Dyes and Pigments 148 (2018) 1–8

Contents lists available at ScienceDirect

Dyes and Pigments

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

Observation of two-way multichannel interaction among Dy and Eu ions in Bi_2SiO_5 nanophosphor

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ARTICLE INFO

Article history:
Received 10 June 2017
Received in revised form
30 July 2017
Accepted 29 August 2017
Available online 1 September 2017

Keywords:
Bi_2SiO_5
Nanophosphors
Energy transfer
White light emission

ABSTRACT

A series of Dy^{3+} and Eu^{3+} ion doped Bi_2SiO_5 nanophosphors were synthesized by hydrothermal method. A comprehensive structural and optical characterization were performed using various techniques including powder X-ray diffraction, UV-Infrared absorption, photoluminescence, time-resolved luminescence technique etc. Crystalline size of the synthesized nanophosphors was found to be ~25 nm, depending on the doping concentration of the active ions. Under the blue light excitations (386 nm and 393 nm) the Dy^{3+}:Bi_2SiO_5 and Eu^{3+}:Bi_2SiO_5 nanophosphors yield characteristic yellowish white light and yellow/red emissions, respectively. In binary co-doped, Dy:Eu:Bi_2SiO_5, excitation of individual ion results from another doped ion, in addition to the emission from resonantly excited ion. Observation of emission from acceptor ions, confirm the effective mutual interaction between the doped ions and existence of two-way energy transfer process. Various energy transfer parameters including the rate of energy transfer efficiency were estimated. A predominate multipole interaction was concluded for the energy transfer through multichannel interaction which yield white light on 350 nm and 386 nm excitations. CIE coordinates were estimated for various excitations which fall well within the gamut of white light.

1. Introduction

In recent years, researchers have developed new luminescent nanomaterials doped with lanthanide elements and explored the possibility of mutual interaction. The interaction between the ions may facilitate the generation of white light and manipulation of colour perception. Lanthanide doped oxide phosphors were reported as potential active sources because of their incomparable luminescent characteristics, good chemical, thermal stability etc [1–4]. The luminescence of trivalent lanthanide ions is a result of transitions within the partially filled 4f shell of the ions. These transitions are parity forbidden leading to low molar absorption coefficients and long luminescent lifetimes [5]. Among lanthanide elements Dy^{3+} ion is known to emit two characteristic intense sharp peaks; 1) blue (~480 nm) and 2) yellow (574 nm) region corresponding to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^6H_{13/2}$ transitions [6]. Due to the presence of complementary colours, it is possible to obtain white light from Dy^{3+} ion activated luminescent materials by adjusting the intensity ratio of yellow and blue colours [7,8]. Unfortunately, the colour render index (CRI) of single Dy^{3+} doped phosphors is very low due to lack of red colour component [9]. To improve colour render index of the white light, red colour needs to include which is possible by coexistence of red colour emitting element with Dy^{3+} ion. For red emission, among lanthanide elements, Eu ion is a preferable choice due to its sharp and bright emission at ~613 nm. In the present study we have included different concentrations of Eu^{3+} ions in single Dy^{3+} doped system [10,11]. Various efforts have been done, in Dy:Eu codoped system, to explore the possibility of white light in glassy hosts [12,13] and nanophosphors [14]. Good host is very important for efficient luminescence of lanthanide ions. In the present work we have explored interaction between Eu^{3+} and Dy^{3+} ions in Bi_2SiO_5 nanophosphor host. Bi_2SiO_5 host provide advantage of wide band gap (3.5 eV) which makes host transparent upto 350 nm.

In the present work, we have excited singly doped and codoped nanophosphors with various UV-blue radiations to explore multichannel interactions between the ions and possibility of white light tuning. We have concluded the efficient mutual interactions among both the active ions which yield a bright white colour emission. Estimation of CIE coordinates reveal the improved white light emission which fall well in gamut of white light in CIE diagram.

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http://dx.doi.org/10.1016/j.dyepig.2017.08.054
0143-7208/

2. Synthesis and characterizations

2.1. Chemicals

The following chemicals were used for sample synthesis: Bismuth Nitrate [$Bi(NO_3)_3 \cdot 5H_2O$], Sodium Silicate [$Na_2SiO_3 \cdot 9H_2O$] (99%), Dysprosium Oxide [Dy_2O_3] (99.9%), Europium Oxide [Eu_2O_3] (99.99%), Nitric acid (HNO_3) and Ammonia Hydroxide [NH_4OH]. These chemicals were purchased from Sigma Aldrich Company and used as it was received.

2.2. Synthesis

Pure Bi_2SiO_5 nanophosphors and doped with Dy and Eu^{3+} ions activated were prepared by using hydrothermal method. In a typical synthesis process, $Bi(NO_3)_3 \cdot 5H_2O$ and $Na_2SiO_3 \cdot 9H_2O$ taken into ratio of 2: 1 M concentration which was diluted in 15 ml distilled water with mild heating. For synthesis of doped Bi_2SiO_5 samples, different nitrate solutions of lanthanide ions were prepared by dissolving appropriate amount of Dy_2O_3 and Eu_2O_3 in 2 ml concentrate Nitric acid (68%) in diluted solution of $Bi(NO_3)_3 \cdot 5H_2O$ and $Na_2SiO_3 \cdot 9H_2O$. Under vigorous stirring, the pH value of the mixture was adjusted to 09 by adding ammonia solution. After stirring for 30 min, the mixture was transferred into a Teflon-lined autoclave of capacity ~150 ml. The autoclave was sealed and heated under autogenous pressure at 180 °C for 48 h. Subsequently, autoclave was allowed to cool down to room temperature naturally. The white products were collected by centrifuge process and washed with distilled water several times. The obtained powder was dried at 100 °C for 12 h to remove moisture. A white powdered sample of Bi_2SiO_5 was obtained by annealing it at different temperatures viz. 500 °C/3 h, 600 °C/3 h and 800 °C/3 h. The concentration of lanthanide ions is given in x mol % (x = 0.5, 1, 1.5, 2) is denoted as 1.5Dy or as 1.5Dy:1Eu in rest of the manuscript.

