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Optical properties of trivalent samarium-doped $Ba_5Zn_4Y_8O_{21}$ nanodiametric rods excitable by NUV light

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ABSTRACT

A series of reddish-orange $Ba_5Zn_4Y_{8-x}O_{21}$:xSm^{3+} (x = 0.04–0.24) nanophosphors were synthesized via urea-assisted solution combustion method and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), diffuse reflectance (DR) and photoluminescence (PL) spectroscopy. Rietveld analysis infers that Y^{3+} ions can be well-substituted by Sm^{3+} ions without any major alteration in the crystal structure of host matrix. Moreover, as no JCPDS data was available for the host, the lattice parameters and refined atomic positions were determined for both, the host as well as the doped sample. TEM investigation revealed the nanodiametric rods of almost smoothly-surfaced morphological character. The optical band-gap of the host (5.36 eV) was calculated from DR spectra and also performed theoretically in density functional theory (DFT) framework using CASTEP code. On NUV excitation, the nanophosphor exhibits the characteristic emission peaks of Sm^{3+}, which can be credited to $^4G_{5/2} \rightarrow {}^6H_J$ (J = 5/2, 7/2, 9/2, 11/2) transitions. The optimum Sm^{3+} concentration for better luminescence was found to be 1.5 mol%. The critical distance (20.49 Å) elicits the right mechanism responsible for concentration quenching (dipole-dipole). The detailed analysis of PL decay curves gave the radiative lifetime (1.11 ms), overall rate of non-radiative relaxation (240.16 s^{-1}) and most importantly, the quantum efficiency of $^4G_{5/2}$ electronic state (78%). The CIE color coordinates unveiled an almost pure reddish-orange emitter, which finds potential applications in phosphor-converted white light emitting diodes (PC-WLEDs) under NUV excitation.

1. Introduction

The global energy demand is urging human civilization not only to invent new eco-friendly energy sources but is also expecting to use the current ones in a more efficient and cost effective manner [1]. Therefore, nano-scaled phosphor materials with prominent luminous efficacy and high thermal stability are becoming the urgent demand of recent white light generation applications like LED bulbs, plasma displays, solid state laser devices; and the research target in this field of nanotechnology is accelerating day by day at an extremely fast rate [1–4]. Furthermore, in addition to the aforementioned devices, rare-earth ions activated novel inorganic nanophosphors also show promising applications in numerous other fields like optical markers, field emission displays, quantum counters and solar cells; which makes them extremely remarkable for research purpose [5–9]. Hence, in order to reduce the global illumination load on power plants across the world, phosphor-converted white light emitting diodes (PC-WLEDs) have attracted tremendous attention to replace the conventional incandescent and fluorescent lamps in the view points of their long lasting performance, low electric requirements, good reliability, extraordinary luminescence efficiency, fast response and eco-friendly features [10]. Generally, white LEDs are fabricated using a combination of blue InGaN LED chip (λ_{ex} = 450–470 nm) with a coating of Ce^{3+} doped yellow-emitting phosphor material YAG ($Y_3Al_5O_{12}$:Ce^{3+}). However, this leads to a low color rendering index due to insufficient red component for solid state lighting (SSL) [10]. Therefore, an alternative approach for the fabrication of white LEDs involves the coating of ultra-violet (UV) or near ultra-violet (NUV) LED chips (λ_{ex} = 350–420 nm) with tricolor RGB (Red-Green-Blue) phosphor, is of great importance and demands material scientists to invent

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new red or reddish-orange, blue and green phosphors to solve this problem [4,11].

Now, being an essential component in RGB phosphor based WLEDs, Eu^{3+} and Sm^{3+} doped nano-scaled phosphors have been explored extensively due to very sharp spectral bands arising from intra 4*f* transitions (4*f*→ 4*f*) in the emission spectra. This results in high lumen output, less internal scattering, high surface to volume ratio and outstanding luminescence characteristics [12–14]. Hence, the search for a proper host material with enhanced luminescence properties for such type of devices is still a significant issue for material scientists. Moreover, trivalent Sm^{3+} ($4f^5$) is one of the important rare-earth dopant, as it has been well proved to be an excellent activator for various inorganic host lattices to generate orange-red emission for various display techniques and other applications [4,15]. This encouraged the author to explore some samarium doped nanophosphors for white light illumination; and consequently, in the present paper, a reddish-orange nanophosphor $Ba_5Zn_4Y_{8-x}O_{21}$:xSm^{3+} with advanced optical properties as well as high chromatic stability for phosphor based white LEDs has been reported via solution combustion route. In the previous reports of rare-earth doped $Ba_5Zn_4Y_8O_{21}$, Fu and co-workers presented an up-conversion phosphor [16]; while the only down-conversion phosphor involving the structural characteristics and luminescent properties of Eu^{3+} doped $Ba_5Zn_4Y_8O_{21}$ was reported by Dalal and co-workers [17]. A related host $Ba_5Zn_4Gd_8O_{21}$ has also been investigated extensively by Suo et al. and other researchers in recent time [9,18–21]. However, up to now, there is no report on down-conversion $Ba_5Zn_4Y_8O_{21}$:Sm^{3+} nanophosphor by any of the synthesis route; and this is the first report of Sm^{3+} doped $Ba_5Zn_4Y_8O_{21}$ nanophosphor. The reddish-orange emission color of Sm^{3+} activator ions in oxide host lattice due to ${}^4G_{5/2} \rightarrow {}^6H_J$ (J = 5/2, 7/2, 9/2, 11/2) transitions, makes them favourable component for PC-WLEDs [22]. Since, no JCPDS data is available for $Ba_5Zn_4Y_8O_{21}$ host; the author used Rietveld refinement technique to study the effect of doping of Sm^{3+} ions on the crystal structure parameters of $Ba_5Zn_4Y_8O_{21}$ host material [23]. It is well known that host with only bivalent metal ions like Zn^{2+} or Ba^{2+} are perfect candidate for the doping of bivalent lanthanide ions like Eu^{2+}; while host having trivalent metal ions are suitable for trivalent lanthanide doping. This is due to the similarity in oxidation state, which results in minimum defect incorporation and thus imparts maximum luminescence. This makes the yttrium, gadolinium or lanthanum based hosts as the perfect choice for Sm^{3+} doping [24,25]. The X-ray diffraction analysis confirms that $Ba_5Zn_4Y_8O_{21}$ crystallizes in tetragonal phase with *I*4/*m* (87) space group and unit cell dimensions are found to be a = 13.7615 Å, b = 13.7615 Å, c = 5.7052 Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, V = 1080.45 Å^3 with two formula units per unit cell.

