High Eu\(^{3+}\) concentration quenching in \(Y_3TaO_7\) solid solution for orange-reddish emission in photonics†

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We report the synthesis of a \(Y_3TaO_7\) solid solution containing a high Eu\(^{3+}\) concentration (from 7 up to 50 mol%) and investigate how Eu\(^{3+}\) influences the \(Y_3TaO_7\) crystallization process. To this end, we evaluate the \(Y_3TaO_7\) structural features and photoluminescence properties after Eu\(^{3+}\) introduction into the \(Y_3TaO_7\) lattice. The higher the Eu\(^{3+}\) ion concentration, the more stable the crystallization process of the \(Y_3TaO_7\) phase seems to be. The Eu\(^{3+}\)-containing \(Y_3TaO_7\) displays intense orange-reddish, broad band emission because Eu\(^{3+}\) occupies different symmetry sites in the host and causes inhomogeneous broadening. Eu\(^{3+}\) emission quenching due to Eu\(^{3+}\) concentration is negligible up to 30 mol% and absolute quantum yield values of up to nearly 30% were obtained, making Eu\(^{3+}\)-containing \(Y_3TaO_7\) interesting materials for application as high-intensity emitters in photonics.

1. Introduction

Inorganic materials have been extensively used as rare earth ion (RE\(^{3+}\)) hosts. In particular, metal oxide (\(M_2O_3\)) matrices have been largely employed for this purpose because they present tunable structures, are chemically and thermally stable, exhibit optical transparency over a wide spectral range (UV-NIR), and have a high refractive index and low phonon energy, which all enable their large-scale application in photonics.\(^1\)–3 One of the challenges in photonics is the development of materials that allow the incorporation of a high concentration of RE\(^{3+}\), avoiding rare earth cluster formation. The high solubility of RE\(^{3+}\) into the host, prevents effective concentration quenching process. As a consequence, these materials can exhibit high emission brightness and intensity, which are requirements for applications in lighting, displays, bioimaging, among others. In this sense, there is a crescent emphasis have been given to fluorite (CaF\(_2\))-related crystal structures as RE ion hosts.\(^4\)–15 The fluorite cubic structure has a general composition of \(MO_2\) per unit cell, where \(M\) is a tetra-valent metal. Compounds derived from the fluorite structure have aroused growing interest: several materials can be synthesized by replacing the \(M^{4+}\) cations with ions of different valences. This substitution generates oxygen vacancies for charge compensation.\(^5\)–18

Compounds with the general formula \(A_xM_2O_7\) (\(A = \text{RE and } M = \text{Ti, Sn, Zr, Hf}\)) are a class of oxides with fluorite-related structures.\(^19\) Depending on the ratio between the \(A^{3+}\) and \(M^{4+}\) ionic radii \((r_A/r_M)\), the compound generally crystallizes in fluorite (lower ratio) or pyrochlore crystal structure (higher ratio).\(^20\) In the latter structure, \(M^{4+}\) and \(A^{3+}\) are coordinated with six and eight oxygen atoms, respectively.\(^21\) Substitution introduces two oxygen vacancies for charge compensation. Pyrochlore and weberite (another kind of crystal structure with the same stoichiometry as pyrochlore) are anion-deficient fluorite-related superstructures.\(^17\) Only a few recent works about fluorite-related structures doped with high RE ion concentrations have been published.\(^22,23\)

Ternary RE ion compounds (\(\text{RE}_3\text{MO}_7\)) are also fluorite-related structures that are closely related to the weberite structure, but replacement is different. The four \(M^{4+}\) ions of the fluorite unit cell are replaced with three \(\text{RE}\)\(^{3+}\) ions and one \(M^{5+}\) ion (\(M = \text{Nb, Ta, Sb, Ru, Ir, Os, Re, etc.}\)), and one oxygen vacancy arises per fluorite cell.\(^8\)–17 Significant differences between the \(\text{RE}^{3+}\) and \(M^{5+}\) ionic radii lead to cation ordering at the metal sites and to oxygen vacancy ordering at the anion sites.\(^8\)–16 This structure exhibits distinct \(\text{RE}^{3+}\) configuration—seven and eight coordination ions, where REO\(_7\) exist between MO\(_6\)–REO\(_8\) layers.\(^17\) Depending on \(\text{RE}^{3+}\) and \(M^{5+}\), the structure and space group in which \(\text{RE}_3\text{MO}_7\) compounds crystallize vary, and many polymorphic modifications can be obtained only on the basis of processing conditions.\(^24\) The magnetic properties of fluorite-based materials have been studied to a large extent, and their
high versatility has been demonstrated through their application in different areas.\textsuperscript{7,8,25-28} Some structural studies on RE\textsuperscript{3+}-doped fluoride-related structures have shown that RE\textsuperscript{3+} ions are considerably soluble in their hosts. Besides the zirconates and hafnates cited above, there have been reports on tantalates, niobates, and antimonates with high RE\textsuperscript{3+} dopant ion concentration.\textsuperscript{9,11-16} Similar ionic radii and valence mean that the RE\textsuperscript{3+} dopant ions preferentially substitute the RE ions of the oxide structure.\textsuperscript{29} These complex structures provide a spatial arrangement where the distance between two Eu\textsuperscript{3+} ions allows a higher accommodation of these ions into the lattice without lead to concentration quenching, differently than other oxides.\textsuperscript{9} These characteristics make this type of structure interesting for application as high-intensity emitters in photonics.

