Credit Author Statement

Development of a simple process to obtain luminescent YVO₄:Eu³⁺ nanoparticles for Fiber Optic Dosimetry

Luciana Mentasti: methodology, investigation, writing- original draft.

Nahuel Martínez: methodology, investigation.

Ileana A. Zucchi: writing- review and editing, supervision.

Martín Santiago: writing- review and editing, conceptualization, supervision, funding acquisition.

Gastón Barreto: methodology, writing- original draft, funding acquisition, project administration.
Dissolution of $\text{Y(NO}_3\text{)}_3$ in water
Dissolution of $\text{Eu(NO}_3\text{)}_3$ in water
Dissolution of $\text{NH}_4\text{VO}_3$ in water
Dissolution of $\text{NH}_4\text{NO}_3$ in water
Dissolution of $(\text{NH}_4)_2\text{CO}$ in water

Precursors mixing
Yellow solution

Water evaporation 70°C
Red gel

Heating 200°C
Combustion

Annealing

$0.95(\text{Y(NO}_3\text{)}_3)+0.05(\text{Eu(NO}_3\text{)}_3)+\text{NH}_4\text{VO}_3+3(\text{NH}_4)_2\text{CO}+3\text{NH}_4\text{NO}_3$
$\rightarrow Y_{0.90}\text{Eu}_{0.00}\text{VO}_4+14\text{H}_2\text{O}+8\text{N}_2+3\text{CO}_2$

$\text{YVO}_4\text{Eu}^{3+}$ nanoparticles
Development of a simple process to obtain luminescent YVO$_4$:Eu$^{3+}$ nanoparticles for Fiber Optic Dosimetry

Luciana Mentasti$^a$, Nahuel Martinez$^a$, Ileana A. Zucchi$^b$, Martín Santiago$^a$ and Gastón Barreto$^a$*

$^a$ Center for Research in Physics and Engineering of the Center of Buenos Aires Province, CIFICEN (UNCPBA-CONICET-CICPBA). Pinto 399, B7400JWI, Olavarría, Buenos Aires, Argentina.

$^b$ Institute of Materials Science and Technology, INTEMA (UNMDP-CONICET), J. B. Justo 4302, 7600 Mar del Plata, Argentina

*Corresponding author, mail: gbarreto@fio.unicen.edu.ar. Av. del Valle 5737, Olavarría (CP7400), Buenos Aires, Argentina.

Abstract

YVO$_4$:Eu$^{3+}$ is a red emitter phosphor commercially available as micrometric powder due to its high luminescence efficiency under electron-beam excitation. Although some published results have demonstrated the potential of using this micrometer material in Fiber Optic Dosimetry systems, there is no information regarding its use on a nanometric scale. In order to obtain a nanometric material with high luminescent efficiency, a simple synthetic combustion method was developed and the results were compared with both, those of a commercial material and those obtained by a typical coprecipitation synthesis. A single crystalline phase was obtained when the combustion route was employed for the preparation meanwhile two crystalline phases were obtained via coprecipitation synthesis. The particle size of YVO$_4$:Eu$^{3+}$ obtained by combustion route ranges from 55 up to 200 nm. Fourier Transform Infrared Spectroscopy and Thermogravimetric Analysis indicated that annealing at 600°C promote the degradation of the impurities that remained adsorbed onto nanoparticles surface after the synthesis. However, to improve the Radioluminiscense intensity, an annealing process at 1000 °C was required. The method allows obtaining a nanometric material with a scintillation intensity almost twice higher than that of the commercial powder.

Keywords: Optical materials, chemical synthesis, crystal structure, luminescence, optical spectroscopy
1. Introduction

In recent years, phosphor materials have become more and more attractive for several applications. They are used from cathode ray tubes and plasma display panels to biological labels and luminescence immunoassay, including other fields. Dosimetry in radiotherapy treatments is another possible application of phosphors. Fiber Optic Dosimetry (FOD) is a technique known as an alternative to traditional dosimetry systems. FOD allows in vivo measurements of dose rate, using a small scintillator attached to the end of an optical fiber. The scintillator could be either an organic or inorganic phosphor. When the scintillator is irradiated with high energy beams, the Radioluminescence (RL) emitted is in general proportional to the dose rate absorbed by the phosphor [1].

