



Upconversion and infrared emission of $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped $\text{SiO}_2\text{-Gd}_2\text{O}_3$ obtained by sol-gel process

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Abstract

This work reports on the preparation of materials based on $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped $\text{SiO}_2\text{-Gd}_2\text{O}_3$ via sol-gel process. The 0.4 mol% of Er^{3+} ions was fixed and the amount of Yb^{3+} ions changed as 1.8, 5 and 9 mol% in order to evaluate the photoluminescence properties as a function of the Yb^{3+} ions concentration. The prepared xerogels were heat-treated at 900, 1000 and 1100 °C for 8 h. X-ray diffraction analyses of the heat-treated materials confirmed the formation of the Gd_2O_3 cubic phase embedded in the SiO_2 host, demonstrating the effective incorporation of RE^{3+} ions in the structure. The Scherrer's equation verified that the sizes of Gd_2O_3 nanocrystallites are between 31 and 69 nm and directly dependent on the heat-treatment temperature. Under excitation at 980 nm all materials showed upconversion phenomena, and the intensities of the emissions in the green and red regions showed to be directly dependent on power pump of laser, quantity of Yb^{3+} ions and heat-treatment temperature. The materials also showed emission in the infrared region with the maximum around 1530 nm, assigned to the transition of $^4\text{I}_{13/2} \longrightarrow ^4\text{I}_{15/2}$ of the Er^{3+} ions, region known as technological C-telecom band used in optical amplification.

Keywords: $\text{SiO}_2\text{-Gd}_2\text{O}_3$ ceramic, rare earths, photoluminescence, C-telecom window

1. Introduction

Rare earth (RE^{3+}) doped materials have had a great impact on industry, society and research due to their importance in the development of devices with essential technological properties. These ions have been highlighted in the development of advanced technological devices due to their differentiated properties when incorporated into host matrix with desirable characteristics including low phonon energy of the network, appropriate refractive index, and chemical stability among others [1].

Some properties like photoluminescence [2], magnetism [3] and energy conversion [4] of RE^{3+} ions are associated to the splitting of 4f levels assigned to the

inter-electronic interactions, spin-orbit coupling and the ligand field effect on the RE^{3+} ions when present in host matrices [5].

Among the RE^{3+} ions, Er^{3+} ions have an interesting photoluminescent property that stands out among the other RE^{3+} ions when incorporated into host matrices with low energy phonon lattices. This ion shows emission in the infrared region, at about 1550 nm, that is assigned to the $^4\text{I}_{13/2} \longrightarrow ^4\text{I}_{15/2}$ transition, which enables Er^{3+} ions to be applied in the development of optical amplifiers in the third telecommunication window [6].

Besides the characteristic emission at 1550 nm of Er^{3+} ions, another emission mechanism may occur resulting in emissions in the visible region. A short distance between Er^{3+} ions caused by the large concentration of these ions in the host matrix, contributes to the red and green region emissions from the upconversion

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process [7,8]. These characteristics make them excellent ions for research in development of new materials for applications in solid state lasers [9] and energy conversion devices [4].

The Yb^{3+} ion absorbs energy around 980 nm, in the same region as Er^{3+} ion, however, the Yb^{3+} ions have great cross section absorption in the infrared region, 10 times more efficient than Er^{3+} ions. In this sense, Yb^{3+} ions can efficiently absorb in the 980 nm region and act as an Er^{3+} ion sensitizer, transferring energy to the Er^{3+} ions, contributing to an increase of the photoluminescence emission efficiency [10]. The energy transfer between Yb^{3+} and Er^{3+} ions occurs because the $^2\text{F}_{5/2}$ energy level of the Yb^{3+} ion is resonant with $^4\text{I}_{11/2}$ energy level of the Er^{3+} ion.

Due to the large applicability of materials containing RE^{3+} ions, in the last several years many efforts have focused on the development of efficient host matrices. In the literature, several papers report on the Er^{3+} -doped binary oxide systems containing SiO_2 obtained by sol-gel process. Emphasized from these papers are the SiO_2 - TiO_2 [11], HfO_2 - SiO_2 [12], SiO_2 - ZrO_2 [13], SiO_2 - Nb_2O_5 [14], and SiO_2 - Ta_2O_5 [15] with excellent optical properties, in the visible and infrared region.

Systems based on Gd_2O_3 - SiO_2 have proven to be efficient matrices for $\text{Er}^{3+}/\text{Yb}^{3+}$ ions [16] due to the properties of Gd_2O_3 including: low phonon energy lattice around 600 cm^{-1} [17], good chemical and thermal stability which allows use at different temperatures, easy routes used in the synthesis [18,19] and low change in the lattice parameters during the incorporation of RE^{3+} ions in the Gd_2O_3 structure associated to the proximity between the ionic radii of RE^{3+} ions. It is important to take into account the efficiency of the energy transfer from the Gd^{3+} ions to the RE^{3+} ions when the materials are excited in the UV-vis region (below $\sim 350\text{ nm}$) [20]. In accordance with Zeng *et al.* [16], the presence of SiO_2 on the surface of the $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped Gd_2O_3 - SiO_2 nanoparticles showed much higher upconversion photoluminescence emission in the visible range. Similar paper was reported by Wang *et al.* [21] where material based on the monodisperse rare earth-doped SiO_2 - Gd_2O_3 showed intense photoluminescence emissions. However, they have not shown the influence of the heat treatment temperature in the photoluminescent properties of the materials. In the present paper the authors report on optimizing the presence of Yb^{3+} in the Er^{3+} -doped Gd_2O_3 - SiO_2 as sensitizers.