Fu \textit{et al.}\textsuperscript{29} reported that the Y\textsubscript{3}TaO\textsubscript{7} crystalline phase consists of an orthorhombic \textit{Ccmm} space group with unit cell parameters related to the fluoride-type cubic structure ($a_{\text{cubic fluorite}} = 5.3$ Å); the relation is $a = 2a_c$, $b = \sqrt{2}a_c$, and $c = \sqrt{2}a_c$ for the Y\textsubscript{3}TaO\textsubscript{7} crystalline structure. In this structure, Y\textsuperscript{3+} coordinates with seven or eight oxygen atoms, whereas Ta\textsuperscript{5+} coordinates with six oxygen atoms. Molchanov \textit{et al.}\textsuperscript{31} described that Y\textsubscript{3}TaO\textsubscript{7} starts to decompose at high annealing temperatures (above 900 °C) and precipitates as Ta\textsubscript{2}O\textsubscript{5}, which reacts with the former compound to give a polymorphic crystalline phase M-YTaO\textsubscript{4}. According to our previous report,\textsuperscript{32} at lower Eu\textsuperscript{3+} concentrations (up to 5.0 mol%), Eu\textsuperscript{3+} ions incorporated into the host delay YTaO\textsubscript{4} formation.

Introduction of impurities, such as dopant ions, into a crystalline host, is an effective method to manipulate and to control the properties of a material, including its crystalline structure, phase transition, and grain size and shape, among others. The choice of dopant ion is based on similarities between the dopant and the host ions, like the ionic radius, valence, and chemical properties.\textsuperscript{33} The dopant ion can occupy either a substitutional or an interstitial site in the host lattice.\textsuperscript{34,35} The dopant may be either partially soluble or co-soluble in the host lattice, forming a solid solution and stabilizing a crystalline phase. Therefore, the properties of the solid solution can be tailored for specific applications. In this sense, Eu\textsuperscript{3+} doping into the Y\textsubscript{3}TaO\textsubscript{7} lattice can be used not only to study the photoluminescence properties of the resulting solid but also to manipulate the crystalline structure. This is desirable because a pure yttrium tantalate phase is difficult to obtain, due to its polymorphism properties.\textsuperscript{36,37}

In this paper, we explore Eu\textsuperscript{3+} solubility within Y\textsubscript{3}TaO\textsubscript{7}. We discuss how the incorporation of higher Eu\textsuperscript{3+} concentrations into Y\textsubscript{3}TaO\textsubscript{7} affects host stabilization and luminescence features. First, we synthesize Eu\textsuperscript{3+}-doped Y\textsubscript{3}TaO\textsubscript{7} solid solutions with higher Eu\textsuperscript{3+} concentration (from 7 up to 50 mol%) to investigate how Eu\textsuperscript{3+} influences YTaO\textsubscript{4} crystallization. Next, we evaluate the Y\textsubscript{3}TaO\textsubscript{7} structural features after Eu\textsuperscript{3+} is introduced into the lattice and assess the matrix photoluminescence properties, with Eu\textsuperscript{3+} functioning as a structural local-probe. We will show that the matrix excited state lifetime only decreases at the highest Eu\textsuperscript{3+} concentration employed herein. Rising Eu\textsuperscript{3+} concentrations elicit negligible Eu\textsuperscript{3+} emission quenching, which makes the application of these materials as high-intensity emitters in photonics especially interesting.

2. Experimental procedure

2.1 Eu\textsuperscript{3+}-doped Y\textsubscript{3}TaO\textsubscript{7} synthesis

Y\textsubscript{3}TaO\textsubscript{7} doped with higher Eu\textsuperscript{3+} concentration (from 7 to 50 mol%) was prepared by the sol-gel methodology. Tantalum ethoxide (Sigma-Aldrich, 99.98%), Y(NO\textsubscript{3})\textsubscript{3} (Sigma-Aldrich, 99.8%), and Eu(NO\textsubscript{3})\textsubscript{3} ethanolic solution were used as precursors. The Eu(NO\textsubscript{3})\textsubscript{3} stock solution was prepared from dissolving EuO\textsubscript{2} in HNO\textsubscript{3} aqueous solution, followed by drying at 80 °C and addition of anhydrous ethanol. This solution concentration was carefully confirmed by complexometric titration with EDTA using xylentol orange as an indicator at pH 5.8. The reaction was carried out by basic catalyst with NH\textsubscript{4}OH 0.56 mol L\textsuperscript{-1} (Cinética, 24.5%). The reaction mixture was stirred for 1 h, and the resulting solid was separated by centrifugation. Part of the solid was annealed at 900 °C, whereas the other part of the solid was annealed at 1100 °C for 2 h. The Eu\textsuperscript{3+} quantity in each sample was related to the Y and Ta molar total amount and ranged from 7 to 50 mol%. Samples were labeled SX, with $X = 7, 10, 15, 20, 30$ and 50 mol%. A detailed description of sample preparation can be found elsewhere.\textsuperscript{32}

