

# Upconversion luminescence of Er<sup>3+</sup>/Yb<sup>3+</sup> doped Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH phosphor powders

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## ARTICLE INFO

### Keywords:

Strontium hydroxide phosphate  
Biocompatibility  
Upconversion phosphors  
Lanthanides  
Energy transfer  
Photodynamic therapy

## ABSTRACT

Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH co-doped with Er<sup>3+</sup> and Yb<sup>3+</sup> powder phosphors were synthesized by urea combustion method. The crystal structure was analyzed using X-ray diffraction (XRD). Particle morphology was analyzed using a Jeol JSM 7800F thermal field emission scanning electron microscope (FE-SEM) and the chemical composition analysis was carried out using an Oxford Instruments AzTEC energy dispersive spectrometer (EDS) attached to the FE-SEM. Upconversion emission was measured by using a FLS980 Spectrometer equipped with a 980 nm NIR laser as the excitation source, and a photomultiplier (PMT) detector. The XRD data of the Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH powder exhibited characteristic diffraction patterns of the hexagonal structure referenced in the standard JCPDS card number 00-033-1348. The sharp peaks revealed the formation of crystalline Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH. The powders were made up of hexagonal nanospheres. The enhanced red emission due to the <sup>4</sup>F<sub>9/2</sub> → <sup>4</sup>I<sub>15/2</sub> transitions of Er<sup>3+</sup> was observed and was attributed to up conversion (UC) energy transfer from Yb<sup>3+</sup>. The upconversion energy transfer mechanism from Yb<sup>3+</sup> to Er<sup>3+</sup> is discussed.

## 1. Introduction

Strontium hydroxide phosphate (Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH) has attracted great interest in modern material due to its outstanding biocompatibility and bioactivity properties [1]. It has been extensively used as a bone cement filter, in laser materials and also in the development of industrial phosphors [2]. The ionic radius of the Sr<sup>2+</sup> ion is 1.12 Å and it is similar to ionic radii of many dopant ions such as lanthanides that are used as luminescent centres in many light emitting materials (phosphors) [3,4]. Therefore strontium hydroxide phosphate is a promising host for preparation of phosphors including upconversion phosphors due to among other things, ease of incorporation of lanthanides, short distance between atomic positions that can be occupied by dopant ions such as erbium (Er<sup>3+</sup>) and high solubility ytterbium (Yb<sup>3+</sup>) [5].

In this study, Er<sup>3+</sup> and Yb<sup>3+</sup> co-doped Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH phosphors were prepared by urea combustion method. Yb<sup>3+</sup> was used as a sensitizer of upconverted red photoluminescence from Er<sup>3+</sup>. Although a single Er<sup>3+</sup> ion is sufficient to produce upconversion effect, co-doping is usually necessary to enhance its emission (by a transfer of NIR primary excitation energy) since many lanthanides including Er<sup>3+</sup> have low absorption cross-section leading to a weak emission [6]. Yb<sup>3+</sup> is usually used as a sensitizer for upconversion photoluminescence due to its larger absorption cross-section in the near infrared (NIR) region (850–1050 nm). Er<sup>3+</sup> ions emits green

and red upconverted photoluminescence associated, respectively, with the <sup>4</sup>S<sub>3/2</sub> → <sup>4</sup>I<sub>15/2</sub> (at ~ 560 nm) and <sup>4</sup>F<sub>9/2</sub> → <sup>4</sup>I<sub>15/2</sub> (at ~ 660 nm) transitions when the ions are excited either directly using the NIR radiation or through the NIR excitation of the Yb<sup>3+</sup> sensitizer [7]. Light energy in wavelengths in the range of 600–900 nm (far red to NIR) can penetrate living tissues to a depth about 8–10 mm because they are not blocked by water or blood in the body [8,9]. Therefore these wavelengths can be used in light therapy for treating surface wounds, cuts, scars and cancerous cells. In this paper, we demonstrate enhancement of red emission from Er<sup>3+</sup> at ~ 660 nm through sensitization by NIR excitation of Yb<sup>3+</sup>. In other words, primary excitation energy was harvested by Yb<sup>3+</sup> and subsequently transferred non-radiatively to Er<sup>3+</sup> enhancing its red emission. Our red emitting Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH:Er<sup>3+</sup>,Yb<sup>3+</sup> material can be used in light therapy to activate photosensitizers for treatment of cancer or photodynamic therapy. We evaluated the structure, particle morphology and upconversion luminescence of Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH:Er<sup>3+</sup>,Yb<sup>3+</sup> phosphor. A mechanism of energy transfer from Yb<sup>3+</sup> to Er<sup>3+</sup> is presented. We will not report on the application of our materials in photodynamic therapy.