Among the different routes for synthesis of new materials, the sol-gel process is very interesting and has often been used in the synthesis of materials containing rare earth ions [11–15]. The sol-gel process allows for good homogeneity of the precursor solution and thus controls the refractive index of the final materials by just changing the molar ratio between metals in the precursor solution. All these parameters lead to the control of shape, crystallinity, size of the particles, and elimination of by-products present in the final material [22–24].

Taking these ideas into account, the focus of this paper was to obtain $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped Gd_2O_3 - SiO_2 prepared by the sol-gel process. The concentration of the Yb^{3+} ions as sensitizers of Er^{3+} under excitation at 980 nm and the heat treatment temperature were changed in order to evaluate the influence on the photoluminescent properties of the materials. The structural properties of the resulting materials are also presented and discussed.

II. Experimental

The materials studied in this work were prepared by the sol-gel process using TEOS (Sigma Aldrich, 98%) as Si^{4+} precursor. Er_2O_3 (Sigma Aldrich, 99.99%), Yb_2O_3 (Sigma Aldrich, 99.99%) and Gd_2O_3 (Sigma Aldrich, 99.99%) were dissolved in hydrochloric acid, and then a solvent exchange was performed with anhydrous ethanol, obtaining alcohol solutions of Er^{3+} , Yb^{3+} and Gd^{3+} ions. These solutions were titrated with EDTA 0.01 mol/l at room temperature. To obtain the SiO_2 -based materials containing Gd_2O_3 , the precursors were mixed in the molar ratio of $\text{Si}^{4+}/\text{Gd}^{3+}$ equal 70/30. The systems were doped with 0.4 mol% of Er^{3+} and Yb^{3+} ions were added in amount of 1.8, 5 and 9 mol%, both in relation to the total amount of Gd^{3+} and Si^{4+} ions. The corresponding amount of TEOS was added in a beaker, followed by a proper volume of concentrated HCl to reach the 50:1 ratio of TEOS:HCl. The volume was then diluted to 10 ml with anhydrous ethanol. In another beaker, the corresponding volumes of anhydrous ethanol solution containing Gd^{3+} ions was added with ethanol solution containing Er^{3+} and Yb^{3+} ions. The final volume of this solution was also diluted to 10 ml with anhydrous ethanol. Both solutions were kept under stirring for 15 min. The solutions were then mixed and kept under stirring for an additional 15 min to promote the hydrolysis and formation of the sol. The sols were kept in an oven at approximately 100°C for 24 h to obtain the xerogels, which were crushed in an agate mortar followed by heat-treatment at 900, 1000 and 1100°C for 8 h.

The crystalline structure of the powders obtained after different heat treatment were characterized by X-ray diffraction analysis (XRD 6000, Shimadzu) with $\text{CrK}\alpha = 2.2897\text{ \AA}$ radiation and graphite monochromator, using step of 0.02° in 2θ range of 10 – 80° . The crystallite size was calculated using the Scherrer's equation. Morphology of the final materials after heat-treatment was analysed by scanning electron microscopy (SEM TM-3000, Hitachi). The upconversion emission spectra were collected in the region between 500 and 750 nm using a Spectra Pro 300i spectrometer with a photomultiplier detector. The materials were excited by operating a diode laser at 980 nm with fibre coupled with varying the power excitation pumps from 100 to 225 mW with steps of 25 mW. The infrared photoluminescence spectrum in the region between 1400 and 1700 nm was collected using a diode laser at 980 nm with the power

pump fixed at 300 mW operating the same equipment, however, the InGaAs was used as the detector. All measurements were performed at room temperature.