2.2 Characterization

Powder X-ray diffraction (XRD) measurements were obtained on a Siemens-Bruker D5005-AXS diffractometer. The equipment operates with CuK\textalpha radiation, $\lambda = 1.5418$ Å, and has a graphite monochromator. Diffractograms were recorded at 0.02° s\textsuperscript{-1} for $2\theta$ values ranging from 5.00 to 90.00°. Diffuse Reflectance Spectroscopy (DRS) was performed between 250 and 600 nm, at room temperature, on a Varian Cary 500 Scan spectrophotometer equipped with a Harrick Co Praying Mantis diffuse reflection accessory. Fourier transform infrared (FT-IR) spectroscopy spectra were measured on a PerkinElmer FTIR Spectrum Two instrument spectrometer in the 4000-400 cm\textsuperscript{-1} range, with a resolution of 2 cm\textsuperscript{-1}. Powder samples were mixed with KBr pellets. Photoluminescence steady-state spectra were recorded on a Fluorolog-3 Horiba Scientific (model FL3-22) spectrophuorometer equipped with a FL1073 Horiba photomultiplier and the excitation source used was a 450 W Xe arc lamp. Time-resolved measurements were carried out in a Horiba Jobin Yvon Triax 550 Fluorolog spectrophuorometer, the xenon lamp pulsed mode and a Spex DM302 photomultiplier were employed. Emission decay curves were recorded on a Fluorolog 3 Horiba Scientific (model FL3-22) equipped with a Hamamatsu R928 photomultiplier with xenon lamp pulsed mode. The absolute emission quantum yield values ($q$) were measured at room temperature using a C9920-02 Hamamatsu system. The method is accurate within 10%.

3. Results and discussion

3.1 Structural and vibrational properties

Fig. 1 shows the X-ray diffractograms of the Eu\textsuperscript{3+}-doped samples annealed at 900 or 1100 °C. All crystalline planes correspond to
the Y₃TaO₇ phase (JCPDS 01-071-1346 48-265), a fluorite-related orthorhombic structure with space group Ccmm and unit cell parameters a = 10.486, b = 7.426, and c = 7.448 Å. Six oxygen atoms surround tantalum, in an octahedral arrangement; yttrium atoms are coordinated with seven or eight oxygen atoms. The tantalum and yttrium atoms are organized as a deformed cube with missing oxygen and as a slightly deformed cube, respectively.²⁶

Previously it was demonstrated that rising Eu³⁺ content up to 5.0 mol% leads to a secondary monoclinic crystalline phase named M’-YTaO₄ (JCPDS 24-1425) with space group P12/a1, which is also verified for the non-doped host.³² The Eu³⁺ concentration of 7.0 mol% (sample S7) stabilizes Y₃TaO₇, and the secondary phase is absent. No significant intense peaks related to Eu³⁺-based oxides or secondary crystalline phases appear even in the presence of higher Eu³⁺ concentration in the host, which indicates that Eu³⁺ ions are homogeneously distributed in the lattice, resulting in a solid solution, indicating that Y₃TaO₇ provides high RE ion solubility. The diffractogram of S15 and S30 annealed at 1100 °C display negligible low-intense diffraction peaks corresponding to the M’-YTaO₄ phase, as observed by baseline magnification presented at the right side of Fig. 1. Therefore, this phase is considered as an impurity. The diffraction patterns observed for the samples afford only for the mentioned crystalline phases. No further peaks attributed to RE oxides were detected.

An expanded view of the diffractograms in the 2θ range of 28–35° can be observed in Fig. 1, where the most intense diffraction peaks appear for the Eu³⁺-doped Y₃TaO₇ samples annealed at 900 or 1100 °C. All the diffraction peaks shift to lower 2θ values at higher Eu³⁺ concentration. In agreement with Bragg’s law, it indicates increasing interplanar spacing (d) in the Y₃TaO₇ crystalline structure. Higher interplanar spacing is due to the slightly larger Eu³⁺ ionic radius (1.066 Å) as compared to the ionic radius of the Y³⁺ ions (1.019 Å) that Eu³⁺ substitutes.³⁸ Peak shifts toward lower angles confirm that a substitutional homogeneous solid solution [Y-Eu]₃TaO₇ emerges. The slight difference between the Eu³⁺ and Y³⁺ ionic radii culminates in mismatched sizes, so substitution of Y³⁺ for Eu³⁺ causes a slight lattice expansion.

We reported that Eu³⁺ incorporation into the Y₃TaO₇ host affects crystallization and delays formation of M’-YTaO₄ as a secondary crystalline phase as compared to the undoped sample.³² M’-YTaO₄ formation is pronounced up to a Eu³⁺ concentration of 5.0 mol% because Y₃TaO₇ decomposes and reacts with precipitated Ta₂O₅, to generate YTaO₄.³¹ However, Eu³⁺ concentrations higher than 5.0 mol% induce Y₃TaO₇ phase stabilization because a solid solution arises. Y₃TaO₇ no longer decomposes, so YTaO₄ is absent. The solid solution probably originates in a specific range of Eu³⁺ concentrations higher than 5.0 mol%.

As discussed before, Y₃TaO₇ contains two different Y³⁺ coordination sites in the unit cell: one-third of the Y³⁺ ions are octacoordinated, whereas two-thirds are heptacoordinated. Hinatsu et al.⁴⁰ recently reported substitution in LnY₂TaO₇ for a series of lanthanides. When larger ions substitute Y³⁺, they preferentially occupy the octacoordinated position, whilst smaller ions tend to engage in heptacoordination. Therefore, unit cell parameters for Ln = Eu³⁺ are a = 10.5287, b = 7.4554, and c = 7.4926 Å; i.e., unit cell dimensions increase due to the presence of larger Eu³⁺ ions in the host.

