

LaPO₄:Er micro-spheres with high NIR luminescent quantum yield

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ABSTRACT

Er-doped LaPO₄ micro-spheres have been synthesized by spray pyrolysis and the near infrared (NIR) properties have been characterized. It has been found that, following an adequate post-annealing treatment, the emission properties are remarkably improved. The NIR luminescence intensity is highly enhanced and its decay time increases to a value almost coincident with the reported radiative lifetime, which implies that the quantum yield approaches $\eta \approx 100\%$. This improvement in luminescence characteristics is probably related to the suppression of residual OH⁻ radicals, that otherwise act as NIR luminescence quenchers, and to the increase in material's crystallinity.

1.- INTRODUCTION

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3 Lanthanide phosphate (LaPO_4) and, in particular, its monoclinic polymorph (monazite),
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5 has been widely used as a host for the preparation of lanthanide- based phosphors. In fact,
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7 doped with Ce and Tb constitutes one of the classical phosphors used in high-quality
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9 fluorescent lighting due to its high quantum yield and stability at high temperature [1-4]. By
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11 varying the dopants (Pr, Nd, Eu, ...) the optical properties can be tuned over a wide spectral
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13 range, with emerging applications in different fields such as biomedicine [5-6], photonic band
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15 gap materials or optical amplification [7-8]. In particular, for optical amplifiers and lasers, Er
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17 becomes the most interesting dopant because of its characteristic emission, at around 1.5 μm ,
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19 coincident with the transparency window of optical fibers [8-9]. Along this line, there has been
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21 a considerable effort along the last years in order to prepare Er doped phosphate particles
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23 incorporated into polymer-based components, in order to improve luminescence characteristics
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25 and trying to achieve long lifetimes and high quantum efficiencies [10-17]. The data reported
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27 in the literature for the 1.5 μm emission lifetime vary within a very large range (60 μs [14] to
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29 3.7 ms [17]), reflecting possibly the large variety of dopants concentration, particle size and
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31 fabrication processes; affecting material's properties such as crystallinity or impurities content
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43 Spray pyrolysis is a well known technique for the synthesis of powdered materials, whose
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45 main advantages are simplicity and continuous character, which, along with its suitability to
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47 control particle size (micrometric) and shape (spherical), make it very attractive for industrial
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49 purposes [18-19]. Recently, this method has been used to prepare LaPO_4 spheres doped with
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51 Ce and Tb ions, which showed a high luminescence efficiency after a post heating treatment at
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53 $>1300^\circ\text{C}$ [20-21]. However, up to our knowledge, this synthesis method has never been applied
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55 to the synthesis of Er-doped LaPO_4 with NIR luminescence.
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In the present work we explore the applicability of the spray pyrolysis procedure for the synthesis of Er-doped LaPO₄ powders with improved NIR luminescent characteristics. It is found that it is possible to prepare LaPO₄:Er micro-spheres with good IR emission characteristics, including a relatively long lifetime. Following an adequate post-annealing treatment, the emission properties are remarkably enhanced, with a significant increase in luminescence intensity and decay time that, as far as we know, exceeds all previously reported values for Er³⁺ in LaPO₄. In fact, the decay time increases to a value almost coincident with the reported radiative lifetime, which implies that the NIR luminescent quantum yield (QY) approaches $\eta \approx 100\%$. We also show that the improvement in luminescence QY is probably related to the suppression of residual OH radicals, that otherwise act as efficient NIR luminescence quenchers, and to a parallel crystallinity increase.

2.- EXPERIMENTAL

2.1.- *Synthesis of samples*

Erbium-doped lanthanum phosphate with nominal composition Er_{0.02}La_{0.98}PO₄ was prepared by pyrolysis of a liquid aerosol generated from an acidic (0.3 mol dm⁻³ HCl) solution 0.049 mol dm⁻³ in lanthanum nitrate (La(NO₃)₃·6H₂O, Fluka, 99%), 0.001 mol dm⁻³ in europium chloride (ErCl₃·6H₂O, Aldrich, 99.9%) and 0.05 mol dm⁻³ in H₃PO₄. This solution was sprayed into an expansion chamber using a glass nozzle and air at constant pressure (0.5 kg cm⁻²) as a carrier gas and the resulting aerosol was introduced into two consecutive furnaces kept at 250 and 600°C, respectively, in which the liquid droplets were first dried and then, thermally decomposed. The so obtained solid particles were collected on a glass filter with a very high efficiency. A more detailed description of the experimental setup can be found in reference [18].