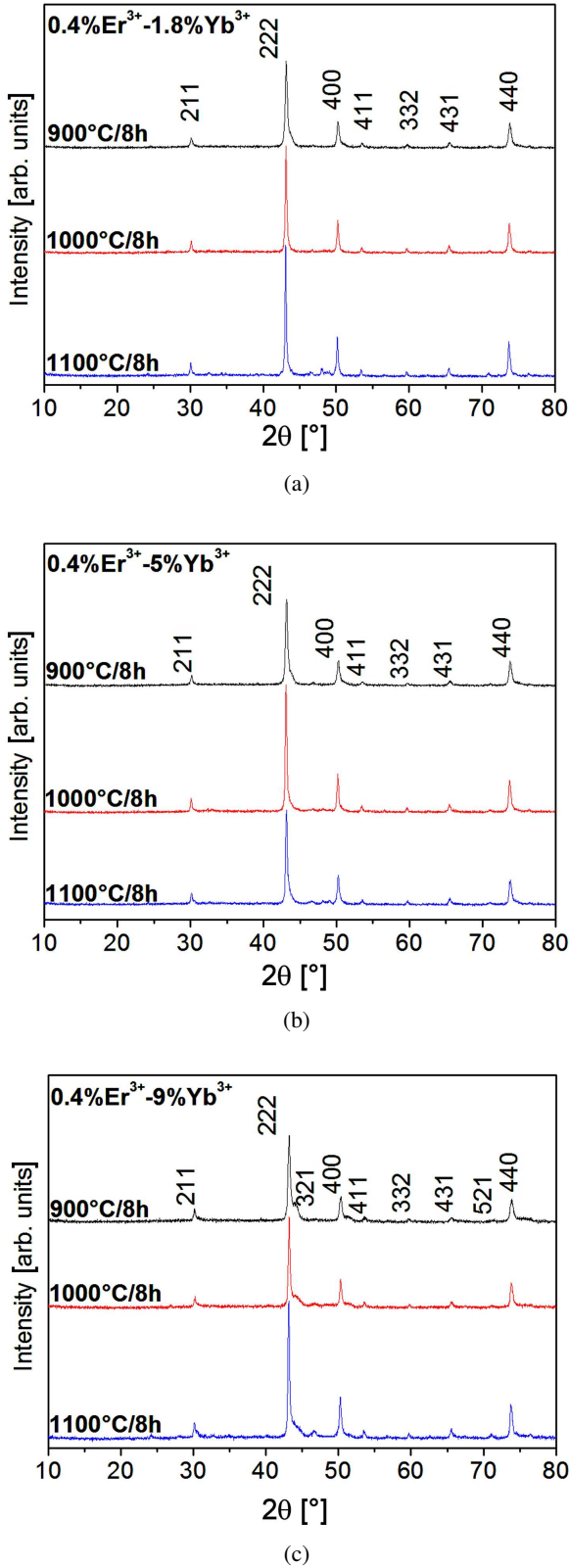


Figure 1. XRD patterns for the materials formed from the 70Si⁴⁺-30Gd³⁺ binary system containing 0.4 mol% of Er³⁺ ions and: a) 1.8 b) 5 and c) 9 mol% of Yb³⁺ ions after different heat-treatment at different temperatures

III. Results and discussion

The crystallinity of the materials and the phases formed after the heat treatment were evaluated by XRD analysis (Fig. 1). All observed peaks were attributed to the reflections of the crystalline planes assigned to formation of the cubic type crystalline phase of Gd₂O₃, being highlighted in the diffractograms the most intense reflections at 211, 222, 321, 400, 411, 332, 431, 521 and 440. The obtained lattice parameters were $a = b = c = 10.813 \text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$ according to the JCPDF card 00-012-0797. It was observed that with increasing the temperature of the heat treatment, an increase of the intensity of reflections occurs, indicating higher volumes of the crystalline portion in the system [25]. No reflections assigned to the secondary phases, such as a Er₂O₃ or Yb₂O₃ phase, are observed for the material containing 1.8 and 5 mol% of Yb³⁺ ions. This indicates the effective introduction of the ions in the host matrix. However, as shown in Fig. 1c, for the systems with the highest concentration of Yb³⁺ ions (9 mol%), there is the onset formation of Yb₂O₃ as secondary phase. This can be verified due to the presence of the reflection positioned around $2\theta = 44^\circ$, which is close to the most intense reflection assigned to the plane (222) of the Gd₂O₃ cubic phase.

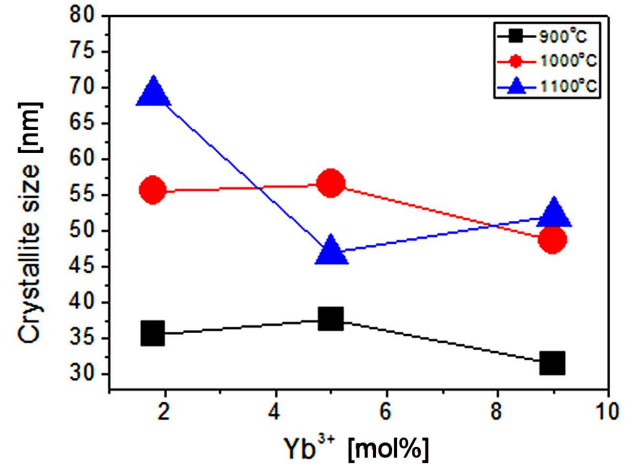


Figure 2. Crystallite size dependence on the mol% of Yb³⁺ ions concentration and the temperature of heat-treatment (the crystallite size was calculated by Scherrer's equation)

Using Scherrer's equation (Equation 1) the nanocrystallite size was determined based on the most intense reflection attributed to the plane (222) located at $2\theta = 43.16^\circ$:

$$D_{hkl} = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where D is the size of crystallite, K is the shape factor (in this work we used 0.89), λ is the wavelength of X-ray ($2.2897 \text{ \AA}$), and β the full width of the half maximum (FWHM) of the most intense peak. The β values were corrected in accordance with Equation 2:

$$\beta = \sqrt{\beta_{exp}^2 - \beta_{inst}^2} \quad (2)$$

where β_{inst} is the instrumental full width of the half maximum and β_{exp} is the experimental full width of the half maximum of the most intense peak in diffractogram. The standard sample used was Silicon with 325 mesh (Shimadzu).

As shown in Fig. 2, the nanocrystallite sizes obtained by Scherrer's equation are between 31 and 69 nm. Increasing the percentage of Yb^{3+} ions from 1.8 up to 5 mol% no significant increase in the size of nanocrystallites are observed, only a reduction in the case of the sample containing 5 mol% of Yb^{3+} ions heat-treated at 1100 °C. However, by increasing the percentage of Yb^{3+} to 9 mol%, a decrease in the nanocrystallite size is clearly observed. The observed decreasing in crystallite size can be associated with two main factors: i) the large amount of dopant ions cause a clustering of dopants on the surface of the material and avoiding the coalescence process; or ii) the possible formation of secondary phases, such as Yb_2O_3 , hindering the formation of Gd_2O_3 crystal due to the lowering of surface energy. Somehow the presence of impurities decreases the surface energy of the Gd_2O_3 preventing the growth of crystals. It is also observed that the nanocrystallite size increases as a function of heat treatment temperature. This behaviour can be associated with the coalescence or aggregation phenomena of nanocrystals due to the higher thermal energy applied on the system by heat-treatment.

