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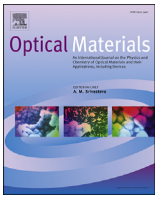

Bright emission via energy transfer from Dy to Tb in Bi_2SiO_5 nanophosphor

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ABSTRACT

The present article discusses the optical and structural properties of Tb and Dy co-doped Bi_2SiO_5 nanophosphors which were synthesized by Co-precipitation method. The synthesized sample contains plate-like morphology of uniform thickness ~200 nm. Prepared samples were found of average crystallite size ~20 nm, which yield bright yellow dominating white emission and green emission, in Dy: Bi_2SiO_5 and Tb: Bi_2SiO_5 nanophosphor, respectively under UV-light excitation. We have reported one-way efficient energy transfer from Dy to Tb ion, which facilitates precise colour tuning ability. The energy transfer phenomenon was well explored using, photoexcitation, photoluminescence and time-resolved luminescence techniques.

1. Introduction

Silicate-based nanophosphors are one of the promising hosts for the doping of lanthanide ions to study down conversion luminescence due to the higher lattice vibration, wide band gap ~3.5 eV, compact crystalline structure, thermal stability, low synthesis cost etc. [1–3]. These phosphors find vast applications in variety of display devices including X-ray screens, fluorescent lamps, solid state lighting etc. [4–6]. In the present article, we have studied comparably less explored Bi_2SiO_5 nanophosphor which was reported as one of the potential hosts for the study of luminescence, photocatalytic activity, hydrogen generation, heavy metal removal etc. [7,8]. Bi_2SiO_5 is among one of the compounds pertaining to the Aurivillius family having Bi_2O_3-SiO_2 binary system. The crystalline structure of Bi_2SiO_5 is composed of layers of $(SiO_3)^{2-}$ pyroxene and $(Bi_2O_2)^{2+}$. These layers are stacked alternatively which provide unique crystalline features. Inspite of wide range of applications, spectroscopic analysis of doped Bi_2SiO_5 nanophoshphor is less studied. In the present article, we have attempted doping of Tb and Dy lanthanide ions in Bi_2SiO_5 nanophoshphor, to search possibility of efficient interaction between the active ions which may yield precise colour tenability. Among lanthanides, Tb^{3+} and Dy^{3+} ions are known to emit bright multicolour luminescence though predominate green and yellow colours, in addition to the various infrared emissions [9,10]. Kang et al. have reported bright green emission from Y_2SiO_5:Tb nanophosphor prepared by spray pyrolysis [11]. Sahu et al. have reported bright white light from $Sr_2MgSi_2O_7$:Dy^{3+} doped sample [3]. Tiwari et al. reports increase in thermoluminescence intensity in Dy doped $Ca_2Al_2SiO_7$ phase which is due to the increase in traps concentration under UV irradiation [12].

The energy of few excited energy levels of Tb and Dy ions, are comparable in UV-blue region. Overlapping of energy levels facilitate efficient interaction between the doped ions, which may promote colour tunability. In this article, we have synthesized Bi_2SiO_5:Tb:Dy co-doped nanophosphor by Co-precipitation technique. Synthesized nanophosphors were excited by UV-blue radiations, which yield bright yellow and green emission. The strong electronic interaction between the ions was also reported in various hosts viz. $Ca_2Al_2SiO_7$, Y_2SiO_5, $SrSiO_3$, $Sr_2MgSi_2O_7$, $Ca_2MgSi_2O_7$ and Sr_2SiO_4 [11–14]. However, interaction was found to be function of doping concentration. Tb:Dy codoped nanophosphor studied in various hosts [15,16]. Our work is focused on the study of Tb ion and energy transfer in Dy:Tb ions in Bi_2SiO_5 nanophosphors. Luminescence investigations of bismuth silicate nanophoshphor doped with Dy^{3+}, Tb^{3+} and energy transfer between Tb^{3+} and Dy^{3+} in Bi_2SiO_5 host were not examined earlier.

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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%), Terbium Oxide [Tb_4O_7] (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 Tb and Dy activator ion were prepared by using Co-precipitation method. In a typical synthesis, $Bi(NO_3)_3 \cdot 5\ H_2O$ and $Na_2SiO_3 \cdot 9.\ H_2O$ taken into 2: 1 M concentration. $Bi(NO_3)_3 \cdot 5\ H_2O$ solution prepared by taken 15 ml distilled water and 1 ml nitric acid. $Na_2SiO_3 \cdot 9.\ H_2O$ solution prepared by taking 60 ml distilled water and then mix both the solution. For synthesis of different activator ion doped Bi_2SiO_5, different solution prepared by dissolving Dy_2O_3 and Tb_4O_7 in Nitric acid 68% molar concentration and add into above solution. Under vigorous stirring, the pH value of the mixture was adjusted to 9 by adding ammonia solution. The solid products were collected and washed with distilled water several times and then dried at 80 °C for 12 h. A white Bi_2SiO_5 powder sample was obtained and annealed at 600 °C for 3 h, on the basis of our previous optimize annealing temperature. Hereafter, x mol % Tb; Dy ion concentrations are given as x Tb; Dy.

