Sensors and Actuators A 331 (2021) 113014

Contents lists available at ScienceDirect

Sensors and Actuators A: Physical

journal homepage: www.elsevier.com/locate/sna

Enhanced upconversion emission of Er^{3+}-Yb^{3+} co-doped $Ba_5(PO_4)_3OH$ powder phosphor for application in photodynamic therapy

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ARTICLE INFO

Article history:
Received 10 June 2021
Received in revised form 25 July 2021
Accepted 1 August 2021
Available online 4 August 2021

Keywords:
Phosphors
Upconversion
Phosphates
Photodynamic therapy

ABSTRACT

Er^{3+}-Yb^{3+} co-doped $Ba_5(PO_4)_3OH$ nanoparticle powder phosphors were successfully synthesized by urea combustion method. The resulting powder phosphors were characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), high resolution scanning electron microscopy (HRSEM), energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS) and photoluminescence spectroscopy (PL). XRD data confirmed crystallization of pure hexagonal phase of $Ba_5(PO_4)_3OH$ and HRSEM images showed formation of ellipsoidal particles. XPS data combined with EDS analysis confirmed the materials composition that corresponds with identification of all the chemical elements constituting the materials. The *in vitro* dark cytotoxicity of the particles confirmed lack of cytocidal behaviour in the absence of light, but considerable photodynamic therapy (PDT) activity was observed upon illumination. Upon excitation using a 980 nm laser, multiple emission peaks in the green and red regions corresponding to the optical transitions of Er^{3+} ion were observed. Upon co-doping with Yb^{3+}, upconverted red emission was detected and this was attributable to non-radiative energy transfer from Yb^{3+} to Er^{3+}. The proposed mechanism of upconversion photoluminescence is discussed.

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1. Introduction

Inorganic phosphates have emerged as preferred host lattices for rare-earths dopant ions to prepare light emitting materials (phosphors) that could be used in a variety of applications such as information displays, medical imaging, theft prevention, advertising, phototherapy lamps, and photodynamic therapy [1]. In addition, phosphates are thermally and chemically stable, biocompatible (able to form bonds with tissues in human bodies) and osteoconductive (permits bone growth on their surfaces) [2]. Barium phosphates are used in a variety of technological applications due to their several exclusive properties such as high thermal expansion coefficient, low viscosity, ultraviolet (UV) transmission, electrical conductivity, high solubility for rare earth ions and non-toxicity [3–5]. Because of their biocompatibility and osteoconductivity, barium phosphates based materials also have potential applications in biomedical fields [6].

In our study, we used the combustion method to prepare erbium (Er^{3+}) and ytterbium (Yb^{3+}) co-doped barium hydroxide phosphate ($Ba_5(PO_4)_3OH$) phosphor materials. $Ba_5(PO_4)_3OH$ has advantages such as low phonon energy, good chemical, photothermal, and photochemical stabilities [7,8]. We studied the structure, particle morphology, electronic states and chemical composition of $Ba_5(PO_4)_3OH:Er^{3+},Yb^{3+}$. In particular, we examined the upconverted red emission of Er^{3+} as a result of non-radiatve energy transfer from Yb^{3+} co-dopant. Er^{3+} has excellent electronic energy level scheme with equally spaced and longer lifetime excited states, which are favourable for upconversion (UC) of near infrared (NIR) light to visible light [9].

Yb^{3+} was used as a sensitizer for upconverted photoluminescence from Er^{3+} because it has a large absorption cross section around the wavelength of 980 nm, therefore it has got the potential to harvest primary excitation energy and transfer it non-radiatively to Er^{3+} enhancing its photoluminescence intensity *via* UC processes [10,11]. As a sensitizer, Yb^{3+} acts to harvest and subsequently transfer the primary NIR excitation energy (absorbed at 980 nm) to excite the second (co-dopant) trivalent rare earth ion (Er^{3+} in our case) that will in turn relax to the ground state, producing up-converted emission in the visible region of the spectrum. Yb^{3+} has two energy

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https://doi.org/10.1016/j.sna.2021.113014
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