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Efficient green and red upconversion emissions in $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped ZnAl_2O_4 phosphor obtained by combustion reaction

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Abstract

Thin ceramic powders of zinc aluminate ZnAl_2O_4 co-doped with Er^{3+} and Yb^{3+} were prepared by a combustion reaction and characterized from the spectroscopic point of view, with the aim of investigating the effect and mechanisms of upconversion emissions. The characteristic cubic spinel structure was predominantly formed for all doped samples, and intense upconversion emission was observed in the green and red spectral regions, under 980 nm diode laser excitation. The upconversion mechanism of both emissions was confirmed to involve two photon absorptions and it was found that the efficiencies of the emissions are considerably enhanced by increasing the Yb^{3+} concentration in relation to Er^{3+} . The results indicate the potential of $\text{ZnAl}_2\text{O}_4:\text{Er}^{3+}, \text{Yb}^{3+}$ phosphor powders for applications in luminescent display panels and other photonic devices.

1. Introduction

Since the discovery of enhanced radiative transition rates in rare-earth (RE^{3+}) doped semiconductor nanoparticles [1], the development of RE metal oxide phosphors with less than 100 nm particle size has received much attention [2–5]. Among the most interesting materials of that kind, the spinel zinc aluminate (ZnAl_2O_4) offers many advantages, such as high thermal and chemical stability, hydrophobic behaviour, high mechanical resistance, low sintering temperature, and high quantum yields [6, 7]. This material presents a close-packed face-centered cubic structure belonging to the $Fd\bar{3}m$ space group, and an optical band gap of 3.8 eV [8], which makes it suitable for photoelectronic devices, such as plasma display panels

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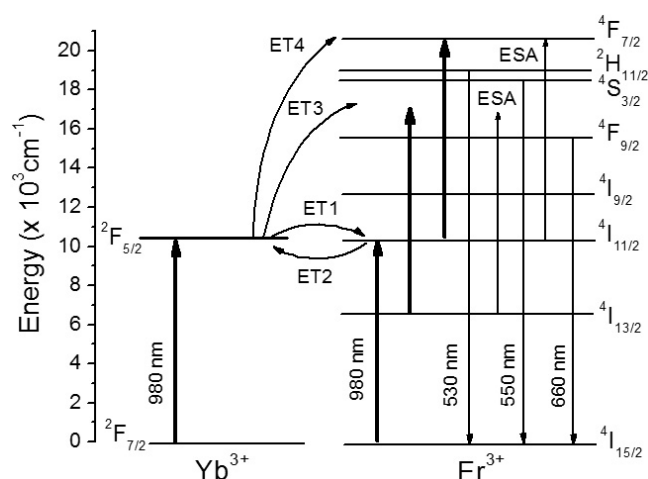


Figure 1. Partial energy level diagrams of Er^{3+} and Yb^{3+} . The pumping transition at 980 nm, and the $\text{Yb} \rightarrow \text{Er}$ (or $\text{Er} \rightarrow \text{Yb}$) energy transfer processes (ET1, ET2, ET3, ET4) are indicated, along with the upconversion emissions, in the green and red spectral regions.

(PDPs), and field emission displays (FEDs) [5]. Based on that, several investigations have been reported on RE ion (Dy^{3+} , Tb^{3+} , Eu^{3+} , Tm^{3+}) doped ZnAl_2O_4 , obtained by different methods [3, 5–7]. The combustion method has been largely used because it is faster and simpler than other methods that require calcination steps, and it leads to high-purity, chemically homogeneous powders, with small and uniform particle size [9].

Concerning the application in luminescent panels, one of the most interesting RE ions is Er^{3+} , with efficient upconversion emissions in the green (${}^2\text{H}_{11/2}$, ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ transitions) and red (${}^4\text{F}_{5/2} \rightarrow {}^4\text{I}_{15/2}$) spectral ranges, that can be pumped by low-cost diode lasers (figure 1). The upconversion process involves a series of non-radiative and radiative mechanisms that result in the generation of photons with higher energy than the excitation photon [10, 11]. In the case of erbium, the excitation can be efficiently pumped at the diode wavelength of 980 nm. Following such a pumping scheme, the procedure of co-doping Er^{3+} doped samples with Yb^{3+} is commonly employed, since this ion has an absorption coefficient around this wavelength that is at least ten times higher than that of Er^{3+} . Thus, it can act as a very efficient sensitizer of the excitation energy, subsequently transferring it to the emitting Er^{3+} [4, 12], as indicated in the partial energy level diagrams in figure 1.

