

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Influence of Li⁺ codoping on visible emission of Y₂O₃:Tb³⁺, Yb³⁺ phosphor



SPECTROCHIMICA ACTA

Anurag Pandey, Vineet Kumar Rai*, Kaushal Kumar

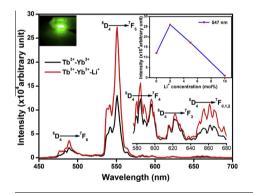
Laser and Spectroscopy Laboratory, Department of Applied Physics, Indian School of Mines, Dhanbad 826004, Jharkhand, India

HIGHLIGHTS

- Y₂O₃:Tb³⁺, Yb³⁺, Li⁺ phosphor has been prepared through combustion process.
- Up/down conversion emission has been investigated using 980 nm/ 303 nm excitation.
- Codoping of lithium enhances the emission intensity throughout the visible region.
- The purity of intense green emission is verified by chromaticity diagram.

G R A P H I C A L A B S T R A C T

Comparison of the upconversion emission spectra of 0.1 mol% Tb^{3+} + 3.0 mol% Yb^{3+} and 0.1 mol% Tb^{3+} + 3.0 mol% Yb^{3+} + 2.0 mol% Li^+ codoped Y_2O_3 phosphors.



ARTICLE INFO

Article history: Received 11 January 2013 Received in revised form 21 March 2013 Accepted 26 August 2013 Available online 2 September 2013

Keywords: Upconversion phosphor Combustion synthesis Cooperative transfer Terbium CIE coordinates

Introduction

ABSTRACT

Upon 980 nm diode laser excitation visible upconversion emission from the Tb^{3+} ions has been observed in combustion synthesized $Tb^{3+}-Yb^{3+}$ codoped Y_2O_3 phosphor. The intensity of upconversion as well as downconversion emission bands has been increased by codoping of Li⁺ ions into $Tb^{3+}-Yb^{3+}:Y_2O_3$ phosphor and the reason behind this increment is discussed. The pump power dependence of upconversion emission bands has shown two-photon absorption process. The cooperative energy transfer from Yb^{3+} to Tb^{3+} ions is supposed to be responsible for the upconversion emission from the Tb^{3+} ions on near infrared excitation. The calculated colour coordinates indicate the purity of intense green emission from present phosphor which is suitable for various photonic applications.

© 2013 Elsevier B.V. All rights reserved.

The research on inorganic luminescence materials having high efficiency, good thermal and chemical stability has revealed wide interests from last few decades. The emission from rare earth ions doped luminescent materials in the optical region of electromagnetic spectrum has been observed through upconversion (UC) and downconversion (DC) processes. Upconversion phosphors have a number of properties that make them striking for photonics applications such as display devices, lighting purposes, solar cells, biological applications, temperature and radiation sensors etc. [1–6]. The visible light emission from the upconverting phosphor materials has some additional advantages in the sense that the component of its every colour is useful for eye vision. Luminescence from triply ionized lanthanides are mainly ascribed to their intra 4f or 5d–4f transitions, characterized by narrow emission lines with high colour purity that suits for present interest. The emission efficiency of lanthanides in solid host material has been achieved near to the theoretical limits, so there seems a possibility for further improvement in emission efficiency of these materials. Search for

^{*} Corresponding author. Tel.: +91 326 223 5404/5282.

E-mail addresses: vineetkrrai@yahoo.co.in, rai.vk.ap@ismdhanbad.ac.in (V.K. Rai).

^{1386-1425/\$ -} see front matter \odot 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.saa.2013.08.109

the relatively high efficient upconverting lanthanide doped luminescent materials under inexpensive 980 nm near infrared (NIR) diode laser excitation is continued till now.

The selection of suitable hosts and dopants mainly depends on their crystal structure, ionic radii, emissive efficiency, thermal conductivity, refractive index, phonon frequency, etc. Numerous oxide and non-oxide hosts have been used by the researchers but some unique features of oxide hosts make them more practical. Among the oxide hosts, Y₂O₃ is very popular due to its versatile features such as high band gap, low phonon frequency, wide transmission region and matching of ionic radii with many rare earth ions [6,7].

Several rare earths and non-rare earths have been doped in various host materials for getting efficient blue, green and red UC emissions [8–13]. Terbium is an interesting rare earth because of its efficient green emission under visible and UV light excitations [7,14–16]. Due to its typical energy level structure the terbium ion cannot be directly excited by 980 nm wavelength radiation, so codoping of another rare earth is necessary to obtain the upconversion emission from terbium ion. Yb³⁺ is an ideal sensitizer for this purpose due to its strong ${}^{2}F_{5/2} \leftarrow {}^{2}F_{7/2}$ absorption transition around 980 nm. The sensitization of Tb³⁺ by Yb³⁺ ions can be expressed in terms of dipole–dipole interactions [17]. The Tb³⁺–Yb³⁺ codoped glasses have been investigated vastly [18–22] but the reports on Tb³⁺–Yb³⁺ codoped phosphors are rare [23]. Yang et al. [23] reported cooperative energy transfer and frequency UC in the Tb³⁺–Yb³⁺ and Nd³⁺–Tb³⁺–Yb³⁺ codoped GdAl₃(BO₃)₄ phosphor upon 980 and 808 nm excitations.