Despite the particular application, phosphor materials have the singular characteristic of acting as optical transducers: they convert ionizing radiation into visible radiation [2]. When a phosphor material returns to ground state after being excited, it emits radiation with a characteristic wavelength that is related with the identity of the chemical structure. In particular, Rare Earth (RE) elements can work as efficient optical activators of this process. They are used as dopants in different hosts. A RE widely employed as optical activator is Europium, which has a red emission at about 620 nm after excitation if present as Eu$^{3+}$ cation [3].

Vanadates, tungstates, molybdates and other complex oxides are ideal hosts for RE dopants [4]. Among them, Yttrium vanadate, YVO$_4$, is the typical host for Europium. YVO$_4$ have a tetragonal zircon type crystalline structure [5]. The atoms are arranged like two distorted tetrahedral, where Yttrium atoms are coordinated by eight Oxygen atoms and Vanadium ones are surrounded by four Oxygen atoms. Doping with Europium generates a substitution process, where Eu$^{3+}$ occupies Y$^{3+}$ sites [2]. Sevic, Rabasovic, Krizan, Savic-Sevic, Mitric, Gilic, Hadzic and Romcevic [6] have reported that doping YVO$_4$ with Eu$^{3+}$ does not change the crystalline structure of the material, but according to Kumari, Baitha and Manam [4] it might generate changes in the interplanar spacing because Eu$^{3+}$ ionic radius is bigger than Y$^{3+}$ radius.

Since 1964 YVO$_4$:Eu$^{3+}$ is a red emitter phosphor commercially available as micrometric powder due to its high luminescence efficiency under electron-beam excitation [7]. For this reason, it has been widely employed by industry as red emitter for CRT screens. The feasibility of using YVO$_4$:Eu$^{3+}$ as FOD detector has been demonstrated by Martínez, Rucci, Marcuzzó, Molina, Santiago and Cravero [1], who employed micrometric YVO$_4$:Eu$^{3+}$ powder to fabricate efficient
scintillators having a volume of 1-3 mm³. However, no analogous studies for nanometric particles have been carried out so far.

Several reports point out that employing nanometric powder enhances overall scintillation yield by reducing optical scattering losses [8, 9]. Also, enhancement of the scintillation yield of nanometric size phosphors -with respect to micrometric ones- has been reported [10, 11]. The mentioned results make the development of YVO₄:Eu³⁺ based nanoparticle scintillators an issue of interest in the framework of the application of this material to scintillation technology.

The synthesis of YVO₄:Eu³⁺ as nanometric powder has been widely studied by several routes. Uitert, Linares, Soden and Ballman [12] synthesized YVO₄:Eu³⁺ via a solid state reaction. This method has some limitations, such as the lack of homogeneity of the product, the requirement of high annealing temperatures, formation of large particles that have to be milled by mechanical treatments, long times of heat treatments, etc.

In contrast, wet chemical methods are a suitable option for nanoparticle synthesis of YVO₄:Eu³⁺ [2]. Yanhong and Guangyan [13] have reported this synthesis by a traditional coprecipitation method. Huignard, Gacoin and Boilot [14] have studied the same route for colloidal YVO₄:Eu³⁺ nanophosphors. Riwotzki and Haase [15] and Rafiaei and Shokouhimehr [16] synthesized YVO₄ nanoparticles doped with different phosphors by hydrothermal methods. In addition, Ansari and Labis [17] reported the synthesis of nanofibers of YVO₄:Eu³⁺ via an hydrothermal route. Also, the synthesis of Europium doped Yttrium Vanadate using sol-gel methods was studied [18, 19] and novel techniques were reported for the synthesis of this material [20, 21]. However, there are some disadvantages associated with the synthetic techniques mentioned above. For example, coprecipitation method requires high annealing temperature to reach crystallinity in the final product and hydrothermal method demands conditions of high pressures, requiring autoclave reactor.

Combustion route is a simple wet chemical method that requires fuels and oxidizers. It takes place when the mixture of precursors and fuels reaches the auto ignition temperature. Auto ignition temperature is the minimum required temperature at which a fuel in contact with air burns spontaneously. An exothermic reaction is carried out during this process, which under certain conditions could produce a flame.