Fig. 2A, B and Table 1 display the bandgap energy determined by using the absorption coefficients (estimated by the reflectance data and the Kubelka–Munk equation⁴¹ – Fig. S1 and S2, ESI†) and the Tauc plot⁴² for direct bandgap. Minor bandgap energy changes were detected, namely, from 4.76 to 4.86 eV for the samples annealed at 900 °C and from 4.71 to 4.85 eV for the samples annealed at 1100 °C. Only the samples S50 at both annealing temperatures showed lower values of band gap (4.54 and 4.66), which agrees with the observed in the XRD analysis. The literature reports a bandgap of 4.6 eV for Y₃TaO₇ (ref. 43) and a higher bandgap value for the resulting solid solution. We notice that the Eu³⁺ incorporation into the host lattice affects the bandgap energy. For samples S7–S50, their close band gap energy values show that a similar structure; i.e., stabilized (Y-Eu)₃TaO₇ solid solution. As already discussed for lower Eu³⁺.
concentrations, these samples have high transparency in the UV range, and there is no luminescence quenching due to host absorption.

The Eu³⁺-doped Y₃TaO₇ samples without annealing and annealed at 900 or 1100 °C were analyzed by FTIR (Fig. S3†). After annealing, the spectra indicate full removal of water and organic substances, which could decrease luminescence and quantum emission efficiency by the non-radiative process through excited-state deactivation. The higher frequency band is around 820 cm⁻¹ (Ta—O—Ta stretching vibration⁴⁴), highlighting that Y₃TaO₇ has relatively low phonon energy.

### 3.2 Luminescent properties

Fig. 3 depicts the excitation spectra of samples S7–S50 annealed at 900 or 1100 °C, monitored through the Eu³⁺ ⁷F₀ → ⁵D₂ transition at 607.0 nm. A broadband with more than one contribution in the UV region, centered at around 270 nm, emerges in all the spectra. It corresponds to charge transfer (CT) from an O²⁻ (2p) partially filled shell to a Eu³⁺ (4f) filled shell and from the tantalate group, which is associated with the charge transfer between O²⁻ to Ta⁵⁺.⁴⁵,⁴⁶ Moreover, the other contribution is associated with the host absorption. As observed previously, the energy gap values are approximately 4.8 eV (from 251 to 254 nm), which also corresponds to the range of the observed broadband and indicates the energy transfer from host lattice to Eu³⁺ excited states.⁴⁷–⁴⁸ Also, sharp peaks above 350 nm are characteristic of Eu³⁺ f-f transitions. The bands at 360, 394, 415, 462, and 529 nm are assigned to transitions from the ground state ⁷F₀,₁ to ⁵D₄, ⁵L₄, ⁵D₃, ⁵D₂, and ⁵D₁, respectively. These spectral profiles are very similar to the spectral profiles of pure Y₃TaO₇ and of Y₃TaO₇ with lower Eu³⁺ concentrations (0.1 and 0.5 mol%).³²

We recorded the emission spectra of Eu³⁺-doped Y₃TaO₇ samples annealed at 900 or 1100 °C (Fig. 4) under excitation at the CT band (~275 nm). The emission spectra under excitation at the Eu³⁺ f-f transitions at 394 (⁷F₀ → ⁵L₄) and 464 nm (⁷F₀ → ⁵D₂) are depicted in Fig. S4†. These spectra contain mostly broad bands centered at 578, 590–595, 605–633, 653, and 710 nm, which refer to ⁵D₀ → ⁷F₉ (⁹ = 0, 1, 2, 3, and 4), respectively.

The samples annealed at 900 °C have emission spectra with very broad bands (full-width-at-half-maximum of, fwhm, ~9 nm), independently of the selected excitation wavelengths, as already noticed.³² The Y₃TaO₇ crystalline structure contains two possible coordination sites for Y³⁺ ions; i.e., hepta- and octa-coordination. Eu³⁺ probably replaces Y³⁺ in the two different symmetry sites and is randomly distributed. In these spectra, Eu³⁺ occupies the same average symmetry site. The broad (fwhm ~ 70 cm⁻¹) ⁵D₀ → ⁷F₀ transition detected in all the spectra suggests that Eu³⁺ occupies more than one symmetry site (without inversion center in accordance with the higher relative intensity of the ⁵D₀ → ⁶F₂ transition). The fact that the samples annealed at 900 °C display a similar spectral profile indicates high correspondence in terms of Eu³⁺ distribution in similar local-coordination symmetry sites. Eu³⁺-doped fluorite-related compounds with pyrochlore structure, such as rare-earth zirconates, hafnates, niobates, and tantalates, exhibit a similar spectral profile with analogous broad bands.¹¹,²²,²³,⁴⁹–⁵¹

The samples annealed at 1100 °C have slightly different spectra even in the presence of the same crystalline phase, as discussed previously. Concerning broadening, the samples

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**Table 1** Optical band gap energy values obtained from the Tauc plot for the Eu³⁺-doped Y₃TaO₇ samples annealed at 900 or 1100 °C

| Sample | Host absorption (±0.01 eV) |
|--------|----------------------------|
|        | 900 °C | 1100 °C |
| S7     | 4.79   | 4.85   |
| S10    | 4.86   | 4.83   |
| S15    | 4.76   | 4.84   |
| S20    | 4.83   | 4.83   |
| S30    | 4.78   | 4.71   |
| S50    | 4.64   | 4.66   |

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**Fig. 2** Tauc plot of Eu³⁺-doped Y₃TaO₇ annealed at (A) 900 °C and (B) 1100 °C.
annealed at 1100 °C clearly have the same pattern as the samples annealed at 900 °C. Depending on the excitation wavelength, a sharper peak at 611.5 nm stands out. When this sharper peak occurs more evidently, the $^5D_0 \rightarrow ^7F_0$ transition tends to disappear. This different emission profile resembles the Eu$^{3+}$ emission profile in M$^2$-RETaO$_4$. In conclusion, most of the Eu$^{3+}$ ions are occupying Y$_3$TaO$_7$ symmetry sites. However, as the temperature increases, and M$^2$-YTaO$_4$ is minimally formed, Eu$^{3+}$ tends to occupy M$^2$-YTaO$_4$ symmetry; that is, Eu$^{3+}$ substitutes Y$^{3+}$ in a C$_2$ site. Although this secondary phase is not evident in the XRD analysis, the photoluminescence spectra clearly indicate the formation of a distinct phase for the samples annealed at 1100 °C.