The samples heat treated at 900 °C were analysed by SEM to evaluate the morphology of the formed materials. Figure 3 shows that the materials present homogeneity, with the formation of plates on the order of micrometers. The presence of nanoparticles is also observed that can be associated with the SiO_2 and Gd_2O_3 compounds. This morphology is evidence of the formation of a ceramics, in which Gd_2O_3 clusters were formed around the SiO_2 plates. The increasing of Yb^{3+} ion concentration does not affect the morphology of the materials.

As shown in Fig. 4, even when using the lowest excitation power, all materials containing Er^{3+} and Yb^{3+} ions show upconversion photoluminescence emission. The emission bands in the spectra localized in the green region (510–575 nm) of the electromagnetic spectrum are assigned to the $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transitions, and in the red region (625–700 nm) associated with the $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transition. These bands are observed in all upconversion emission spectra, and are assigned to the intraconfigurational $f-f$ transitions of Er^{3+} ions [26].

In the upconversion emission spectra, the amounts of Yb^{3+} ions are shown to have an important role in the intensity of emissions. The samples heat-treated at 900 °C showed greater photoluminescence intensity, and with increasing of concentration of Yb^{3+} ions, a reduction of the intensity of the emission bands is seen. This

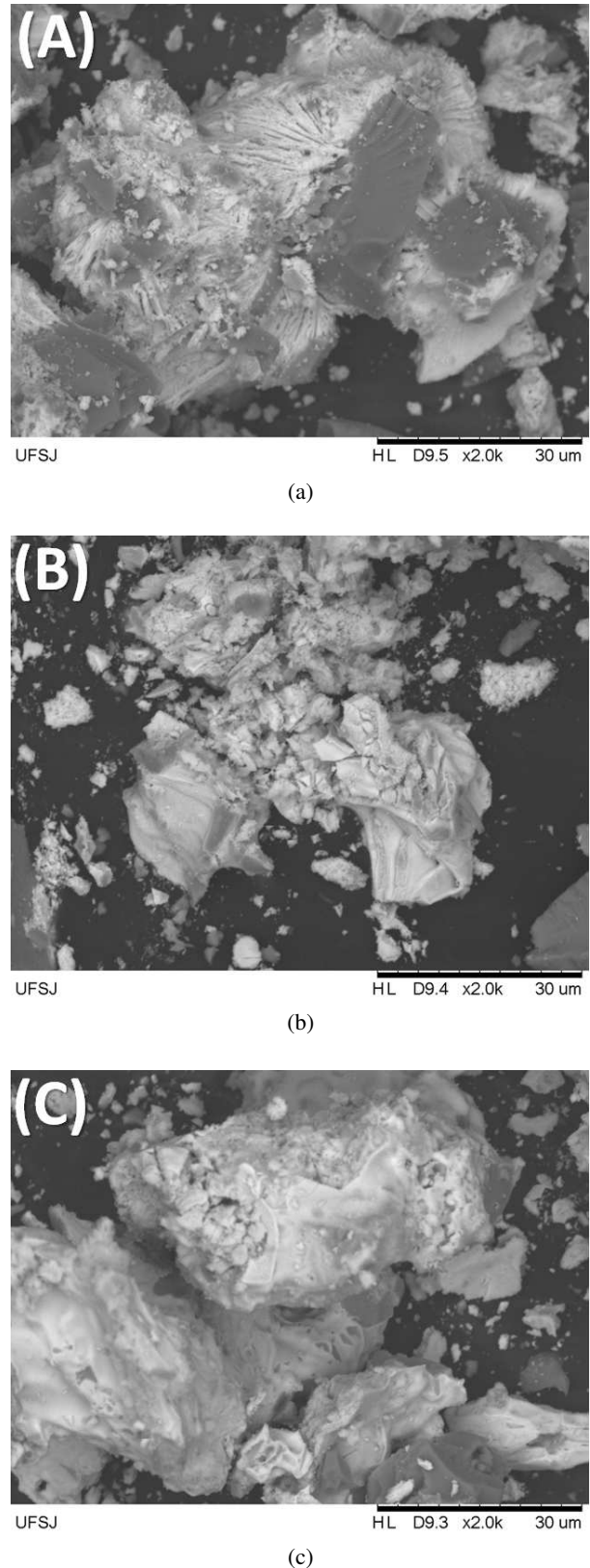


Figure 3. SEM images of 70Si-30Gd materials heat treated at 900 °C containing 0.4 mol% Er^{3+} and: a) 1.8, b) 5 and c) 9 mol% of Yb^{3+} ions

behaviour may be related to the phenomena of cross-relaxation due to a high concentration of these ions. The increasing concentration of Yb^{3+} ions promotes the

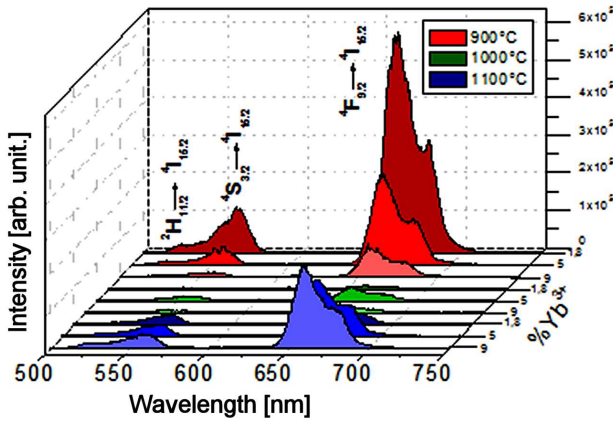


Figure 4. Upconversion emission spectra of the material based on $70\text{Si}^{4+}\text{-}30\text{Gd}^{3+}$ containing 0.4 mol% of Er^{3+} ions and with different percentages of Yb^{3+} ions heat-treated at 900, 1000 and 1100 °C, under excitation at 980 nm with a diode laser (the power pump fixed at 100 mW)

