Particle morphology and luminescence properties of green emitting $\text{Ba}_2\text{SiO}_4\text{:Eu}^{2+}$ through hydrothermal reaction route

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Abstract

Green-emitting $(\text{Ba}_{0.97}\text{Eu}_{0.03})_2\text{SiO}_4$ phosphors of different morphologies and particle sizes were prepared by varying the conditions of hydrothermal synthesis. Single-phase powders were obtained at 250°C and autogeneous pressure followed by post annealing at 900°C for 1h. The ethanol/water ratio, hydrothermal reaction time, NaOH/Ba²⁺ ratio and silicon precursor strongly influence the particle size and morphology. The particle size, having spherical or needlelike shapes, ranges from 200 nm to 3 μm, depending on those parameters. These phosphors show strong absorption in the near UV range and the photoluminescence emission spectra consist of a strong broad green band centered around 514 nm. Furthermore, the emission intensities are dependent on the ethanol to water ratio, and 55-79% of that of micron-sized powders with a quantum efficiency of 94%.

Keywords: Ba_2SiO_4 , phosphor, solid-state lighting, hydrothermal synthesis

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Introduction

Solid-state lighting (SSL) as white light sources based on light-emitting diodes (LEDs) are considered as next generation lighting because of their outstanding properties of high efficiency, longer life and reliability, and low temperature performance [1-3]. A common SSL technology for generating white light involves using a blue-emitting InGaN LED with a yellow-emitting phosphor, $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ and another red-emitting phosphor for color correction [4,5]. White-emitting LEDs in which a near UV-LED is combined with red, green, and blue phosphors are being investigated due to less current droop of the LEDs and a better control over the color-rendering index and color temperature through the manipulation of phosphor blends [6-8]. For this near UV-LED approach, the broad green-yellow emitting $(\text{Ba},\text{Sr})_2\text{SiO}_4:\text{Eu}^{2+}$ phosphor has been shown to have high quantum efficiency [9-12]. Previous work has shown that the quantum efficiencies of micron-sized powders under 400 nm excitation are ~95% and these phosphors show good thermal stability up to 150°C [13,14]. However, the most reported preparation methods of these phosphors are through traditional solid-state reaction methods that involve a high temperature annealing step (>1200°C) [10-12,15-18]. Recently, solution-based chemical synthesis techniques have been used due to their advantages of low synthesis temperature and phase homogeneity and smaller particle size of the powders. Among these methods, the hydrothermal method is a promising solution-based chemical approach with good control over the particles size and their distribution, phase homogeneity, and morphology [19-22].

Hydrothermal synthesis is a method for crystallizing ceramic powders directly from an

aqueous solution at elevated temperature ($T > 25^{\circ}\text{C}$) and pressure ($P > 100\text{ kPa}$) [22]. The reaction occurs in a sealed vessel and occurs over a prolonged time ($\sim 24\text{ h}$). There are very few reports on the synthesis of Eu^{2+} activated silicate phosphors by the hydrothermal method. Lu et al. [23] reported various morphologies (“hedgehog-like”, spherical, porous irregular, and worm-like) of $\text{Ba}_{1-x}\text{Si}_x\text{O}_4:\text{Eu}^{2+}$ ($x = 0.33, 0.5, 0.6$) were found, depending on the value of x . The ratio of Sr/Si and the hydrothermal reaction time significantly affected the powder morphology of $\text{SrSiO}_3:\text{Eu}^{3+}$ [24]. These results demonstrated that unique powder morphologies could be obtained by hydrothermal synthesis. Although some progress has been made to control the morphology of silicate phosphors by hydrothermal synthesis, there are no reports, to the best of our knowledge, on variation of luminescence properties (photoluminescence (PL) emission and quantum efficiency) with the synthetic parameters.

In this work, for the first time the luminescence properties of $(\text{Ba}_{0.97}\text{Eu}_{0.03})_2\text{SiO}_4$ phosphors prepared by the hydrothermal method are presented. The morphology of the powders depending on the ratio of ethanol and water, Si precursor, the amount of precipitation agent and reaction time were investigated and the PL emission intensities are compared.

Experimental

First, tetra-ethoxysilane (TEOS, 99.9%, Sigma Aldrich) (1.09 ml) was added to ethanol (10-40 ml) with a few drops of nitric acid (68 – 70%, EM Science). The resultant solution was stirred for 15 min. Next, $\text{Ba}(\text{NO}_3)_2$ (99.999%, Alfa Aesar) and Eu_2O_3 (99.999%, Alfa Aesar) in the desired molar ratios were dissolved in 20 ml of a dilute nitric acid aqueous solution.