Table S1† shows the $^5D_0 \rightarrow ^7F_2/5D_0 \rightarrow ^7F_1$ intensity ratios, calculated from the respective area of each transition, fitted by Lorentzian functions, for all the Eu$^{3+}$ doping concentrations and sample annealing temperatures. The samples annealed at 1100 °C have lower $^5D_0 \rightarrow ^7F_2/5D_0 \rightarrow ^7F_1$ ratios than the samples annealed at 900 °C mainly because fewer structural defects exist at higher annealing temperature, as discussed based on bandgap energy measurements. In general, Eu$^{3+}$ occupies slightly higher symmetry sites in the samples annealed at 1100 °C. However, the difference between the samples is not significant, suggesting that Eu$^{3+}$ is still in the same average symmetry sites.

Besides, it is also important to take the presence of Eu$^{3+}$ in a different symmetry site into account for the samples S15 and S30 annealed at 1100 °C. The spectral profile of Eu$^{3+}$ in Y$_3$TaO$_7$ symmetry sites can be seen for these samples in a magnified view and it will be discussed later. The more intense $^5D_0 \rightarrow ^7F_2$ transition band at 611.5 nm corresponds to Eu$^{3+}$ occupying M$^2$-YTaO$_4$ sites.

In order to demonstrate the occupation of Eu$^{3+}$ ions in two different symmetry sites of Y$_3$TaO$_7$ and M$^2$-YTaO$_4$ hosts, Fig. 5 shows the emission spectra for S15 at 1100 °C under different excitation wavelengths. Although the S15 sample annealed at 900 °C shows the crystallization of a single-phase, its emission spectrum was used as a reference to estimate the Eu$^{3+}$ in Y$_3$TaO$_7$ emission of the sample annealed at 1100 °C. In Fig. 5 it is possible to observe the change in the S15 at 1100 °C sample spectral profile at different excitation wavelengths. The gray patterned area in each spectrum corresponds to the normalized

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**Table S1†**

| Sample | $^5D_0 \rightarrow ^7F_2/5D_0 \rightarrow ^7F_1$ Ratio |
|--------|--------------------------------------------------|
| S7     | Lower                                            |
| S10    | Lower                                            |
| S15    | Lower                                            |
| S20    | Lower                                            |
| S30    | Lower                                            |
| S50    | Lower                                            |

In conclusion, most of the Eu$^{3+}$ ions are occupying Y$_3$TaO$_7$ symmetry sites. However, as the temperature increases, and M$^2$-YTaO$_4$ is minimally formed, Eu$^{3+}$ tends to occupy M$^2$-YTaO$_4$ symmetry; that is, Eu$^{3+}$ substitutes Y$^{3+}$ in a C$_2$ site. Although this secondary phase is not evident in the XRD analysis, the photoluminescence spectra clearly indicate the formation of a distinct phase for the samples annealed at 1100 °C.
spectrum of S15 at 900 °C, which has a pure Y₃TaO₇ phase and then multiplied by the indicated factor to adjust under the obtained spectra of S15 at 1100 °C. For this estimate, all spectra were normalized.

Under CT band excitation, at 275.0 nm, Eu³⁺ ions that are distributed into Y₃TaO₇ lattice are preferentially activated. The contribution of the band that corresponds to YTaO₄ CT band is smaller at this excitation wavelength. Under excitation at 393.0 nm, the major contribution comes from the Eu³⁺ in M’-YTaO₄ host, results in sharper spectra. In Fig. 6B, under 394.0 nm excitation, it is possible to activate almost only the Eu³⁺ into M’-YTaO₄, with C₂ symmetry. Under 392.5 nm excitation, Eu³⁺ ions in both hosts are activated. Even performing a time-resolved emission measurement under 392.5 nm excitation (Fig. S7†), it was not possible to distinguish different symmetry site besides the diminishing of the peak referent to Eu³⁺ into M’-YTaO₄, at 611.5 nm, which possess lower lifetime than Eu³⁺ ions into Y₃TaO₇.

Fig. 6A shows the excitation spectra with fixed emission at two different wavelengths (607.0 and 611.5 nm), evidencing that the bands observed for ⁵D₀ → ⁷F₂ transition come from different symmetry sites. Eu³⁺ ions into Y₃TaO₇ lattice provides the large spectral profile and Eu³⁺ into M’-YTaO₄ host, results in sharper spectra. For the samples annealed at 1100 °C under excitation at CT band with emission at 607 nm (the curves under excitation at 393 and 464 nm are presented in Fig. S6, ESI†). The samples display an almost single exponential behavior and have been fitted by using a first-order exponential. This indicates that even Eu³⁺ ions exist in different symmetry sites, the lifetime values are close to each other. We obtained τ₁ lifetimes values from decay curves for each sample under different excitation wavelengths (see Table 3).

