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Europium-activated barium/strontium silicates for near-UV light emitting diode applications

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ABSTRACT

This paper reports on the luminescence properties of submicron-sized green-yellow emitting $(Ba_{1-x}Sr_xEu_{0.03})_2SiO_4$ $(0 \le x \le 1)$ phosphors. These phosphors were prepared by a modified sol–gel/Pechini method. The X-ray diffraction analysis shows that the single phase products are obtained. The particle size - ranges from 200 to 500 nm with a spherical or needlelike shape depending on x. These phosphors show strong absorption in the near UV range and the photoluminescence emission spectra consist of a strong broad green-yellow band centered between 512 and 570 nm, depending on x. Furthermore, the phosphors have high quantum efficiencies: 94% for $x=0$ and 85% for $x=0.25$. The emission lifetime at 400 K is 97% of that at 40 K, demonstrating good thermal stability.

1. Introduction

White light sources based on light-emitting diodes (LEDs) are the next generation lighting source because of their outstanding properties, such as high efficiency, longer life and reliability and a low temperature of performance [1–3]. Blue LEDs with $Y_3Al_5O_{12}:Ce^{3+}$ yellow-emitting phosphors are now commercially used as light sources to generate white light. Recently, white LEDs in which a near UV-LED is combined with blue, green- and red-emitting phosphors have been investigated extensively due to less current droop of the LED and better control over color rendering index and color temperature through manipulation of phosphor blends [4–6]. These phosphors require strong absorption in the near-UV range, which can be obtained from dipole-allowed 4f–5d transition in rare earth activated ions [7,8] such as Ce^{3+} and Eu^{2+} in a suitable host.

For the near UV-LED approach, the broad green-yellow emitting $(Sr,Ba)_2SiO_4:Eu^{2+}$ phosphors have been studied [9–14]. However, despite these efforts, superior luminescence properties for LED application have not been fully realized. Furthermore, the powders were mostly prepared by solid-state reaction resulting in micron-sized powders which have higher scattering loss that reduces the light extraction efficiency.

In this work, luminescence properties of sub-micron sized $(Ba_{1-x}Sr_xEu_{0.03})_2SiO_4$ phosphors prepared by the sol–gel/Pechini method are presented. A 3 at% Eu^{2+} concentration that substitutes for Ba^{2+} or Sr^{2+} was selected because it was previously found to have the highest emission intensity and quantum efficiency [15]. The effects of x, crystal structure and temperature dependence on luminescence properties were examined.

2. Experimental

First, tetra-ethoxysilane (TEOS, 99.9%, Sigma Aldrich) (2.18 ml) was added to ethanol (20 ml) with several drops of nitric acid (68–70%, EM Science) and water. The resultant solution was stirred for 30 min. Next, $Sr(NO_3)_2$ (99.9%, Sigma Aldrich) and $Ba(NO_3)_2$ (99.999%, Alfa Aesar) and Eu_2O_3 (99.999%, Alfa Aesar) in the desired molar ratios were dissolved in a dilute nitric acid solution. Note that $Ba(NO_3)_2$ of high purity (above 99.99%) is required for dissolution to be complete in water or nitric acid solutions. After the solution became transparent, the required amount of silica sol was added to the mixture under stirring. Subsequently, 4.2 g citric acid ($C_6H_8O_7 \cdot H_2O$, EMD), which acted as a chelating agent for the metal ions, and 2.23 ml ethylene glycol (C_2H_6OH, Fischer Scientific) were introduced (molar ratio=1:1:2). Then, 2.5 g polyethylene glycol (PEG, $(C_2H_4O)_nH_2O$,

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molecular weight=20,000, Sigma Aldrich), used as a cross-linking agent, was added to the aqueous solution. The mixture was well stirred to achieve uniformity and was then placed in a water-bath at 80 °C to warm overnight so that the solution would hydrolyze into a sol and then into a gel. The gel was heated to 1000 °C for 1 h in air to remove the carbon and organic material. Next the gel was calcined at 1200 °C for 10 h in a slightly reducing atmosphere (a mixture of 5% H_2 and 95% N_2).

