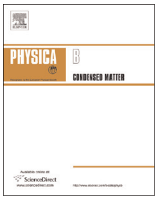
Physica B ■ (■■■■) ■■■–■■■

Contents lists available at ScienceDirect

Physica B

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



White light emitting $LaGdSiO_5:Dy^{3+}$ nanophosphors for solid state lighting applications

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A R T I C L E I N F O

Article history:
Received 12 May 2015
Received in revised form
18 September 2015
Accepted 1 October 2015

Keywords:
Phosphors
Photoluminescence
Oxyorthosilicates
Solid State Lighting

A B S T R A C T

Powdered dysprosium (Dy^{3+}) doped Lanthanum gadolinium oxyorthosilicate ($LaGdSiO_5$) mixed phosphors were synthesized using urea-assisted solution combustion method. The X-ray diffractometer analysis showed that the samples crystalized in the pure monoclinic mixed phase of $LaGdSiO_5$. The crystallite size and the lattice strain calculated from the X-ray diffraction peaks using Williamson–Hall equation varied from 12 nm to 16 nm and 1.6×10^{-2} to 2.43×10^{-2} respectively. The photoluminescence (PL) emission spectra recorded using 425, 454 and 475 nm excitation wavelengths exhibit characteristic similar to the YAG:Ce phosphor pumped InGaN LED system, by absorbing portion of the excitation energy and re-emitting it. The emission spectra were characterized by radiative recombination at 425, 454, 475, 485 and 575 nm depending on the excitation wavelength. These emission line are ascribed to the $f\rightarrow f$ transitions of Dy^{3+}. The peak intensity and hence the color of the emitted visible light were dependent on the concentration of Dy^{3+}. The International Commission on Illumination (CIE) color coordinates of (0.336, 0.313) and (0.359, 0.361) were obtained for Dy^{3+} molar concentration of 0.05 and 3.0 mol% when the emission was monitored using 454 nm and 475 nm respectively. The band gap measured from the reflectance curve using Tauc plot initially decreased with increasing Dy^{3+} concentration, but at higher concentration, it started to increase. These materials were evaluated for solid state lighting application.

1. Introduction

The most important property of any phosphor is its quantum efficiency (i.e. its brightness) which is the ratio of the number of photons that a phosphor absorbs to the number of photons it emits. Self-absorption, band gap, density, thermal and the chemical stability and decay time are other important properties of phosphors. Phosphors are often graded based on these properties with the superior ones having higher quantum efficiency, minimal self-absorption, wide band gap, high density, high thermal and chemical stability and fast decay time [1,2]. Rare-earth oxyorthosilicates (R_2SiO_5, R=La or Gd) crystals have demonstrated outstanding characteristics of good host for various rare-earth ions. For instance, they have shown wide band gap of about 6.0 eV, high quantum efficiency, minimal self-absorption, high density, fast decay time [1], and good thermal and chemical stability [3,4]. Some R_2SiO_5 has shown quantum efficiency twice as that of germanium oxide (BGO) [5], and life time about five times less than BGO [6]. These properties gives R_2SiO_5 the excellent host ability to accommodate many rare-earth ions for various phosphor applications [7–13].

R_2SiO_5 are produced from 1:1 composition of binary rare-earth silicate (R_2O_3–SiO_2) system. They are classified into two monoclinic structure groups (small and large ionic radius rare-earth ions) in accordance with the size of the ionic radius of the rare-earth ion. The small ionic radii rare-earth ions in R_2SiO_5 include all the light rare-earth elements and Tb (La–Tb) while the large ionic radii rare-earth ions in R_2SiO_5 include all the heavy rare-earth elements except Tb (Y, Dy–Lu). The small ionic radius radii rare-earth ions in R_2SiO_5 have monoclinic crystallographic point group with space group $C2/c$ and $B2/b$ belonging respectively to the low ($X1$) and high ($X2$) temperature phases. The large ionic radii rare-earth ions in R_2SiO_5 have monoclinic crystallographic point group with space group $P21/c$ and $12/a$ belonging to the low and high temperature phases respectively. Both La_2Sio_5 and Gd_2SiO_5 belong to the small ionic radii rare-earth ions in R_2SiO_5 crystals and they have two crystallographic sites R1 and R2 coordinated by 7 and 9 oxygen atoms respectively and linked together by tetrahedral SiO^{4-} ions [14–16].