The upconversion efficiency can also be enhanced by proper choice of the host matrix, and in this respect, low phonon energy is a desirable characteristic to minimize the probability of non-radiative decays in the near-infrared and visible spectral regions. The ZnAl_2O_4 host presents a maximum phonon energy of 840 cm^{-1} , comparable to that of efficient metal oxide upconversion hosts such as SrTiO_3 [4], Y_2O_3 [2, 13], TiO_2 [14], etc.

In this work, we present the spectroscopic investigation of upconversion emissions in $\text{ZnAl}_2\text{O}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ powder samples prepared by the combustion reaction method. The aim is to explore the possibilities of applications of this oxide material as a phosphor, for luminescent display panels, as well as other photonic devices.

2. Experimental details

A set of $\text{Zn}[\text{Al}_{1.9}\text{RE}_{0.1}]\text{O}_4$, ($\text{RE} = \text{Er}^{3+} + \text{Yb}^{3+}$) powders, with the $\text{Er}:\text{Yb}$ ratio varying up to 1:6, was synthesized using the combustion reaction method. For instance, the sample labelled

1:1 was doped with (0.05 mol Er^{3+} + 0.05 mol Yb^{3+}), whereas the sample labelled 1:5 was doped with (0.017 mol Er^{3+} + 0.083 mol Yb^{3+}), etc.

The combustion reaction method involves a mixture of oxidizing reagents containing the metal ions, in this case, graded aluminium and zinc nitrates ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$: Merck), rare-earth oxides (Er_2O_3 and Yb_2O_3 : Aldrich), and urea [$\text{CO}(\text{NH}_2)_2$: Synth], as the reducing agent. The initial composition of such mixture is calculated based on the total valence number of the reacting elements, so as to favour the desired $\text{Er}^{3+}/\text{Yb}^{3+}$ proportion, using the concepts of chemistry of the propellants [15]. The solutions were heated on a hot plate up to 480 °C, until auto-ignition occurred (combustion). After combustion, the products, in the form of white porous flocks, were transferred to a pre-heated furnace at 500 °C, and treated for about 15 min for the elimination of volatiles (from the decomposition of urea and the nitrates), that could have remained due to the short time of the reactions. The flocks were then mashed in an agate mortar and the powders were sieved (325-mesh sieve; 44 nm).

Ground-state absorption spectra were measured in a Perkin-Elmer spectrophotometer model Lambda 900, in the 700–1700 nm range. For these measurements, the powders were dispersed and pressed in KBr pellets. The upconversion spectra were obtained using as the excitation source a homemade diode laser emitting at 980 nm. The powder samples were measured in capillary tubes, and their luminescent signals were filtered by a Thermo Jarrel Ash model 82497 single monochromator (0.3 m), being collected by an RCA 31034 photomultiplier, and amplified by a lock-in amplifier model PAR 128.

3. Results and discussions

The combustion reactions to form $\text{ZnAl}_2\text{O}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ powders were characterized by a very explosive behaviour, accompanied by the formation of a yellow flame. For the 1:5 $\text{Er}^{3+}:\text{Yb}^{3+}$ doped sample, for instance, a flame temperature of 760 °C was measured with an optical pyrometer, and the flame lasted 11 s. As the Yb/Er ratio increased to values higher than 5, small increases (~15%) in time and temperature were observed. According to x-ray diffraction data (not shown), there is predominant formation of the ZnAl_2O_4 spinel structure for all the samples, but despite the high temperature of such fast reactions, the presence of traces of ZnO and Yb_2O_3 oxides was also identified. This effect is more pronounced for samples with higher RE^{3+} doping concentrations, as similarly observed by Barros *et al* [5] for Eu^{3+} and Tb^{3+} doped ZnAl_2O_4 samples prepared under the same conditions. The reason for this probably lies in the significantly larger ionic radii of RE^{3+} ions (0.88 nm for Er^{3+} , 0.85 nm for Yb^{3+}), which, while preferably substituting smaller Al^{3+} ($r = 0.53$ nm), in the six-coordinated octahedral sites of ZnAl_2O_4 spinel, introduce structural distortions ultimately leading the system to a low solubility limit. Thus, to minimize this effect, an optimum concentration of RE^{3+} must be selected. From the studied set of samples, it was found that the sample which exhibits desirable spectroscopic properties, while not compromising the structure of the host matrix significantly, is the one doped with 1:5 $\text{Er}^{3+}:\text{Yb}^{3+}$. Therefore, the representative results hereafter presented are those obtained for this sample.

