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Visible upconversion in Er^{3+}/Yb^{3+} co-doped $LaAlO_3$ phosphors

Vijay Singh [a,*], V.K. Rai [b], N. Singh [a], M.S. Pathak [a], M. Rathaiah [c], V. Venkatramu [c], Rahul V. Patel [d], Pramod K. Singh [e], S.J. Dhoble [f]

[a] Department of Chemical Engineering, Konkuk University, Seoul 143 701, Republic of Korea
[b] Department of Applied Physics, Indian School of Mines, Dhanbad, 826 004, Jharkhand, India
[c] Department of Physics, Yogi Vemana University, Kadapa 516 003, India
[d] Department of Food Science and Biotechnology, Dongguk University-Seoul, Ilsandong-gu, Goyang-si, Gyeonggi-do, 410 820, Republic of Korea
[e] Materials Research Laboratory, Sharda University, Greater Noida 201 310, India
[f] Department of Physics, RTM Nagpur University, Nagpur 440 033, India

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ABSTRACT

The Er^{3+} doped and Er^{3+}/Yb^{3+} co-doped $LaAlO_3$ phosphors have been synthesized by the combustion method and characterized their structural, morphological, elemental, vibrational and optical properties. The optical absorption and upconversion properties of the synthesized phosphors have been studied. Upon co-doping Yb^{3+} ions into Er^{3+}:$LaAlO_3$, the blue, green and red upconversion emissions of Er^{3+} ions have been enhanced about ~20, ~54 and ~22 times, under 978 nm laser excitation. The observed upconversion emissions could be due to excited state absorption in Er^{3+}:$LaAlO_3$, whereas energy transfer is dominant mechanism in Er^{3+}/Yb^{3+}:$LaAlO_3$ phosphors. The tuning in the color emitted from the synthesized phosphors towards the green region has been found due to incorporation of the Yb^{3+} ions. With increase in the pump power, the color emitted from the co-doped phosphor is not tuned significantly, showing its applicability in making the green display devices.

1. Introduction

Trivalent lanthanide (Ln^{3+}) doped inorganic materials have attracted great attention due to their potential applications in optical devices such as optical fiber amplifiers, light converters, sensors, solid state lasers, and displays [1–4]. Among different families of Ln^{3+}-doped crystalline materials, oxide crystals are of great interest due to their unique optical properties, such as long fluorescent lifetime, large Stokes shift, their high chemical durability and thermal stability [5]. In particular, perovskite type oxides of general formula ABO_3 (the size of A cation is larger than B) is interesting to study. Lanthanum aluminate ($LaAlO_3$) with a perovskite-type structure is important one for many applications such as substrates for superconductors, magnetic and ferromagnetic thin films, and luminescent host materials [6,7]. This is basically due to its special properties such as good thermal stability with high melting point (2180 °C) which can minimize the interfacial dislocations [8], good dielectric properties, high relative permittivity ($\epsilon_r = 23$), high quality factor (6800) and very small temperature coefficient of resonant frequency (−44 ppm/K) [9]. For instance, the $LaAlO_3$ is considered as a typical dielectric material with band gap energy ~5–6 eV [10], can be used as a host material for full-color phosphor applications [11].

Near-infrared (NIR) to visible light conversion in Ln^{3+} ion doped materials has great importance not only to understand the mechanisms of interaction between the Ln^{3+} ions in different hosts but also for their application in upconversion lasers, bio-labels, and bio-assays [12,13]. Among Ln^{3+} ions, the Er^{3+} is a promising ion for upconversion applications since it provides ladder type intermediate levels with long lifetimes, which are easily populated with low cost diode lasers. There has been a growing interest in upconverting phosphor compounds, which emit visible radiation when excited with infrared light. In fact, upconversion lasing emissions in infrared and visible range have been achieved in several Er^{3+} doped phosphor materials [14,15].

In recent years, $LaAlO_3$ material has been well synthesized and characterized [7,16–20]. Liu et al. [7,16] reported the synthesis of Ln^{3+} doped $LaAlO_3$ (Ln^{3+} = Sm, Tb and Tm) powders using a pechini-type sol-gel process and investigated their photoluminescence and cathodoluminescence properties. Mao et al. [17] proposed $LaAlO_3$:Eu full color phosphor which could be great potential for application to white light-emitting devices. Thermally stimulated luminescence and electron spin resonance investigation on gamma irradiated $LaAlO_3$:Eu^{3+} phosphor was reported by Singh et al. [18]. Fu and Liu [19] investigated photoluminescence and X-ray luminescence properties of the $LaAlO_3$:Eu^{3+} nanophosphors. Dong et al. [20] synthesized Eu^{3+} doped $LaAlO_3$ phosphors through sol-gel process and investigated luminescent properties. Our literature survey shows as of now limited information is available on Ln^{3+} doped $LaAlO_3$ phosphors and in particular, no investigations on Er^{3+} doped and Er^{3+}/Yb^{3+} co-doped $LaAlO_3$ phosphors.