Currently, many wet-chemical methods such as sol-gel method [26], hydrothermal synthesis [27] and combustion synthesis [28] are being widely used to synthesize rare earth doped nanocrystals in suitable particle-size range. Compared to other conventional means, we have reported the urea-assisted solution combustion approach for phosphor processing in the present investigation, as it has been well proved to be a fast technique to prepare high purity, single-phased, non-agglomerated nanocrystals of regular morphology and excellent homogeneity at relatively lower temperature in short interval of time [28,29]. Surface morphological properties and particle size were analyzed by transmission electron microscopy (TEM). The optical band-gap of the host was calculated from diffuse reflectance spectra and also checked theoretically along with density of states from density functional theory using CASTEP code [30]. The photoluminescence excitation and emission studies of the synthesized nanophosphors signify their efficient behaviour in RGB based white LEDs. The critical distance for energy transfer was found and used to illustrate the actual mechanism responsible for concentration quenching in nearby Sm^{3+} ions. The detailed study of photoluminescence decay curves gave the radiative lifetime, overall rate of non-radiative relaxation and the quantum efficiency of ${}^4G_{5/2}$ electronic state. Finally, the calculation of CIE color coordinates from emission spectra in MATLAB program revealed the pure reddish-orange emitter, indicating that these nanophosphors find promising applications in phosphor-converted white light emitting diodes (PC-WLEDs) under NUV excitation.

2. Experimental

2.1. Material and synthesis

Sm^{3+} doped $Ba_5Zn_4Y_8O_{21}$ samples with different concentration of samarium ions (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mol % with respect to Y^{3+} ions) were synthesized via solution combustion route [28]. Stoichiometric compositions of high purity (Sigma Aldrich) analytical grade ($Ba(NO_3)_2$), ($Zn(NO_3)_2 \cdot 6H_2O$), ($Y(NO_3)_3 \cdot 6H_2O$), ($Sm(NO_3)_3 \cdot 6H_2O$) and urea (NH_2CONH_2) as a fuel were weighed and dissolved in minimum amount of distilled water in a 400 mL pyrex beaker by continuous stirring the solution to get a homogenous redox mixture. The molar ratio of metal nitrates to organic fuel (O/F) was determined by knowing the total oxidising and reducing valencies of the oxidizer and the fuel, respectively [28]. The mixture was then introduced into a preheated furnace maintained at 500 °C for a short time. The reaction mixture goes through fast dehydration and foaming accompanied by disintegration, releasing large amount of inflammable gaseous products. This exothermic combustion process provides chemical energy for the reaction resulting in the formation of white crystalline product. During the course of reaction, urea was oxidized by nitrate ions and acts as fuel for redox reaction. The basic combustion reaction for $Ba_5Zn_4Sm_{0.12}Y_{7.88}O_{21}$ nanophosphor synthesis may be described as follows:

$$41.667Ba(NO_3)_2 + 33.333Zn(NO_3)_2 \cdot 6H_2O + 65.667Y(NO_3)_3 \cdot 6H_2O + Sm(NO_3)_3 \cdot 6H_2O + 291.667NH_2CONH_2 \rightarrow 8.333Ba_5Zn_4Y_{7.88}Sm_{0.12}O_{21} + 466.667N_2(g) + 1183.333H_2O(g) + 291.667CO_2(g)$$

Finally, the products were taken out of the furnace, cooled to room temperature and ground to powder form in an agate mortar. All the products were then placed into an alumina crucible and sintered at 1000 °C for 3 h, crushed again and reheated for another 6 h at the same temperature to complete the reaction. At last, the white crystalline product obtained, that was used for further characterizations such as powder X-ray diffraction, photoluminescence investigation and diffuse reflectance measurements.

2.2. Materials characterization

In order to analyze the crystal structure parameters and phase purity of $Ba_5Zn_4Y_8O_{21}$:Sm^{3+} samples, X-ray powder diffraction (XRD) measurements were performed carefully on a high resolution Rigaku Ultima-IV X-ray powder diffractometer using Cu Kα irradiation at 40 kV tube voltage and 40 mA tube current supply. The 2θ angular ranges of all the diffraction data sets were recorded from 10° to 80° with scanning speed of 2° min^{-1} and stepping angle was maintained at 0.02°. The qualitative and quantitative phase analysis of the sample (1.5 mol%) was inspected using Rietveld refinement technique by means of GSAS (General Structure Analysis System) program [31,32]. The basis crystallographic information file (CIF) used for Rietveld refinement was setup using $Ba_5R_8Zn_4O_{21}$ (R = trivalent lanthanide) host lattice [23].