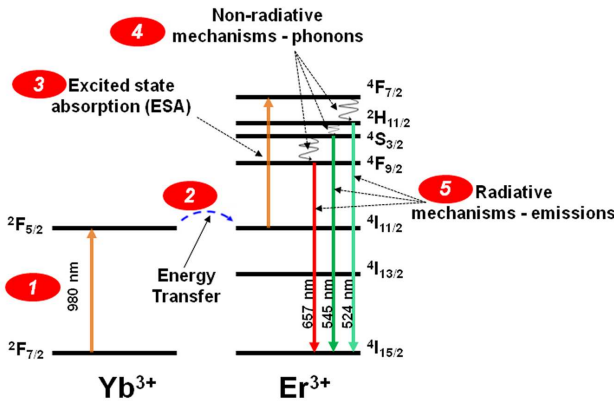


Figure 5. Diagram of energy levels of Er^{3+} and Yb^{3+} ions with a simplified ETU mechanism followed an ESA process resulting in the emissions at 524, 545 and 657 nm by Er^{3+} ions

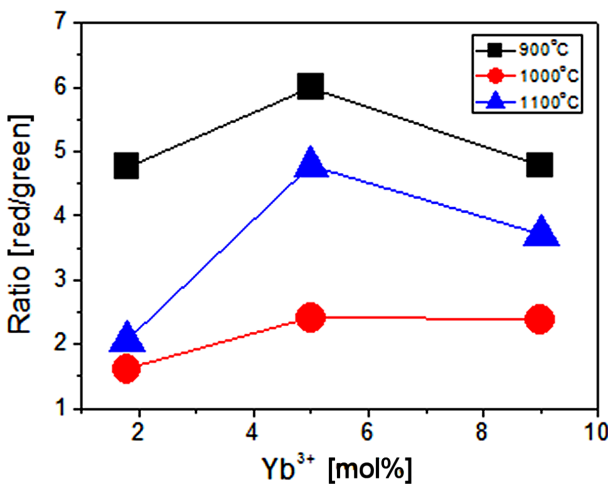


Figure 6. Ratio of the areas assigned to the ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$ and ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2} - {}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ assigned to the Er^{3+} ions as a function of heat-treatment temperature and the % of Yb^{3+} ion concentration under excitation at 980 nm with a diode laser (the power pump fixed at 100 mW)

reduction of distances between them, resulting in the increasing of the cross relaxation process of ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ energy level. Consequently, this effect decreases the probability of mechanisms via ETU process occurring in the Er^{3+} , resulting in low intensity of the upconversion emission.

The materials heat-treated at 1000 °C showed the lowest upconversion intensity in comparison to the all materials reported here. In these materials, predominant emission mechanisms can be in the 1.5 μm region, when from the ${}^4\text{I}_{13/2}$ excited state occurs radiative decay to the ${}^4\text{I}_{15/2}$, consequently reducing the probability of occurring of the upconversion process.

On the other hand, the materials heat-treated at 1100 °C showed the increasing of the emission intensity as a function of Yb^{3+} ions concentration. As determined by Scherrer's equation, these materials present higher crystallite sizes that contribute to the increasing of distance among ions, reducing the process via cross relaxation and favouring the upconversion mechanisms.

Contrary to the materials heat-treated at 1100 °C, the crystallite sizes of the materials heat-treated at 900 °C were lower. At this point it is necessary to take into account that the higher Yb^{3+} ions concentration can result in low distance among them favouring the cross relaxation process.

The upconversion process observed in the materials can occur by two predominant types of mechanisms: ESA (Excited State Absorption) and ETU (Energy Transfer Upconversion). Literature [27] has shown that the ETU process is two orders of magnitude greater than the ESA process, and with the use of Yb^{3+} ions as a sensitizer, is certainly the predominant mechanism.

The ESA involves the Er^{3+} electronic excitation from its ground level ${}^4\text{I}_{15/2}$ to its excited state ${}^4\text{I}_{11/2}$ for a photon resonant to the ${}^4\text{I}_{11/2}$ energy level, a process called Ground State Absorption (GSA). Then the second photon promotes the excitation of Er^{3+} ions to the higher energy states like ${}^4\text{F}_{7/2}$ from which, after non-radiative processes, emits light from the ${}^2\text{H}_{11/2}$, ${}^4\text{S}_{3/2}$ or ${}^4\text{F}_{9/2}$ energy levels positioned at 524, 545 and 657 nm, respectively.

The ETU process is represented in a simplified way in Fig. 5. This energy transfer involving Yb^{3+} and Er^{3+} ions occurs due to the energy level ${}^2\text{F}_{5/2}$ of the Yb^{3+} ion being resonant with the energy level ${}^4\text{I}_{11/2}$ of the Er^{3+} ion, and after this energy transfer process, the second photon results in enough energy to promote the Er^{3+} electrons from ${}^4\text{I}_{11/2}$ level to the higher energy excited states like ${}^4\text{F}_{7/2}$. Further, the same as in ESA, after non radiative processes, radiative decays may occur from the ${}^2\text{H}_{11/2}$, ${}^4\text{S}_{3/2}$ and ${}^4\text{F}_{9/2}$ levels emitting at 524, 545 and 657 nm, respectively.