 $Tb^{3+}-Yb^{3+}$ codoped Y_2O_3 down conversion phosphor has also been investigated earlier [24]. Yuan et al. [24] reported energy transfer mechanism upon excitation at ${\sim}483$ nm in the $Tb^{3+}-Yb^{3+}$ codoped Y_2O_3 phosphor. They found that the excited Tb^{3+} ions in the 4f-5d state relax down nonradiatively to the 5D_4 level and transfer its excitation energy cooperatively to two Yb^{3+} ions i.e. Tb^{3+} (5D_4) \rightarrow $2Yb^{3+}$ (${}^2F_{5/2}$) and can be used in silicon solar cell panels to reduce thermalization loss. But here we desire to study the optical properties of $Tb^{3+}-Yb^{3+}$ codoped Y_2O_3 phosphor upon NIR excitation at 980 nm. It is reported that codoping of Li⁺ ions in very small quantity play an important role in enhancement of luminescence intensity [25,26]. So, we have tried to observe the effect of Li⁺ codoping on visible UC and DC emissions of $Tb^{3+}-Yb^{3+}$ codoped Y_2O_3 phosphor.

In the present work we have synthesised the $Tb^{3+}-Yb^{3+}$ and $Tb^{3+}-Yb^{3+}-Li^+$ codoped Y_2O_3 phosphors through solution combustion process. The phase and crystallite size of synthesized phosphors has been determined with the help of X-ray diffraction (XRD) measurement. The presence of impurities in developed phosphor has been detected from the Fourier transform infrared (FTIR) spectroscopy. The UC and DC emission studies upon 980 nm and 303 nm excitations have been performed and explained. The effect of Li⁺ codoping and subsequent enhancement of visible emission is also discussed. The purity of intense green emission observed from sample has been visualised by CIE coordinates on increasing pump power densities.

Experimental

Sample preparation

 $Tb^{3+}-Yb^{3+}$ and $Tb^{3+}-Yb^{3+}-Li^+$ codoped Y_2O_3 phosphor powders have been prepared by mixing the starting materials, namely Y_2O_3 , Tb_2O_3 , Yb_2O_3 and Li_2CO_3 through solution combustion method using urea as the organic fuel. The composition of phosphor samples were

$$(100 - x - y)Y_2O_3 + xTb_2O_3 + yYb_2O_3$$
(i)

where *x* = 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 mol% and *y* = 1.0, 3.0, 5.0 mol% and

$$(100 - x - y - z)Y_2O_3 + xTb_2O_3 + yYb_2O_3 + zLi_2CO_3$$
 (ii)

where *x* = 0.1 mol%, *y* = 3.0 mol% and *z* = 0.0, 2.0, 5.0, 10.0 mol%.

The desired amount of starting materials was dissolved in nitric acid (HNO₃) to obtain the transparent nitrate solutions of the mentioned raw materials. All the transparent solutions were mixed together and then urea was added to the solution as a reducing agent. Now the solution was heated at 80 °C and stirred simultaneously to form the transparent gel. The transparent gel was placed in a crucible and rapidly heated in an electric furnace preheated to 650 °C. After few minutes, the solution becomes foamed and the flame was produced which lasted in 2–3 min. The crucible was immediately removed from the furnace. The resultant fluffy mass was taken out and crushed into fine powder using pestle and mortar. The formed phosphor powders were given heat treatment at 800 °C for 2 h. The obtained fine phosphor powders were used for further characterization purposes.

Characterization

The X-ray diffraction pattern of synthesized phosphors have been recorded by an X-ray powder diffractometer using Cu K α_1 radiation ($\lambda = 0.154$ nm). The Fourier transform infrared (FTIR) spectra of the samples were recorded in 500–4000 cm⁻¹ range. The room temperature UC emission spectra were recorded using a Princeton triple grating monochromator (Acton SP-2300) attached with a photomultiplier tube (PMT). The photoluminescence studies were carried out using Fluorescence Spectrophotometer within the 450–750 nm wavelength range. The samples were pumped by a diode (CW) laser operating at 980 nm with beam spot size 1.4 mm and all the measurements have been performed at room temperature.

Results and discussion

X-ray diffraction analysis

To investigate phase composition, crystallization and the crystallite size of the synthesized material, the X-ray diffraction (XRD) patterns of 0.1 mol% $Tb^{3+} + 3.0 \text{ mol}\% Yb^{3+}$ and 0.1 mol% $Tb^{3+} + 3.0 \text{ mol}\% Yb^{3+} + 2.0 \text{ mol}\% Li^+$ codoped Y_2O_3 phosphors were recorded (shown in Fig. 1). From Fig. 1 no extra peak in Li⁺ codoped sample has been observed which assured that the Li⁺ ions replace Y^{3+} ions and occupy the sites of the lattice.

The diffraction peaks observed at $2\theta = 29.49^{\circ}$ is the strongest one corresponding to the plane (222). The other main diffraction peaks were observed at 20.93°, 34.14°, 48.92°, 57.89° and 79.09°

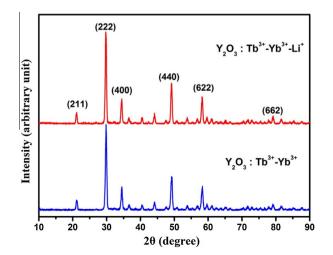


Fig. 1. XRD pattern of Tb³⁺-Yb³⁺ and Tb³⁺-Yb³⁺-Li⁺ codoped Y₂O₃ phosphors.

Download English Version:

https://daneshyari.com/en/article/7673253

Download Persian Version:

https://daneshyari.com/article/7673253

Daneshyari.com