Samples with higher Eu³⁺ concentration (S7–S50) behave in the same way as samples doped with lower Eu³⁺ concentration (0.1 up to 5.0 mol%). The samples annealed at 1100 °C have higher τ₁ values, which refer to greater elimination of species (like OH groups) that deactivate the Eu³⁺ excite state. We already observed that Eu³⁺-doped Y₃TaO₇ has a long lifetime (about 1.80 ms for the sample containing Eu³⁺ at 0.5 mol%, annealed at 1100 °C). The lifetime of samples with higher Eu³⁺ concentration (S7–S50) that have stabilized Y₃TaO₇ crystalline phase is longer than that of the samples with lower concentration (up to 5 mol%).

Analysis of these samples under the same excitation wavelength and with Eu³⁺ concentration higher than 20 mol% shows that these samples have reduced τ₁/e values. Although the S30 and S50 samples exhibit strong luminescence, the lifetime values suggest quenching by concentration: a shorter Eu³⁺ ion – Eu³⁺ ion distance promotes energy transfer. Energy migration combined with host defects explains such quenching.

For the samples annealed at 1100 °C that exhibited the sharp peak at 611.5 nm (Fig. 4B, S4B and D†), we measured the lifetime of both peaks that are assigned to ⁵D₀ → ⁷F₂ transition, the large one at λ_em = 607.0 nm (as can be seen in Fig. 7 and Table 2) and the sharp one at λ_em = 611.5 nm. The decay curves of these samples for this last-mentioned wavelength were adjusted with the non-single exponential fit, that was not reported here, and the τ₁/e values are exhibited in Table 3. Lower τ₁/e values were obtained under excitation at 393.0 and 464.0 nm with emission fixed at 611.5 nm than the values obtained with the emission at 607.0 nm.

The shorter lifetime values may be related to increasing Eu³⁺ content to structural changes (Y₃TaO₇ → M’-YTaO₄) because Eu³⁺ in the latter phase has a shorter lifetime. Eu³⁺ ions that occupy symmetry sites in this structure have a shorter lifetime.
and lower symmetry (C2). Photoluminescent measurements and lifetime decay curves of most of the samples annealed at 1100 °C have shown the presence of the M0.YTaO4 crystalline phase, which had not been detected in the XRD diffractograms. The lifetime values of the samples showed in Table 3 are similar to those values of samples doped with 1, 2, and 5 mol% of Eu3+ concentration.

In order to observe the quenching effect as a function of Eu3+ concentration, Fig. S7† brings \( \tau_{1/e} \) values for each sample, measured with emission fixed at 607.0 nm for the \( ^5D_0 \rightarrow ^7F_2 \) transition, for evaluation in the Y3TaO7 host. Samples S10 and S7 have a longer lifetime, for samples annealed at 900 °C and 1100 °C, respectively. Although lifetime decreases slightly from S7 to S20, their \( \tau_{1/e} \) values are close. Samples S30 and S50 have significantly lower lifetime values, indicating that quenching due to concentration takes place. The lifetime dependence on the excitation wavelength is another argument supporting distinct local-coordination sites. Also, the presence of CTB intermediate state in near-resonance with the \( ^5D_0 \) emitting level mediating energy transfer is known to induce a lifetime increases relative to its intrinsic or natural lifetime measured under direct intra-4f6 excitation (393.0 and 464.0 nm).

It is possible to describe the behavior of the \( ^5D_0 \) excited state lifetime values decreases as a function of Eu3+ ions concentration from the following equation:55,56

\[
\tau_{\text{obs}} = \frac{\tau_0}{1 + (r/Q)^p}
\]

where \( \tau_{\text{obs}} \) is the experimental lifetime value, \( \tau_0 \) is the radiative lifetime (ideal), \( r \) is Eu3+ ions concentration, \( Q \) is the quenching concentration and \( p \) is the phenomenological parameter that gives curve profile. The graphs inserted in Fig. 7 show the dependence of \( ^5D_0 \) lifetime as a function of Eu3+ ions concentration up to 50 mol% of Eu3+ under excitation at CTB (the graphs referent to excitation at 393 and 464 nm excitation are shown in Fig. S8†). The lifetime values of the samples doped with 0.1 and 0.5 mol%52 were included in this calculus since the Eu3+ are in the same symmetry sites of the samples presented in this work.

The best fit obtained from the equation data for each curve is represented by a red line. Therefore, the average calculated parameters were: \( \tau_0 = 1.62 \pm 0.01 \text{ ms}, Q = 32 \text{ mol\%}, \) and \( p = 5 \) for the samples annealed at 900 °C and \( \tau_0 = 2.01 \pm 0.01 \text{ ms}, Q = 29 \text{ mol\%}, \) and \( p = 5 \) for the samples annealed at 1100 °C.

### Table 2

| Annealing temperature (°C) | Sample | CTB  | 393.0 nm | 464.0 nm |
|---------------------------|--------|------|----------|----------|
| 900                       | S7     | 1.74 | 1.68     | 1.59     |
|                           | S10    | 1.75 | 1.73     | 1.66     |
|                           | S15    | 1.68 | 1.48     | 1.52     |
|                           | S20    | 1.54 | 1.53     | 1.52     |
|                           | S30    | 1.00 | 1.01     | 1.00     |
|                           | S50    | 0.13 | 0.12     | 0.12     |
| 1100                      | S7     | 2.18 | 2.14     | 2.00     |
|                           | S10    | 2.16 | 2.10     | 2.02     |
|                           | S15    | 2.08 | 1.96     | 1.96     |
|                           | S20    | 1.87 | 1.81     | 1.81     |
|                           | S30    | 0.86 | 0.96     | 0.90     |
|                           | S50    | 0.17 | 0.18     | 0.19     |