These complex upconversion mechanisms involving Er^{3+} and Yb^{3+} ions were recently deepened by Anderson *et al.* [27]. As observed previously, the materials show predominant emission in the red region, and the

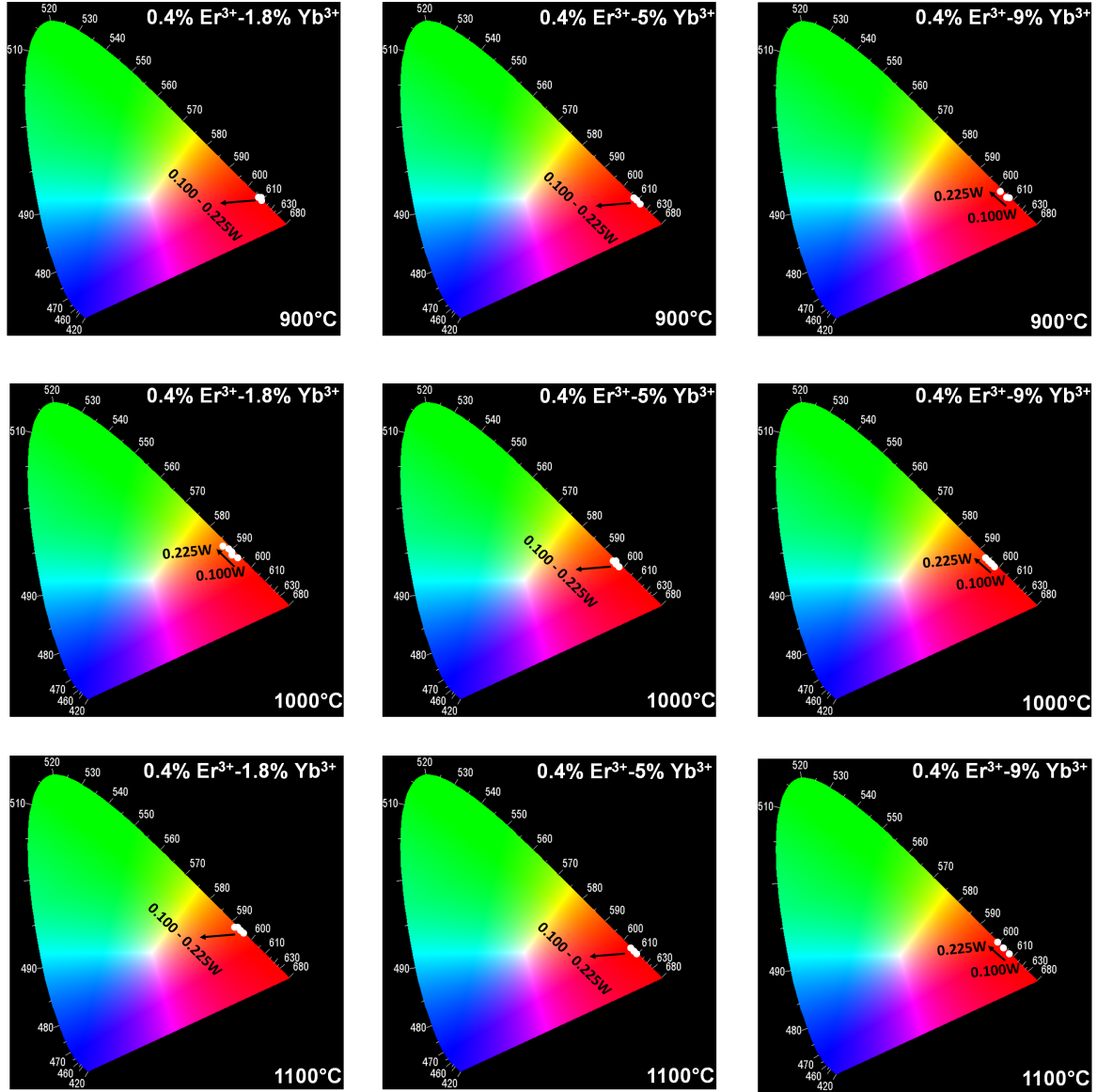


Figure 7. Chromaticity diagram (CIE) of $70\text{Si}^{4+}\text{-}30\text{Gd}^{3+}$ materials containing Er^{3+} and Yb^{3+} ions

ratio between red and green emissions are shown in Fig. 6. It can be seen, that the materials heat-treated at 900°C showed higher emission intensity in the red region, with 4 to 6 times more intensity than the emission in the green region. As it was previously explained the large amount of Yb^{3+} ions used in the preparation of the materials contributes significantly to the population of the states responsible for the emission in this region due to the increase of non radiative mechanisms.

According to Perrella *et al.* [28], the high concentration of RE^{3+} ions in Er^{3+} -doped system contributes to the increase of non-radiative mechanisms, favouring the population of the states responsible for the emission in the red region.

