

Combustion synthesis and upconversion luminescence properties of Er³⁺, Yb³⁺ doped gadolinium oxide nanophosphor

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Abstract

Gd₂O₃: Er³⁺, Yb³⁺ Nanophosphor prepared by combustion synthesis method. Optical and Upconversion luminescence properties of rare earth doped nanophosphors were studied. The nanophosphors were characterized using Scanning electron microscopy, X-ray diffraction and ultraviolet-visible absorption spectroscopy. The results of XRD show cubic phase can be obtained, the average crystalline size could be calculated as 38 and 49nm respectively, which coincided with the results from SEM images. The UV- Vis optical spectra were also studied. Upconversion luminescence spectra of samples under the range of 980 nm, excitation were investigated. The strong red and weak green emission was observed. The possible upconversion luminescence mechanisms for Er³⁺, Yb³⁺ doped gadolinium nanophosphor were also discussed.

Keywords: Combustion synthesis, luminescence properties, nanophosphor

INTRODUCTION

In recent years, numerous investigations have deal with upconverting phosphor compounds that produce emitted photons with a higher energy than the excitation photon energy via a two-or-more-photon system. Such materials are composed typically of trivalent rare-earth sensitizer (e.g., Yb³⁺, Er³⁺, and Sm³⁺) and activator (e.g., Er³⁺, Ho³⁺, Pr³⁺, and Tm³⁺) ions, acting in a multiphoton process [1]. Gadolinium oxide has been extensively used in many different applications [2-4]

Much work has proved that the local environment of active ions plays an important role in Upconversion luminescent properties of nanoparticles, and the local environment of active ions is associated with synthesis method of nanoparticles. Upconversion (UC) luminescence in these materials mainly originates from the electronic transitions within the 4f shell of the rare earth ions, which is sensitive to the composition and the structure of the host material. It is well established that materials with lower phonon energy are required as the hosts for luminescent ions to minimize nonradiative losses. This is important especially for the Upconversion process, because these are very sensitive to quenching by high energy vibrations according to the energy gap law [5]. The current interest in this field is focused on synthesizing nanophosphor materials using improved techniques and looking for their new applications. Out of various phosphors, Er³⁺/Yb³⁺ doped Gd₂O₃ upconversion (UC) nanophosphors has been found to be highly efficient and has been successfully used in different applications [6-11].

The upconversion materials doped with Er³⁺ ions and sensitized with Yb³⁺ ions have been widely studied. Because not only Er³⁺ ions possesses a favorable metastable energy levels with longer excited states, but also Yb³⁺ ions have a large absorption cross section around 980 nm, and can efficiently transfer the excitation energy to Er³⁺ ions [12].

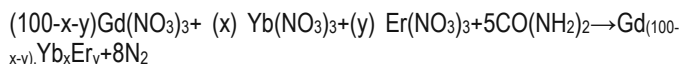
Nanoscale phosphors may have a number of potential advantages over traditional micron-sized phosphors. Such nanosized phosphor particles are reported to be somewhat different in their electrical, optical, and structural characteristics. It is reported that

these differences in electrical and optical characteristics of very small particles are caused by quantum effects due to their high surface to volume ratio, which increases the band gap by reduction of the number of allowable quantum states in the small particles, and improves surface and interfacial effects [13, 14]

In this paper, Gd₂O₃:Er³⁺, Yb³⁺ nanophosphor have been prepared by combustion synthesis in which we use urea as a fuel and reducing agent also and studied Upconversion luminescence excited with the 976 nm wavelength. The structural properties of samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-VIS optical spectra.

EXPERIMENTAL DETAIL

In this study Gadolinium Nitrate (99.99% Sigma Aldrich) Erbium Nitrate (99.99% Sigma Aldrich) and Ytterbium Nitrate (99.99% Sigma Aldrich), Urea were used as starting raw material. To prepare Gd₂O₃: Er³⁺, Yb³⁺, These Gd(NO₃)₃, Er(NO₃)₃ and Yb(NO₃)₃ were mixed according to the stoichiometry equation Given Bellow



According to the above reaction, for (Gd_{0.95}Er_{0.03}Yb_{0.02})₂O₃ we take the suitable amount above material in a beaker and then a suitable amount of urea was added to prepare the precursor solution and kept stirring for 30 min. Finally this sample was transferred to crucible and fired in a furnace then water was evaporated quickly and soon a vigorous redox reaction occurred, the whole process went on for a few seconds at 600°C. Finally Gd₂O₃: Er³⁺, Yb³⁺ nanophosphor with different concentration were obtained.

