Dyes and Pigments 122 (2015) 22–30

Contents lists available at ScienceDirect

Dyes and Pigments

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

Photoluminescence and Judd–Ofelt analysis of Eu^{3+} doped $LaAlO_3$ nanophosphors for WLEDs

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ARTICLE INFO

Article history:
Received 12 February 2015
Received in revised form
31 May 2015
Accepted 2 June 2015
Available online 14 June 2015

Keywords:
$LaAlO_3:Eu^{3+}$
Phosphor
Photoluminescence
CIE
CCT
Combustion process

ABSTRACT

Europium doped lanthanum aluminate nanophosphors were synthesized by a combustion process using Oxalyl di-hydrazide as fuel. The nanophosphors calcined at 900 °C for 3 h were characterized by PXRD, FTIR spectroscopy, SEM and TEM. The average crystallite size determined by TEM and Scherrer's method was found to be in the range 20–50 nm. The characteristic emission peaks (λ_{exi} - 395 nm) recorded at ~ 591, 616, 646 and 696 nm ($^5D_0 \rightarrow {}^7F_{j=0,1,2,3}$) may be attributed to the 4f–4f intra shell transitions of Eu^{3+} ions. The estimated CIE chromaticity co-ordinates were calculated from emission spectra, were close to the national television standard committee value of red emission. Correlated color temperature was found to be 1929 K.

1. Introduction

The demand for developing efficient luminescent materials including suitable hosts for lanthanide ions remains highly desirable. It is known that Perovskite structured lanthanum aluminate ($LaAlO_3$) has attracted much interest for its wide range of applications owing to its fascinating physical and chemical properties. Recent photoluminescence studies indicated that $LaAlO_3$ was a good host material for lanthanide ions, due to its wide-band gap (~5.6 eV), significantly low phonon energy (146–159 cm^{-1}) and good transparency over the visible light range [1]. The luminescence of Eu^{3+} ions was especially useful for probing the local structure of luminescent centers in a host lattice. Lin et al. [2], investigated systematically the luminescence of Eu^{3+} in different lattice sites of $La_2CaB_{10}O_{19}$, and paved the way for the investigation on multiple-sites luminescence of Eu^{3+} [3]. Therefore, the spectroscopic properties of Eu^{3+} in different host lattices are important not only for possible industrial application but also for basic research.

Trivalent doped rare earth ions find a wide range of applications including in security ink, bar codes, anti-counterfeiting ink and display applications [1]. Further luminescent materials, doped with Eu^{3+} ions were widely studied for their high efficiency and proper Commission International de I' Eclairage (CIE) chromaticity coordinates. Eu^{3+} doped phosphors were effectively excited by near-UV and blue light, as a result these phosphors emit a strong red color which is attributed to 4f–5d transitions. It involves broad spectral line width as occurred for low valence rare-earth ions which crystal field related and can be tuned by the size and the crystal structure [4]. The $LaAlO_3$ host doped with rare earth ions exhibits some interesting applications such as long lasting phosphor, X-ray imaging, light emitting display (LED),

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http://dx.doi.org/10.1016/j.dyepig.2015.06.002
0143-7208/

lasers, plasma displays and environmental monitoring [5]. Various wet and soft synthesis methods including polymerized complex method using citric acid and ethylene glycol route have been reported [6–8]. Several chemical routes are used for preparing finer and homogeneous powders of $LaAlO_3$ with Poly Vinyl Alcohol (PVA) with metal nitrate synthesis [9], sol–gel process [10], EDTA gel route [11], co-precipitation method [12], pyrolysis using triethanolamine and combustion synthesis with urea, glycine and ODH as fuels [13–15].

Luminescence efficiency of phosphors can be altered by changing their compositions. Great improvements in luminescence efficiency of phosphors were observed by doping with even very small quantities of dopants/co-dopants. Currently, the research on efficient and inexpensive nanophosphors is a challenging problem for new luminescent materials. Use of those phosphor materials in light emitting diode (LEDs) was a major step in solid state lighting technology. However, white light emitting diodes (WLEDs) are consider to be the next generation lighting system because of their excellent properties (high luminous efficiency, low power consumption, environmentally friendly features (nontoxic), reliability and long life) [16–18].

Combustion techniques have emerged as an important synthesis technique for aluminate nanoparticles for being very simple experimental set-up, provides molecular level of mixing, high degree of homogeneity, time saving, more economical, affords ultra-pure, higher surface area product can be obtained [19]. The solution combustion synthesis may be a promising synthesis method for commercial needs. In comparison with other methods, the powders obtained by the combustion synthesis method was generally more homogeneous, have less impurities and have higher surface areas than powders prepared by conventional methods [20].

This paper presents the synthesis and characterization of $LaAlO_3:Eu^{3+}$ nanophosphors, prepared by combustion synthesis using Oxalyl di-hydrazide (ODH) as a fuel. The structural details and optical properties of the synthesized phosphors are investigated by PXRD, TEM, FTIR and SEM. In addition the effect of europium substitution on photoluminescence (PL) properties are investigated for their possible usage in lighting applications.

