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Multifunctional possible application of the Er^{3+}/Yb^{3+}-coped Al_2O_3 prepared by recyclable precursor (aluminum can) and also by sol-gel process

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ABSTRACT

The evolution of research on luminescent phosphors led to research on materials doped with rare earth ions (RE^{3+}), not only because of their photoluminescent properties, but also for their potential applications in photonics. The search for new photoluminescent materials has led to an investigation of the photoluminescence of RE^{3+} present in an aluminum oxide (Al_2O_3) matrix. This oxide has a transparent window on the short ultraviolet to near infrared, excellent mechanical properties and good chemical stability. Within this context, this work aims to obtain Al_2O_3: Er^{3+}/Yb^{3+}. The preparation of Al_2O_3: Er^{3+}/Yb^{3+} involved two synthesis processes. For the co-precipitation process, rings of aluminum cans were used as precursors, and for the sol-gel process, the precursor used was tri-sec-butoxide aluminum. From the XRD results, high heat-treatment temperatures were observed to favor the formation of the α-Al_2O_3 phase and low temperatures were observed to favor the formation the γ-Al_2O_3 phase. The analysis of the photoluminescence emission spectra when excited at 980 nm, showed the up-conversion phenomenon with an emission in the visible region. The emission spectra also showed emission between 1400 and 1650 nm, with a maximum at about 1530 nm. The materials exhibit efficient energy absorption in the infrared region, with light emission in the visible region. Furthermore, the spectra show an intense emission in the infrared region assigned to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+}, demonstrating excellent potential to be used in optical amplifier device at the third telecommunications window.

1. Introduction

During the last few years, luminescent materials have been considered technologically important components, serving as the basics for the functionality and success of many communication, lighting and imaging systems [1–4].

The continuous evolution of research of these materials in nanoscale structures and well controlled devices, has led to research in rare earth (RE^{3+}) doped materials [5–7]. Thus, the luminescence of the RE^{3+} has attracted much attention because of their potential applications in photonics due to their photoluminescent properties, known since the 20th century [8–11]. Such applications include generator imaging devices, traditional lighting devices such as cathode ray tubes, fluorescent lamps, light emitting diodes, field emission displays, lasers [9], solar cells [12], biological markers [6] in sensors technology [13], in uniform fiber Bragg grating (FBG) [14], optical bistable device (OBD) [15], and more.

The RE^{3+} doped host matrix that have photoluminescence properties, have narrow emission lines that come from intraconfigurational f-f transitions due to the weak interaction of electrons with the 4f ligands [16–18]. Transitions involve the partially occupied 4f orbital having transitions forbidden by Laporte rule [19]. However these f-f emissions

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are allowed and intense compared to other transitions, due to spin-orbit coupling effect, the intraconfigurational mixtures, the symmetry of the crystal field and other effects [18]. Depending on the RE^{3+} present, the emissions can occur from the ultraviolet to the infrared region with greater intensity that is dependent on properties of the host matrix [20,21]. These characteristics have attracted attention for use in technological science materials and also to improve the fundamental studies to understand precisely what properties are involved [9]. Among the extensive research on RE^{3+}, there has been a great interest especially in Er^{3+}, due to its *up-conversion* efficiency in the visible region [6]. Furthermore, these ion doped materials also contribute to the transmission signal amplification in the third telecommunications window [22].

Materials doped with Er^{3+} when excited at 980 nm, exhibit an emission band attributed to $^4I_{15/2} \rightarrow {}^4I_{11/2}$, in the infrared region with maximum at 1550 nm, a fundamental characteristic for applications in telecommunications systems and optical amplification devices [23,24]. In this way, the Erbium Doped Fiber Amplifier (EDFA) has gained great attention. The wavelength used in telecommunications systems is positioned in the "Third Window of Telecommunications" (C-Telecom) [25]. This region is divided into three different regions: S band (region between 1460 nm and 1530 nm), C band (region between 1525 nm and 1565 nm) and L band (region between 1570 nm and 1610 nm). Therefore, it is of great industrial interest the development of materials that offer adequate optical and spectroscopic properties to operate in the regions between 1400 nm and 1650 nm [26,27].

In order to contribute to a higher Er^{3+} emission efficiency, since the absorption cross section in the 980 nm region of this ion is very low, around 1.7×10^{-21} cm^2 [11,12], Yb^{3+} is used as sensitizer. The Yb^{3+} absorption band extends over a broader region of wavelength, between 850 and 1080 nm [9,28], being the most intense at 980 nm [8,29]. The co-doping of Yb^{3+} produces enhancement of intense absorption due to the high cross section of Yb^{3+}, about 11.7×10^{-21} cm^2, ten times more efficient than the Er^{3+}, thus increases the optical pumping. Therefore the Yb^{3+} ion can act effectively as a sensitizer of the Er^{3+}, due to resonance conditions between both, together with an efficient energy transfer (ET) from the emission spectral overlap between Yb^{3+} of the transition $^2F_{5/2} \rightarrow {}^2F_{7/2}$ and absorption Er^{3+} of the transition $^4I_{15/2} \rightarrow {}^4I_{11/2}$ [6,12,22]. This process is much more efficient than the excitation directly on Er^{3+}. The efficiency of an optical fiber is related to the increased bandwidth of communication systems (C-Telecom). An optical fiber with a broadened band in this region, allows transporting several wavelengths of light simultaneously. Thus purely optical devices are replacing semiconductor based electronic devices, due to some advantages such as increased transmission speed and distance, broad emission band, resistance to electromagnetic interference, low attenuation of transmitted signal strength and null electrical conductivity. Therefore, fiber based systems are undergoing a period of evolution with the objective of high efficiency in the field of telecommunications, for example, the amplification of the emission signal achieved by the incorporation of rare earth ions in the fiber [4,30].

