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Color tuning of $Y_3Al_5O_{12}$:Ce phosphor and their blend for white LEDs

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Abstract

Gadolinium or lanthanum co-doped (0.5 mole) yttrium aluminum garnet doped with cerium phosphors were synthesized by a citric acid gel method and the effect of co-dopants on the structural and luminescent properties were studied. A significant peak shift in the photoluminescence spectra of yttrium aluminum garnet doped cerium was observed from 535 to 556 and 576 nm for gadolinium or lanthanum co-doped phosphors, respectively. The color tuned phosphor were blended with yttrium aluminum garnet doped cerium which showed a considerable improvement in the Commission International De Eclairage chromaticity co-ordinate values of gallium nitride based blue light emitting diode pumped white light. White light emitted from yttrium aluminum garnet doped cerium shows a Commission International De Eclairage value of (0.229, 0.182) whereas the yttrium aluminum garnet doped cerium phosphor blended with gadolinium or lanthanum co-doped phosphor shows (0.262, 0.243) and (0.295, 0.282), respectively. These results demonstrate the possibility to use these phosphor blends to enhance the white light generation in the field of white-light emitting diode solid-state lighting.

Keyword : B. Luminescence

1. Introduction

Major developments in wide band gap III–V nitride compound semiconductors have lead to the commercial production of highly efficient light emitting diodes (LEDs) [1–3]. Tuning of LED monochromatic emission to various colors including realization of white light is possible by using phosphors which emit blue, green, yellow and red wavelengths simultaneously. Currently, lot of yellow color phosphors have been developed based on yttrium aluminum garnet doped Cerium ($Y_3Al_5O_{12}$:Ce), Sr_2SiO_4:Eu, Sr_3SiO_4:Eu, Ca-α-SiAlON:Eu [4–7]. These phosphors are used for the conversion of blue emission from blue LEDs into white light emitting LEDs. It is well established that Ce doped $Y_3Al_5O_{12}$, denoted as YAG:Ce, has been found to be an efficient phosphor material, because the 4f–5d transition of the Ce^{3+} ion shows a maximum absorbance in the blue region thus converting GaN based blue LED radiation into a very broad intense yellow emission band. White light is then a result of the combination of this yellow emission with the non-absorbed blue emission from the blue LED [8–12]. However, there is a lack of emission toward

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the red region which directly suppresses the color rendering index (CRI) of blue LED conversion of YAG:Ce emission for white light generation. If some how YAG:Ce emission could be made to cover the red wavelength region also, it is possible to improve the color rendering index (CRI) of white light emission [9]. In this aspect, studies have been carried out to substitute larger dopant ions, viz. (Gd^{3+}i.r. = 0.938 Å or La^{3+}i.r. = 1.032 Å) at the Y^{3+} site and Ga^{3+} (0.620 Å) at the Al^{3+} (0.535 Å) site, respectively to achieve red and blue shift in the emission spectra of YAG:Ce [10,13]. These larger ions, when substituted at the Y^{3+} site bring about changes in the electronic band structure due to crystal field modifications which in turn affect the Ce emission characteristics. Moreover, such higher ionic size ions when substituted drastically reduce the emission efficiency [11]. We have in this paper reported the Gd and La (0.5 mole) co-doped YAG:Ce phosphor prepared by citric acid gel method. We show that if this material was blended with YAG:Ce an improvement in CIE chromaticity co-ordinate value is seen without much compromise in the emission intensity.

2. Experimental

To prepare phase pure YAG:Ce and Gd or La co-doped YAG:Ce phosphor at low temperature with a homogenous mixing of atomic elements at molecular level, we have adopted a citric acid gel method. Appropriate amounts of the corresponding metal nitrates with the required amount of citric acid were dissolved in water. The solution was continuously stirred for several hours at 80 °C to form a transparent gel. The beaker containing the gel was heated at 400 °C until a yellowish fluffy precursor was formed. Then the precursor was heated at 800 °C for 4 h and finally heated at 1100 °C for 6 h in a reducing atmosphere. X-ray diffraction studies were carried out using Seifert XRD 3000P powder diffractometer with Cu Kα radiation. The elemental composition analyses were carried out using energy dispersive X-ray (EDX) analysis probe attached to a scanning electron microscope (SEM) instrument (Philips). Excitation and emission spectra were obtained using a Fluorolog (USA), fluorescence spectrophotometer with a 450 W Xe lamp as the excitation source. The emission spectra of the phosphors with a blue LED excitation (456 nm) and their corresponding (CIE) chromaticity color co-ordinates were measured using an Ocean Optics USB2000 optical fiber based fluorescence spectrophotometer. All the measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows the X-ray powder diffraction pattern of YAG:Ce phosphor in which Y is replaced either by Gd or La (0.5 mole). The amount of Ce was taken as 0.05 mole and its oxidation state is +3. The patterns are indexed based on

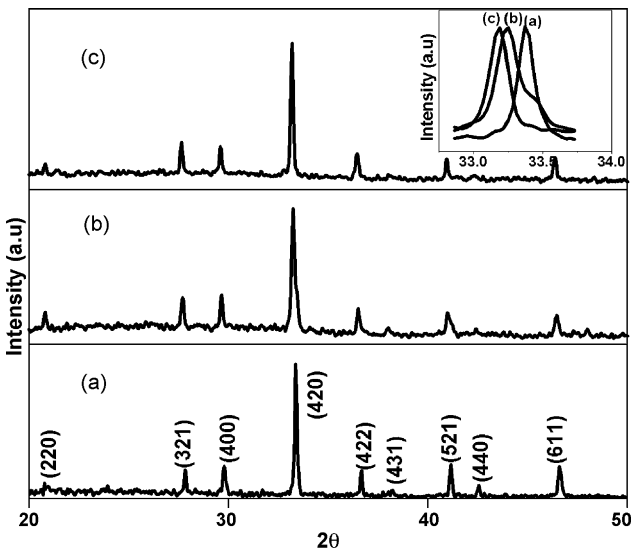

Fig. 1. Powder X-ray diffraction patterns of (a) YAG:Ce, (b) YAG:Ce (Gd 0.5 mole), (c) YAG:Ce (La 0.5 mole) phosphor. Inset shows shift in (4 2 0) plane towards lower 2θ angle.