* Corresponding author.
E-mail address: vijayjiin2006@yahoo.com (V. Singh).

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Hence, there is need to explore the infrared to visible energy conversion in Er^{3+} doped and Er^{3+}/Yb^{3+} co-doped $LaAlO_3$ phosphors.

The Er^{3+} doped and Er^{3+}/Yb^{3+} co-doped $LaAlO_3$ phosphors were prepared by combustion route. The advantages of this synthesis method are possibility to prepare complex composition, good homogeneity through mixing at the molecular level, safe, fast and required low temperature. In recent years, authors have shown that, by combustion synthesis, variety of complex oxides could be synthesized relatively at low temperatures [21,22]. A similar method was employed to produce Er^{3+}:$LaAlO_3$, co-doped with Yb^{3+} phosphor powders, in which urea has been employed as a fuel. The synthesized samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive analysis of X-ray (EDX), FTIR spectroscopic techniques for their structural, morphological and vibrational properties. The optical and upconversion properties have been studied by using diffuse reflectance and emission spectroscopy.

2. Experimental

$LaAlO_3$:$Er_{(0.03)}$ and $LaAlO_3$:$Er_{(0.03)}$,$Yb_{(0.05)}$ were prepared by the combustion of $La(NO_3)_3 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Er(NO_3)_3 \cdot 5H_2O$, $Yb(NO_3)_3 \cdot 5H_2O$ and urea (NH_2CONH_2) as precursor materials. The optimal oxidizer:fuel ratio where the fuel and nitrates react completely was determined to be the stoichiometric composition. To perform the combustion reaction the appropriate materials were placed in a glass beaker of 100 ml capacity and mixed with de-ionized water. The resulting solution was allowed to react at 80 °C for 20 min. to obtain a homogenous solution. Then the solution was introduced into a muffle furnace preheated to 550 °C. After the reaction (which lasts about 5 min), the materials were crushed with a mortar and pestle and placed in 50 ml alumina crucibles to be heat-treated to 900 °C for 4 h. The resulting powder was used for further characterization.

X-ray diffraction data were recorded on an X'Pert Pro Diffractometer (Panalytical) using CuKα_1 radiation ($\lambda = 1.5406$ Å) in the 2θ range of 10° to 80°. Morphology was determined using a scanning electron microscope (SEM, Hitachi S-3200N, Japan). Their chemical compositions were analyzed using the energy dispersive X-ray (EDX) attached to the SEM. FT-IR spectra were taken using a Perkin-Elmer RX1 instrument in the range from 4000 to 400 cm^{-1}. The UV–Vis absorption spectra of the samples were measured in diffuse reflectance mode using a Cary 6000i UV–Vis-NIR spectrophotometer equipped with an integrating sphere. The upconversion emission spectra of powder samples were measured with a Fluorolog 3–22 spectrometer (Jobin Yvon) combined with a continuous wave 978 nm laser diode (LYPE 30-SGWL978-F400). The powder samples inside the spectrometer were excited at 978 nm laser via an optical fiber. All the measurements were carried out at room temperature.

3. Results and Discussion

3.1. Powder X-ray Diffraction: Structural Studies

The structure and phase purity of combustion derived Er^{3+}:$LaAlO_3$ and Er^{3+}/Yb^{3+}:$LaAlO_3$ phosphors are studied by XRD. The measured XRD pattern of (a) Er^{3+}:$LaAlO_3$ and (b) Er^{3+}/Yb^{3+}: $LaAlO_3$ phosphors are shown in Fig. 1. The perovskite structure with the crystalline planes of (012), (110), (202), (024), (122), (300), (220) and (312) are matched with that of pure $LaAlO_3$ (JCPDS no. 082-0478). It was observed that $LaAlO_3$ has a pure rhombohedral phase having centro-symmetric space group R-3c (No. 167) with perovskite structure. As the ionic radii of Er^{3+} (~88 pm) and Yb^{3+} (~85 pm) ions are similar to the ionic radii of La^{3+} ions (~103 pm). The Er^{3+}/Yb^{3+} ions occupy the La^{3+} ion crystallographic site with D_3 point symmetry [19]. There is no additional signature in the XRD pattern of the synthesized $LaAlO_3$ phosphors {Fig. 1 (a) & (b)} which imply that the dopants were incorporated into the structure of $LaAlO_3$ and its single phase formation. The

