Enhanced red luminescence quantum yield from Gd\(^{3+}\)/Eu\(^{3+}\) : CaLa\(_2\)ZnO\(_5\) phosphor spheres for photonic applications

K. Naveen Kumar\(^a\), L. Vijayalakshmi\(^b\), Jong Su Kim\(^b\)

\(^a\) Clean Energy Priority Research Center, Yeungnam University, Gyeongsan, Gyeongbuk 38541, Republic of Korea
\(^b\) Semiconductor Nanodevice Research Lab. (SNRL), Department of Physics, College of Science, Yeungnam University, Gyeongsan, Gyeongbuk 38541, Republic of Korea

**Abstract**

Novel bright red emission was obtained from co-doped Gd\(^{3+}\)/Eu\(^{3+}\) : CaLa\(_2\)ZnO\(_5\) (CLZO) phosphor spheres. We have successfully synthesized co-doped Gd\(^{3+}\)/Eu\(^{3+}\) : CLZO phosphor spheres by citrate sol-gel method. Structural and morphological analysis was carried out by XRD and FE-SEM. EDX and XPS studies were employed to analyze the presence of elements and their ionic states respectively. The complex formation studies were carried out by the FTIR spectral study. The photoluminescence spectral profiles confirm the dazzling red emission has been observed at 626 nm (\(\text{5D}_0 \rightarrow \text{7F}_2\)) from the Eu\(^{3+}\) : CLZO phosphors under the excitation of 467 nm. Upon increasing the Eu\(^{3+}\) concentration, the photoluminescence performance has also increased remarkably. The optimized concentration of the Eu\(^{3+}\) was noticed at 12 mol%. Upon co-doping with Gd\(^{3+}\) ions to Eu\(^{3+}\) : CLZO phosphors, the red emission pertaining to Eu\(^{3+}\) was appreciably enhanced through energy transfer from Gd\(^{3+}\) to Eu\(^{3+}\) ions. The energy transfer mechanism was substantiated by several fluorescent methods such as lifetime decay dynamics and quantum efficiencies. Commission International de l’Eclairage (CIE) 1931 chromaticity coordinates (x-y) calculated for singly doped and co-doped CLZO samples. The CIE coordinates were found to be (0.6644, 0.3355) and (0.6688, 0.3311) respectively, which were good consistent with the standard values of NTSC surprisingly. Correlated color temperature (CCT) value was evaluated for optimised co-doped sample and it was found to be between 2000-5000 K which could be more preferable red component for warm white light applications. The lifetime and quantum efficiency of the optimized co-doped sample have been evaluated as 1.102 ms and 69% respectively. The ravishing red emission of the Gd\(^{3+}\)/Eu\(^{3+}\) : CLZO phosphor spheres which suggests that these phosphor materials could be promising candidates for red luminescent optical devices.

**Keywords:** Phosphor, Red emission, Energy transfer

1. Introduction

Rare earths contained complexes have been an attractive material for past few decades because of their large stokes shifts, greater luminescence efficiency and prominent photophysical properties. These materials are most preferable for high performance luminescence devices, biological fluorescence labes, display devices, targeted drug delivery along with multimodal imaging capability and sensor applications [1]. With respect to ever increasing energy demands and the environmental concerns, it is imperative for the development of high efficiency light sources for reducing the energy consumption and environmental pollution. In view of reducing the global power consumption in day to day life, W-LED technology has become an interesting way of research over traditional fluorescent lighting sources because of their potential features such as low power consumption, high efficiency and long lifetime. W-LEDs which are considered as a modern generation of photonic systems, can conquer the aforementioned shortcomings because of their advantages such as environmental friendliness, low power consumption, high efficiency and long lifetime. However, W-LED technology has some shortcomings such as a poor color rendering index (CRI), short lifespan and high color correlated temperatures due to red color deficiency [2]. The usage of W-LEDs in industrial and commercial fields is often limited due to low red spectral component in the fabrication. Lanthanide ions such as Europium (Eu), Erbium (Er) and other elements have been used as dopants in an appropriate host matrix for tunable emission features. In this context, CaLa\(_2\)ZnO\(_5\) (CLZO) has been found to be an excellent host material for incorporation of the above mentioned rare earth ions [3]. Among all the rare earth elements, the trivalent europium (Eu\(^{3+}\)) has been identified as a promising candidate for potential red luminescence under UV
radiation because of its unique atomic properties, thermal stability and chemical durability. The Eu\(^{3+}\) emission is ascribed to f-f electronic transitions which is independent of the shape and size and it is located from 560 to 725 nm. Eu\(^{3+}\) ion is a familiar red emitting RE ion due to its unique electronic transition of \(^5D_0 \rightarrow ^7F_2\) [4]. However, the greater red emission of Eu\(^{3+}\) could be obtained at a higher optimized concentration of Eu\(^{3+}\) ions in host matrix. This emission could be abruptly reduced after further optimized concentration due to concentration quenching effect. To overcome this concentration quenching, there are several methods have been established to improve the emission performance of the Eu\(^{3+}\) ions in the host matrices which are increasing the ion concentration and co-doped with suitable secondary sensitizer ions [5]. Nevertheless, there are so many reports on the florescence features with increasing the concentration of Eu\(^{3+}\) ions [6]. But significant results may not be obtained by increasing the concentration. Hence, we have approached another way to increase the fluorescence enhancement of Eu\(^{3+}\) ions with the host lattice. We have been undertaken an appropriate sensitizer rare earth ion such as Gd\(^{3+}\) which is well defined in earlier reports. We can obtain a strong red emission from Eu\(^{3+}\) ion doped phosphor spheres by sensitizing with Gd\(^{3+}\) ions. Here, Gd\(^{3+}\) ions acting as sensitizer and Eu\(^{3+}\) ions acting as activators. The successful emission photons corresponding to Gd\(^{3+}\) ions may absorb by Eu\(^{3+}\) ions with the host matrix under UV/Vis excitation source. The possible energy transfer may occur between sensitizer and activator at a particular wavelength of excitation. In order to enhance the red color index and fluorescence efficiency, Gd\(^{3+}\) ions have been undertaken to co-dope along with Eu\(^{3+}\) ions in CaLa\(_2\)ZnO\(_5\) (CLZO) phosphors in our present work. Interestingly, we obtained remarkable results than our previous reports that the potential red emission is improved by co-doping strategy with Gd\(^{3+}\) ions under the excitation of 276 nm. The energy transfer phenomenon has been systematically elucidated by several fluorescence dynamics.