1 The obtained powdered samples were calcined at different temperatures (up to 950 °C)
2 for 4 h, using a heating rate of 10 °C min⁻¹.
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5 **2.2.- Characterization techniques**

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8 The morphology of the particles was examined by scanning electron microscopy (SEM-
9 FEG) (Model S4800, Hitachi).
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12 The quantitative composition of the samples (Er/La mol ratio) was determined by the ICP
13 technique (Model Ultima 2, Horiba Jobin Yvon).
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17 The Fourier transform infrared spectra (FTIR) were recorded in a Jasco FT/IR-6200
18 Fourier transform spectrometer. For this purpose, the samples were diluted in KBr pellets.
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20 Thermogravimetric analyses (TGA) were performed (Q600 TA Instrument) in air atmosphere
21 using a heating rate of 10 °C min⁻¹.
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29 The crystalline phases present in the samples were identified by X-ray diffraction (XRD)
30 (Model X'Pert Pro, Panalytical). Unit cell parameters of the sample calcined at 950 °C were
31 determined by Rietveld refinement, using the X'Pert HighScore Plus software, from the XRD
32 data collected at intervals of 0.02° (2θ) for an accumulation time for interval of 10 s. The
33 crystallographic data for the LaPO₄ structure were taken from reference [22].
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42 Crystallite size was evaluated according to the Scherrer formula from the (2 0 0) XRD
43 reflection at 2θ ~ 26.8° or from the SEM pictures taken at high magnification.
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48 Optical absorption spectra in the UV-Visible and near infrared range were measured by
49 using a Perkin Elmer Lambda 1050 spectrophotometer. For that purpose the particles were
50 mounted in a specially designed holder, constructed by using a 100 μm thick spacer, with a 10
51 mm × 5 mm rectangular opening, sandwiched by two microscope slide covers. The LaPO₄:Er
52 powders were included filling the cavity.
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1 Luminescence was obtained either under CW or pulsed excitation, at different
2 wavelengths, using several sources. For CW measurements either an Ar⁺ laser (Spectra
3 Physics, model 2040E), Ti: Sapphire laser (Spectra Physics, model 3900) or a diode laser
4 (LIMO FQ-A 0063) have been used. The luminescent signal was dispersed by using a
5 Princeton Instrument monochromator (ARC SpectraPro 500-i model) and detected with a
6 Judson InGaAs photodiode (G 5883). For lifetime measurements, excitation was performed by
7 using the diode laser, in pulsed configuration, and the transient luminescence was averaged and
8 recorded with a digital Tektronix TDS 420 oscilloscope.
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10 **3.- RESULTS AND DISCUSSION**

11 ***3.1.- Structural characterization***

12 The Er content (Er/Er+La mol ratio) of the synthesized Er_{0.02}La_{0.98}PO₄ sample
13 experimentally determined (1.95%) was in agreement with the nominal value (2%). An
14 illustrative SEM picture of this sample (as prepared) is presented in the upper part of Figure 1,
15 which shows that it consisted of spherical particles of broad size distribution (< 10 μm). The
16 XRD pattern obtained for these spheres (Fig. 2, lower curve) was consistent with monoclinic
17 LaPO₄ [JCPDS file 1-83-651] with low crystallinity as revealed by the broadening of the XRD
18 reflections. In fact, the crystallite size, estimated for this sample by using the Scherrer formula,
19 was much smaller (12 nm) (Table 1) than the size of the spheres (Fig. 1), manifesting their
20 polycrystalline character. The FTIR spectrum of this sample displayed bands at >1200 cm⁻¹
21 mainly due to the lattice vibrations [23], along with a much less intense absorption at 1380 cm⁻¹
22 corresponding to the unreacted nitrate anions and two broad bands at 1630 and 3390
23 attributed to adsorbed water [24] (Fig. 3). Nevertheless, the possible contribution to the latter
24 band of OH⁻ anions of different origin cannot be neglected. The TGA curve recorded for this
25 sample presented a weight loss of 6 % in the 25-800 °C range (Fig. 4). Such a weight loss must
26 be ascribed to the release of such impurities as suggested by FTIR spectroscopy (Fig. 3). Thus,
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the nitrate disappeared in the spectrum of the sample heated at 600°C, whereas the intensity of the water bands weakened and completely disappeared at 800°C. No further changes were observed on further heating at higher temperatures up to 950 °C.