The required amount of fuels is given by the relationship between oxidizing and reducing components. According to Jain, Adiga and Pai Verneker [22] \( \phi_e \) is defined as the ratio between total amounts of oxidizing elements and reducing elements in the mixture. The combustion could be complete, fuel-rich or lean-rich depending on \( \phi_e \) value. If \( \phi_e = 1 \), the reaction is...
stoichiometrically balanced and the combustion is complete. In order to minimize damages on environment and avoid production of toxic gases the most suitable option is to work in complete combustion conditions.

Combustion route is a feasible method for the synthesis of luminescent materials, especially for RE doped ones due to its low temperature conditions and short reaction times [2, 23-27]. There are few reports that studied the synthesis of YVO₄:Eu³⁺ via a combustion route. Ekambaram and Patil [28] reported the synthesis of different vanadates doped with Europium (including Yttrium) using ammonium nitrate and 3-methylpyrazole-5-one as fuels. However, they did not report the particle size neither the study of any luminescent property. Kumari, Baitha and Manam [4] studied the synthesis of YVO₄:Eu³⁺ via a combustion route using urea as fuel but they also found a phase of Y₂O₃ in formation. Shokouhimehr and Rafiaei [29] and Rafiaei, Kim and Shokouhimehr [30] compared the effect of different fuels and different solvents in photoluminescence properties and phosphor nanostructure and Rafiaei and Shokouhimehr [31] studied the impact of alumina crucible dimensions in luminescence properties of YVO₄:Eu³⁺. Sevic, Rabasovic, Krizan, Savic-Sevic, Mitric, Gilic, Hadzic and Romcevic [6] reported the formation of YVO₄:Eu³⁺ pure nanoparticles (from 37 to 71 nm) via a combustion route using urea and ammonium nitrate as fuels, but the selected amounts of reagents do not match with those conditions for complete combustion requirements [22]. Recent works have shown efficient cathodoluminescence of sub-micrometer-sized YVO₄:Eu³⁺ samples fabricated by hydrothermal synthesis, which points out the possibility of using YVO₄:Eu³⁺ nanoparticles for ionizing radiation detection [32].

In this work, with the aim of developing a scintillator based on YVO₄:Eu³⁺ nanoparticles suitable for FOD, YVO₄:Eu³⁺ nanoparticles were synthesized employing a combustion method. The reported strategy involves the comparison of the structural and the luminescent properties of YVO₄:Eu³⁺ nanoparticles obtained by the traditional coprecipitation method and combustion route using urea and ammonium nitrate as fuels. The response of the YVO₄:Eu³⁺ nanoparticles to electron irradiation was also evaluated in order to assess the feasibility of using these compounds as detector of ionizing radiation.

2. Material and methods

2.1 Synthesis

YVO₄ nanoparticles were synthesized by two different methods: coprecipitation and combustion route. In both cases, the effect of Eu³⁺ as dopant was studied, so the samples were
synthesized undoped and doped with 5% mol of Eu$^{3+}$. This concentration has shown to render the most efficient emission of Eu$^{3+}$ doped into this host [33].

Coprecipitation method was reproduced as reported by Yanhong and Guangyan [13]. The starting chemicals were Y(NO$_3$)$_3$.6H$_2$O (Sigma-Aldrich 99.8%), Eu(NO$_3$)$_3$.5H$_2$O (Sigma-Aldrich 99.9%), NH$_4$VO$_3$ (Biopack>99%) and NaOH (Anedra 99.3%). For the undoped sample, 40 mL of a NH$_4$VO$_3$ solution 0.05 M was adjusted to pH 12.5 with a NaOH solution. 40 mL of a Y(NO$_3$)$_3$ solution 0.05 M was added dropwise. The mixture was then heated at 60˚ C under magnetic stirring for 1 h. The white opalescent colloid resulting was filtered, washed, dried at 60˚ C and annealed for 2.5 h at 1000˚ C if required. The procedure for the doped sample was analogous, except that instead of using 40 mL of Y(NO$_3$)$_3$ solution 0.05 M as before, 38 mL of Y(NO$_3$)$_3$ solution plus 2 mL of Eu(NO$_3$)$_3$ solution 0.05 M were employed. The chemical reaction involved is shown in (1).

\[
(1 - x)Y(NO_3)_3 + xEu(NO_3)_3 + NH_4VO_3 \rightarrow Y_{1-x}Eu_xVO_4
\]  

(1)

where x=0 for the undoped sample and x=0.05 for the doped sample.

