Tunable green/red luminescence by infrared upconversion in biocompatible forsterite nanoparticles with high erbium doping uptake

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ABSTRACT

Nanoparticles represent a promising platform for diagnostics and therapy of human diseases. For biomedical applications, these nanoparticles are usually coated with photosensitizers regularly activated in a spectral window of 530−700 nm. The emissions at 530 nm (green) and 660 nm (red) are of particular interest for imaging and photodynamic therapy, respectively. This work presents the $Mg_2SiO_4:Er^{3+}$ system, produced by reverse strike co-precipitation, with up to 10% dopant and no secondary phase formation. These nanoparticles when excited at 985 nm show upconversion emission with peaks around 530 and 660 nm, although excitation at 808 nm leads to only a single emission peak at around 530 nm. The direct upconversion of this biomaterial without a co-dopant, and its tunability by the excitation source, renders $Mg_2SiO_4:Er^{3+}$ nanoparticles a promising system for biomedical applications.

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1. Introduction

In the recent past, rare earth doped nanoparticles rose as a topic of growing interest due to their distinct optical properties [1]. Crystalline structures doped with rare earth ions exhibit well-defined absorption and emission lines and do not undergo photo-bleaching [2,3], making these nanoparticles extremely advantageous for biomedical applications. In crystalline nanoparticles, the absorber and emitter ions inside the structure are shielded from the outside environment, thus there is little or no quenching related to the biological medium in which it they are inserted [4–7].

For biomedical applications, these nanoparticles are usually coated with photosensitizers activated in a spectral window of 530−700 nm [6,8,9] and the location of light exposure is controlled; it is therefore possible to target specific cells, such as bacterial cells or tumors. The emissions around 530 nm (green) and 660 nm (red) are of particular interest for imaging and photodynamic therapy (PDT) [6,8,9], as they also activate a variety of anticancer drugs [10−15]. However, these wavelengths have reduced tissue penetration, rendering large internal areas virtually inaccessible to diagnosis and treatment purposes. One way to avoid the above-mentioned problem is to shift the excitation wavelength to the near infrared region (NIR). In this spectral region, biological tissues allow high light penetration with minimal absorption, enabling the light to reach targets in deep positions inside living organisms [8,16]. Therefore, NIR excitation sources can be used with higher

intensity and/or exposure time than ultraviolet (UV) and visible (Vis) sources, without causing significant damage to the exposed tissue.

When inserted in specific hosts, rare-earth ions such as Ho^{3+}, Eu^{3+} and Er^{3+} present upconversion emission, i.e. these systems are able to absorb two or more low energy photons and emit at higher energy ranges [17–21]. Recently, upconversion nanoparticles (UCNPs) excited in the NIR have been widely applied in biomedicine. At 800 nm, water and hemoglobin have a minimal NIR absorption and the heating effect is therefore considerably reduced. Overheating may induce cell and tissue damage [4,15,22]. Thus, efforts are being made to adjust the UCNPs excitation window [8,9,23]. Research on platforms based on upconversion is still at an initial state focusing on the manufacturing of nanoparticles. The development of platforms such as UCNPs with tunable emission — particularly the green and red emissions — could represent an important improvement for their application, since with the same system it would be possible to activate different functions by the careful choice of the excitation wavelength [24,25].

The erbium (III) ion presents upconversion when excited at different NIR wavelengths, emitting in the UV–Vis range [10,18,26]. The wavelength and intensity of the absorption and emission lines vary in accordance to the host [27]; in other words, a dopant ion may have distinct optical properties depending on the host in which it is inserted [28]. Forsterite (Mg_2SiO_4) is a biocompatible material with high dielectric constant ($εr = ~7$) [29,30], elevated transparency in the UV–Vis–NIR range [31] and great physico-chemical stability even under extreme conditions ($\geq 1800\ °C$ and a wide range of pH) [29,32,33]. These properties make forsterite an excellent candidate for biological and optical applications. However, it has not yet been extensively studied in the aforementioned fields.

We present for the first time, to the best of our knowledge, the erbium-doped forsterite (Mg_2SiO_4:Er^{3+}) system. Homogeneous nanoparticles of Mg_2SiO_4:Er^{3+} were produced by a low cost technique, namely reverse strike co-precipitation (RSC). This is a simple and effective way to produce large amounts of high quality single-phase nanopowder that are loosely agglomerated [34,35]. Downconversion and upconversion photoluminescence were measured with excitation at 985 and 808 nm. Interestingly, the produced Mg_2SiO_4:Er^{3+} nanoparticles presented different upconversion emissions depending on the NIR wavelength excitation.

