

Sensitization Effect of Yb³⁺ in Upconversion Luminescence of Eu³⁺ Codoped Y₂O₃ Phosphor

Anurag Pandey, Riya Dey and Vineet Kumar Rai*

Laser and Spectroscopy Laboratory, Department of Applied Physics, Indian School of Mines, Dhanbad-826004, Jharkhand, India

Abstract

For structural information, the X-ray diffraction analysis of Y₂O₃:Eu³⁺ phosphors codoped with Yb³⁺ synthesized by combustion synthesis process has been performed. The upconversion emission study of the Y₂O₃:Eu³⁺ phosphor codoped with Yb³⁺ ions on excitation with 980 nm diode laser in the visible region has been done. The upconversion emissions corresponding to the Eu³⁺ ions is due to sensitization from Yb³⁺ ions in developed phosphor, and has been explained on the basis of cooperative energy transfer process. The orange colour emitted from the codoped samples is visualized by CIE diagram. The results show the applicability of the present phosphor as suitable NIR (near infrared) to visible upconverter, and in other photonic devices.

Keywords: Combustion synthesis; Cooperative emission; Photoluminescence; Rare earths

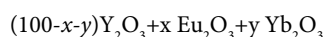
Introduction

The rare earths (RE) doped luminescent materials have been the subject of significant interest in recent years due to their potential applications in different fields [1-4]. In these materials, mainly the rare earth elements are responsible for the generation of radiation of light of different color by changing the dopants, which are useful for various applications [5,6]. Several oxide host materials are available for the preparation of rare earth doped luminescent materials, but the Y₂O₃ is chosen due to their high optical band gap, low phonon frequency and ionic radii comparable with most of the rare earths. Several studies have been reported on synthesis and optical characterisation of nanocrystalline Eu³⁺ doped phosphors [7,8]. But, the upconversion (UC) emission with NIR excitation in singly Eu³⁺ doped materials is not possible. So, in order to get visible UC emission from Eu³⁺ ion, another rare earth ion can be used as sensitizer to excite Eu³⁺ ions. In our previous study, we have excited Eu³⁺ ion by a 980 nm laser using Er³⁺ as sensitizer and studied its UC behavior [9]. In most of the cases, Yb³⁺ ion is taken as the sensitizer because of its higher absorption cross-section corresponding to 980 nm excitation.

In the present work, we have synthesized Y₂O₃:Eu³⁺-Yb³⁺ phosphors through solution combustion synthesis process. The XRD analysis and upconversion emission studies of the synthesized material have been performed, and the process responsible for the UC emissions is discussed in detail.

Experimental Procedure

The Eu³⁺, Yb³⁺ codoped Y₂O₃ Phosphor powders have been prepared by low temperature solution combustion method. The compositions of the compounds used were as follows:



where x=1.0 mol%, y=1.0, 3.0, 5.0 mol%.

Firstly, the Y₂O₃, Eu₂O₃ and Yb₂O₃ were dissolved in HNO₃ to convert in the form of nitrates. The nitrate forms of host and dopants were mixed with urea solution and stirred about 2 hours at 65°C, till transparent gel was obtained. The formed gel was taken in an alumina crucible and placed inside an electrical furnace preheated at 600°C where combustion took place. The obtained samples were grinded to

get fine and homogeneous powder, and then heat treated at higher temperature about 800°C. These heat treated samples have been used for further measurements.

Results and Discussion

X-ray diffraction analysis

The X-ray diffraction pattern of heat treated Eu³⁺, Yb³⁺ codoped Y₂O₃ phosphor has been shown in Figure 1. The observed peaks matches very well with the peaks of JCPDS card no. 25-1200. The results indicated cubic structure of synthesized material with lattice parameters a=b=c=10.60 Å and α=β=γ=90°. The average crystallite size of developed phosphor has been found around 20 nm using well known Scherrer's formula [10].

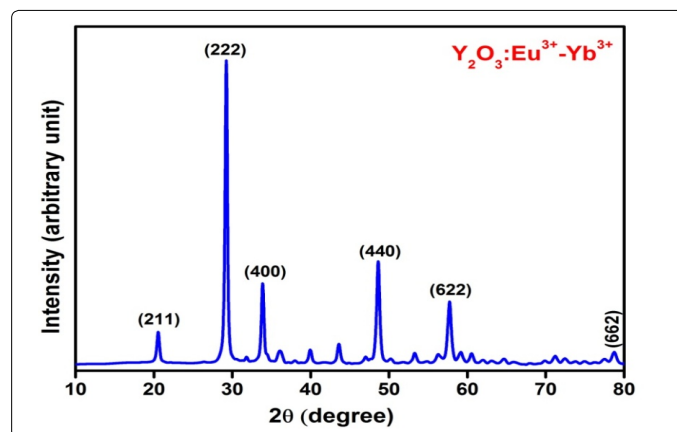


Figure 1: XRD pattern of Eu³⁺, Yb³⁺ codoped Y₂O₃ phosphor.

*Corresponding author: Vineet Kumar Rai, Laser and Spectroscopy Laboratory, Department of Applied Physics, Indian School of Mines, Dhanbad-826004, India, Tel: +91-326-223-5404/5282; E-mail: vineetkrai@yahoo.co.in; rai.vk.ap@ismdhanbad.ac.in

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Upconversion emission study

The UC emission spectra of Eu³⁺, Yb³⁺ codoped Y₂O₃ phosphor upon excitation at 980 nm with fixed Eu³⁺ (1.0 mol%) and varying Yb³⁺ (1.0, 3.0, 5.0 mol%) concentrations have been recorded, and for 1.0 mol% Eu³⁺+3.0 mol% Yb³⁺ combination the maximum UC emission intensity has been observed. In Figure 2, we have shown the UC emission spectra corresponding to the optimized concentration of Eu³⁺ and Yb³⁺ ions. The Eu³⁺ ions cannot be excited directly by using a 980 nm diode laser excitation due to unavailability of energy levels in Eu³⁺ ions. But, in the Eu³⁺, Yb³⁺ codoped system upconversion emission spectrum is observed (Figure 2). This indicates that the Eu³⁺ ions are excited due to presence of the Yb³⁺ ions. The UC emission bands peaking about 526 nm, 550 nm, 586 nm, 611 nm and 658 nm are assigned as ⁵D₁→⁷F₀, ⁵D₁→⁷F₂, ⁵D₀→⁷F_{0,1}, ⁵D₀→⁷F₂ and ⁵D₀→⁷F₃ transitions of Eu³⁺ ion, respectively [11]. The orange colour light emitted from synthesized sample can be seen by naked eyes.

No UC emission bands have been observed in Eu³⁺ doped phosphor, but are found in the Eu³⁺, Yb³⁺ codoped phosphor. This is basically due to sensitization of Eu³⁺ ions by Yb³⁺ ions via cooperative energy transfer process. The contribution of two Yb³⁺ ions have been observed in UC emissions from Eu³⁺, Yb³⁺ codoped materials [11]. A simplified energy level scheme of Eu³⁺ and Yb³⁺ ion is shown in Figure 3.

The Yb³⁺ ions from its ²F_{7/2} ground state are firstly excited to the ²F_{5/2} state, and then transfer their energy cooperatively in such a way that one of them (acceptor) after gaining energy from the another one (donor) occupies the virtual state (V) (i.e. ²F_{5/2}+²F_{5/2}→²F_{5/2}). After that the excited Yb³⁺ ions from its virtual state transfer their excitation energy directly to the ground state Eu³⁺ ions and promoting them to the ⁵D₁ and ⁵D₀ level of Eu³⁺ ions [12]. Then, the relaxations from ⁵D₁ and ⁵D₀ levels gives radiative emissions at ~526 nm, ~550 nm, ~586 nm, ~611 nm and ~658 nm, corresponding to the ⁵D₁→⁷F₀, ⁵D₁→⁷F₂, ⁵D₀→⁷F_{0,1}, ⁵D₀→⁷F₂ and ⁵D₀→⁷F₃ transitions, respectively.

The CIE color coordinates corresponding to 1.0 mol% Eu³⁺-y mol% Yb³⁺ (y=1.0, 3.0, 5.0 mol%) codoped Y₂O₃ phosphors have been calculated as shown in Figure 4. The calculated values of color coordinates are found to be (0.56, 0.41), (0.57, 0.40), (0.58, 0.40), respectively. This does not show any significant variation in color emitted from the phosphor with increasing content of the Yb³⁺ ions, which makes such phosphor materials suitable to use in display devices.

Conclusion

The cubic structured Eu³⁺, Yb³⁺ codoped Y₂O₃ phosphors have been

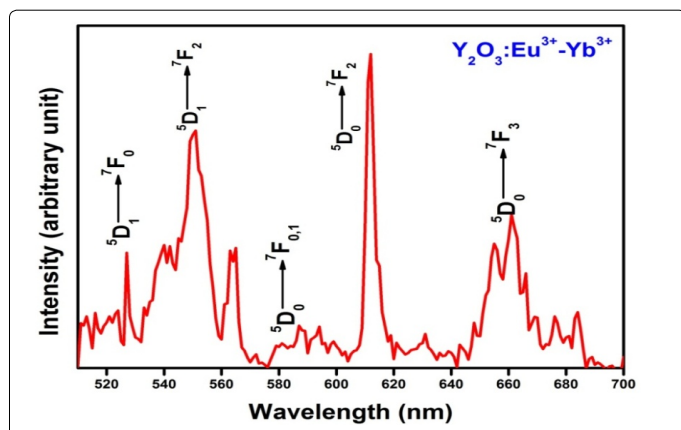


Figure 2: Upconversion emission spectrum of Eu³⁺, Yb³⁺ codoped Y₂O₃ phosphor.

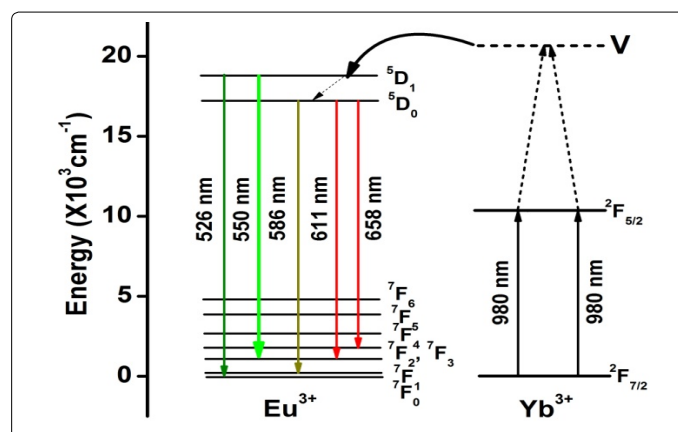


Figure 3: Energy level diagram of Eu³⁺ and Yb³⁺ ions with possible transition schemes.

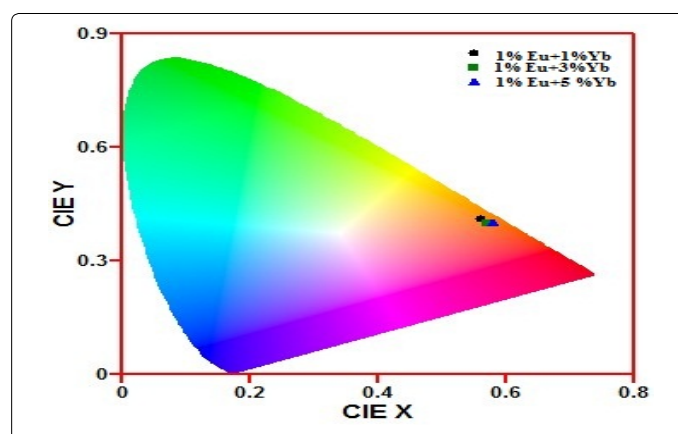


Figure 4: Color coordinates of Eu³⁺-Yb³⁺ codoped Y₂O₃ phosphor.

synthesized via low temperature combustion technique successfully. The average crystallite size ~20 nm has been confirmed with the help of XRD analysis. The study of upconversion emission observed from the synthesized phosphor by 980 nm excitation support the possibility of cooperative energy transfer from Yb³⁺ to Eu³⁺ ions. The color emitted from the developed phosphors is confirmed from CIE diagram. The present study shows utility of the Eu³⁺, Yb³⁺ codoped Y₂O₃ phosphors as NIR to visible upconverter, and its applicability for the development of other photonic devices.

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