2. Experimental studies

2.1. Materials preparation

Single doped and co-doped CLZO phosphors with Eu\(^{3+}/\text{Gd}^{3+}\) ions were prepared by employing traditional citrate sol-gel method. The high purity raw materials of calcium nitrate tetrahydrate Ca(NO\(_3\))\(_2\) 4H\(_2\)O, lanthanum nitrate hexahydrate La(NO\(_3\))\(_3\) 6H\(_2\)O, zinc nitrate hexahydrate Zn(NO\(_3\))\(_2\) 6H\(_2\)O, citric acid monohydrate HOC(COOH) (CH\(_2\)COOH)\(_2\). H\(_2\)O, europium nitrate hexahydrate Eu(NO\(_3\))\(_3\) 6H\(_2\)O, gadolinium nitrate hexahydrate Gd(NO\(_3\))\(_3\) 6H\(_2\)O were purchased from Sigma Aldrich and taken in a stoichiometric ratio. These chemicals were dissolved in 200 ml distilled water homogeneously under continuous stirring at room temperature for 2 h. Then, 8 mol% of citric acid monohydrate was added to this solution as a chelating agent such that the molar ratio of total metal cations to citric acid should be in the ratio of 1:3. This solution was again stirring for 1 h for solution homogeneity. The obtained solution was capped and kept under 80 °C of homogeneous heating for 1 h, after that cap was removed and then heating continued for 6 h. Then the brownish wet gel was kept under 120 °C in a heated oven for 24 h for xerogel. The xerogel was heated with 400°C for 4 h and found black color flakes, then sintered at 900 °C for 6 hours. Then the obtained powder samples were collected for further studies.

2.2. Characterisation

XRD profiles of Eu\(^{3+}\), Gd\(^{3+}\) doped and co-doped CLZO phosphor spheres were recorded on SEIFERT 303 TT X-ray diffractometer (XRD) with CuK\(_\alpha\) (1.5405 Å) which operated at 40 kV and 50 mA of voltage and currents respectively. The XRD measurement is recorded the 20 value from 10° to 90° with a speed of scan is 10°/min. The FT-IR spectral analysis data were recorded by EO-SXB IR spectrometer in the wavenumber range of 4000–450 cm\(^{-1}\). The morphological studies and elemental analysis were carried out by High Resolution FE-SEM-I (JSM 7401F) attached with EDS system. X-ray photoelectron spectroscopy studies were carried out (Thermo Scientific K-Alpha) using an Al Ka X-ray source (1486.6 eV). Photoluminescence (excitation and emission) spectral analysis of Eu\(^{3+}\): CLZO, and Eu\(^{3+}/\text{Gd}^{3+}\): CLZO phosphors were obtained on Scinco FluoroMate FS-2 Visible Fluorescence Spectrometer with Xe-arc lamp of 150 W power as an excitation source for a study state emission spectrum measurement. To estimate the absolute luminescence quantum efficiency of the phosphor samples, an integrating sphere equipped with an Edinburgh spectrometer (Model FLS900) instrument has been used for measuring the integrated fraction of luminous flux and radiant flux with the standard method.

3. Results and discussion

3.1. XRD, FE-SEM and EDS analysis

X-ray diffraction patterns of the optimized CLZO, Eu\(^{3+}\) (12 mol%): CLZO, Gd\(^{3+}\) (1 mol%): CLZO and Eu\(^{3+}\) (12 mol%)/Gd\(^{3+}\) (1 mol%): CLZO phosphor spheres are represented in Fig. 1. The tetragonal structure has been explored for these prepared phosphors and it is confirmed from evaluation of 2θ values and D-spacing. The present CLZO crystallographic structure is well similar to that of structure related to BaLa\(_2\)ZnO\(_5\), BaNd\(_2\)ZnO\(_5\) and BaSm\(_2\)ZnO\(_5\) which had already well consistent with the tetragonal structure in earlier reports [7,8]. No significant changes in the structure were observed by incorporation of rare earth ions in the basic crystal. No new phase has been emerging in the XRD patterns upon doping and co-doping, which confirms the incorporation of rare earth ions into the lattice. The Eu\(^{3+}\) ions and Gd\(^{3+}\) ions are preferably occupied La\(^{3+}\) ion sites due to the proximity between both of them with respect charge and ionic radius. The average crystallite size of the co-doped Eu\(^{3+}/\text{Gd}^{3+}\): CLZO phosphor powder sample has been calculated as ∼180 nm from the Scherrer equation. After making a closer examination of Fig. 1, we have been observed that the XRD peaks at 20 angle of 28.89° and 29.77° are found to be slightly shifted to lower angle side by doping with Eu\(^{3+}\) ions compared to undoped sample. Moreover, the lattice parameters are also increases compared to the un-doped sample. The shifting of the peak position to