Note that $\text{Ba}(\text{NO}_3)_2$ of high purity (> 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 in ethanol was added to the mixture under stirring. One sample was prepared using colloidal silica (~20 nm diameter 40% in water, Alfa Aesar) as the Si source. Subsequently, 20 ml of 1M NaOH solution as a precipitating agent was added very slowly (~1 ml/min) to that mixture under stirring (molar ratio of Ba/Si/NaOH=2:1:4.6-6). Then, the mixture was transferred into a 45 mL Teflon®-lined stainless steel autoclave (Model: Parr 4744), which was then sealed and kept at 250 °C. After 12 or 24 h, the resulting white product was centrifuged and washed with ethanol several times, and dried at 60 °C for 3 h. The $(\text{Ba}_{0.97}\text{Eu}_{0.03})_2\text{SiO}_4$ phosphors were obtained by annealing the dried samples in a weak reducing atmosphere (a mixture of 5% H_2 and 95% N_2) at 900 °C for 1 h. This annealing temperature was chosen as it was found this was the minimum temperature required to fully crystallize $(\text{Ba}_{0.97}\text{Eu}_{0.03})_2\text{SiO}_4$ synthesized by a co-precipitation method [25].

The crystalline phases of the annealed powders were identified by X-ray diffraction (XRD). The particle morphology and size were measured using a field emission scanning electron microscope (FESEM, XL30, Philips). 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.

Results and discussion

XRD patterns of the $(\text{Ba}_{0.97}\text{Eu}_{0.03})_2\text{SiO}_4$ powders depending on post-annealing temperature, hydrothermal reaction time and ethanol to water ratio (EtOH/water) are shown in Fig. 1(a)-(c), respectively. The as-synthesized sample (12 h) does not show the presence of

Ba₂SiO₄, as shown in Fig. 1(a), but contains the unreacted precursors. However, after annealing at 900 °C for 1 h in a reducing atmosphere, the resultant powders are single phase BaSiO₄ (space group *Pmcm*, lattice constants $a = 0.5818$ nm, $b = 1.0231$ nm, $c = 0.7519$ nm [17]; JCPDS 26-1403), as shown in Fig. 1(a). It should be noted that the annealing temperature required to obtain single phase powders is significantly lower than that required by the traditional solid-state reaction method (~1200°C).

The crystalline phase of the powders is dependent on the hydrothermal reaction time. The powders prepared by hydrothermal reaction for 12 h contained, in addition to Ba₂SiO₄, SiO₂ and BaSiO₃. In contrast, the powders with 24 h reaction time are single phase Ba₂SiO₄, as shown in Fig. 1(b). Furthermore, the phases that develop are dependent on the amount of ethanol in the solution, as shown in Fig. 1(c). Compared to the samples prepared with lower ethanol/water ratios (EtOH/H₂O = 0.25 and 0.5), with a higher ratio (EtOH/H₂O = 1.0) BaSiO₃ and SiO₂ are present, as shown in Fig. 1(c). Specifically, there are distinctive peaks for $2\theta \sim 27^\circ$ and 32° for the sample of EtOH/H₂O = 1, ascribed to the presence of BaSiO₃ (orthorhombic with space group of P212121 (#19), JCPDS 70-2112) whereas these peaks are not clearly shown in the XRD patterns of the sample of EtOH/H₂O = 0.25 and 0.5. According to the phase diagram for BaO•SiO₂, the line compound Ba₂SiO₄, is flanked by BaO and BaSiO₃ [15]. The presence of incompletely reacted intermediate compounds implies that the solubility of the precursors is apparently too low for complete dissolution to occur.

SEM micrographs of (Ba_{0.97}Eu_{0.03})₂SiO₄ depending on the ratio of ethanol and water and hydrothermal reaction time are shown in Fig. 2(a)-(d). All samples were post-annealed at 900 °C for 1 h. As the EtOH/water ratio increased, the particle diameter increased from 300 nm to 3 μm. For EtOH/water = 0.25, the single-phase particle diameters are ~350 nm and

the shape is spherical, as shown in Fig. 2(a). For EtOH/water = 0.5, the particles are also spherical and uniform with diameters of ~ 500 nm consisting of both Ba_2SiO_4 and a minor amount of BaSiO_3 , as shown in Fig. 2(b). For EtOH/water = 1, the particles are severely agglomerated and the aggregate diameter is over $3\text{ }\mu\text{m}$, as shown in Fig. 2(c). The particle size dependence on the EtOH/water may be attributed to the difference of vapor pressure of the solvent in the autoclave. As the EtOH/water ratio increases, the vapor pressure of the solution during hydrothermal reaction increases. Therefore, the pressure on the precursor is higher at larger ethanol concentrations. This causes the particles to agglomerate at larger concentrations of ethanol. A similar explanation has also been proposed to interpret the surface area and agglomeration of TiO_2 nanoparticles prepared by hydrothermal synthesis, wherein the surface area of TiO_2 increased with increasing EtOH/water ratio, resulting in aggregation of TiO_2 particles [26].