2. Experimental

Nano-scale erbium doped forsterite powder was synthesized via RSC similarly as the pure forsterite powder described by Zampiva at al. [36]. In order to produce Mg_2SiO_4:Er^{3+} (2g), Mg $(NO_3)_2 \cdot 6H2O$ 99% (8.14g), Si$(OC_2H_5)_4$ (TEOS) 98.5% (3.17 mL) and x (0%, 1%, 3%, 5%, 7%, 10%, 20% mol) of Er$(NO_3)_3 \cdot 5\ H_2O$099.9% were dissolved in a solution of ethanol (40 mL) and HNO_3 70% (3 mL). All reagents were purchased from Sigma-Aldrich. The reaction follows the stoichiometry described below (Eq. (1)):

$$2\ Mg(NO_3)_2 + Si(OHC_2H_5)_4 + x\ Er(NO_3)_3 \rightarrow Mg_2SiO_4:\ Er^{3+} + x\ N_2 + 8\ CO_2 + 12\ H_2O + x\ O_2 \tag{1}$$
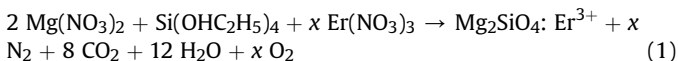
The samples crystallinity was evaluated by X-ray diffraction (XRD) using a PHILIPS diffractometer (model X'Pert MPD), 40 kV, 40 mA and Cu anode and the crystallite size was calculated by Scherrer's equation. The specific surface area of the calcined powders were determined by the Brunauer–Emmett–Teller nitrogen gas adsorption method (BET, Micromeritics ASAP2020 gas absorption). Raman spectroscopy was carried out using a Renishaw inVia microRaman System with a 532 nm wavelength laser. X-ray

photoelectron spectroscopy (XPS, ESCA 3000-VG Microtech) was performed using Al-Kα radiation for the initial survey as well as for the high resolution measurements. The morphology was characterized by scanning electron microscopy (SEM, JEOL-JSM 6060) at an accelerating voltage between 10 and 20 kV and transmission electron microscopy (TEM, JEM 2010) at 200 kV. The powder samples were dispersed with ethanol, which was dropped onto silicon glass and dried at 60 °C for 2 h. The produced films were then analyzed via absorbance spectroscopy in the UV–Vis–NIR range using an Ocean Optics spectrophotometer. For the emission analyses, the powders were pressed into pellets with a thickness of 1 mm. Photoluminescence measurements were performed in a Micro-PL system (HORIBA Jobin Yvon) with a solid-state laser excitation source (Quantum Laser) operating at 532 nm with 100 mW output power. The emission spectra in the UV–Vis–NIR were obtained by exciting the samples at 808 and 985 nm with an intensity of up to 1 W cm^{-2}; the signals were collected and analyzed by a monochromator equipped with a photomultiplier for signal detection in the visible region (500–700 nm) and with a Ge photodetector for signal detection in the infrared region (1440–1700 nm).

3. Results and discussion

The XRD analysis (Fig. 1) showed that with the variation of erbium concentration in the samples from 0 to 10% mol a single phase of forsterite is observed (synthetic forsterite, PDF# 34-189). In the Mg_2SiO_4: Er^{3+} 20% diffractogram, the presence of magnesium oxide (MgO, PDF # 45-946) is observed, indicating saturation of the host structure and the beginning of competing phase formation. Although structure saturation has occurred, no erbium oxide peaks are observed (Er_2O_3 PDF # 08-0050).

Via Scherrer's calculation, with increasing Er^{3+} concentration in the structure, the crystallites undergo a small gradual growth, ranging from 15 ± 3 nm for the Mg_2SiO_4 sample to 25 ± 2 nm for the Mg_2SiO_4:Er^{3+} 20% sample. Despite the growth of the crystallites, no significant lattice changes were observed according to the XRD analysis. In addition, the surface area analysis by BET, showed
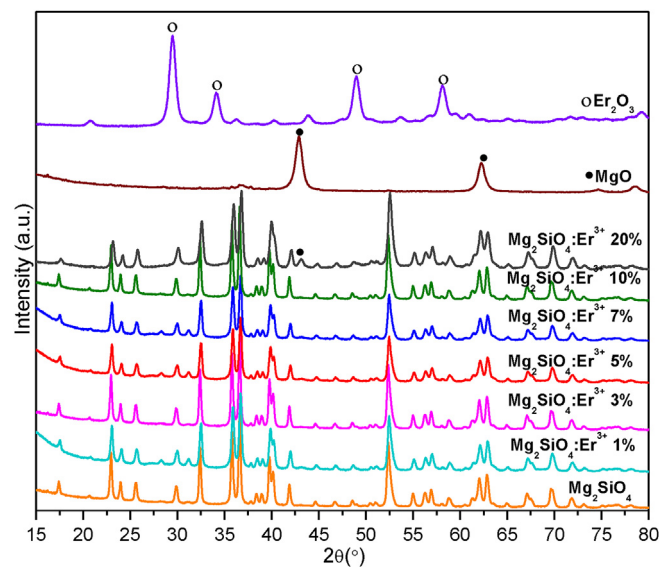

Fig. 1. X-ray diffractograms of commercial MgO, Er_2O_3 and synthesized Mg_2SiO_4 with different Er^{3+} doping concentration. From 0 to 10% a single phase of forsterite is observed. In the Mg_2SiO_4: Er^{3+} 20% diffractogram, the presence of MgO indicates saturation of the host structure.