It should be noted that the thermal treatment also gave rise to a sharpening of the XRD peaks (Fig. 2) indicating an increase of sample crystallinity, accompanied by a change in the microstructure of the spheres, as illustrated in Fig.1 for the sample heated at 950 °C, in which the spheres appeared clearly composed by much smaller aggregated crystallites. The size of such crystallites was found to progressively increased from 12 nm, for the as prepared sample to 50-150 nm, after heating at 950 °C (Table 1).

The incorporation of Er³⁺ to the LaPO₄ structure was evidenced by EDS analysis and from the measurement of the unit cell parameters obtained for the sample calcined at 950 °C, which were lower than those corresponding to an undoped sample (Table 2), in agreement with the smaller size of the Er³⁺ cation in the ninefold coordination present in the monoclinic structure (1.062 Å,) when compared with that of La³⁺ (1.216 Å) [25]; although the definitive confirmation of Er incorporation is provided by the presence of characteristic absorption and emission bands associated to Er³⁺ ions, which are discussed in the following section.

3.2.- Optical characterization

Figure 5 shows the room temperature absorption spectra of the LaPO₄:Er³⁺ powders. The absorption bands of Er³⁺ ions are clearly visible, and identified in the figure with the labels of the corresponding excited multiplets.

Figure 6 shows the near-infrared (NIR) luminescence spectra of Er³⁺ in LaPO₄, under NIR excitation, using a Ti: Sapphire laser at $\lambda_{exc} \approx 800$ nm, corresponding to the $^4I_{15/2} \rightarrow ^4I_{9/2}$ transition, as indicated in the inset. It basically consists on a single broad emission, extending from 1.45 μ m to 1.65 μ m, which corresponds to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition, although a careful inspection of spectra allows also identifying a very weak emission at around 980 nm,

1 corresponding to the ${}^4I_{11/2} \rightarrow {}^4I_{15/2}$ transition. The emission is coincident to that obtained after
 2 excitation to other multiplets, either the ${}^4I_{11/2}$ multiplet using a diode laser operating at $\lambda_{\text{exc}} \approx$
 3 980 nm, or to the upper ${}^4F_{7/2}$ multiplet using an Ar^+ laser at $\lambda_{\text{exc}} \approx 488$ nm, in accordance with
 4 the results previously reported by other researchers [11]. This confirms that $\text{LaPO}_4:\text{Er}$ is an
 5 excellent NIR emitting material that can be efficiently pumped to different Er-multiplets, from
 6 where a non-radiative cascade ultimately populates the ${}^4I_{13/2}$ multiplet, from where the 1.5 μm
 7 emission occurs, as indicated in the inset. This characteristic is one of the recognized
 8 advantages of phosphate materials to be used for optical lasers and amplifiers [8-9].

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 20 Nevertheless, the luminescence intensity of our particles is dependent of the thermal
 21 treatment given to the samples. As prepared material displays a relatively low luminescent
 22 intensity, which is substantially increased by calcination. In figure 6 the IR luminescence of
 23 samples annealed at different temperatures is represented and it is apparent that the
 24 luminescence is strongly increased when compared to as prepared powders.

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 33 In order to explore more quantitatively the variations in the NIR luminescence quantum
 34 yield of the $\text{LaPO}_4:\text{Er}$ powders, the dependence of the fluorescence decay time of the 1.5 μm
 35 emission (${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition) for samples subjected to different calcination temperatures,
 36 has been investigated. The results are presented in Figure 7, where the luminescence decay
 37 after pulsed laser excitation is presented. It can be clearly observed that the NIR luminescence
 38 lifetime increases as the temperature of calcination is raised.

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 49 The luminescence decays are not single exponentials but they can be conveniently
 50 described by using a double exponential decay, as it has been observed in many other
 51 powdered materials [26-30]:

$$52 \quad I(t)/I_0 = A_S \exp(-t/\tau_{\text{short}}) + A_L \exp(-t/\tau_{\text{long}}) \quad (1)$$

The calculated decays are represented by the continuous lines in figure 7 and the corresponding fitting parameters are summarized in Table 3, together with the average decay time, defined as:

$$\langle \tau \rangle = \frac{\int_0^{\infty} tI(t)dt}{\int_0^{\infty} I(t)dt} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \quad (2)$$

From the data collected in Table 3, it can be observed that while pristine material has a relatively short average lifetime (around 0.76 ms) it is lengthened with calcination, reaching a value $\langle \tau \rangle \approx 6.47$ ms when calcined at 950 °C. This last value is very close to the reported radiative lifetime ($\tau_{\text{rad}} \approx 6.71$ ms) [17]. The relative weight of the fast and slow components varies also with calcination temperature. While the fast component represents almost a 40% of the emission, its intensity is reduced as the calcination temperature increases, and the longest component becomes dominant, reaching an 80% of the emission for the samples calcined at 950 °C.