The ground-state absorption spectrum of this sample is displayed in figure 2. The observed transitions are attributed according to the partial energy levels diagrams of Er^{3+} and Yb^{3+} in figure 1. The spectrum presents the absorption bands of Er^{3+} in the two most useful near-infrared diode laser pumping wavelengths, which are 800 and 980 nm. The latter is actually preferred to excite Er^{3+} infrared and upconversion emissions because, in singly doped samples, it presents an absorption coefficient typically three times higher than at 800 nm. In the spectrum of figure 2 the 980 nm band shows even higher intensity because it is actually a superposition

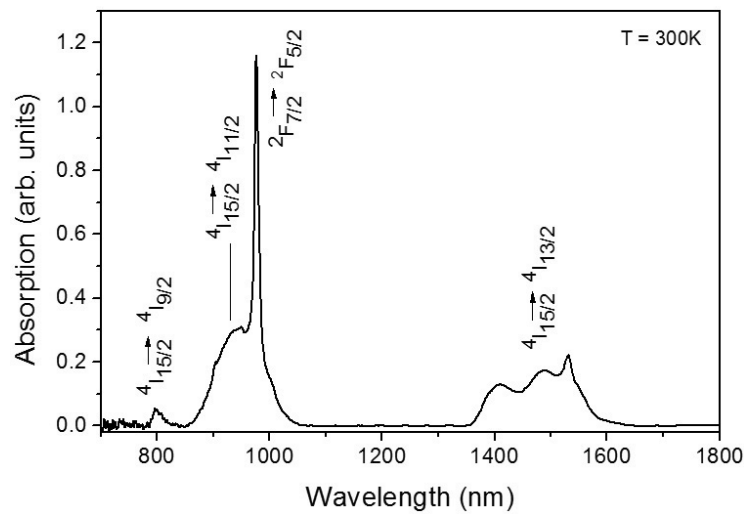


Figure 2. Near-infrared ground-state absorption spectrum of the $\text{ZnAl}_2\text{O}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ (1:5) sample. The transitions from $\text{Er}^{3+} 4\text{I}_{15/2}$ and from $\text{Yb}^{3+} 2\text{F}_{7/2}$ are indicated by the bands.

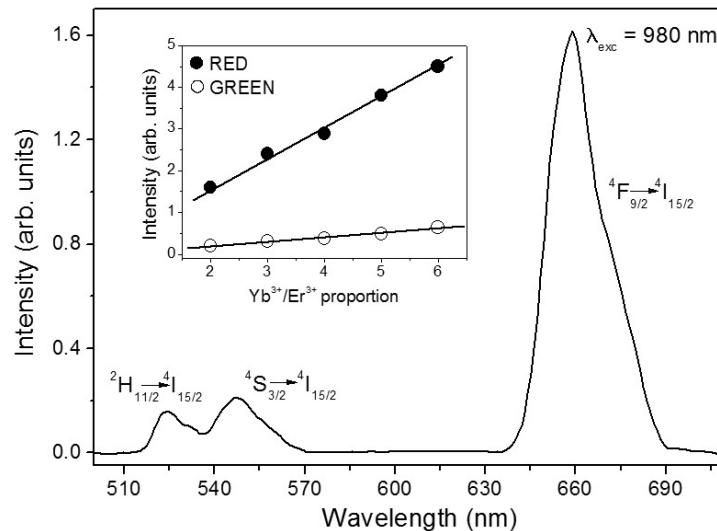


Figure 3. Upconversion spectrum of the $\text{ZnAl}_2\text{O}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ (1:5) sample. The excitation was done at 980 nm, and the green and red emissions transitions are attributed according to the diagram in figure 1. The inset presents the integrated red and green upconversion emission intensity dependence on the $\text{Yb}^{3+}/\text{Er}^{3+}$ molar proportion.

of Er^{3+} ($4\text{I}_{15/2} \rightarrow 4\text{I}_{11/2}$) and Yb^{3+} ($2\text{F}_{7/2} \rightarrow 2\text{F}_{5/2}$) transitions. As previously cited, Yb^{3+} has an absorption coefficient at least ten times higher than Er^{3+} at this wavelength region, so it usually acts as a very efficient sensitizer for Er^{3+} .

Figure 3 presents the room-temperature upconversion spectrum of the 1:5 doped $\text{ZnAl}_2\text{O}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ sample, obtained with diode excitation at 980 nm. The originated green and red emissions are quite efficient, being perceived with the naked eye, even for low pump powers (20 mW). The bands in the range 510–570 nm correspond to transitions from the upper

states ${}^2\text{H}_{11/2}$ and ${}^4\text{S}_{3/2}$ to the ground state ${}^4\text{I}_{15/2}$, and the band around 660 nm corresponds to the ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$ transition. It is noted that these bands present considerably large half widths (10 nm around 520 nm, 17 nm around 540 nm, 22 nm around 660 nm), due to the high local heating of the sample grains, caused by efficient Yb^{3+} absorption. In this case, not only are the lower Stark components of the emitting levels ${}^2\text{H}_{11/2}$, ${}^4\text{S}_{3/2}$ and ${}^4\text{F}_{9/2}$ responsible for the emissions, but also the upper ones, which are thermally populated. The excitation mechanisms of such upconversion emissions can be understood by examining the diagrams in figure 1.

