} ions, respectively. The possible mechanism responsible for these emissions involves, first, the Yb^{3+} transition: $^2F_{7/2} \rightarrow ^2F_{5/2}$, resonant with the IR excitation. Next, subsequent efficient ET processes from Yb^{3+} to Tm^{3+} ions populate Tm^{3+}: $^3H_5$, $^3F_{3,2}$ and $^1G_4$ levels, involving 1, 2 and 3 photons, respectively, while the $^1D_2$ level would correspond to a 4-photon UC process, assisted by the cross relaxation (CR) mechanism $^3F_{3,2} + ^3H_4 \rightarrow ^3H_6 + ^1D_2$ of Tm^{3+} ions [8, 39-42] (see energy level diagram in the right inset in Fig.5).

In addition, other UC emissions are also observed in the NIR and UV ranges of the spectra. On one hand, the emission at 802 nm, ascribed to $^3H_4 \rightarrow {}^3H_6$ transition, is achieved after non-radiative de-excitation from $^3F_{3,2}$ level. On the other hand, UV emissions at 362, 350 and 290 nm are assigned to $^1D_2 \rightarrow {}^3H_6$, $^1I_6 \rightarrow {}^3F_4$ and $^1I_6 \rightarrow {}^3H_6$ transitions respectively, where the upper excited level, $^1I_6$, can be efficiently populated by ET from Yb^{3+} ions by the channel $Yb^{3+}: {}^2F_{5/2} + Tm^{3+}: {}^1D_2 \rightarrow Yb^{3+}: {}^2F_{7/2} + Tm^{3+}: {}^1I_6$, (see right inset in Fig.5). It should be noticed that the emissions coming from these levels, $^1D_2$ and $^1I_6$, have not been previously observed in Yb^{3+}-Tm^{3+} co-doped Sr_2LuF_7 NCs [27]. It can also be seen that by increasing the pump power, high-energy UC emissions, from $^1D_2$ and $^1I_6$ levels, enhance faster than the other UC emissions. This fact implies that pump power density results critical in optimizing the population of higher energy levels and therefore in obtaining more efficient UC emissions, in particular in the UV range. Besides, a progressive change of the relative intensities in the UC emissions can be also observed, when increasing the heat-treatment temperature of these nGCs, from 300 to 700 ºC (see left inset in Fig.5), showing a shortening of interionic distances, favouring the ET processes and thus enhancing the high energetic UC emissions.

Finally, in order to complete the luminescent study, UC spectra of $1.0Yb^{3+}$-$0.1Er^{3+}$ and $1.0Yb^{3+}$-$0.1Ho^{3+}$ co-doped nGCs heat-treated at 700 ºC, were measured under 980 nm excitation at 200 mW pump power (see Fig.6(a) and (b) respectively). Moreover, corresponding precursor glasses heat treated at 200 ºC were measured under the same conditions, showing a luminescence practically negligible (not shown). For the Yb^{3+}-Er^{3+} co-doped nGCs, the observed emission peaks at 407, 523-541 and 654 nm can be assigned to $^2H_{9/2} \rightarrow {}^4I_{15/2}$ (blue), $^4S_{3/2}({}^2H_{11/2}) \rightarrow {}^4I_{15/2}$ (green) and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ (red) transitions of Er^{3+} ions (see energy levels diagram in the inset of Fig.6(a)). On the other hand, the corresponding UC emission spectrum of Yb^{3+}-Ho^{3+} co-doped nGCs presents red and green emissions, located at 540 and 650 nm, which are assigned to the $^5S_2({}^5F_4) \rightarrow {}^5I_8$ and $^5F_5 \rightarrow {}^5I_8$ transitions of Ho^{3+} ions respectively (see energy level diagram in the inset of Fig. 6(b)).

The UC mechanism in Yb^{3+}-Er^{3+} and Yb^{3+}-Ho^{3+} co-doped systems has been extensively investigated [20, 43]. Under 980 nm excitation, an initial ET from Yb^{3+} ions in the $^2F_{5/2}$ excited level to the Ho^{3+} or Er^{3+} ions, populates the $^5I_6$ and $^4I_{11/2}$ levels respectively. Next, a second ET from Yb^{3+} ions populates the corresponding emitting

levels (see insets in Fig.6), giving rise to intense red and green emissions in both co-doped nGCs systems, involving 2-photon processes. Moreover, in both cases the contribution of the green emission is dominant, as it is quantified by the CIE formalism [44], with corresponding colour coordinates (0.308;0.668) for Yb^{3+}-Er^{3+} and (0.309;0.674) for Yb^{3+}-Ho^{3+} co-doped nGCs, located near the border of the green region. Moreover, taking into account that the colour coordinates for the Yb^{3+}-Tm^{3+} co-doped nGCs, also treated at 700 ºC, are (0.183;0.106) located near the border of the blue region, it should be possible to generate white light through the adequate combination of Yb^{3+}, Tm^{3+} and Er^{3+} or Ho^{3+} ions doping level in the present Sr_2LuF_7 nGCs. Research along this line is currently been carried out.