3. Characterization

The particle morphology and size were measured using a field emission scanning electron microscope (FESEM, XL30, Philips). The crystalline phases of the annealed powders were identified by X-ray diffraction (XRD) and the peak and phase analysis were identified by an XRD analysis program (JADE, Materials Data, Inc.). Photoluminescence (PL) measurements were taken using a Jobin-Yvon Triax 180 monochromator and SpectrumOne charge-coupled device detection system, using a 450 W Xe lamp as the excitation source. The low temperature measurements were preformed on a Jobin-Yvon Fluorolog-3 system with a 450 W Xe excitation lamp. A cryostat was mounted in the sample chamber of the Fluorolog system and liquid nitrogen was used to cool the sample. Quantum efficiency (QE) measurements were made using a 400 nm laser diode as the excitation source. Powdered phosphor samples were dispersed in a silicone gel and cured. The samples were then placed in a 25.5 cm sphere and three measurements were taken following the method outlined in Ref. [16].

4. Results and discussion

Ba_2SiO_4 has an orthorhombic structure having P_{mcn} (space group #62) and Sr_2SiO_4 has two crystalline structures, which are the high temperature α-phase that crystallizes in the orthorhombic space group, P_{mab} (space group #62) and the low temperature β-phase with a monoclinic space group $P_{21/c}$ (space group # 14). The transformation temperature is ~85 °C [17–19]. Both of the phases can coexist, as the α→β phase transition temperature is low and the phase transformation is completed by the rearrangement of short-range order without breaking of ionic bonds [17,18]. Furthermore, Sr_2SiO_4 and Ba_2SiO_4 can form a continuous solid solution [14]. The XRD patterns of the $(Ba_{1-x}Sr_xEu_{0.03})_2SiO_4$ (x=0, 0.5, 0.75, 1) powders are shown in Fig. 1. For x=0, 0.5 and 0.75, the powders show the single α-phase (JCPDS 39-1256). The XRD patterns are shifted to higher angles at larger x because of the substitution by smaller cation ($r_{Sr} < r_{Ba}$). The distinguishing peaks for the β-phase (JCPDS 38-0271), which are near 2θ=27.7° and 32.4°, are not present, indicating that single α-phase was obtained. For Sr_2SiO_4, the α- and β-phases coexist and the amount of β-phase is approximately 40%, as determined by the XRD program (JADE). This mixture is attributed to the sluggish α→β transformation that was incomplete after sintering.

SEM micrographs of $(Ba_{1-x}Sr_xEu_{0.03})_2SiO_4$ (x=0, 0.25, 1) are shown in Fig. 2(a)–(c), respectively. As x increased, the particle shape transformed from spherical to needlelike. For Ba_2SiO_4 (x=0), the particle size is near 500 nm and is spherical, as shown in Fig. 2(a). With an addition of Sr to Ba_2SiO_4 structure, needlelike particles appeared and both spherical and needlelike shapes are observed at x=0.25 as shown in Fig. 2(b). The needles are ~200 nm in length and ~70 nm wide and the spherical particles are 100–200 nm in diameter, although the powders are agglomerated due to high temperature annealing (1200 °C). For Sr_2SiO_4 (x=1) in Fig. 2(c), the shape is mainly needlelike. The needles are 0.5–1.5 μm in length and ~60–70 nm wide; the aspect ratio is 5–20.