In singly Er^{3+} doped samples, the 980 nm photons are responsible for the excitation of the ${}^4\text{I}_{11/2}$ level, which can also populate the lower-lying ${}^4\text{I}_{13/2}$ through multiphonon decay. Besides possibly originating near-infrared emissions around 1550 and 2800 nm, both these metastable levels can undergo excited-state absorptions (ESAs) of 980 nm photons, leading to excitation of upper ${}^4\text{F}_{9/2}$ and ${}^4\text{F}_{7/2}$ levels. Given the small energy gap separating the levels ${}^4\text{F}_{7/2}$ and (${}^2\text{H}_{11/2}$, ${}^4\text{S}_{3/2}$), the latter are rapidly populated via multiphonon decay from ${}^4\text{F}_{7/2}$. Additional non-radiative decay from ${}^4\text{S}_{3/2}$ can also populate level ${}^4\text{F}_{9/2}$, favouring the red emission (${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$). If the Er^{3+} concentration is high enough to allow the interaction of these ions, various cross relaxation energy transfers (not shown), involving levels ${}^4\text{I}_{11/2}$ and ${}^4\text{I}_{13/2}$, can also take place, playing a role in the excitation of the upper levels.

In $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped samples however, though the aforementioned processes are also possible, the $\text{Yb} \rightarrow \text{Er}$ energy transfers (ET1, ET3 and ET4 in figure 1) are known to be the most significant contribution for Er^{3+} 980 nm upconversion excitation. In the dominant ET1 process, an Yb^{3+} ion excited to ${}^2\text{F}_{5/2}$ state decays non-radiatively to ground-state ${}^2\text{F}_{7/2}$, transferring its energy to an Er^{3+} ion in the ground state and exciting it to ${}^4\text{I}_{11/2}$. From this point there can be ET4 (${}^2\text{F}_{5/2}$, ${}^4\text{I}_{11/2} \rightarrow {}^2\text{F}_{7/2}$, ${}^4\text{F}_{7/2}$) or non-radiative decay to ${}^4\text{I}_{13/2}$ followed by ET3 (${}^2\text{F}_{5/2}$, ${}^4\text{I}_{13/2} \rightarrow {}^2\text{F}_{7/2}$, ${}^4\text{F}_{9/2}$), not to mention the ESA processes. As for the $\text{Er} \rightarrow \text{Yb}$ energy transfer (ET2), resonant to ET1, its probability depends on the product between the energy transfer rates and the lifetimes of the levels involved. Thus, it is desirable that ${}^2\text{F}_{5/2}$ (Yb) has a longer lifetime than ${}^4\text{I}_{11/2}$ (Er), so that $\text{Yb} \rightarrow \text{Er}$ predominates. Indeed, by analysing the inset in figure 3, it is verified that as the Yb^{3+} concentration increases with respect to Er^{3+} , there is a linear increase in integrated intensities of the red and green emissions (up to 1:6 Er:Yb proportion). This is an indication of the efficient $\text{Yb} \rightarrow \text{Er}$ energy transfers. The steeper increase in intensity of red emission might be due to the ET3 process that, differently from ET4, is responsible for excitation of ${}^4\text{F}_{9/2}$ only.

Another interesting characteristic of the Er^{3+} green upconversion emissions derives from the fact that the populations of the thermally coupled ${}^2\text{H}_{11/2}$ and ${}^4\text{S}_{3/2}$ are, as to be expected, highly dependent on temperature, and this is a useful feature for the construction of optical temperature sensors [16, 17]. Figure 4 presents the upconversion spectra in the region 500–580 nm of the 1:5 doped sample, as a function of pump power. For comparison, these spectra were normalized by the peak intensities of the ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ transition. It can be seen that as the pump power (and consequently the temperature) increases, the ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$ emission is increasingly favoured. The temperature-dependent intensity ratios of these two transitions can then be used to build a scale [18]. Since the ZnAl_2O_4 structure is chemically stable for temperatures higher than 800 °C, and $\text{Er}^{3+}/\text{Yb}^{3+}$ doped samples present high emission efficiencies, it is suggested that this material, used in the ceramic form, is an interesting candidate for high-temperature sensing. Traditionally, the materials studied for this purpose were fluoride glasses with low transition temperature T_g (~ 500 °C) [19], which thus limited application to low temperatures.