Combustion route was carried out for an oxidizer/fuel ratio equal to 1 [2]. The starting chemicals were Y(NO$_3$)$_3$.6H$_2$O (Sigma-Aldrich 99.8%), Eu(NO$_3$)$_3$.5H$_2$O (Sigma-Aldrich 99.9%), NH$_4$VO$_3$ (Biopack>99%); (NH$_2$)$_2$CO (Anedra 99%) and NH$_4$NO$_3$ (Stanton 99%) as fuels, all of them in analytical grade. The chemical reaction can be symbolized as follows, analogous to that reported by Foka K. E. [34]:

\[
(1 - x)Y(NO_3)_3 + xEu(NO_3)_3 + NH_4VO_3 + 3(NH_2)_2CO + 3NH_4NO_3 \rightarrow Y_{1-x}Eu_xVO_4 + 14H_2O + 8N_2 + 3CO_2
\]  

(2)

where x= 0 for the undoped sample and 0.05 for the doped sample.

For instance, 3.03 g of Y(NO$_3$)$_3$.6H$_2$O, 0.18 g of Eu(NO$_3$)$_3$.5H$_2$O, 0.97 g of NH$_4$VO$_3$, 1.50 g of (NH$_2$)$_2$CO and 2.00 g of NH$_4$NO$_3$ were separately dissolved in distilled water. Each solution was slowly added to the Y(NO$_3$)$_3$ solution. The resulting yellow solution was then concentrated by heating at 70 °C under magnetic stirring until free water evaporated. Then, the as-prepared red gel was heated at 200°C in a heating mantle for 2 h until the combustion was completed. A foamy orange powder was obtained and certain fractions were annealed at 600, 800 or 1000 °C for 2.5 h. For the undoped sample the proceeding was analogous, all amounts were the same except that of Y(NO$_3$)$_3$.6H$_2$O, which was 3.19 g.

\[\text{2.2 Characterization techniques}\]
X-Ray Diffraction (XRD) analysis of the samples were carried out on a Philips 3020 diffractometer with CuKα radiation (λ = 1.54 Å) and Ni filter at 34 kV and 40 mA. All patterns were recorded in the 2θ range from 15˚ to 70˚ with a step size of Δ2θ= 0,04˚.

Fourier Transform Infrared Spectroscopy (FTIR) data were obtained on a Nicolet Magna 550 spectrometer with Nernst filament source, Germanium film with ICs beamsplitter and DTGS pyroelectric detector. The patterns were obtained from 400 cm\(^{-1}\) to 4000 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\) after making pellets of the samples diluted in KBr via hydraulic press machine.

TEM images were taken in a transmission electron microscope Jeol JEM 2100 with B6La filament at 200 kV. These images were processed using Image J software and the histograms for particle sizes were carried out in Origin Pro 8.

Thermogravimetric Analysis (TGA) of the nanoparticles were performed in a Q500 TA Instrument thermogravimetric analyzer. Tests were carried out at a heating rate of 10 °C/min from 30 to 900 °C in air atmosphere. The samples were about 10 mg in all cases.

The excitation and emission spectra were obtained in a Varian Cary Eclipse fluorescence spectrophotometer. Measurements were recorded at a scan rate of 600 nm/min and with a spectral resolution of 5 nm. The Decay times of the luminescence signals were also investigated. The samples were excited with UV pulses (266 nm) from the fourth harmonic of a Continuum Surelite II Nd:YAG pulsed laser. The light coming from the sample was filtered to get rid of spectral components having wavelength shorter than 520 nm. Luminescence was detected by means of a Hamamatsu-H7360-03 photon counting head. The emission light was recorded for 60 seconds at a pulse frequency of 10 Hz. Pulses were averaged and fitted with a two-component exponential decay function to obtain characteristic lifetimes (τ\(_1\) and τ\(_2\)) of the UV-excited emission.

Radioluminescence (RL) measurements were carried out to assess the scintillation yield of each sample. The results were compared with those from a commercial sample of YVO\(_4\):Eu\(^{3+}\) kindly provided by Phosphor Technology Ltd. (United Kingdom). Commercial powder has an average particle size of 5 μm (according to the manufacturer specifications). Samples were irradiated at room temperature by resorting to a 10 mCi opthalmic 90Sr beta-source rendering a dose rate of 0.022 Gy/min at the sample position. The intensity of the scintillation light was recorded with a Hamamatsu H7360-03 photon counting head. This light detector has a spectral window ranging from 300 up to 850 nm.

