

White light emission from Eu^{3+} co-activated $\text{Ca}_2\text{Gd}_8\text{Si}_6\text{O}_{26}:\text{Dy}^{3+}$ nanophosphors by solvothermal synthesis

E. Pavitra, G. Seeta Rama Raju, Jae Su Yu*

Department of Electronics and Radio Engineering, Institute for Laser Engineering, Kyung Hee University, 1 Seocheon-dong, Giheung-gu, Yongin-si, Gyeonggi-do 446-701, Republic of Korea

Received 30 December 2012; received in revised form 4 January 2013; accepted 17 January 2013
Available online 1 February 2013

Abstract

$\text{Ca}_2\text{Gd}_8(\text{SiO}_4)_6\text{O}_2$ (CGS) nanophosphors with different concentrations of single-doped Dy^{3+} ions and co-doped $\text{Dy}^{3+}/\text{Eu}^{3+}$ ions were prepared by a solvothermal synthesis. Very fine particles in the nanometer range could be achieved by this method, as evidenced by transmission electron microscope measurements. The hexagonal phase of the oxyapatite structure was confirmed by X-ray diffraction patterns. The energy transfer between Eu^{3+} and Dy^{3+} ions was investigated by photoluminescence excitation and emission properties. These phosphors had absorption bands in the UV and NUV region, which are suitable for the emission wavelength of UV or NUV light-emitting diodes (LEDs). With increasing the Eu^{3+} ion concentration, the emission peak intensity corresponding to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition increased and the yellow (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$) emission intensity also increased compared to the blue (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$) emission intensity due to the increased energy transfer between Dy^{3+} to Eu^{3+} ions. Thus, the Eu^{3+} ions compensated the red emission component of the Dy^{3+} doped CGS nanophosphors. Such phosphors are expected to have potential applications for NUV based white LEDs.

© 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: C. Optical properties; D. Apatite; Solvothermal process; White light emission

1. Introduction

Solid-state lighting becomes a smart strategy for energy saving, safety (lack of toxic mercury), reliability, maintenance, and eco-friendly characteristics, with its promise of being about 10 times more efficient than the incandescent lighting [1–3]. Besides, oxide-based phosphors activated with trivalent rare-earth ions are particularly important in the application of generating artificial light for next-generation field-emission display devices and white light-emitting diodes (WLEDs) due to their stable physical and chemical properties. At present, primarily two general approaches are being explored to yield WLEDs: blue LED chip coated with yellow phosphor and the tri-band (red, green, and blue) based WLEDs, which have been fabricated by pumping with UV-A (320–400 nm) LED sources [4–6]. In both approaches, highly-efficient

and long-lived phosphor materials that are well matched to the excitation conditions of the diode should be necessarily developed and thus their spectral emission properties produce a high color rendering index (> 95).

Recently, among the various kinds of synthetic oxyapatites, the ternary rare-earth-metal silicate with the oxyapatite structure of $\text{Ca}_2\text{RE}_8(\text{SiO}_4)_6\text{O}_2$ ($\text{RE} = \text{Y}/\text{Gd}$) as an efficient host lattice for well-organized excitation induced tunable luminescent properties of various rare-earth (RE) ions and mercury-like ions [7]. The ternary CGS host lattice belongs to the family of oxyapatite $\text{M}_4^{\text{I}}\text{M}_6^{\text{II}}(\text{XO}_4)_6\text{O}_2$ hexagonal structures with space group $P6_3/m$, where M^{I} and M^{II} positions correspond to the two distinct low symmetry (C_3 and C_s) crystallographic sites, which accommodate metal ions such as divalent alkaline-earth or RE^{3+} elements. In the CGS host lattice, Ca^{2+} and Gd^{3+} ions are randomly distributed in the C_3 point symmetry of the 9-fold coordinated 4f site, and Gd^{3+} ions are completely occupied in the C_s point symmetry of 7-fold coordinated 6h sites. Both sites are very suitable for the luminescence of RE^{3+} ions owing

*Corresponding author. Tel.: +82 31 201 3820; fax: +82 31 206 2820.
E-mail address: jsyu@khu.ac.kr (J.S. Yu).

to their low symmetry features. The X-site is occupied by P-block elements such as P, As, Si, or Ge [2,8].

Among the RE³⁺ ions, dysprosium (Dy³⁺) ions exhibit strong luminescence in a variety of lattices, leading to both blue (⁴F_{9/2}→⁶H_{15/2}) and yellow (⁴F_{9/2}→⁶H_{13/2}) emissions. By appropriate adjustment of yellow-to-blue intensity ratio (*Y/B*) values, it is possible to obtain near-white emission [9,10]. But, unfortunately, Dy³⁺ single-doped CGS phosphors suffer from a lack of red component. In order to compensate the red component, Eu³⁺ ions were also introduced into CGS host lattice because it is one of the most important activators among RE ions due to the rich red emission from the ⁵D₀→⁷F₂ transition [10].

To the best of our knowledge, until now, no reports have been found on the detailed luminescent properties of Dy³⁺ single-doped and Eu³⁺/Dy³⁺ co-doped CGS nanophosphors by a solvothermal process. It is well known that the phosphors with fine particle size and narrow size distribution offer the possibility of high resolution and high luminescence efficiency. In this work, the structural and detailed luminescence properties of Dy³⁺ single-doped and Dy³⁺/Eu³⁺ co-doped nanophosphor samples by varying the concentrations were systematically investigated and the energy transfer between the Dy³⁺ and Eu³⁺ ions was also discussed.