2. Experimental

2.1. Sample preparation

$LaAlO_3$ doped with Eu^{3+} (1–9 mol %) phosphors are prepared by solution combustion method in a very short time (less than 5 min). La $_{0.99}$ $Eu_{0.01}AlO_3$ (1 mol %) prepared using 3.217 g of lanthanum nitrate [$La(NO_3)_3.6H_2O$ (99.9% purity) Sigma Aldrich], 0.033 g europium nitrate [Eu $(NO_3)3$ (99.9% purity) Himedia], 2.13 g of aluminum nitrate [$Al(NO_3)_3.9H_2O$ (99.9% purity) Sigma Aldrich] are used as oxidizers (O) and 3.54 g of lab prepared ODH [$C_2H_6N_4O_2$] is used as fuel (F) [21]. All the starting materials are taken in stoichiometric ratios [F/O = 1] and dissolved in minimum quantity of doubled distilled water in a cylindrical Pyrex Petri dish of approximately 300 ml capacity and mixed thoroughly using a magnetic stirrer (maintained at 500 rpm) for ~ 4 min. The stoichiometry of the redox mixture used for the combustion synthesis was calculated based on the total oxidizing and reducing valencies of the compounds [16]. Then the Petri dish containing this solution was introduced into a pre heated muffle furnace by maintaining temperature at 500 ± 10 °C. Initially the solution boiled resulting in a transparent gel. Shortly thereafter, the reaction mixture undergoes dehydration and ignites at one spot with liberation of large amount of gaseous products (oxides of nitrogen and carbon). The combustion propagated throughout the reaction mixture without further need of any external heating, as the heat of reaction is sufficient for the decomposition of the redox mixture. The entire combustion process is completed in less than 5 min leaving behind the final product; leaving a white powder with an extremely porous structure. The foamy product was ground into a fine powder using agate-mortar and calcined at 900 °C for 3 h. Similar experimental procedure has been used for other compositions (3,5,7 and 9 mol %). The flow chart for the synthesis of the sample was given in Fig. 1. The chemical equation assumed for the combustion synthesis is given by

$$La(NO_3)_3 + Al(NO_3)_3 + C_2H_6N_4O_2 \rightarrow LaAlO_3 + 3H_2O + 5N_2 + CO_2 + 6O_2 \quad (1)$$

2.2. Characterization

The crystalline nature of the powder sample is characterized by PXRD using X-ray diffractometer (Shimadzu) (operating at 50 kV and 20 mA by means of CuK_α (1.541 Å) radiation with a nickel filter at a scan rate of $2^\circ min^{-1}$). Fourier transform infrared (FTIR) studies of the samples are performed with a Perkin Elmer FTIR spectrophotometer (Spectrum-1000). The surface morphology of the product is examined by Scanning Electron Microscopy (SEM) using Hitachi table top (SEM) (Model TM 3000) (accelerating voltage up to 20 kV using Tungsten filament). Transmission Electron Microscopy (TEM) analysis is performed on a JEOL, JEM-2100 (accelerating voltage up to 200 kV, with LaB_6 filament) equipped with EDS having 1.5 Å resolutions. Photoluminescence studies are made using Horiba, (model fluorolog-3) Spectroflourimeter at RT using 450 W xenon as excitation source. Fluor Essence™ software is used for spectral analysis.

3. Results and discussion

Fig. 2 shows the PXRD patterns of undoped and Eu^{3+} (1–9 mol %) doped $LaAlO_3$ nanophosphor calcined at 900 °C for 3 h. The diffraction patterns are in good agreement with the standard JCPDS File No. 31- 22 confirming pure rhombohedral structure with Space Group: R3m (no. 160). Further, introduction of an activator (Eu^{3+}) did not influence the crystal structure but certainly modified the lattice parameters due to the difference in the ionic radii between

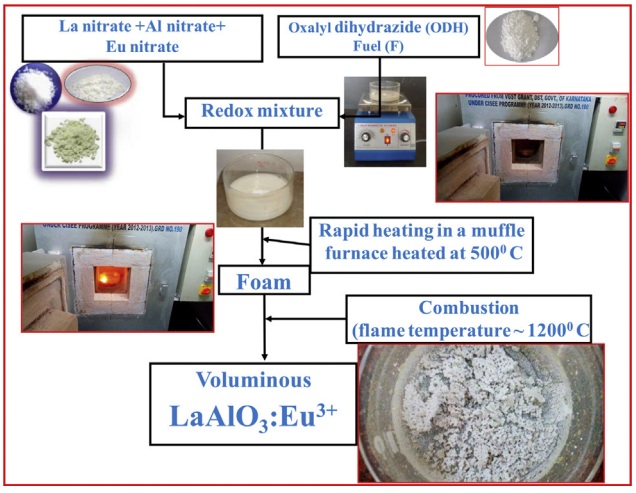

Fig. 1. Flow chart for the synthesis of Eu^{3+} (1–9 mol %) doped $LaAlO_3$.