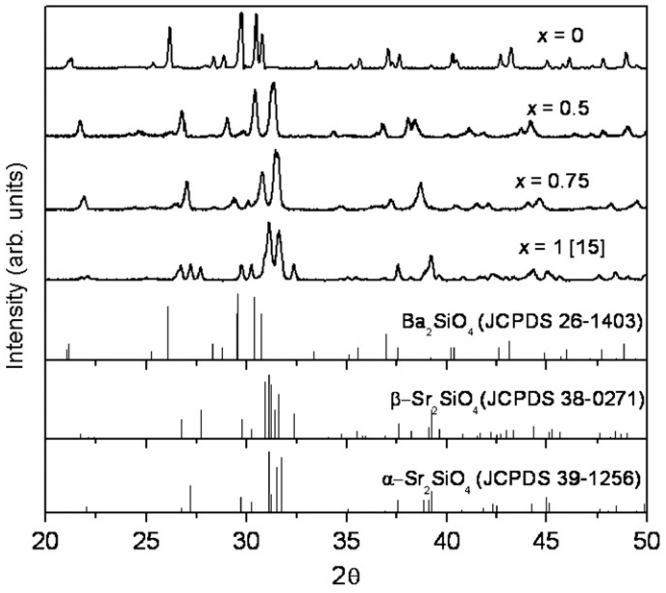

Fig. 1. XRD patterns of $(Ba_{1-x}Sr_xEu_{0.03})_2SiO_4$ (x=0, 0.5, 0.75, 1) phosphors. The pattern at x=1 is from Ref. [15].

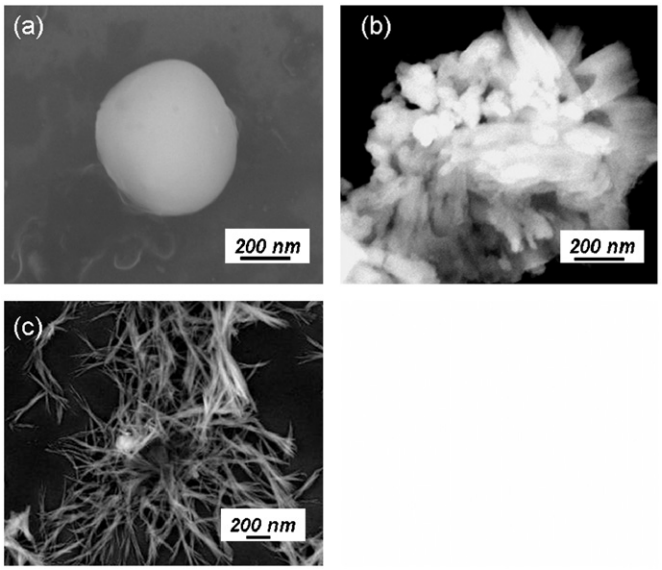

Fig. 2. SEM micrographs of $(Ba_{1-x}Sr_xEu_{0.03})_2SiO_4$ at (a) x=0, (b) x=0.25 and (c) x=1.

Fig. 3(a) shows the PL emission and excitation and reflection spectra of $(Ba_{0.97}Eu_{0.03})_2SiO_4$. The excitation wavelength for PL emission spectra is 380 nm. The PL spectrum consists of a green band centered around 512 nm and the excitation spectrum shows the broad band centered around 360 nm. In addition, a strong absorption in the UV to near UV spectral region is observed, which is above 80% as shown in Fig. 3(a). Fig. 3(b) presents PL emission spectra of $(Ba_{1-x}Sr_xEu_{0.03})_2SiO_4$ (x=0, 0.25, 1) under 380 nm excitation. The emission band center changes from 512 to 565 nm depending on x and is attributed to the allowed $4f^65d \rightarrow 4f^7$ transition [7,8]. Quantum efficiencies of these phosphors are 94% at x=0, 85% at x=0.25 and 75% at x=1 under 400 nm excitation. These high quantum efficiencies indicate that $(Ba_{1-x}Sr_xEu_{0.03})_2SiO_4$ phosphors are very promising green-yellow emitters for application in white-emitting UV-LEDs. The emission peak position as a function of x is shown in Fig. 3(c). The emission peak is observed to be dependent on x. The peak position