This increase in the NIR luminescence decay time can also be expressed in terms of the luminescence quantum yield (η) that can be calculated as:

$$\eta = \frac{A_{\text{rad}}}{A_{\text{Total}}} = \frac{A_{\text{rad}}}{A_{\text{rad}} + A_{\text{no-rad}}} = \frac{\tau_{\text{exp}}}{\tau_{\text{rad}}} \quad (3)$$

where $A_{\text{rad}} = 1/\tau_{\text{rad}}$ represents the radiative transition rate and is equal to the reciprocal radiative lifetime, whereas $A_{\text{total}} = A_{\text{rad}} + A_{\text{no-rad}} = 1/\tau_{\text{exp}}$ represents the total transition rate which includes radiative plus all possible non-radiative channels such as multiphonon relaxation or energy transfer to luminescence quenchers. The total de-excitation rate, in the case of a single exponential decay, is the reciprocal of the measured lifetime (τ_{exp}). In our case, where the decay is multicomponent, we have taken the reciprocal of the average decay time (eq. (2)) as a

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representative figure to represent the average transition rate and luminescent quantum yield. Its value is incorporated in the last column of Table 3 and represented in Figure 8 vs. calcination temperature. It can be observed that as prepared material has a modest (11 %) luminescent quantum yield, which increases monotonously with calcination temperature, reaching values substantially higher and even approaching the theoretical limit of 100 % when calcination is performed above 900 °C.

In fact, this possibility is not unrealistic considering that in other materials, the luminescence quantum efficiency of the ${}^4I_{13/2}$ Er^{3+} level approaches such theoretical 100 % limit [31-37]. The non-radiative component of the decay includes, in general, intrinsic multiphonon de-excitation of the ${}^4I_{13/2}$ multiplet plus other extrinsic de-excitation channels, which include impurities quenching that is particularly relevant in nano- and submicrometer sized materials. If these additional extrinsic channels are suppressed, the only non-radiative channel remaining is the intrinsic multiphonon component. And this rate decreases exponentially with the number of phonons needed to bridge the gap between the emitting and the lower lying level [38-43].

For the 1.5 μm emission of Er^{3+} , the gap between the emitting ${}^4I_{13/2}$ multiplet and the lower lying ${}^4I_{15/2}$ ground state is sufficiently high ($\Delta E \approx 6500 \text{ cm}^{-1}$) to preclude efficient non-radiative de-excitation. We can make an estimation of the multiphonon decay rate considering that it can be expressed as :

$$A_{no-rad} = \beta \exp[-\alpha(\Delta E - 2\hbar\Omega)] \quad (4)$$

where ΔE is the energy gap, $\hbar\Omega$ is the phonon energy of the host material and α and β are parameters characteristic of the material. The host dependence of the non-radiative decay rate

1 is basically governed by its phonon energy, while the parameters α and β are relatively
2 insensitive to the host [42, 43].
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5 We may therefore make a reasonable estimation by using the parameters reported for
6 phosphate glasses ($\alpha \approx 4,7 \times 10^{-3}$ cm, $\beta \approx 6,2 \times 10^7$ s⁻¹ [42]), and it is obtained that even in the
7 high phonon energy material that is LaPO₄ ($\hbar\Omega \approx 1100$ cm⁻¹ [44]), the calculated multiphonon
8 transition rate is: $A_{\text{no-rad}} \approx 0.1$ s⁻¹, which is much smaller than the reported radiative rate ($A_{\text{rad}} \approx$
9 149 s⁻¹ (= 1/6.71 ms)) and hence a luminescence quantum efficiency close to 100% would be
10 expected, provided that extrinsic quenching factors would be efficiently suppressed.
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22 At this point we should consider that it is generally accepted the detrimental effect of
23 impurities on the luminescence efficiency, acting as quenchers. Particularly OH⁻ radicals are
24 known to be efficient Er³⁺-luminescence quenchers [45-56], because of its vibration energy and
25 that only 2 phonons are needed to match the energy gap of the 1.5 μm emission. In fact, it has
26 been demonstrated in phosphate glasses that there is a direct relationship between OH⁻ content
27 and the reduction of the observed luminescence lifetime [55].
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38 As we have indicated above in relation to the FTIR spectra and TGA curves (Figures 3
39 & 4), the LaPO₄:Er microspheres synthesized in the present work incorporate some OH⁻ (and
40 nitrate) radicals, which are efficiently suppressed upon calcination at 800°C. A similar result
41 has been also reported, for Nd-doped LaPO₄ [50]. Therefore, our luminescence results are
42 perfectly compatible with the above mentioned arguments and the fact that in LaPO₄ it is
43 possible to remove very efficiently remaining impurities by calcination. Nevertheless, we
44 cannot exclude the possibility that other factors accompanying the calcination process could
45 also contribute to the enhancement of the luminescence quantum efficiency, particularly for
46 higher calcination temperatures (above 800 °C), where most impurities have been eliminated.
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increase in crystallite size (see figure 2 and Table 1), may therefore be responsible of the observed improvement in the quantum yield at higher temperatures.