Conclusions

A novel transparent Eu^{3+} -doped or Yb^{3+}-Tm^{3+}, Yb^{3+}-Er^{3+} and Yb^{3+}-Ho^{3+} co-doped nGCs containing cubic Sr_2LuF_7 NCs, confirmed by XRD and HRTEM images, were successfully developed by the sol-gel method and posterior thermal treatments. The use of Eu^{3+} as structural probe ion revealed different environments for RE ions and suggested that an important fraction of these ones are located into the nanocrystalline Sr_2LuF_7 phase. Main UV, VIS and NIR UC emissions were analysed in the Yb^{3+}-Tm^{3+} co-doped nGCs as a function of pump-power and heat-treatment temperature. Green and red UC emissions were observed in Yb^{3+}-Er^{3+} and Yb^{3+}-Ho^{3+} co-doped nGCs and their corresponding ET mechanisms were described. Results obtained suggest that these systems can be considered for potential optical applications as high efficient UV-VIS up-conversion materials in solid state lasers and photonic integrated devices.

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Figure captions

Fig.1. XRD patterns of RE^{3+} doped-Sr_2LuF_7 nGCs heat-treated at indicated temperatures. Inset shows the transmittance curve of the transparent nGC heat-treated at 700 ºC.

Fig. 2. (a) TEM and (b) HRTEM images of RE^{3+} doped-Sr_2LuF_7 nGCs heat treated at 700 ºC. Inset shows the power spectrum (FFT patern) and filtered higher-contrasted image of the squared NC.

Fig. 3. Emission spectra of Eu^{3+} doped-Sr_2LuF_7 nGCs heat-treated at indicated temperatures, exciting at 392 nm. All spectra have been normalized at 590 nm ($^5D_0\rightarrow$ $^7F_1$ transition). Energy levels diagram of Eu^{3+} ions is included in the inset.

Fig. 4. Excitation and emission spectra of Eu^{3+} doped-Sr_2LuF_7 nGCs heat-treated at 700 ºC, detecting and exciting at indicated wavelengths. Excitation spectra have been normalized at 525 nm ($^7F_0\rightarrow^5D_1$ transition) and the emission spectra at their corresponding maxima. Inset shows photoluminescence decay curve of this nGC, excited at 392 nm, monitoring the 592 nm emission.

Fig. 5. UC emission spectra of $1.0Yb^{3+}$-$0.1Tm^{3+}$ co-doped-Sr_2LuF_7 nGCs (mol%) heat treated at 700 ºC, under excitation at 980 nm, at indicated pump powers. Right inset shows the energy level diagrams of Yb^{3+} and Tm^{3+} ions with main UC emissions and corresponding population mechanisms. Left inset shows UC emission spectra of $1.0Yb^{3+}$-$0.1Tm^{3+}$ co-doped-nGCs (mol%) heat-treated at indicated temperatures, under excitation at 980 nm and 200 mW of pump power, along with a photograph of the nGC heat treated at 700 ºC. All spectra have been normalized at 802 nm ($^3H_4\rightarrow^3H_6$ transition).

Fig. 6. UC emission spectra of (a) $1.0Yb^{3+}$-$0.1Er^{3+}$ and (b) $1.0Yb^{3+}$-$0.1Ho^{3+}$ co-doped-nGCs (mol%) heat treated at 700 ºC, under excitation at 980 nm and 200 mW of pump power. Insets show the energy level diagrams of Er^{3+} and Ho^{3+} ions and their corresponding photographs. Spectra have been normalized at their corresponding maxima.
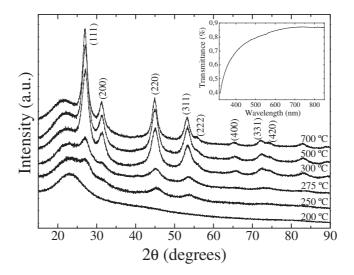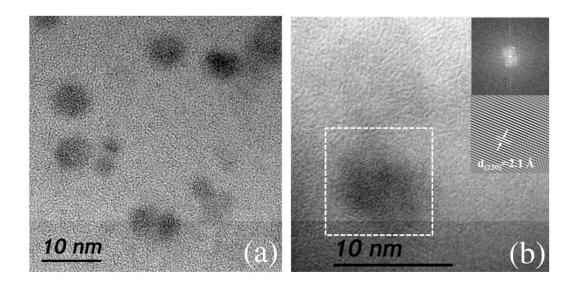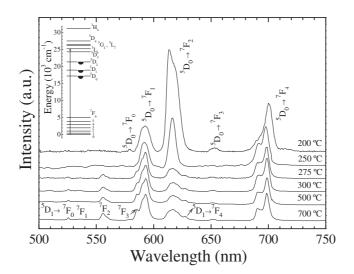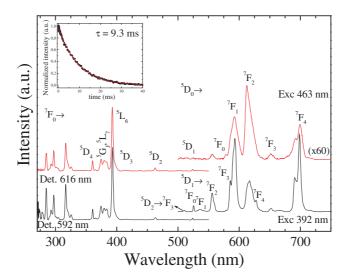
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