2. Experimental details

Nanocrystalline CGS host lattices doped with Dy³⁺ and Eu³⁺ ions were prepared by the solvothermal process with the composition of Ca₂(Gd_{8-(x+y)}Dy_xEu_y)Si₆O₂₆ (*x*=0.5, 1, 2 mol%; *y*=1, 2, 3 mol%). The appropriate amounts of high-purity grade calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O), gadolinium nitrate hexahydrate (Gd(NO₃)₃·6H₂O), dysprosium nitrate pentahydrate (Dy(NO₃)₃·5H₂O), europium nitrate pentahydrate (Eu(NO₃)₃·5H₂O), and tetraethyl orthosilicate (Si(OC₂H₅)₄) were dissolved in 70 ml of 2-propanol. All reagents were taken without any further purification and stirred vigorously using the magnetic stirrer until the formation of homogeneous solution and then transferred into a stainless steel autoclave with a Teflon liner (140 ml capacity and 50% filling). Then, it was heated to 230 °C at a rate of 2 °C/min and maintained for 5 h with continued magnetic stirring (at 180 rpm) to make stable networks between the reactants. After gradually cooling down to room temperature, the precipitate was separated by a centrifugal separator with 5000 rpm for 5 min and then dried at 100 °C for a day in ambient atmosphere. Finally, the dried powder was annealed at 1200 °C for 5 h. The experiment was repeated at similar conditions as functions of Dy³⁺ and Eu³⁺ ion concentrations.

The X-ray diffraction (XRD) patterns of the CGS samples were recorded by using a powder X-ray diffractometer (Mac Science, M18XHF-SRA) with CuK=1.5406 Å. The morphology of the samples was examined by using a field-emission transmission electron microscope (FE-TEM: JEOL, JEM-2100F). The Fourier transform infrared (FTIR) spectra of the CGS samples were

measured by using a Thermo Nicolet-5700 spectrophotometer. The room-temperature photoluminescence (PL) spectra were recorded on a Photon Technology International (PTI, USA) fluorimeter with a Xe-arc lamp of power 60 W.

3. Results and discussion

Fig. 1 shows the XRD patterns of pure CGS, CGS:Dy³⁺ and CGS:Dy³⁺/Eu³⁺ nanophosphors sintered at 1200 °C. All the diffraction peaks correspond to the hexagonal phase of the oxyapatite structure with space group *P*6₃/*m*, which are in well agreement with the standard JCPDS card [PDF (28-0212)]. No impurity phase caused by RE ions can be noticed at the current doping level, indicating that the Dy³⁺ and Eu³⁺ ions are completely dissolved into the Gd³⁺ sites of CGS host lattice. It is well known that the pure phase is favorable for luminescent properties of phosphors. Generally, the crystallite size can be estimated by using the Scherrer equation, $D_{hkl}=(k\lambda)/(\beta \cos \theta)$, where *D* is the average grain size, *k*(0.9) is a shape factor, λ is the X-ray wavelength (1.5406 Å), and β and θ are the full width at half maximum and the diffraction angle of an observed peak, respectively. The strongest diffraction peaks were used to calculate the crystallite sizes of CGS nanophosphors sintered at 1200 °C, which yields an average value of about 72 nm. The crystallinity of the CGS phosphors with different concentrations of Eu³⁺/Dy³⁺ ions was the same because the energy supply was constant. The inset of Fig. 1 shows the TEM image of the CGS:1 mol% Dy³⁺ (i.e., CGS:1Dy³⁺) sample annealed at 1200 °C. From the TEM image, it is clear that the particles are in the nanometer range.

The FTIR spectrum of the CGS:1Dy³⁺ nanophosphors annealed at 1200 °C is shown in Fig. 2. Typically, the bands at 3572 cm⁻¹ and 630 cm⁻¹ originated from the

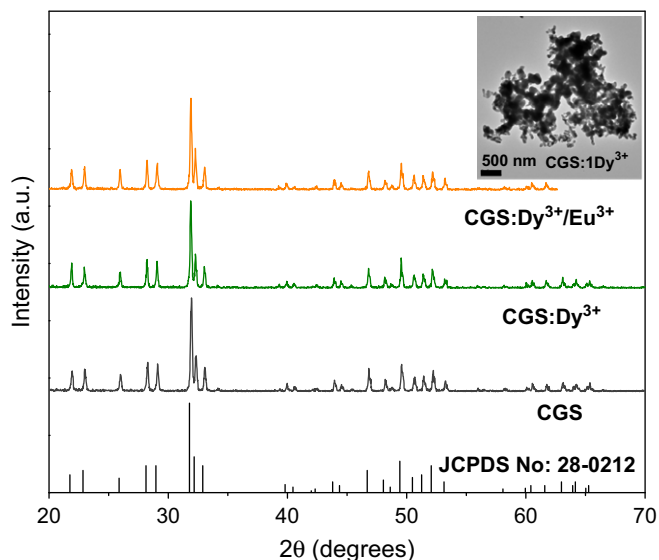


Fig. 1. XRD patterns of pure CGS, Dy³⁺ single-doped CGS, and Dy³⁺/Eu³⁺ co-doped CGS nanophosphors (inset shows the TEM image of CGS:1Dy³⁺).

Download English Version:

<https://daneshyari.com/en/article/1462756>

Download Persian Version:

<https://daneshyari.com/article/1462756>

[Daneshyari.com](https://daneshyari.com)