## 2. Experimental

Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH co-doped Er<sup>3+</sup>/Yb<sup>3+</sup> phosphor powders were synthesized by combustion method using urea as a fuel. This synthesis

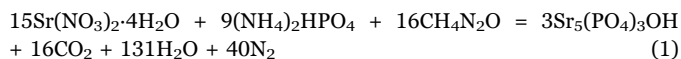
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<http://dx.doi.org/10.1016/j.physb.2017.06.040>

Received 11 April 2017; Received in revised form 11 June 2017; Accepted 13 June 2017  
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method is quick, simple and uses inexpensive raw materials. Lately it is one of the preferred methods to prepare different nanomaterials. The following starting materials with 99% purity were used for the preparation of materials reported in this paper: strontium nitrate (6 M  $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), di-ammonium hydrogen phosphate ((4 M  $\text{NH}_4)_2\text{HPO}_4$ ), erbium nitrate ( $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ), ytterbium nitrate ( $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) with different concentrations of  $\text{Er}^{3+}$  (in the range of 0.1–7 mol%),  $\text{Yb}^{3+}$  (7 mol%), and  $\text{Er}^{3+}:\text{Yb}^{3+}$  (3:1–7 mol%), and urea ( $\text{CO}(\text{NH}_4)_2$ ). When a complete reaction is assumed, the theoretical equation for the formation of  $\text{Sr}_5(\text{PO}_4)_3\text{OH}$  is given by:



All reagents, in stoichiometric amounts, were dissolved in 2 ml of distilled water and the mixture was stirred vigorously for 15 min until a thick homogenous solution was formed. The solution was kept in a furnace maintained at 600 °C. The solution boiled, underwent dehydration and decomposed while generating combustible gases such as  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{H}_2\text{O}$ . The combustion ashes were cooled to room temperature and were ground gently using a pestle and mortar resulting in a fine powder. The materials synthesized were  $\text{Sr}_5(\text{PO}_4)_3\text{OH}$ ,  $\text{Sr}_5(\text{PO}_4)_3\text{OH}:\text{Er}^{3+}$ ,  $\text{Sr}_5(\text{PO}_4)_3\text{OH}:\text{Yb}^{3+}$  and  $\text{Sr}_5(\text{PO}_4)_3\text{OH}:\text{Er}^{3+},\text{Yb}^{3+}$ . All the powders were annealed at 800 °C in air.