3. Results and discussion
3.1 Structure characterization

XRD measurements were performed on the nanoparticles to extract information about their crystalline structure.

Figure 1 shows the diffraction profiles recorded for the undoped nanoparticles synthesized by coprecipitation method and combustion route. For both cases, patterns corresponding to the as-synthesized nanoparticles and after annealing at 1000˚C are shown. As can be seen, the as-synthesized nanoparticles show broad diffraction peaks and weak signals, typical of low crystallinity nanoparticles. In contrast, the annealed nanoparticles exhibit narrow and more intense diffraction peaks, indicating an improvement in crystallinity due to the annealing. For identification purpose, these patterns were compared with those reported in the Crystallography Open Database (COD). A single crystalline phase is identified in combustion nanoparticles which corresponds to YVO$_4$ (9009764 COD). Instead, two crystalline phases were identified in coprecipitation nanoparticles, Y$_2$O$_3$ and YVO$_4$. The crystalline phase corresponding to Y$_2$O$_3$ was identified by the diffraction peak at 2θ = 29.2˚ assigned to the reflections from the (222) plane of the Y$_2$O$_3$ crystal lattice (1009015 COD). Semiquantitative analysis results are 95% YVO$_4$ and 5% Y$_2$O$_3$.

Figure 2 compares the XRD patterns of doped and undoped samples synthesized by coprecipitation method after annealing at 1000 °C. The doped nanoparticles show three crystalline phases identified as YVO$_4$, Y$_2$O$_3$ and Eu$_2$O$_3$ according to reported in COD. In addition, the highest intensity peak corresponds to Y$_2$O$_3$, indicating that this is the crystalline phase that is present in the highest proportion (semiquantitative analysis results are 52% Y$_2$O$_3$, 26% Eu$_2$O$_3$ and 22% YVO$_4$). Attending that the main objective of this work is the synthesis of doped YVO$_4$ due to its subsequent technological application as scintillator nanoparticles suitable for FOD, the focus will be centered on the nanoparticles obtained by combustion synthesis.

Figure 3 shows XRD patterns of doped nanoparticles synthesized by combustion route (as-synthesized and annealed at 1000°C) and, as reference, the pattern corresponding to the undoped nanoparticles annealed at 1000°C. All diffraction peaks are in good agreement to those reported in COD for YVO$_4$ structure. No additional peaks that could suggest the presence of another crystalline phase in doped samples are observed. This is strong evidence that can justify the substitution of Y$^{3+}$ by Eu$^{3+}$ into YVO$_4$ structure [6]. It can be observed that peak positions in doped samples are slightly shifted towards lower 2θ values. According to Kumari, Baitha and Manam [4], it could be due to the higher ionic radius of Eu$^{3+}$ with respect to Y$^{3+}$. It
would increase crystalline network size and consequently the crystallite size, $D$, whose value can be calculated using Scherrer equation [35]:

$$D = \frac{\lambda}{B \cos \theta}$$

where $K$ is a factor related to crystallite shape (0.9 is generally a good approximation), $B$ the width of the X-ray diffraction peak in radians, $\lambda$ the X-ray wavelength (0.15405 nm) and $\theta$ the diffraction angle. According to maximum intensity peak, the estimated crystallite sizes are listed in Table 1. The increment in the values of “$D$” also highlights the effect of annealing on crystallinity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing temperature</th>
<th>$D$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YVO$_4$</td>
<td>-</td>
<td>24</td>
</tr>
<tr>
<td>YVO$_4$</td>
<td>1000°C</td>
<td>43</td>
</tr>
<tr>
<td>Y$<em>{0.95}$Eu$</em>{0.05}$VO$_4$</td>
<td>-</td>
<td>31</td>
</tr>
<tr>
<td>Y$<em>{0.95}$Eu$</em>{0.05}$VO$_4$</td>
<td>1000°C</td>
<td>54</td>
</tr>
</tbody>
</table>

Table 1: Crystallite size ($D$) estimated by Scherrer equation.

### 3.2 Morphological characterization

Figure 4 shows TEM images of the nanoparticles synthesized by combustion route. In all of them, it can be clearly seen that nanoparticles are agglomerated. In as-synthesized samples a) and c), the nanoparticles present low crystallinity (attending to XRD data previously shown) but have an apparently homogenous morphology. In annealed samples b) and d), the nanoparticles are bigger, with an improved crystallinity but with a more heterogeneous morphology. These images put on evidence that the annealing promotes coalescence and aggregation processes that increase nanoparticle size and result in more polyhedral shapes.