### Table 3

| Samples | \( ^5D_0 \) excited state lifetimes (ms) for Eu3+-doped yttrium tantalate samples annealed at 1100 °C with emission fixed at 611.5 nm and under excitation at 393.0 nm and 464.0 nm |
|---------|---------------------------------------------------------------------------------|
|         | 393.0 nm | 464.0 nm |
| S7      | 1.42     | 1.41     |
| S10     | 1.41     | 1.48     |
| S15     | 1.26     | 1.31     |
| S20     | —        | 1.41     |
| S30     | 0.70     | 0.80     |

Fig. 7 PL decay curves for curves for the Eu3+ \( ^5D_0 \) excited state under excitation at CTB of Eu3+ doped Y3TaO7 samples annealed at (A) 900 or (B) 1100 °C with fixed emission at 607.0 nm. Inset: lifetime values (\( \tau_{\text{obs}} \)) as a function of Eu3+ concentration (from 0.1 [30] up to 50 mol%) under excitation at CTB. The lines are visual guides.
These yttrium tantalate samples had exhibited a high quenching concentration at about 30 mol% of Eu³⁺ ions, a much higher value than the observed for other materials, such as zirconates, hafnates,²²,²³ antimonates, for example. The high quenching concentration of Eu³⁺ ions in this host can be attributed to the facility of substitution of these ions in the place of Y³⁺ ions of the host, therefore, the RE³⁺ ions have high solubility in this host due to the similarity of ionic radii.

Judd–Ofelt intensity parameters, radiative ($A_{\text{rad}}$) and non-radiative ($A_{\text{nrad}}$) transition probabilities were calculated based on emission spectra under excitation at 393 nm shown at Fig. S4.⁹ The refractive index used to calculate these parameters was 1.8, estimated by using specular reflectance on a film prepared using the same precursors as the powders, by dip-coating technique.²⁴ The calculated values were based on the characteristic spectra of Y₃TaO₇ as well as the comparison with the experimental lifetime values, where the emission was fixed at the Y₃TaO₇ ⁵D₀ → ⁷F₂ transition (~607 nm). The quantum efficiency values were omitted due the very close values between the $\tau_{\text{exp}}$ and $\tau_{\text{rad}}$ calculated. Therefore, the calculated quantum efficiency for some samples showed values higher than 100%. This is an indicative that the refractive index value used for the calculations do not corresponds to the real value of the samples, affecting the obtained value. The powder annealing can result in a material with less densification, smaller refractive index value and, thus, a higher lifetime value. This behavior can be observed in nanostructured materials. For example, in Y₂O₃:Eu³⁺ samples where the radiative lifetime is 0.9 ms (calculated and measured from a monocrystal), for particulated nanostructured materials, the experimental lifetime value is highly dependent on the annealing temperature. Previous studies showed that lifetime values higher than 0.9 ms, and as the material was annealed at higher temperatures or for longer time, there was a reduction in these lifetime values.⁷,⁸ This fact can explain the higher $\tau_{\text{exp}}$ found for these yttrium tantalate samples.

Even though, this group of samples has presented higher values of radiative transition probabilities ($A_{\text{rad}}$) and $\tau_{\text{rad}}$ than the group of samples with lower Eu³⁺ concentration.²⁴ In the previous work, it was shown that these samples clearly show the presence of M³⁺-YTaO₄ phase. To show the influence of Eu³⁺ ions located in this phase on $A_{\text{rad}}$ and $\tau_{\text{rad}}$, it was calculated these values based on the almost isolated emission spectra of sample S15 annealed at 1100 °C depicted in Fig. 6B ($\lambda_{\text{em}} = 394$ nm) and the $\tau_{\text{exp}}$ presented in Table 4 ($\lambda_{\text{exp}} = 611.5$ nm). The quantum efficiency value calculated for this sample was 57%.

Table 4 lists the experimental $\Omega_{2}$ and $\Omega_{4}$ intensity parameter values for all the samples and the refractive index value used was 1.8. The values of sample S15 at 1100 °C marked (⁎) are referent of the same emission spectra referred previously (Fig. 6B).

The samples with higher Eu³⁺ concentration have presented higher $\Omega_{2}$ than the samples with lower concentration.²⁴ The environment could become more polarizable and less symmetric, which agrees with the $^5D_0 \rightarrow ^7F_j$ transition of Eu³⁺ ions in the Y₃TaO₇ host (Table S1).³²

Absolute emission quantum yield was measured and the obtained values are shown in Table 5. Under excitation at CTB (250 and 280 nm), the values were about 10%. For other fluorite-type structure materials, the obtained values were 15–18% for