The particle morphology is also dependent on the hydrothermal reaction time. Compared to the samples prepared for 24 h in Fig. 2(a)-(c), the morphology of the 12 h reacted samples is needlelike as shown in Fig. 2(d). The needles are $\sim 1.5\text{ }\mu\text{m}$ in length and ~ 150 nm wide (aspect ratio = 10). It appears at shorter reaction times under hydrothermal synthesis conditions, there is an initial preferential growth direction resulting in anisotropic particle morphologies. As the reaction proceeds, the particles subsequently have enough time to spheroidize to minimize total surface energy.

SEM micrographs of the powders as a function of the concentration of the precipitating agent (NaOH), the NaOH/ Ba^{2+} ratio, and different Si precursor are shown in Fig. 4(a)-(d). All samples were reacted for 24 h with EtOH/water = 0.5 and post-annealed at $900\text{ }^\circ\text{C}$ for 1 h, resulting in the single phase $(\text{Ba}_{0.97}\text{Eu}_{0.03})_2\text{SiO}_4$. As the NaOH/ Ba^{2+} ratio increased from

2.3 to 3, the particle size increased from 200 nm to 800 nm. For $\text{NaOH}/\text{Ba}^{2+} = 2.3$, the particle size is $\sim 200\text{-}300$ nm with a spherical shape, but the particles are agglomerated, as shown in Fig. 3(a). For $\text{NaOH}/\text{Ba}^{2+} = 2.8$, ellipsoidal (major axis: 500-600 nm, minor axis: 300-400 nm) and needle-like (1.5 μm in length and 70 nm in diameter) particle morphologies coexist, as shown in Fig. 3(b). At $\text{NaOH}/\text{Ba}^{2+} = 3$, the particles are agglomerated with particle diameters between 600-800 nm, as shown in Fig. 3(c). The particle size dependence on $\text{NaOH}/\text{Ba}^{2+}$ may be attributed to the reaction rate. As the $\text{NaOH}/\text{Ba}^{2+}$ ratio increases, the reaction rate increases, which allows the particles to grow rapidly in a preferential direction and then subsequently to become agglomerated.

The morphology and size of the powders prepared with colloidal silica as a Si precursor is shown in Fig. 3(d). Needle-like particles are observed, similar to those with a higher $\text{NaOH}/\text{Ba}^{2+}$ ratio prepared with TEOS (Fig. 3(b)), but the quantity and size of the needle-like particles having lengths of 3-5 μm and widths of ~ 150 nm (aspect ratio 30-50) are larger. This indicates the growth of the needles was rapid, most likely due to preferred anisotropic nucleation on the surface of the spherically-shaped silica particles.

Fig. 4 shows the PL emission spectra of $(\text{Ba}_{0.97}\text{Eu}_{0.03})_2\text{SiO}_4$ depending on the ratio of ethanol to water ($\text{EtOH}/\text{H}_2\text{O} = 0.25\text{-}1$). The excitation spectrum consists of a broad band between 310-430 nm [27]. The excitation wavelength chosen for the PL emission spectra was 380 nm. The PL spectrum consists of a green band centered around 514 nm. The emission band center is attributed to the allowed $4f^65d \rightarrow 4f^7$ transition of Eu^{2+} [28,29]. It is noted that there is no noticeable sharp line emission attributable to the $4f\text{-}4f$ transition for Eu^{3+} in the spectra, indicating the valance of Eu in the Ba_2SiO_4 structure has completely transformed from Eu^{3+} to Eu^{2+} during post-synthesis annealing. For a $\text{EtOH}/\text{H}_2\text{O} =$ ratio of 1

(Ba₂SiO₄+BaSiO₃ mixture), the emission band center is red-shifted and broader. This is due to the BaSiO₃:Eu²⁺ emission, which has an emission centered at ~560 nm [30,31]. The emission intensity increased with increasing the EtOH/H₂O ratio, which can be attributed to the increasing particle size (Fig. 2(a)-(c)). The relative intensities compared to powders with 94% quantum efficiency prepared by sol-gel/Pechini method [14] are 55%, 66%, and 79% at ratios of 0.25, 0.5 and 1, respectively. In general, the quantum efficiency can be roughly estimated by the ratio of the numbers of photon out (related to emission intensity) to the numbers of photon in (related to absorption of the light). Assuming the absorption of each sample is comparable despite of different size of the powders, the rough estimated quantum efficiency of the samples is 52%, 62% and 74% for EtOH = 0.25, 0.5 and 1, respectively.