Figure 5 shows histograms of the nanoparticle size calculated by TEM image analysis. Starting with the undoped samples, 96% of as-synthesized nanoparticles (histogram (a)) have particle sizes below 14 nm, 52% of them are in the range of 6-10 nm. In the case of the annealed nanoparticles (histogram (b)), 95% of the nanoparticles have particle sizes lower than 250 nm with a 51% of them comprised between 100-150 nm. The analysis clearly shows the effect of heat treatment on increasing particle size.

Analogously for doped samples, 95% of as-synthesized nanoparticles (histogram (c)) have particle sizes lower than 14 nm with a 52% of them comprised between 6-10 nm. According to
histogram (d), after the annealing, 79% of the nanoparticles have particle sizes lower than 250 nm while 55% of them are in the range of 50-200 nm.

From the comparison between annealed nanoparticles (doped and undoped), it is noted that the maximum particle size registered for the undoped nanoparticles was around 400 nm meanwhile for the doped nanoparticles (synthesized under the same conditions) it was significantly higher, around 550 nm.

The differences observed between the values obtained for the crystallite size (D, Table 1) and for the particle size (calculated from TEM images) can be justified based on the dislocations and defects present in the structures of the nanoparticles. These two parameters would have the same value in the ideal case in which the grains were simple perfect crystals. In the present case, TEM images show agglomeration and several defects that interrupt the periodicity of the crystalline structure. Therefore, an individual particle may contain a number of crystallites defined as coherently diffracting regions [36, 37].

3.3 Surface Characterization

FTIR spectra for YVO₄:Eu³⁺ nanoparticles synthesized by coprecipitation and combustion methods after annealing are shown in Figure 6. Combustion sample presents two characteristic bands. The intense band observed around 812 cm⁻¹ is characteristic of V-O bond vibration, particularly of VO₄³⁻ group. Another band with lower intensity is located around 453 cm⁻¹. It is associated with the vibration of the Y-O bond [4, 38]. There are no evidences that suggest that the sample could have any impurity adsorbed on the surface. Considering XRD data shown previously, it can be concluded that YVO₄:Eu³⁺ nanoparticles obtained by combustion route after annealing correspond to a pure compound.

On the other hand, FTIR spectrum of coprecipitation nanoparticles shows at least four characteristic bands. The two located around 839 and 476 cm⁻¹ are characteristic of V-O and Y-O bond vibrations, respectively. There is another band near 766 cm⁻¹ that can be attributed to N-O bond vibration corresponding to some precursor that could have been adsorbed on the surface [39]. As XRD data showed, this sample has three crystalline phases: YVO₄, Y₂O₃ and Eu₂O₃ with yttrium oxide in majority. In FTIR spectrum of coprecipitation sample, the most intense band is the one located in 476 cm⁻¹ (in combustion sample is the one located in 812 cm⁻¹). It could indicate that there are more Y-O bonds that increase the intensity of the band, due to the presence of Y₂O₃ crystalline phase. However, FTIR analysis does not show any evidence
of Eu₂O₃ formation, probably because Eu-O bonds have characteristic vibrations that appear at frequencies lower than 400 cm⁻¹[40].

Figure 7 shows FTIR spectra of YVO₄ nanoparticles obtained by combustion route. There are five characteristic bands in the as-synthesized sample. The two located around 812 and 453 cm⁻¹ are attributed to V-O and Y-O bond vibration respectively. The broad peak near 3410 cm⁻¹ could be assigned to O-H stretching vibrations and the one located around 1640 cm⁻¹ to O-H bending vibrations [38]. The band near 1380 cm⁻¹ is characteristic of C-O bending vibrations [4]. There could be another peak not well defined around 1310 cm⁻¹ associated with the presence of NO₃⁻ group vibration [41]. Therefore, there are impurities associated with precursors that might be adsorbed on nanoparticle surface. Figure 7 also shows the spectra corresponding to the annealed samples at two different temperatures (600 and 1000 °C) in order to evaluate the effect of annealing temperature on the nanoparticles composition. As can be seen, impurity bands almost disappear in FTIR spectra as the annealing temperature increases, likely due to temperature-activated surface degradation processes. Furthermore, there are no significant differences between doped and undoped FTIR spectra after annealing at 1000 °C. It could indicate that the presence of Eu³⁺ does not change the composition of the nanoparticles surface.