The morphologies and sizes of the rare earth doped Gd₂O₃ were determined by X-ray diffraction studies with Cu K α radiation ($\lambda=1.5418 \text{ \AA}$). XRD data were collected over the range 20°-80° at room temperature. The X-ray diffraction patterns have been obtained data from X-ray powder diffractometer. The particle size was

determined using the sherrer's formula.

The Shimatzo 1700 UV-VIS spectrometer is used to obtain the optical absorption spectra of Er³⁺, Yb³⁺ Doped Gadolinium Nanophosphor. For Upconversion studies the samples was excited by using of IR light having 950-980 nm Wavelength. All of the measurements were carried out at room temperature.

RESULTS AND DISCUSSION

Structural characterization of Gd₂O₃:Er³⁺,Yb³⁺ :-

XRD analysis

The XRD spcrta of Gd₂O₃:Er³⁺,Yb³⁺ nanophosphors show in fig 1 fired at 600°C. Four different peaks are obtained at 2θ values of 30.04°, 34.12°, 48.20° and 57.56°. and the peaks correspond to diffraction at (211), (222), (400) and (622) planes, respectively and sample are in the cubic structure. All diffraction patterns are in good agreement with JCPDS NO.43-1015 reference, the size of the particles has been computed from the width of first peak using Debye Scherrer formula [15]. The size of particle in the range of 38 to 49 nm.

SEM analysis

Fig.2 shows the SEM images of Gd₂O₃: Er³⁺,Yb³⁺ nanophosphor. The microphotograph of the sample prepared at 600 nm by combustion synthesis shows. According to the observation by SEM, the particle sizes are around 60 nm to 155 nm for samples prepared by combustion methods, respectively. A deviation in the estimated particle sizes by SEM and X-ray diffraction may be approximately same and identical to each other.

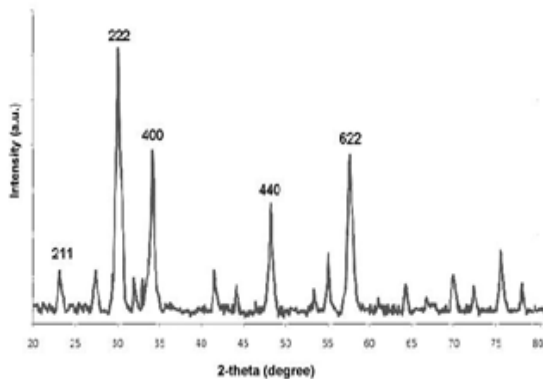


Fig 1. XRD pattern of Gd₂O₃: Er³⁺, Yb³⁺

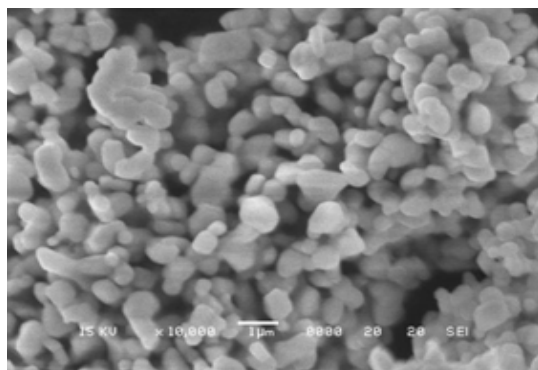


Fig 2. SEM images of Gd₂O₃: Er³⁺, Yb³⁺

nanoparticles

UV-Vis analysis

The absorption spectra of the pure and Er³⁺,Yb³⁺ Gd₂O₃ doped are presented in Fig.3(a), in the range of 200nm -550nm optical absorption edge was obtain at 238 nm for pure Gd₂O₃ and 232 nm Er³⁺,Yb³⁺ doped Gd₂O₃. The band Gap energy of the sample corresponding the absorption edge is found in the range 5.21 eV to 5.35eV.