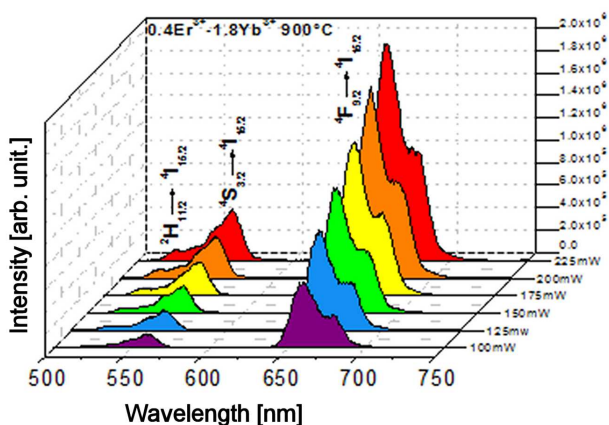
Vetrone *et al.* [29] observed the same trend in the increase of Yb^{3+} ions concentration in the Y_2O_3 materials, and concluded that the initial cross-relaxation mechanism in neighbouring Er^{3+} ($^4\text{F}_{7/2} \longrightarrow ^4\text{I}_{11/2}$) and Yb^{3+} ($^2\text{F}_{5/2} \longrightarrow ^2\text{F}_{7/2}$) ions followed by the

$^4\text{F}_{7/2} \longrightarrow ^4\text{F}_{9/2}$ and $^4\text{F}_{9/2} \longrightarrow ^4\text{I}_{11/2}$ mechanisms directly populated the $^4\text{F}_{9/2}$ state, favouring the mechanisms of red emissions. Similar effect was observed by Guo *et al.* [17], who showed that the great enhancement of red emission and diminishment of green emission of Er^{3+} in $\text{Gd}_2\text{O}_3\text{:Er+Yb}$ were caused by $\text{ET}(^4\text{I}_{13/2}(\text{Er}) + ^2\text{F}_{5/2}(\text{Yb}) \longrightarrow ^4\text{F}_{9/2}(\text{Er}) + ^2\text{F}_{7/2}(\text{Yb}))$ and $\text{ET}(^4\text{F}_{7/2}(\text{Er}) + ^2\text{F}_{7/2}(\text{Yb}) \longrightarrow ^4\text{I}_{11/2}(\text{Er}) + ^2\text{F}_{5/2}(\text{Yb}))$ processes, respectively.

By using the upconversion emission spectra obtained from the materials $70\%\text{Si}\text{-}30\%\text{Gd}$ doped with Er^{3+} and Yb^{3+} ions the CIE (*Commission Internationale d'Eclairage*) diagram of chromaticity was built, as shown in Fig. 7. The white points positioned on the chromaticity diagram represent the emission colours for all materials obtained, in which the materials showed a predominant emission in the red region, according to the profiles observed for the emission spectra. Due to the proximity of points to the edges of the diagrams it

Table 1. X and Y values calculated based on the CIE diagram for the composition 70Si-30Gd doped with Er³⁺ and Yb³⁺ ions

Sample	Current [mW]	900 °C		1000 °C		1100 °C	
		X	Y	X	Y	X	Y
70Si-30Gd doped with 0.4% Er ³⁺ - 1.8% Yb ³⁺	100	0.66	0.336	0.57	0.408	0.599	0.392
	125	0.661	0.335	0.553	0.427	0.602	0.39
	150	0.658	0.338	0.554	0.428	0.595	0.397
	175	0.657	0.339	0.586	0.398	0.597	0.396
	200	0.655	0.342	0.563	0.422	0.593	0.399
	225	0.654	0.342	0.567	0.419	0.588	0.405
70Si-30Gd doped with 0.4% Er ³⁺ - 5% Yb ³⁺	100	0.659	0.336	0.599	0.39	0.648	0.346
	125	0.672	0.323	0.609	0.382	0.658	0.337
	150	0.665	0.329	0.609	0.383	0.654	0.34
	175	0.666	0.329	0.606	0.385	0.658	0.338
	200	0.664	0.331	0.604	0.388	0.656	0.34
	225	0.664	0.331	0.606	0.386	0.654	0.341
70Si-30Gd doped with 0.4% Er ³⁺ - 9% Yb ³⁺	100	0.65	0.343	0.587	0.399	0.652	0.342
	125	0.655	0.339	0.607	0.382	0.636	0.358
	150	0.631	0.36	0.611	0.378	0.636	0.358
	175	0.656	0.337	0.601	0.388	0.636	0.359
	200	0.652	0.341	0.604	0.386	0.622	0.371
	225	0.651	0.342	0.602	0.387	0.62	0.373

**Figure 8.** Emission intensity as a function of the laser power pump for material 70Si⁴⁺-30Gd³⁺ containing 0.4 mol% Er³⁺ and 1.8mol% of Yb³⁺ ions heat-treated at 900 °C for 8 h

is concluded that it is a pure colour emission and with variation of the power of the laser pump, no significant changes in the position of the emission colour were observed. The coordinates obtained by the CIE diagrams are presented in the Table 1, and the values of X and Y obtained had little variation for all samples, a result expected due to the spectra profiles of the materials.

Figure 8 shows that the emission intensity is directly dependent on the excitation power source. The presented results describe only the material containing 0.4 and 1.8 mol% of Er³⁺ and Yb³⁺ ions, respectively, heat-treated at 900 °C, which are representative for all other samples obtained in this paper. From the obtained results by increasing the excitation source power, the predominant colour emission is independent of the laser power used, and this predominant emission in the red region is attributed to non-radiative processes that contribute to the population of ⁴F_{9/2} levels.