The selection of the host matrix suitable for the doping of rare earth ions is fundamental in developing efficient materials for optical application, since the matrix and the intentionally added impurity play an important role in the luminescence optical amplification process, pumping efficiency [7,13,31–34], broad band emission, as well as chemical durability, thermal stability [6,35] and mechanical resistance [22].

However, the search for new photoluminescent materials that have these characteristics, led to the investigation of the photoluminescence of RE^{3+} present in aluminum oxide (Al_2O_3), which has been widely studied as a host material to RE^{3+} [36,37]. This material has significant technological importance, because it offers a large window of transparency, from short ultraviolet to the near infrared region [22,38]. It has excellent mechanical properties, good chemical stability [39,40], hardness and refractory properties which makes it an excellent candidate for optical applications [41], amplifiers [42]and lasers [43]. Aluminum oxide is very popular as a dielectric material. It is believed there are more than 15 different crystallographic phases, which can be subjected to a variety of transitions. The most stable structure, *corundum* (α-Al_2O_3), with a gap E_g = 9.4 eV, is the most widely used for practical application and has been thoroughly studied [44–47]. Other phases of alumina, including γ, δ, η, θ, κ β, χ are metastable polymorphs. They are called transition phases, as are the intermediate steps in the process of obtaining the α-phase during calcination [48,49].

Extensive research on the optical properties of Er^{3+} in the aluminum oxide matrix has shown that it is one of the most suitable matrices for Er^{3+} [33,50,51]. The Al_2O_3: Er^{3+}/Yb^{3+} may be prepared by synthetic techniques in which the parameters that affect the optical properties can be varied [52,53]. For example the following techniques may be used ion implantation [28], pulsed laser deposition [54,55], chemical vapor deposition [56], co-precipitation and combustion [3], sol-gel method [32,43,57], among others.

The possible energy emission mechanisms of these materials can be deducted from the energy matching conditions, which are related to the excitation and energy transfer processes of Er^{3+} and Yb^{3+} ions [8]. Among them, the most important mechanism is the phenomenon of *upconversion*. This phenomenon was defined as a nonlinear optical process in which a wave of continuous light of low energy in the near infrared region (NIR) (typically 980 nm) is converted into visible light of higher energy, from the absorption multiple photons or energy transfer [58,59].

In order to obtain materials that have higher photoluminescence efficiency, researchers studied the effect of energy transfer between the Yb^{3+} and Er^{3+} in the host Al_2O_3 matrix. This material was compared to materials doped with Er^{3+}. Thus, they found that co-doping with Yb^{3+} increased the photoluminescence of the material [29]. The excitation mechanism follows the photoluminescence of Er^{3+} in the $^4I_{13/2}$ level with a wavelength of excitation between 890 and 1030 nm. In the sample doped only with Er^{3+}, a narrow band centered at 980 nm can be excited, the absorption band of Er^{3+} and extends from 955 to 1000 nm. In contrast, when the sample is co-doped with Yb^{3+}, the same issue may be activated on a much larger wavelength range with a sharp peak at 975 nm. This peak is characteristic of Yb^{3+}, referring to the level $^2F_{5/2}$ absorption [60]. However, the sample that is co-doped with Yb^{3+} exhibits an effective energy transfer to Er^{3+}, resulting in an absorption band and more intense emission. Thus considering the intensity of photoluminescence in samples co-doped with Yb^{3+}, this materials have potential application in photonic devices.

The understanding of ion emission properties of Er^{3+} and Yb^{3+} as well as their structural and crystalline properties will be conducted in order to evaluate the best photoluminescent properties of the Al_2O_3 doped with these RE^{3+}. The materials will be prepared in two different ways, by a co-precipitation method and by a sol-gel process.

2. Experimental procedure

Initially the synthesis of the Er^{3+}/Yb^{3+} co-doped Al_2O_3 was carried out using a co-precipitation method. In this synthesis, aluminum can rings and alcoholic solutions of erbium chloride, and ytterbium chloride, previously standardized with 0.01 mol L^{-1} EDTA. 0.5 g of aluminum can rings were dissolved in 13 mL of aqueous 5.0 mol L^{-1} HCl with stirring and heating for 15 min at 60 °C. After the rings completely dissolved, the doping was performed with 0.1, 1 and 3 mol% of Er^{3+}, and then co-doping with 1.2 mol% of Yb^{3+}, relative to the total amount of moles of Al^{3+}. Then the ions were precipitated using an ammonium hydroxide solution NH_4OH (Neon – 28–30%). The precipitate was centrifuged and the material was kept in an oven at 100 °C for 4 days. The materials were crushed in an agate mortar to obtain powders which were heat-treated at 400, 600, 900, 1000, 1100 °C for 4 h to obtain the RE^{3+} co-doped aluminum oxide.

Subsequently, the Er^{3+}/Yb^{3+} co-doped Al_2O_3 was synthesized by a sol-gel process using the tri-sec-butoxide aluminum (Aldrich- 97%)