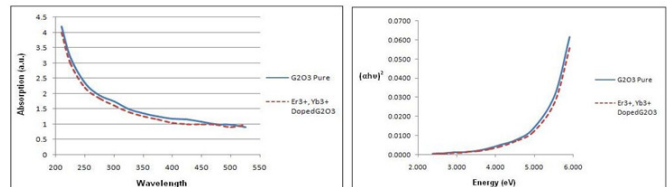


Fig 3(a). Absorption spectra of Gd₂O₃: Er³⁺, Yb³⁺
Fig 3(b). Graph between (ahv)² verses energy of Gd₂O₃: Er³⁺, Yb³⁺

Upconversion emission measurements

The Upconversion emission spectra were recorded in the 300–700 nm wavelength regions with 980 nm excitation. These spectra consist of two groups of upconversion emission peaks around 546-563 nm and 652-683 nm, which are attributed to ²H_{11/2},⁴S_{3/2}→⁴I_{15/2} transition and ⁴F_{9/2}→⁴I_{15/2} transition of Er³⁺ ions[16], respectively. The assignments of upconversion emission bands of Gd₂O₃: Eu³⁺, Yb³⁺ are given in Table 1. It is clear that the red emission was much stronger than that of green emission. We can infer that there are more electrons populated in the ⁴F_{9/2} energy level for samples. The upconversion mechanism in Er³⁺ and Yb³⁺ codoped systems is well known and occurs via a two- photon process of energy from the Yb³⁺ ion to the Er³⁺ ion. A typical energy level diagram for the upconversion emission from Gd₂O₃: Er³⁺,Yb³⁺ ions under 980 nm infrared excitation is shown in Fig.5 [17, 18]. Because the Yb³⁺ ions have a much larger absorption cross section relative to that of Er³⁺ ions around 980 nm, the Er³⁺ ion can be excited from the ground-state ⁴I_{15/2} to the excited—state ⁴I_{11/2} by energy transfer from the excited Yb³⁺ ions,

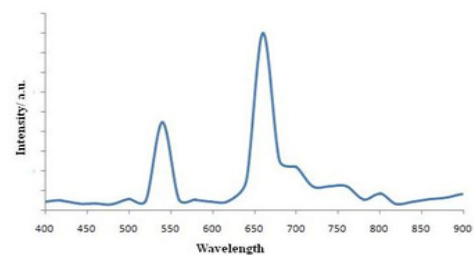


Fig 4(a). Up conversion luminescence spectra

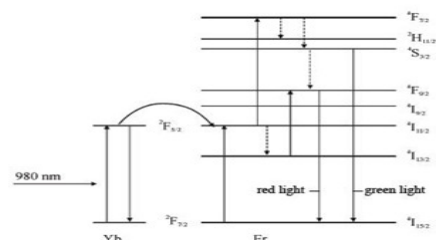
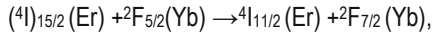


Fig 4(b). Energy level diagram for the upconversion emission under 980 infrared excitation



Which is subsequently excited to the ${}^4F_{7/2}$ state of the Er^{3+} ion by absorbing another Yb^{3+} ion energy, the ${}^4F_{7/2}$ state decays nonradiatively to the ${}^2H_{11/2}$, ${}^4S_{3/2}$ and ${}^4F_{9/2}$ level. The green and red emissions have been observed from the ${}^2H_{11/2}$, ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ and ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions, respectively.

Table 1

Emission assignment	Emission nm	Band range cm^{-1}	Width of emission bands range
${}^4S_{3/2} \rightarrow {}^4I_{15/2}$	546-563 nm	18 315 -17 762	553
${}^4F_{9/2} \rightarrow {}^4I_{15/2}$	652-683 nm	15 337-14 641	696

CONCLUSION

$\text{Er}^{3+}, \text{Yb}^{3+}$ codoped Gd_2O_3 nanophosphor material has been synthesized through combustion method. The XRD patterns show that the samples are cubic structure; the average crystallite size could be calculated as 38 nm and 49 nm, respectively. Upconversion luminescence spectra of samples under the wavelength in the range of 950-980 nm excitations were investigated. The strong red emission of samples were observed, and attributed to ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+} ions.

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