Blue-light excited light emitting diodes (LEDs) have advantages over their UV-light excited counterparts due to the fact that the UV-converted LEDs suffers loss of energy during the conversion of UV-light to white light leading to low luminous efficiency of the LED. This approach also cause the solarization of the resin used for

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http://dx.doi.org/10.1016/j.physb.2015.10.006
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packaging the LED due to the high energy of the UV-light [17]. White light emitting phosphors can be achieved by co-doping a sensitizer and activator into the same host matrix. In this case, the constituents of the white light may be from a single activator at various crystal sites or from different activators [18,19]. Zhang et al. reported white light generated from $NaCaBO_3:Ce^{3+}$, Tb^{3+}, Mn^{2+} single phosphors [20]. Other reports on white light emitting single phosphors by Shaat et al. [21], Lorbeer et al. [22], Guo et al. [23], and Chien-Hao et al. [24]. The major disadvantage of co-doping sensitizer and activator into a single host is the high cost of the these materials, which are required at high concentration to get an efficient result since the distance between the sensitizer and the activator ions are required to be very small (about 1 nm) [25].

To overcome these challenges, a singly doped phosphor, which can generate white light when excited with blue light should be developed. Dy^{3+}-doped matrices can emit blue and yellow light [26] and this has made it one of the choices of an activator for white light emitting phosphors since a co-dopant is not required. The blue emission ($^4F_{9/2}\rightarrow{}^6H_{15/2}$) is a magnetic dipole transition and hardly varies with the crystal field around the Dy^{3+} ions. On the other hand, the yellow emission ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) which is defined as hypersensitive is an electric dipole transition and highly sensitive to the crystal field around Dy^{3+} ions. As a result of the imbalance between the blue and the yellow emission, it is difficult to generate white light from Dy^{3+} doped matrices. Hence the host matrix and the excitation wavelength plays important role in accomplishing this goal. For host matrix without inversion center, Dy^{3+} ions are located in the low symmetry in the host matrix and the yellow emission ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) of Dy^{3+} is stronger than the blue emission ($^4F_{9/2}\rightarrow{}^6H_{15/2}$) [27]. On the other hand, the blue emission can yield stronger emission if the Dy^{3+} ions are doped into a host matrix with inversion center and the Dy^{3+} ions are located in the higher symmetry [28]. Furthermore, when the Dy^{3+} ions are located at or close to the inversion symmetry of the host matrix, both the blue and the yellow emissions of Dy^{3+} yield equivalent emission intensities [29,30]. The excitation wavelength can also influence the emission of Dy^{3+}[31].

Mixing La_2SiO_5 and Gd_2SiO_5 together can leverage the best qualities from these materials. We generated a single host $LaGdSiO_5$ by mixing La_2SiO_5 and Gd_2SiO_5 and doped it with different molar concentrations (x) of Dy^{3+} ions as activator (x=0.05, 0.1, 0.25, 0.75, 1.0, 1.5, 2.0, 3.0 and 5.0). We monitored the photoluminescence (PL) emission with blue light excitation (425, 454 and 474 nm) and part of the incident blue light were absorbed and converted to emission. So, with the combination of the absorbed blue light and the blue emission from Dy^{3+}, we were able to balance the blue and the yellow emission which results in white emission. This is analogous to the InGaN-based YAG:Ce white LED, where InGaN LED is used to excite YAG:Ce yellow emitting phosphor and a portion of the blue light from InGaN LED is absorbed and re-emitted and combination of the blue emission from the InGaN LED and the yellow emission from YAG:Ce can yield white light [32].

2. Experimental

A detailed procedure for the samples preparation was discussed elsewhere [33]. The structure was analyzed using (i) a Bruker D8 Advanced X-ray diffraction diffractometer (XRD) and (ii) a Nicolet 6700 Fourier transform infrared (FTIR) spectroscope. The ultraviolet visible (UV–vis) spectrum was recorded using a Lambda 950 UV–vis spectrometer, while the PL spectra were measured using a Cary Eclipse fluorescence spectrophotometer.