Conclusions

Reported for the first time, the green emitting phosphor, (Ba_{0.97}Eu_{0.03})₂SiO₄ with sub-micron particle sizes were prepared by hydrothermal synthesis. Post-synthesis annealing at 900 °C results in single phase powders with a spherical morphology. This annealing temperature is significantly lower than that required for the powders prepared by solid-state reaction. By controlling the ratio of ethanol to water, reaction time, the amount of precipitating agent and silicon precursor, different size particles can be obtained which have a spherical or needle-like shape. These phosphors show strong green emission band centered around 514 nm under 380 nm excitation. The emission intensities are still 55-79% of the micron-sized powders that have a quantum efficiency of 94%. More optimization is needed to bring the efficiency to the level of the micron-sized particles

prepared by solid-state methods.

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List of Figure Captions

- 1 X-ray diffraction patterns of hydrothermally synthesized $(\text{Ba}_{0.97}\text{Eu}_{0.03})_2\text{SiO}_4$ phosphors: (a) as-synthesized (bottom) and post-annealed at 900°C for 1 h (top), (b) 12 (bottom) or 24 h (top) hydrothermal reaction time (post-annealed at 900°C for 1 h) and (c) ethanol to water ratio (post-annealed at 900°C for 1 h).
- 2 SEM micrographs of $(\text{Ba}_{0.97}\text{Eu}_{0.03})_2\text{SiO}_4$ prepared with the ratio of ethanol and water of (a) 0.25, (b) 0.5 and (c) 1 for 24 h hydrothermal reaction time. (d) ethanol to water ratio = 0.5 for 12 h reaction time. All samples are post-annealed at 900 °C for 1 h.
- 3 SEM micrographs of $(\text{Ba}_{0.97}\text{Eu}_{0.03})_2\text{SiO}_4$ prepared with a ratio of NaOH to Ba^{2+} of (a) 2.3, (b) 2.8 and (c) 3 with an ethanol to water ratio = 0.25. (d) $\text{NaOH}/\text{Ba}^{2+} = 2.3$ prepared with colloidal silica as a precursor of Si. All the samples of hydrothermal reaction time are 24 h and post-annealed at 900 °C for 1 h.
- 4 Photoluminescence emission spectra of $(\text{Ba}_{0.97}\text{Eu}_{0.03})_2\text{SiO}_4$ under 380 nm excitation showing the dependence on the ratio of ethanol to water. The photoluminescence emission intensity of a sample prepared by sol gel synthesis is shown for comparison [14].

Figure 1

Figure 1. X-ray diffraction patterns of hydrothermally synthesized $(\text{Ba}_{0.97}\text{Eu}_{0.03})_2\text{SiO}_4$ phosphors: (a) as-synthesized (bottom) and post-annealed at 900°C for 1 h (top), (b) 12 (bottom) or 24 h (top) hydrothermal reaction time (post-annealed at 900°C for 1 h) and (c) ethanol to water ratio (post-annealed at 900°C for 1 h).

Figure 2

Figure 2. SEM micrographs of $(\text{Ba}_{0.97}\text{Eu}_{0.03})_2\text{SiO}_4$ prepared with the ratio of ethanol and water of (a) 0.25, (b) 0.5 and (c) 1 for 24 h hydrothermal reaction time. (d) ethanol to water ratio = 0.5 for 12h reaction time. All samples are post-annealed at 900°C for 1h.

Figure 3

Figure 3. SEM micrographs of $(\text{Ba}_{0.97}\text{Eu}_{0.03})_2\text{SiO}_4$ prepared with the ratio of NaOH to Ba^{2+} of (a) 2.3, (b) 2.8 and (c) 3 with the ethanol to water ratio = 0.25. (d) NaOH/ Ba^{2+} = 2.3 prepared with colloidal silica as a precursor of Si. All the samples of hydrothermal reaction time are 24 h and post-annealed at 900°C for 1h.

Figure 4

Figure 4. Photoluminescence emission spectra of $(\text{Ba}_{0.97}\text{Eu}_{0.03})_2\text{SiO}_4$ under 380 nm excitation showing the dependence on the ratio of ethanol to water. The photoluminescence emission intensity of a sample prepared by sol gel synthesis is shown for comparison [14].