4.- CONCLUSION

We may therefore conclude that it is possible to synthesized Er-doped LaPO₄ submicron-sized spheres that, upon a simple calcination process at 950 °C, are effectively released of undesirable luminescence quenchers and, simultaneously, the crystallinity is improved, which allows to reach a very high luminescence quantum yield (96 %) in the 1.5 μm Er³⁺ emission (⁴I_{13/2} → ⁴I_{15/2} transition).

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FIGURE CAPTIONS

Fig. 1.- SEM micrographs for the LaPO₄:Er sample as prepared and after heating at 950°C.

Fig. 2.- XRD pattern obtained for the LaPO₄:Er sample as prepared and after heating at different temperatures

Fig. 3.- FTIR spectra obtained for the LaPO₄:Er sample as prepared and after heating at different temperatures

Fig. 4.- TGA curve obtained for the LaPO₄:Er sample.

Fig. 5.- Absorption spectrum of Er³⁺ ions in LaPO₄ microspheres. The absorption bands are labeled indicating the absorbing multiplet from the ⁴I_{15/2} ground state.

Fig. 6.- Near infrared luminescence spectra of Er³⁺-doped LaPO₄ microspheres after different calcination temperatures. The inset shows a partial energy level diagram indicating the main optical transitions involved in the photoluminescence process.

Fig. 7.- Luminescence decays of the 1.5 μm emission of Er³⁺-ions in LaPO₄ microspheres subjected to different calcination temperatures. The lines correspond to the least-squares fitting using a bi-exponential decay (eq. (1)), with the parameters summarized in Table 3.

Fig. 8.- Luminescence quantum yield (circles), calculated as $\langle \eta \rangle = \langle \tau \rangle / \tau_{\text{rad}}$, as function of the calcination temperature. The line has been drawn to guide the eye.

Table 1. Crystallite size of the LaPO₄:Er sample as prepared and after heating at different temperatures.

Temperature (°C)	Crystal size (nm)	Technique
As prepared	12	XRD
600	15	XRD
700	18	XRD
800	37	XRD
900	50	XRD
950	50-150	SEM

Table 2. Unit cell parameters measured for the LaPO₄:Er sample heated at 950 °C and for an undoped LaPO₄ sample prepared under similar conditions.

	a/Å	b/Å	c/Å	V/Å³
LaPO ₄	6.5126(2)	7.0762(2)	8.2913(3)	306.84670
Er _{0.02} La _{0.98} PO ₄	6.5069(1)	7.0683(1)	8.2813(2)	305.8756

Table 3. Fitting parameters of the 1.5 μm luminescence decay of Er^{3+} ions in LaPO_4 , using a double exponential dependence (eq. (1)). The luminescent quantum yield ($\langle\eta\rangle = \langle\tau\rangle/\tau_{\text{rad}}$) is calculated using the average experimental decay time (eq. (2)) and the radiative decay time reported in [17].

Calcination Temperature (°C)	A_S	τ_S (ms)	A_L	τ_L (ms)	$\langle\tau\rangle$ (ms)	$\langle\eta\rangle$ (%)
As prepared	0.42	0.16	0.58	0.85	0.76	11
600	0.35	0.49	0.65	1.74	1.57	23
700	0.40	0.67	0.60	2.26	2.00	30
800	0.17	1.24	0.83	4.42	4.25	63
900	0.24	1.91	0.76	5.98	5.60	84
950	0.17	1.53	0.83	6.70	6.47	96