2.3. Characterizations

The crystalline phases of the prepared samples were identified by X-ray diffraction patterns on Rigaku mini diffractometer (MiniFlex-2, Japan) machine using Graphite filtered Cu-K_α radiation ($\lambda = 1.54$ Å) operated at 40 kV and 100 mA with a scanning rate of 2°/min in the range 10–80°. Crystallite sizes were estimated from Debye-Scherrer's relation $D = K\lambda/\beta \cos\theta$ where, λ is the X-ray wavelength, θ is the angel of the Bragg diffraction peak (in radian) and β is the line width at half maximum. Crystal Strain was estimated by W-H plot ($\beta \cos\theta$ vs 4 $\sin\theta$) using equation: $\varepsilon = \beta/4 \tan\theta$. The Fourier Transform Infrared (FTIR) spectra of the samples were recorded on Carry eclipse 6300 machine (JASCO, Japan) in the range of 400–4000 cm^{-1}. Excitation and photoluminescence spectra of the prepared samples were carried out on RF-530 Spectrofluorophotometer (Shimadzu, Japan) in the range of 200–800 nm. The estimated Chromaticity coordinates calculated by Go-CIE software based on CIE 1931. Photoluminescence decay measurements were recorded with pulsed 386 nm radiation of Xe-lamp (450 W) as an excitation source using Fluorolog-3 (Horiba, Japan). Lifetimes of the radiative levels were estimated by fitting as exponential function to the decay curves.

3. Results and discussion

3.1. Crystalline phase analysis

3.1.1. Effect of annealing

The X-ray diffraction (XRD) patterns of the undoped as-synthesized and annealed (500 °C/3 h, 600 °C/3 h and 800 °C/3 h) Bi_2SiO_5 samples were monitored and depicted in Fig. 1. As-synthesized sample consist of few broader peaks overlying weak background which indicate coexistence of crystallization and amorphous contents. It was observed that the peaks get sharper on annealing at elevated temperature. On further annealing at 600 °C/3 h the background of the pattern was completely removed and peaks get much sharper and clearly visible. In case of undoped annealed (600 °C/3 h) sample, XRD pattern obtained was found to be matched well with Orthorhombic symmetry of Bi_2SiO_5 phase (JCPDS No. 36-0287) [15]. When the same sample was annealed at 800 °C/3 h Bragg's peak intensity increases and slightly shifted towards higher angle side. In this pattern, we have identified an impurity phase of $Bi_4Si_3O_{12}$ (JCPDS No. 76-1726) [16], in addition to Bi_2SiO_5 phase. Peak sharpening and intensity improvement indicates precipitation of comparably big sized Bi_2SiO_5 crystals. In case of as-synthesized undoped sample mean crystallite size was estimated ~7 nm but crystallite size increases after annealing. The mean crystallite size was estimated using Debye-Scherrer's equation in case of annealed sample and found to be ~25 ± 3 nm. The effect of annealing temperatures on the crystalline parameters and doped ion are compared in Table 1. Efforts were made to analysis the Bragg's peaks using Debye-Scherrer's equation and detail obtained are tabulated in Table 1. It has been observed that the crystallite size increases while strain decreases with increasing annealing temperature.

3.1.2. Effect of doping

We have monitored the consequence of Dy^{3+} and Eu^{3+} ions presence in crystalline lattice using X-ray diffraction technique. The XRD patterns of the 1.5Dy, 1.5Dy:1Eu and 1.5Dy:1.5Eu doped Bi_2SiO_5 samples, annealed at 600 °C/3 h, were depicted in Fig. 2. When 1.5Dy ion is doped in the Bi_2SiO_5 nanolattice, Bragg's peaks get improved, in comparison to undoped sample, and several peaks corresponding to crystal planes were visible. When Eu^{3+} ions are also present along with Dy^{3+} ion, diffraction peaks slightly shifted towards higher angle side. Additionally, diffraction peak intensity reduces and gets broadened too. Broadening indicates the smaller crystalline size which was estimated to be ~18 nm. It can be concluded that though doping of Dy^{3+} and Eu^{3+} ions doesn't bring any major change in the crystalline phase but it improves crystallinity up to limited doping concentrations. The observed shifting and broadening indicate possible substitution of Bi^{3+} (117 pm) ions by Eu^{3+} (108.7 pm) and Dy^{3+} (105.2 pm) ions [16].

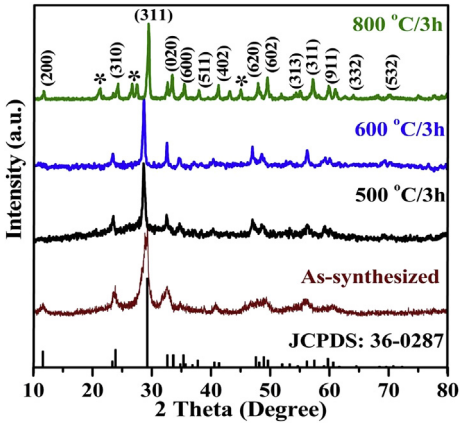

Fig. 1. Powder X-ray diffraction patterns of the undoped as-synthesized, annealed at 500 °C/3 h, 600 °C/3 h and 800 °C/3 h Bi_2SiO_5 crystals synthesized by the hydrothermal method.