Figure 9 shows the emission spectra in the infrared region with the maximum localized around 1531 nm, in which the band is assigned to the transition of ⁴I_{13/2} → ⁴I_{15/2} of the Er³⁺ ion. Under excitation at 980 nm, the Er³⁺ ions are excited from its ground level ⁴I_{15/2} to the excited state ⁴I_{13/2} via photon resonance. Then the non-radiative processes occur and radiative decay from the level ⁴H_{13/2} happens, resulting in strong emission at 1.5 μm. The same emission can occur via ETU process, after energy transfers from the ²F_{5/2} energy level of the Yb³⁺ ion to the ⁴I_{11/2} energy level of the Er³⁺ ion happen.

All materials obtained in this paper present the emission with the maximum at 1531 nm, and make them potential candidates for applications in telecommunication systems such as in the development of optical amplifiers devices in the third telecommunication window [30].

IV. Conclusions

Materials based on Er³⁺/Yb³⁺ co-doped Gd₂O₃-SiO₂ were efficiently obtained by the sol-gel process. The route used to prepare the materials in this work showed very easy way to obtain material with high photoluminescence performance in comparison to other similar materials present in literature. The matrix containing 70 mol% of Si⁴⁺ and 30 mol% of Gd³⁺ was suitable for the incorporation of the Er³⁺ ions (with concentration fixed at 0.4 mol%) and Yb³⁺ ions (with several concentrations). By Scherrer's equation, it was verified that the nanocrystallite size of the materials (70 mol% Si⁴⁺-30 mol% Gd³⁺ doped with 0.4% Er³⁺ and Yb³⁺ in different percentages) is directly dependent on the heat-treatment temperature. The materials had crystallite sizes between 31 and 69 nm. The small change in the size of the crystallite as a function of Yb³⁺ ion

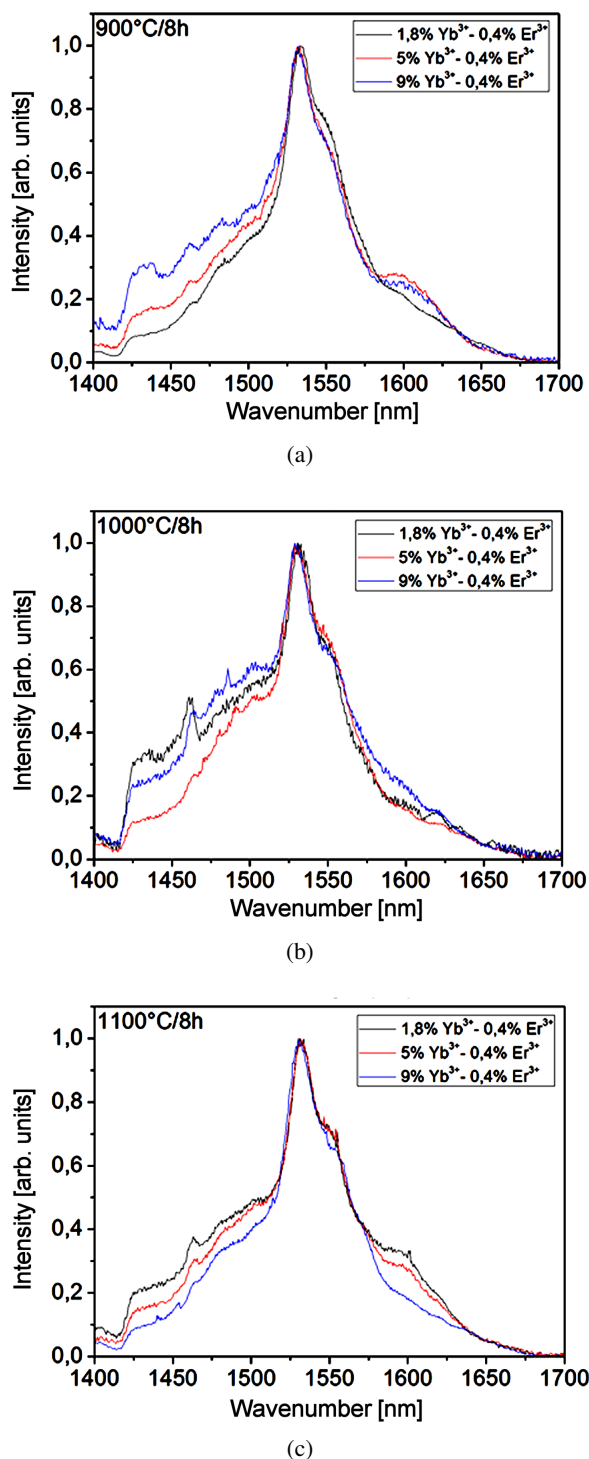


Figure 9. Photoluminescence emission spectra in the 1550 nm region assigned to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of Er^{3+} ions of the material heat-treated at: a) 900 °C, b) 1000 °C and c) 1100 °C for 8 h (the spectra were obtained under excitation at 980 nm with a diode laser - the power pump fixed at 300 mW)

concentration was associated to the surface effect of this ion on the Gd_2O_3 crystals. All prepared materials showed the upconversion emission phenomenon when excited at 980 nm, with bands localized in the green and red regions associated to $^2H_{11/2} \rightarrow ^4I_{15/2}$ or $^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions of the

Er^{3+} ions, respectively. Based on the chromaticity diagram, it can be concluded that the emission in the red region is predominant. The upconversion photoluminescence properties show that the samples annealed at 900 °C present potential for application in laser source and for improving solar cells. The materials obtained also show emission localized around 1530 nm assigned to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of the Er^{3+} ions, under excitation at 980 nm, and can be used in third telecommunication window.

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