## 2.1. Measurements

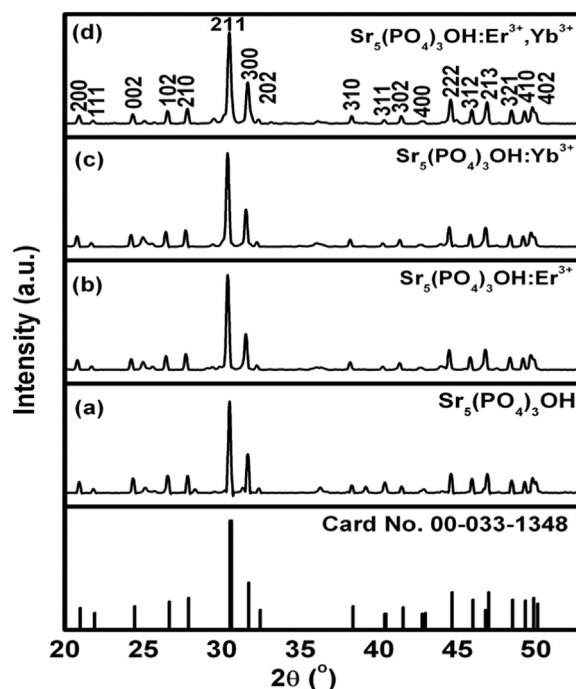
The crystalline structure of the phosphors was analyzed using a Bruker AXS D8 X-ray Diffraction (XRD) with Cu K $\alpha$ 1 radiation ( $\lambda = 1.5406 \text{ \AA}$ ) in the range of 20–60° (2 $\theta$ ). The vibrational bands/modes were analyzed using Fourier Transform Infrared (FTIR) spectrometer. Particle morphology was examined using a Jeol JSM-7800F thermal field emission scanning electron microscope (FE-SEM) coupled with Oxford Aztec 350 X-Max80 Energy x-ray Dispersive Spectroscopy (EDS) which was used to analyse the chemical composition of the phosphors under a vacuum of  $9.634 \times 10^{-5}$  Pa. The absorption and bandgap energy were evaluated using a Perkin Elmer Lambda 950 UV–Vis spectrometer. Upconversion photoluminescence emission was measured by using a photoluminescence (PL) system consisting of a fibre-coupled 980 nm NIR (near infrared) laser as the excitation source, iHR320 Horiba Yvon imaging spectrometer, R943-02 Hamamatsu Photonics photomultiplier (PMT) detector and a SR830 Stanford Research System lock-in amplifier.

## 3. Results and discussion

Fig. 1 shows the XRD pattern of (a)  $\text{Sr}_5(\text{PO}_4)_3\text{OH}$ , (b)  $\text{Sr}_5(\text{PO}_4)_3\text{OH}:\text{Er}^{3+}$ , (c)  $\text{Sr}_5(\text{PO}_4)_3\text{OH}:\text{Yb}^{3+}$  and (d) an indexed  $\text{Sr}_5(\text{PO}_4)_3\text{OH}:\text{Er}^{3+},\text{Yb}^{3+}$  phosphor powders with diffraction peaks corresponding to the standard data referenced in International Center for Diffraction Data (ICDD) Card No. 00-033-1348 [10]. The ionic radii of  $\text{Er}^{3+}$  (1.01 Å) and  $\text{Yb}^{3+}$  (1.01 Å) are slightly smaller than that of  $\text{Sr}^{2+}$  (1.18 Å). Therefore  $\text{Er}^{3+}/\text{Yb}^{3+}$  can be easily substituted into  $\text{Sr}^{2+}$  sites [11]. The narrow and sharp peaks of  $\text{Sr}_5(\text{PO}_4)_3\text{OH}$  powder indicate a highly crystalline structure. The diffraction peaks get broadened by doping with different rare earths, suggesting a systematic decrease in the crystallite size. The crystallite sizes of the powders were calculated by using Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

where  $k$  is the Scherrer's constant (0.98),  $\lambda$  is the wavelength of X-ray (1.54060 Å),  $\beta$  is the full-width at half maxima,  $\theta$  is the Bragg angle of the XRD peak. The diffraction peaks (211, 300, 222, 312, and 213) were used to calculate the crystallite size. The calculated average



**Fig. 1.** XRD results of (a)  $\text{Sr}_5(\text{PO}_4)_3\text{OH}$ ,  $\text{Sr}_5(\text{PO}_4)_3\text{OH}:\text{Er}^{3+}$  ( $\text{Er}^{3+} = 5$  mol%),  $\text{Sr}_5(\text{PO}_4)_3\text{OH}:\text{Yb}^{3+}$  ( $\text{Yb}^{3+} = 3$  mol%) and  $\text{Sr}_5(\text{PO}_4)_3\text{OH}:\text{Er}^{3+},\text{Yb}^{3+}$  ( $\text{Er}^{3+} = 3$  mol% and  $\text{Yb}^{3+} = 7$  mol%) phosphor powders and ICDD Card 00-033-1348.