3.4 Thermal Characterization

In order to contrast the data obtained through FTIR spectra, a Thermogravimetric Analysis (TGA) of the as-synthesized YVO₄:Eu³⁺ nanoparticles obtained by combustion route was carried out (Figure 8). As can be seen, the mass loss takes place in two consecutive steps. The first occurs between 100-200 °C, showing a 5% mass loss. It is immediately followed by the second step comprised between 250-550 °C, which has a lower slope. About 10% of initial mass is lost between these two steps. After that, it seems to be only slight changes in the nanoparticles mass.

Considering also FTIR data, the mass loss shown by TGA data could be due to superficial changes, in particular, to the degradation of impurities that remained adsorbed on surface immediately after reaction.

3.5 Luminescence properties

Figure 9 shows the emission spectra (λex=271 nm) of YVO₄:Eu³⁺ corresponding to the commercial sample (red line) and the combustion sample annealed at 1000°C (black line) normalized with respect to sample weight. The shapes of both spectra fairly match. The
observed emission peaks can be assigned to characteristic transitions of Eu\(^{3+}\) cation. In particular, peaks located at 590, 618, 652 and 699 nm are characteristic of \(5D_0 \rightarrow 7F_J\) \((J=1, 2, 3, 4)\) transitions. Luminescence from higher excited states of Eu\(^{3+}\) can also be identified, namely, peaks at 555 and 595 nm corresponding to \(5D_1 \rightarrow 7F_2\) and \(5D_1 \rightarrow 7F_3\) transitions, respectively [4, 11]. The prominence of the emission corresponding to the \(5D_0 \rightarrow 7F_2\) transition with respect to the intensity of the peak assigned to the \(5D_0 \rightarrow 7F_1\) transition demonstrates that Eu\(^{3+}\) cations occupy sites having low inversion [19]. The presence of \(5D_1\) emission peaks can be possible by taking into account that the vibration energy of VO\(_4^{3-}\) groups is not high enough to depopulate the \(5D_1\) states through the \(5D_0\) level [19]. It is also apparent from Figure 9 that YVO\(_4\):Eu\(^{3+}\) nanoparticles emit more efficiently than micrometric powder under UV excitation. This effect has been also observed in many other phosphors and could be related to the confinement of the longer lifetime excitation of Eu\(^{3+}\) within the nanoparticles [11, 42, 43]. Indeed, the decay lifetimes of the YVO\(_4\):Eu\(^{3+}\)combustion nanoparticles annealed at 1000°C are slightly higher than those corresponding to the commercial sample, as can be seen from Table 2. As can be seen from the table, two exponential decaying signals had to be assumed to consistently fit the experimental data. The values obtained are fairly similar to previous reports, which demonstrates efficient synthesis of YVO\(_4\):Eu\(^{3+}\)nanoparticles [32].

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\tau_1) (s)</th>
<th>(\tau_2) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial YVO(_4):Eu(^{3+})</td>
<td>0.0117 ± 0.0002</td>
<td>0.0633 ± 0.0001</td>
</tr>
<tr>
<td>Combustion YVO(_4):Eu(^{3+}) (1000°C)</td>
<td>0.0128 ± 0.0001</td>
<td>0.0707 ± 0.0002</td>
</tr>
</tbody>
</table>

Table 2: Decay lifetimes of the photoluminescence signal of the commercial sample and of YVO\(_4\):Eu\(^{3+}\)nanoparticles synthesized by the combustion method after annealing at 1000°C.

The dependence of the scintillation yield of the YVO\(_4\):Eu\(^{3+}\) combustion sample as function of the annealing temperature is shown in Figure 10. The RL signal has been normalized to the RL emission of the commercial sample. Maximum relative scintillation is attained after annealing the sample at 1000°C, being the scintillation intensity of this sample almost twice higher than that of the commercial powder. The scintillation signal of the most efficient YVO\(_4\):Eu\(^{3+}\) combustion sample, namely, the sample annealed at 1000°C is compared to that from the commercial sample (Figure 11). Both signals have shown to be stable and repetitive along the irradiation time. The enhancement of the luminescence as the sample is annealed at higher temperature is probably related to the better crystallinity and phase purity achieved by the thermal treatment [32, 44].
According to FTIR and TGA data, there are impurities adsorbed on nanoparticles surface that remain after combustion synthesis. These impurities could provide non-radiative paths to relaxation. These compounds are eliminated when annealing temperature increases, as confirmed by TGA analysis. At the same time higher crystallinity is attained, so improving the scintillation efficiency.