3. Results and discussion

The XRD pattern of the highest and the least concentration of Dy^{3+} (i.e. x=0.05 and x=5.0 mol%) in the $LaGdSiO_5$ matrix were measured to monitor the effect of Dy^{3+} concentration on the structure of the host matrix. As can be seen from Fig. 1, the presence of Dy^{3+} in the host matrix has no significant effect on its structure. This can be as a result of the similarities in the ionic radii of the two host materials and that of the dopant. La^{3+} has ionic radii of 0.110 nm and 0.1216 nm in its seven and nine-fold co-ordinated sites respectively [34], while Gd^{3+} has atomic radii of 0.10 nm and 0.1107 nm in its seven and nine-fold coordinated sites respectively [35,36]. When comparing the atomic radii of these elements to that of Dy^{3+} which are 0.1052 nm and 0.1167 nm in its six and eight-fold coordinated sites [34], it can be seen that they are quite similar in size, and as such Dy^{3+} ions can easily replace any of the two ions without causing any significant effect on the main structure [37]. The XRD patterns match with the standard monoclinic structures of La_2SiO_5 and Gd_2SiO_5 referenced in JCDPS file no: 40–0234 and 74–1795 respectively. The crystallographic planes indicated with the symbol "*" are from La_2SiO_5, while those indicated with "◆"are from Gd_2SiO_5. The average crystallite size (L) and the lattice train (ε) were calculated using the Williamson–Hall equation [38,39] given by Eq. (1).

$$\beta_{hkl}\cos\theta = 4\varepsilon\sin\theta + \frac{K\lambda}{L} \tag{1}$$

where β_{hkl} is the peak width at half maximum of the diffraction peaks, θ is the Bragg angle, λ is the X-ray wavelength in nanometer (nm) and K is a constant usually taken as 0.9 or 0.89. The estimated crystallite sizes and the lattice strains are shown in Table 1.

The stretching mode frequencies of our nanophosphors were determined using Fourier transformed infrared (FTIR) spectroscopy. The FTIR result obtained from $LaGdSiO_5:Dy^{3+}$ 1.0 mol% is shown in Fig. 2. The absorption peak observed around 3605 cm^{-1} have been assigned to the stretching mode of the OH groups, whereas the peak around 665, 880 and 1100 cm^{-1} are the characteristics of Si–O–Si group [40,41]. The peak observed around 455 cm^{-1} is associated with La–OH and Gd–OH bending modes in $La(OH)_3$ and $Gd(OH)_3$ [40,42–45]. The bands at 1380, 1500 and 1655 cm^{-1} are assigned to the bending mode of water, whereas those at 3120 and 3430 cm^{-1} are assigned to the stretching mode of water [40,46,47].

UV–vis reflectance measurement was performed on

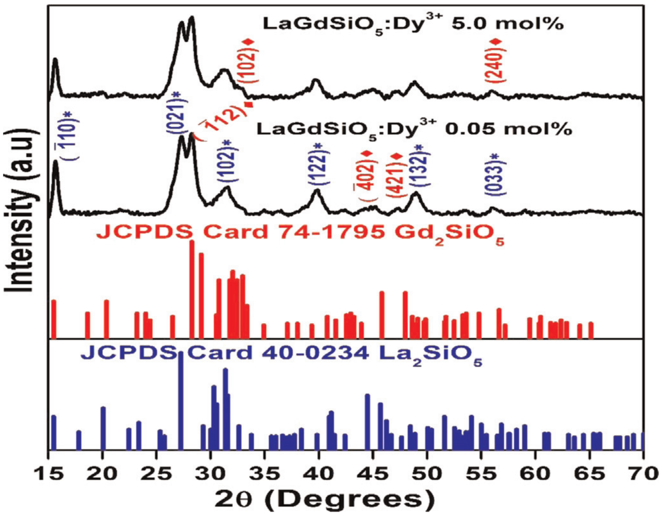

Fig. 1. XRD patterns of $LaGdSiO_5:Dy^{3+}$ $x$mol% (x=0.05 and 5.0) and the standards of La_2SiO_5 and Gd_2SiO_5.

Please cite this article as: S.N. Ogugua, et al., Physica B (2015), http://dx.doi.org/10.1016/j.physb.2015.10.006