**Table 1**

Lattice parameters of different samples calculated from XRD results.

Sample	a (Å)	c (Å)	Crystallite Size (nm)
$\text{Sr}_5(\text{PO}_4)_3\text{OH}$	9.786	7.306	47.1
$\text{Sr}_5(\text{PO}_4)_3\text{OH}:\text{Er}^{3+}$	9.828	7.342	44.4
$\text{Sr}_5(\text{PO}_4)_3\text{OH}:\text{Yb}^{3+}$	9.831	7.345	44.3
$\text{Sr}_5(\text{PO}_4)_3\text{OH}:\text{Er}^{3+},\text{Yb}^{3+}$	9.793	7.312	42.1

crystallite sizes of  $\text{Sr}_5(\text{PO}_4)_3\text{OH}$ ,  $\text{Sr}_5(\text{PO}_4)_3\text{OH}:\text{Er}^{3+}$ ,  $\text{Sr}_5(\text{PO}_4)_3\text{OH}:\text{Yb}^{3+}$  and  $\text{Sr}_5(\text{PO}_4)_3\text{OH}:\text{Er}^{3+},\text{Yb}^{3+}$  are shown in Table 1. The decrease in crystallite size of phosphor powders suggest that incorporation of dopants suppresses the growth of  $\text{Sr}_5(\text{PO}_4)_3\text{OH}$  powder. The peaks corresponding to the crystal plane (210) and (002) were selected to calculate the lattice parameters of the  $\text{Sr}_5(\text{PO}_4)_3\text{OH}$ ,  $\text{Sr}_5(\text{PO}_4)_3\text{OH}:\text{Er}^{3+}$ ,  $\text{Sr}_5(\text{PO}_4)_3\text{OH}:\text{Yb}^{3+}$  and  $\text{Sr}_5(\text{PO}_4)_3\text{OH}:\text{Er}^{3+},\text{Yb}^{3+}$  phosphor powders. The lattice parameters of undoped and doped powders are slightly different, probably due to lattice distortion of the crystal structure [12] caused by incorporation of the dopants.

Fig. 2 shows the crystal structure of  $\text{Sr}_5(\text{PO}_4)_3\text{OH}$  which was drawn by using the Diamond-Visual Crystal Structure Information System program referenced by Inorganic Crystal Structure Database (ICSD) code number 2855. There are two non-equivalent crystallographic sites of Sr, namely Sr1 anions occupy the 4f Wyckoff position at  $z = 0$  and Sr2 anions occupy 6h Wyckoff position at  $z = 1/4$ . The Sr1 and Sr2 atoms are coordinated by six and eight oxygen atoms as the nearest neighbours belonging to the  $\text{PO}_4$  group, respectively. P atoms are connected to oxygen atoms in a tetrahedral arrangements. The atomic coordinates are provided in Table 2.

Fig. 3 shows the FTIR transmission spectra of  $\text{Sr}_5(\text{PO}_4)_3\text{OH}$ ,  $\text{Sr}_5(\text{PO}_4)_3\text{OH}:\text{Er}^{3+}$  ( $\text{Er}^{3+} = 3$  mol%),  $\text{Sr}_5(\text{PO}_4)_3\text{OH}:\text{Yb}^{3+}$  ( $\text{Yb}^{3+} = 7$  mol%) and  $\text{Sr}_5(\text{PO}_4)_3\text{OH}:\text{Er}^{3+},\text{Yb}^{3+}$  ( $\text{Er}^{3+} = 3$  mol% and  $\text{Yb}^{3+} = 7$  mol%) phosphor powders in the wavenumber range of 400–2000  $\text{cm}^{-1}$ . The peak at 592  $\text{cm}^{-1}$  revealing two shoulders is assigned to bending vibrations of O–P–O linkage in the  $\text{HPO}_4^{2-}$  groups indicating the presence of the hydroxyl and phosphate group [13–15]. The little peak

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