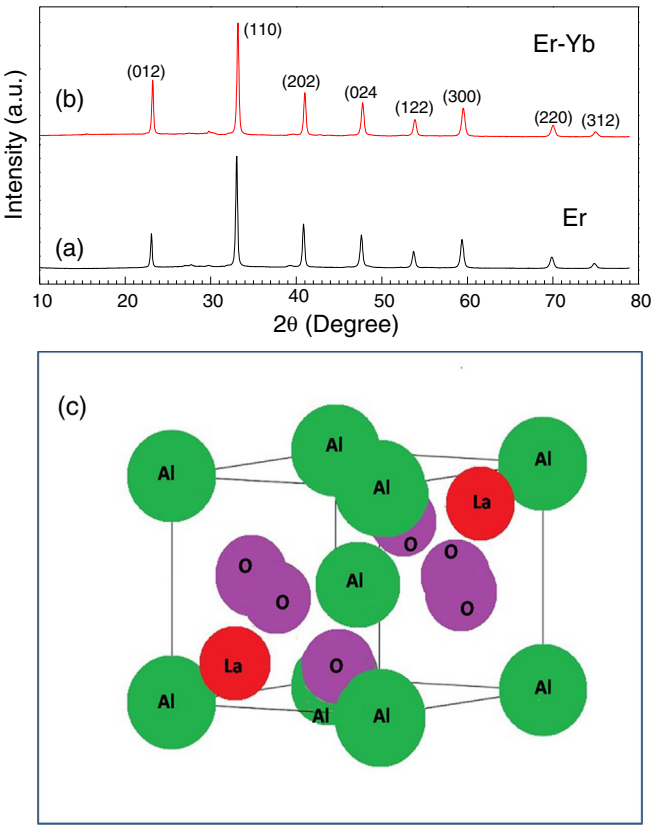

Fig. 1. Powder XRD pattern of (a) Er^{3+}:$LaAlO_3$ (b) Er^{3+}/Yb^{3+}:$LaAlO_3$ phosphors and (c) The crystal structure of $LaAlO_3$ unit cell.

crystal structure of $LaAlO_3$ unit cell is given in Fig. 1(c). The XRD analysis indicates that the dopants do not participate in overall crystal formation except replacing/sitting between few atoms.

3.2. SEM: Morphological and Elemental Analysis

The morphology and elemental analysis of Er^{3+}:$LaAlO_3$ and Er^{3+}/Yb^{3+}:$LaAlO_3$ phosphors have been studied by SEM using backscattered electron detection mode. The black and white SEM micrograph of the Er^{3+}-doped $LaAlO_3$ [Fig. 2(a)] and Er^{3+}/Yb^{3+}:$LaAlO_3$ [Fig. 2(b)] powders shows that crystallites with no uniform shapes and sizes of the order of microns. This non-uniformity of shape and size can be assigned to the non-uniform distribution of temperature and mass flow in the combustion process. For EDX analysis, entire area of the black and white SEM micrographs was analyzed with EDX mapping. The EDX mapping measurements were carried out for Er^{3+}-doped and Er^{3+}/Yb^{3+} co-doped $LaAlO_3$ phosphors to analyze the composition of the clustered particles. EDX elemental mappings (colored images) show the uniform distribution of constituent elements, which indicates a homogeneous distribution of each element in the powders and dopant ions are well dispersed even at the atomic level. Fig. 3(a) and (b) shows the EDX spectra of Er^{3+} doped $LaAlO_3$ and Er^{3+}/Yb^{3+} co-doped $LaAlO_3$ phosphors, respectively. The EDX spectrum demonstrates the presence of La, Al, O, Er and Yb elements in Er^{3+} doped and Er^{3+}/Yb^{3+} co-doped $LaAlO_3$ phosphors.

3.3. FTIR Spectrum: Vibrational Properties

The optical and luminescence properties of optically active Er^{3+} and Yb^{3+} ions depend upon vibrational energies of the $LaAlO_3$ crystallites. These vibrational energies play vital role in de-excitations of optically active ions through multiphonon relaxation. To study the energy of the vibrational modes of $LaAlO_3$, FTIR spectra have been recorded for