In order to prove the proposed upconversion mechanisms, figure 5 presents the dependence of integrated green and red emissions intensities I on excitation power P . For upconversion, it is known that $I \propto P^n$, where n is the number of absorbed pump photons for each

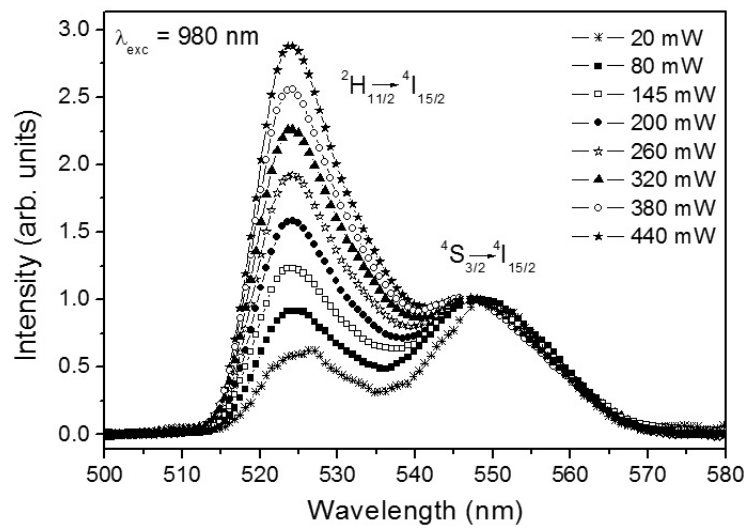


Figure 4. Green upconversion emissions (${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$ and ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$) spectra as a function of diode laser 980 nm pump power of the $\text{ZnAl}_2\text{O}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ (1:5) sample.

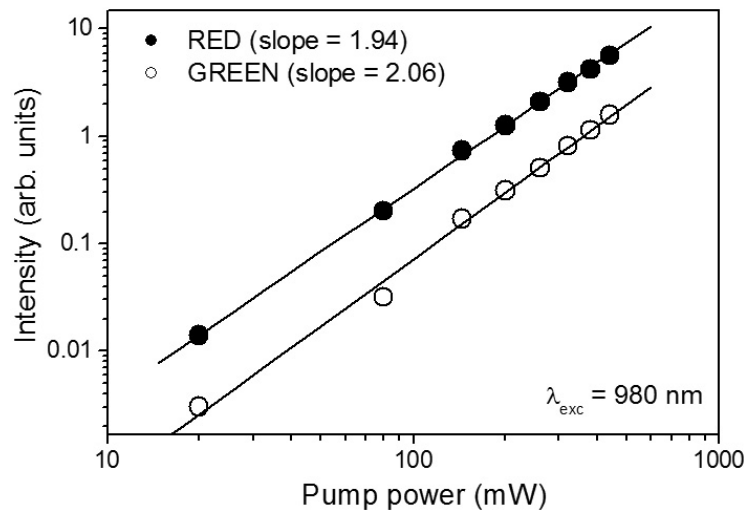


Figure 5. Integrated red and green upconversion emissions (${}^2\text{H}_{11/2}$, ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$) dependence on 980 nm pump power of the $\text{ZnAl}_2\text{O}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ (1:5) sample. Both scales are logarithmic.

emitted unconverted photon. The log–log plots in figure 4 yield linear dependences with slope coefficients of 2.06 for green and 1.94 for red emissions. These results confirm the proposition of two-photon absorptions involved in the upconversion pumping schemes.

4. Conclusions

Based on the results, it is concluded that the combustion reaction method is useful for the synthesis of $\text{ZnAl}_2\text{O}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ powder samples with Er:Yb molar proportion up to 1:6, but

traces of secondary ZnO and Yb₂O₃ oxides are also found in these samples, due to structural distortions caused by the substitution of large RE³⁺ ions in Al³⁺ sites. Still, it is verified that the efficiencies of green and red upconversion emissions in these samples, under 980 nm excitation, is considerably high, and, given the high chemical stability, and the fast, simple and inexpensive preparation of this material, it is a promising candidate for applications as a powder phosphor in plasma display panels (PDPs), field emission displays (FEDs), and other optoelectronic and photonic devices. Additionally, the high upconversion intensities of thermally coupled Er³⁺ levels ²H_{11/2} and ⁴S_{3/2}, associated to the high chemical stability of the host matrix, with respect to high-temperature exposure, also make this material a promising candidate for optical temperature sensors in the ceramic form.

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