| Table 4 | Judd–Ofelt parameters of the Eu³⁺-doped Y₃TaO₇ samples annealed at 900 or 1100 °C under 394 nm excitation |
|---------|-----------------------------------------------------|
| Annealing temperatures | $\Omega_{2}$ (10⁻²⁰ cm²) | $\Omega_{4}$ (10⁻²⁰ cm²) | $A_{\text{rad}}$ (s⁻¹) | $\tau_{\text{rad}}$ (ms) | $\tau_{\text{exp}}$ (ms) |
| 900 °C | | | | | |
| S7 | 7.34 | 4.03 | 592 | 1.69 | 1.63 |
| S10 | 6.76 | 3.97 | 606 | 1.65 | 1.76 |
| S15 | 7.23 | 3.33 | 569 | 1.76 | 1.43 |
| S20 | 7.24 | 3.97 | 584 | 1.71 | 1.51 |
| S30 | 7.40 | 3.51 | 583 | 1.72 | 0.99 |
| S50 | 9.29 | 4.19 | 697 | 1.43 | 0.13 |
| 1100 °C | | | | | |
| S7 | 5.78 | 2.26 | 462 | 2.16 | 2.14 |
| S10 | 6.08 | 2.40 | 481 | 2.08 | 2.09 |
| S15 | 6.57 | 5.38 | 587 | 1.70 | 1.93 |
| S15* | 5.61 | 2.01 | 451 | 2.22 | 1.26 |
| S20 | 5.32 | 2.13 | 431 | 2.32 | 1.78 |
| S30 | 6.69 | 6.42 | 620 | 1.61 | 0.98 |
| S50 | 7.02 | 3.27 | 550 | 1.82 | 0.19 |

| Table 5 | Emission quantum yield values (%) under different excitation wavelengths (250, 280, 320, 393, and 464 nm) of the Eu³⁺-doped Y₃TaO₇ samples annealed at 900 and 1100 °C. The experimental error is 10% |
|---------|-------------------------------------------------------------|
| $\lambda$ (nm) | 900 °C | 1100 °C |
| | S7 | S10 | S20 | S50 | S10 | S20 | S50 |
| 250 | 7.4 | 10.0 | 11.0 | — | 8.8 | 11.0 | 3.9 |
| 280 | 7.1 | 9.9 | 9.3 | — | 7.2 | 10.0 | 1.7 |
| 320 | 2.9 | 4.7 | 5.3 | — | 1.9 | 5.7 | 1.3 |
| 393 | — | 17.0 | 11.0 | 2.5 | 6.0 | 14.0 | 10.0 |
| 464 | — | 29.0 | 15.0 | 2.6 | 16.0 | 15.0 | 7.0 |

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Eu3+ concentration in this case. For zirconates and hafnates, their structures are distorted in such a way that the electric dipole transitions become stronger when Eu3+ is located in sites with an inversion center, because the 5D0 → 7F1 magnetic dipole transition is the strongest emission in this case, and distortions to the symmetry site can be evaluated by splitting of this transition. The emission of the 5D0 → 7F1 transition is orange. For zirconates and hafnates, their structures are distorted in such a way that the electric dipole transitions become stronger. In these structures, the orange emission is stronger when Eu3+ is located in sites with an inversion center because the 5D0 → 7F1 transition dominates in distorted lattices, the local symmetry becomes distorted (deviation from the inversion center), and the red emission component dominates.

The symmetry sites are greatly distorted in Y3TaO7 (ref. 49 and 62) and Y3TaO7. Consequently, these compounds present the 5D0 → 7F1 transition and high-relative intensity 5D0 → 7F2 transition, so emission is redder. In Eu3+-doped Y3TaO7, which belongs to the same space group as Y3TaO7, emission goes from reddish-orange to red with increasing Eu3+ concentration. It is possible to see that the emission of Eu3+ inserted in Y3TaO7 host is reddish-orange almost independently of the increasing of Eu3+ concentration in this case.

The emission becomes redder depending on the amount of M’-YTaO4 in the structure. The higher the Eu3+ concentration, the more stable the Y3TaO7 solid solution, so emission color tends to orange. This indicates that the emission of the compounds is tunable, depends on the structure, and can be tailored by the Eu3+ concentration in the host.

The purity of the emitted color can be characterized from the equation below:

$$\text{Color purity} = \sqrt{\left(x_s - x_i\right)^2 + \left(y_s - y_i\right)^2} \times 100$$

where (x_s, y_s) are the color coordinates calculated from the emission spectra of each sample, (x_i, y_i) are the coordinates of the white illuminant (0.333, 0.333), and (x_d, y_d) are the coordinates of the dominant wavelength. The coordinates of the dominant wavelength used to this calculation were (0.657, 0.334) for 607 nm, corresponding to 5D0 → 7F2 transition. The color purity varied from 95.2–96.3% and 92.6–94.7% for the samples annealed at 900 °C and 1100 °C, respectively, showing the high color purity of this material. These materials can be efficiently excited by UV and blue light generating reddish-orange light, which can be used for several applications such as for lasers, lighting, displays, and the development of warm LEDs. Also, other potential application of the reddish-orange emitters materials is in greenhouses, as artificial light, that can improve the absorption of the chlorophyll of the plants in this region of the spectrum, better than in the green region.

4. Conclusions

We successfully synthesized Y3TaO7 solid solutions containing high Eu3+ concentration, from 7 up to 50 mol%. It was evaluated the Y3TaO7 structural features after Eu3+ introduction into the lattice and also evaluated the photoluminescence properties; Eu3+ ions photoluminescence properties functioned as a structural probe. The higher the Eu3+ concentration, the more stable the Y3TaO7 crystallization. Emission bands were intense (q ~ 30%) and broad (fwhm ~ 9 nm). Inhomogeneous broadening was due to the occupation of Eu3+ ions in a different symmetry sites. Eu3+ emission quenching due to concentration was negligible for the samples containing up to 30 mol%, and quantum yield values of nearly 30% were obtained with excitation in Eu3+ f-f transitions, which makes these materials especially interesting for application as high-intensity emitters in photonics. The results reported here call attention to the design of materials based on the tunability of their emission color through manipulation of their crystalline structure, which can be tailored by controlling the Eu3+ quantity in the sample.

Conflicts of interest

There are no conflicts to declare.

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