2.3. Characterizations

The crystalline phases of the prepared samples were identified by X-ray diffraction patterns on Rigaku mini diffractometer (Mini flex 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 $D = K\lambda/\beta\ \mathrm{Cos}\theta$ 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. Surface morphology was investigated on JSM-6390LV (JEOL, Japan) Scanning Electron Microscope. The Fourier Transform Infrared (FTIR) spectra of the samples were recorded on Alpha II FTIR machine (Bruker) 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).

3. Results and discussion

3.1. Crystalline phase analysis

The XRD patterns of x Tb (x = 0, 1, 2 and 2.5 mol%) doped annealed Bi_2SiO_5 samples were monitored in the range of 10–80° angle (see Fig. 1 [A]). The obtained Bragg's peak patterns were found to be match well with the Orthorhombic system of Bi_2SiO_5 (JCPDS No. 36-0287) [17]. The mean crystallite size of undoped sample was estimated to be ~16 ± 2 nm using Debye-Scherrer's equation. A comparison between the samples with different doping ion concentration was studied. It was observed that the crystalline phase was remaining identical up to 2.5 Tb doping concentration. However, average crystallite sizes increase with the Tb ion concentration in comparison with the undoped Bi_2SiO_5 nanophosphor. The crystalline size of Tb doped samples varies as 1 Tb (~19 nm) < 2 Tb (~20 nm) < 2.5 Tb (~26 nm).

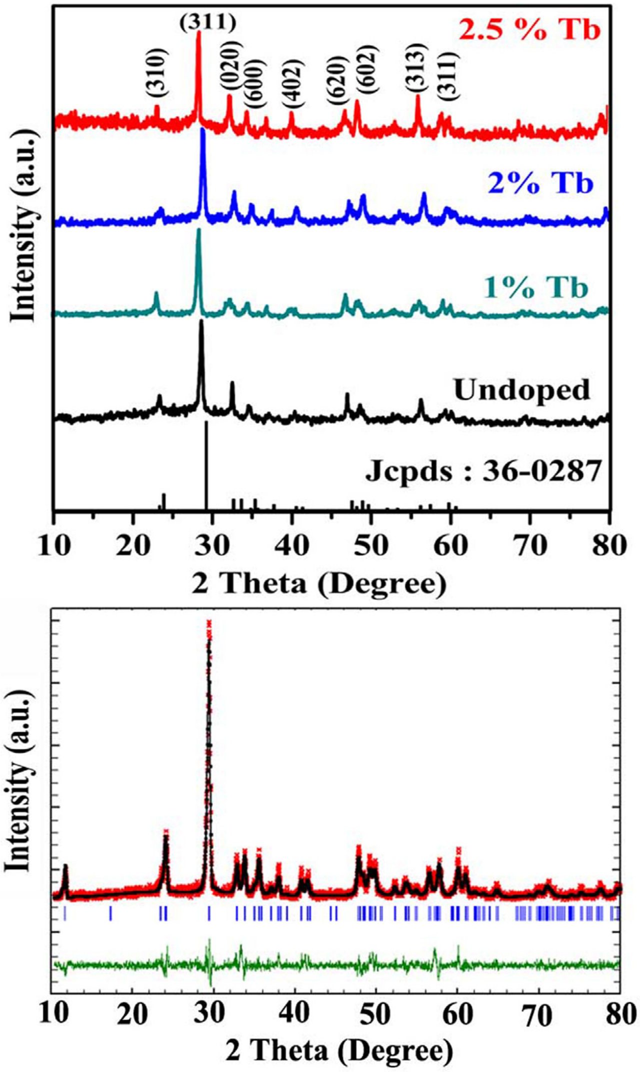

Fig. 1. **[A]** X -Ray diffraction patterns of the x (x = 0, 1, 2 and 2.5 mol%) Tb: Bi_2SiO_5 nanophosphor annealed at 600 °C for 3 h. **[B]** Rietveld refinement of 1Dy:1Tb:Bi_2SiO_5 nanophosphor. The red dots and black line are the observed and calculated intensities. Blue vertical indicate Bragg positions and the green line plots the difference between observed and calculated intensities. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 1 [B] shows the powder X-ray diffraction pattern of Bi_2SiO_5 with full-profile structure refinements of the collected data based on the Rietveld's analysis by Full-Proof software. The Rietveld analysis of 1Dy:1Tb has been carried out for Orthorhombic structure with space group $Cmc2_1$ by appropriate fitting Chi-square $\chi = 2.36$ was found. All the diffraction peaks was successfully indexed according to the lattice constant and space group. Additionally, the results of the final refinements for Bi_2SiO_5 indicated a good agreement between the observed and calculated intensities for the orthorhombic structure.

The surface morphology of Bi_2SiO_5 was examined using Scanning electron microscope and shown in Fig. 2. It can be seen that the most of the particles possess homogeneous plate-like surface morphology with uniform thickness ~200 nm. The observed