From emission spectra it is possible to calculate the chromaticity coordinate values of CIE 1931 Diagram. YVO₄:Eu³⁺ is a red-emitting phosphor so their coordinates are around this region of CIE Diagram. As seen in Figure 12, both commercial and combustion samples have almost the same coordinates (x=0.63 and y=0.37), which are similar to those previously reported [4, 6].

The particles synthesized by the combustion method have high crystallinity, an homogenous morphological distribution and nanometric particle sizes. In turn, the synthesis method is simple, fast and does not require sophisticated equipment. The luminescent behavior is promising for its application as a scintillator in the technological design of new composite materials for FOD. In a next stage the development of a composite material will be carried out to be used as a sensor at the ends of an optical fiber.

4. Conclusions

In order to synthesize YVO₄:Eu³⁺ nanoparticles a thorough analysis of two different preparation methods, namely, coprecipitation and combustion routes, was carried out. Nominally pure and Europium doped samples were obtained in order to evaluate crystalline structural changes when Eu³⁺ replaces Y³⁺ cation into the YVO₄ host.

In the sample prepared by coprecipitation, two different crystalline phases were obtained (yttrium oxide and yttrium vanadate). Probably due to the coexistence of multiple phases and related quenching effects of radiation-induced luminescence, the RL intensity of this sample was almost undetectable.

In contrast, a unique crystalline phase was obtained when the combustion route was employed for the preparation. In this case, particle size ranges from 55 up to 200 nm. FTIR and TGA analysis indicated that annealing at 600°C promote the degradation of the impurities that remain adsorbed on nanoparticles surface after synthesis. However, to improve the RL intensity, it was necessary to anneal the nanocrystalline powder at 1000°C. After this thermal treatment, RL intensity of this sample was almost twice higher than that of the commercial microcrystalline sample. Emission spectra under UV excitation are characteristic of f-f
electronic transitions of Eu$^{3+}$ cation. CIE 1931 Diagram indicates that combustion sample have
the same coordinates than commercial YVO$_4$:Eu$^{3+}$.

Combustion route is a technically simple and inexpensive synthesis method to obtain
YVO$_4$:Eu$^{3+}$ nanoparticles, which could be employed to develop suitable scintillators for Fiber
Optic Dosimetry due to their good structural and optical properties.

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Figure Captions

Figure 1. XRD patterns of undoped samples synthesized via coprecipitation method and combustion route.

Figure 2. XRD patterns of coprecipitation YVO₄ samples.

Figure 3. XRD patterns of combustion YVO₄ samples.

Figure 4. TEM images of YVO₄ samples. a) undoped, as-synthesized b) undoped, annealed at 1000°C c) doped, as-synthesized d) doped, annealed at 1000°C

Figure 5. Size histograms for YVO₄ samples. a) undoped, as-synthesized b) undoped, annealed at 1000°C c) doped, as-synthesized d) doped, annealed at 1000°C

Figure 6. FTIR analysis for YVO₄:Eu³⁺ samples.

Figure 7. FTIR spectra of YVO₄:Eu³⁺ combustion samples.

Figure 8. Thermogravimetric Analysis for YVO₄:Eu³⁺ combustion sample.

Figure 9. Emission spectra of YVO₄:Eu³⁺ samples excited at 271 nm

Figure 10. RL intensity of YVO₄:Eu³⁺ sample synthesized by combustion route at different annealing temperatures, normalized to the RL of the commercial sample.

Figure 11. Radioluminescence signal from the YVO₄:Eu³⁺ sample annealed at 1000°C and the commercial sample.

Figure 12. CIE 1931 Diagram
Highlights

Combustion route is a simple synthesis method to obtain YVO$_4$:Eu$^{3+}$ nanoparticles.

Radioluminescence intensity is twice higher than that of microcrystalline sample.

YVO$_4$:Eu$^{3+}$ synthesized are suitable scintillators for Fiber Optic Dosimetry.
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: