Sensitization Effect of Yb$^{3+}$ in Upconversion Luminescence of Eu$^{3+}$ Codoped Y$_2$O$_3$ 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 Y$_2$O$_3$:Eu$^{3+}$ phosphors codoped with Yb$^{3+}$ synthesized by combustion synthesis process has been performed. The upconversion emission study of the Y$_2$O$_3$:Eu$^{3+}$ phosphor codoped with Yb$^{3+}$ ions on excitation with 980 nm diode laser in the visible region has been done. The upconversion emissions corresponding to the Eu$^{3+}$ ions is due to sensitization from Yb$^{3+}$ 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 Y$_2$O$_3$ 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 Eu$^{3+}$ doped phosphors [7,8]. But, the upconversion (UC) emission with NIR excitation in singly Eu$^{3+}$ doped materials is not possible. So, in order to get visible UC emission from Eu$^{3+}$ ion, another rare earth ion can be used as sensitizer to excite Eu$^{3+}$ ions. In our previous study, we have excited Eu$^{3+}$ ion by a 980 nm laser using Er$^{3+}$ as sensitizer and studied its UC behavior [9]. In most of the cases, Yb$^{3+}$ 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 Y$_2$O$_3$: Eu$^{3+}$-Yb$^{3+}$ 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 Eu$^{3+}$, Yb$^{3+}$ codoped Y$_2$O$_3$ Phosphor powders have been prepared by low temperature solution combustion method. The compositions of the compounds used were as follows:

(100-x-y)Y$_2$O$_3$+x Eu$_2$O$_3$+y Yb$_2$O$_3$

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

Firstly, the Y$_2$O$_3$, Eu$_2$O$_3$, and Yb$_2$O$_3$ were dissolved in HNO$_3$ 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 Eu$^{3+}$, Yb$^{3+}$ codoped Y$_2$O$_3$ 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 Eu$^{3+}$, Yb$^{3+}$ codoped Y$_2$O$_3$ phosphor.](image-url)
Upconversion emission study

The UC emission spectra of Eu\(^{3+}\), Yb\(^{3+}\) codoped Y\(_2\)O\(_3\) phosphor upon excitation at 980 nm with fixed Eu\(^{3+}\) (1.0 mol\%) and varying Yb\(^{3+}\) (1.0, 3.0, 5.0 mol\%) concentrations have been recorded, and for 1.0 mol% Eu\(^{3+}\)+3.0 mol% Yb\(^{3+}\) 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 Eu\(^{3+}\) and Yb\(^{3+}\) ions. The Eu\(^{3+}\) ions cannot be excited directly by using a 980 nm diode laser excitation due to unavailability of energy levels in Eu\(^{3+}\) ions. But, in the Eu\(^{3+}\), Yb\(^{3+}\) codoped system upconversion emission spectrum is observed (Figure 2). This indicates that the Eu\(^{3+}\) ions are excited due to presence of the Yb\(^{3+}\) ions. The UC emission bands peaking about 526 nm, 550 nm, 586 nm 611 nm and 658 nm are assigned as \(^7F_0 \rightarrow ^{5}D_1\), \(^7F_1 \rightarrow ^{5}D_1\), \(^7F_0 \rightarrow ^{5}D_2\), \(^7F_0 \rightarrow ^{5}D_2\), and \(^7F_0 \rightarrow ^{5}D_3\) transitions of Eu\(^{3+}\) 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 Eu\(^{3+}\) doped phosphor, but are found in the Eu\(^{3+}\), Yb\(^{3+}\) codoped phosphor. This is basically due to sensitization of Eu\(^{3+}\) ions by Yb\(^{3+}\) ions via cooperative energy transfer process. The contribution of two Yb\(^{3+}\) ions have been observed in UC emissions from Eu\(^{3+}\), Yb\(^{3+}\) codoped materials [11]. A simplified energy level scheme of Eu\(^{3+}\) and Yb\(^{3+}\) ion is shown in Figure 3. The Yb\(^{3+}\) 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. \(^2F_{5/2} \rightarrow ^2F_{5/2} \rightarrow ^2F_{7/2}\)). After that the excited Yb\(^{3+}\) ions from its virtual state transfer their excitation energy directly to the ground state Eu\(^{3+}\) ions and promoting them to the \(^7D_1\) and \(^7D_0\) level of Eu\(^{3+}\) ions [12]. Then, the relaxations from \(^7D_1\) and \(^7D_0\) levels gives radiative emissions at ~526 nm, ~550 nm, ~586 nm, ~611 nm and ~658 nm, corresponding to the \(^7D_1 \rightarrow ^{5}D_0\), \(^7D_1 \rightarrow ^{5}D_1\), \(^7D_0 \rightarrow ^{5}F_{5/2}\), \(^7D_0 \rightarrow ^{5}F_{2}\), and \(^7D_0 \rightarrow ^{5}F_{3}\) transitions, respectively.

The CIE color coordinates corresponding to 1.0 mol\% Eu\(^{3+}\)-y mol\% Yb\(^{3+}\) (y=1.0, 3.0, 5.0 mol\%) codoped Y\(_2\)O\(_3\) 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 Yb\(^{3+}\) ions, which makes such phosphor materials suitable to use in display devices.

Conclusion

The cubic structured Eu\(^{3+}\), Yb\(^{3+}\) codoped Y\(_2\)O\(_3\) phosphors have been 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 Yb\(^{3+}\) to Eu\(^{3+}\) ions. The color emitted from the developed phosphors is confirmed from CIE diagram. The present study shows utility of the Eu\(^{3+}\), Yb\(^{3+}\) codoped Y\(_2\)O\(_3\) phosphors as NIR to visible upconverter, and its applicability for the development of other photonic devices.

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