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Bi^{3+}, Eu^{3+}-doped $Ba_9Y_2Si_6O_{24}$ phosphors based on the site-selected substitution

Heejun Yun, Sung-Hoon Kim, Sangmoon Park*

Center for Green Fusion Technology and Department of Engineering in Energy & Applied Chemistry, Silla University, Busan, 46958, Republic of Korea

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Luminescent materials having the composition of $Ba_{9\text{-}3(m+n)/2}Bi_mEu_nY_2Si_6O_{24}$ and $Ba_9Y_{2\text{-}m\text{-}n}Bi_mEu_nSi_6O_{24}$ (m = 0.001–0.1, n = 0–0.1) were prepared using a solid-state reaction method in air. The X-ray diffraction patterns of the resulting phosphors were analyzed and the peak positions were indexed. The excitation and emission spectra of the phosphors were investigated using photoluminescence spectroscopy. Critical emission quenching was observed in $Ba_9Y_2Si_6O_{24}$ as a function of the Bi^{3+} content at relatively low concentrations of the activators; furthermore, the quantum efficiency, critical distance, and energy transfer mechanism of Bi^{3+}-doped $Ba_9Y_2Si_6O_{24}$ phosphors based on site-selected substitution were investigated. The dependence of the luminescence intensity of the Eu^{3+} co–doped (n = 0–0.1) host lattices on the Bi^{3+} content (m = 0.025) in $Ba_{9\text{-}3(m+n)/2}Bi_mEu_nY_2Si_6O_{24}$ and $Ba_9Y_{2\text{-}m\text{-}n}Bi_mEu_nSi_6O_{24}$ phosphors was also studied. After the substitution of Eu^{3+} ions for Ba^{2+} or Y^{3+} ions in the Bi^{3+}-doped $Ba_9Y_2Si_6O_{24}$ lattice, we obtained emission spectra of the samples upon excitation with 332 and 373 nm radiations. Co-doping of Eu^{3+} into the Bi^{3+}–doped host structure enabled the effective energy transfer from Bi^{3+} to Eu^{3+} on excitation with 332 nm radiation, and these mechanisms are discussed in this paper. The desired Commission Internationale de l'Eclairage values, including emissions in blue, green, white, and orange wavelength regions, were realized with the phosphors.

1. Introduction

Phosphor-converted white light-emitting diodes (LEDs) are commonly used as solid-state light sources in various applications such as lamps, automobiles, imaging, agriculture, and medicine [1,2]. Typically, such LEDs have phosphors containing rare-earth Ce^{3+} or Eu^{2+} activators with a blue LED chip or cooperative phosphors containing Ce^{3+}-Mn^{2+} or Eu^{2+}-Mn^{2+} with near-ultraviolet (NUV) excitation [3–6]. The Ce^{3+} and Eu^{2+} activators of the LED phosphors typically show highly efficient and broad band emission because of f–d transitions occurring in them. Moreover, the broad band emission due to d–d transitions of Mn^{2+} ions can be increased through energy transfer in host lattices by co-doping with a Ce^{3+} or Eu^{2+} sensitizer. In addition, Tl^{+}-like ions, along with Bi^{3+}, Sn^{2+}, Sb^{3+}, and Pb^{2+} ions, can be used as localized luminescent centers that show broad band emission in host structures due to s–p transitions [1,7]. The ground and the excited states of the $6s^2$ and 6s6p configurations of Bi^{3+} ions in the host lattice have $^1S_0$ and triplet ^3P_J (J = 0, 1, 2) transitions, respectively. Furthermore, while the $^3P_1$ or $^1P_1$ excited states may exist via spin-orbital coupling, the $^1S_0 \rightarrow {}^3P_0$ and $^1S_0 \rightarrow {}^3P_2$ transitions are cannot [7,8]. Bi^{3+} activators act as luminescent centers in the host lattices that depend on the coordination number, covalence, bond volume polarizability, and the current charge [9–12]. The emission of Bi^{3+} ions in the blue-to-green wavelength region of the spectrum is a result of split energy levels in a different site symmetry of host structures [12–14]. The larger Stokes shift of Bi^{3+} emission occurred when Bi^{3+} ions exist in C_2 asymmetry in the Y_2O_3 host lattice, which has C_2 and S_6 symmetry. In host lattices such as $Sr_2Y_8(SiO_4)_6O_2$ and Y_2SiO_5, the larger Stokes shift of Bi^{3+} emission occurred when Bi^{3+} ions occupied the lower-coordination numbered Y^{3+} sites, which exhibit stronger crystal field interactions [12–15]. Bi^{3+} ions also play the role of sensitizers in various luminescent hosts, and transfer energy to rare-earth activators such as Eu^{3+} or Sm^{3+} ions, which can enhance the red light emission with tunable emission wavelength; such emissions are suitable for applications involving a high color rendering index [12,14,16–20].

The $Ba_9Y(Sc)_2Si_6O_{24}$ host structure has a trigonal crystal structure with an R-3H space group as shown in Fig. 1. It contains three

* Corresponding author.
E-mail address: spark@silla.ac.kr (S. Park).

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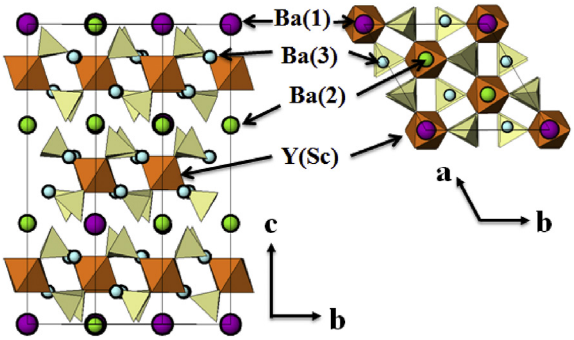

Fig. 1. The structure of $Ba_9Y(Sc)_2Si_6O_{24}$ host lattice.

9-, 10-, and 12-fold Ba^{2+} ions, octahedrally coordinated $Y^{3+}(Sc^{3+})$ ions, and a tetrahedrally coordinated Si^{4+} ions. Broad-band-emitting phosphors of Ce^{3+}, Ce^{3+}-Mn^{2+}, Eu^{2+}, or Eu^{2+}-Mn^{2+} doped $Ba_9Y_2Si_6O_{24}$ were investigated in previous studies [21–24]. In this report, the luminescence properties of phosphors co-doped with Bi^{3+} and Eu^{3+} [$Ba_{9-3(m+n)/2}Bi_mEu_nY_2Si_6O_{24}$ and $Ba_9Y_{2-m-n}Bi_mEu_nSi_6O_{24}$ (m = 0.001–0.1, n = 0–0.1)] based on the Ba^{2+} and Y^{3+} site substitution in the $Ba_9Y_2Si_6O_{24}$ host lattice are discussed. These optical materials were prepared and their X-ray diffraction patterns were analyzed. The photoluminescence (PL) spectra were also analyzed. These exhibited efficient emissions in the blue-green wavelength region of the spectrum, assigned to the s–p transitions of the Bi^{3+} emitter in the orthosilicate hosts. The quantum efficiency (QE), critical distance, and energy transfer mechanism were investigated. Moreover, the PL spectra of orthosilicate phosphors co-doped with Bi^{3+} and Eu^{3+} were monitored. The dependence of the luminescence intensity and the energy-transfer mechanism of the Eu^{3+} co-doped (n = 0–0.1) host lattices on the Bi^{3+} content (m = 0.025) were also studied. Using these phosphors, the desired Commission Internationale de l'Eclairage (CIE) values, including tunable emission light wavelengths throughout blue, green, white, and orange wavelength regions of the spectra were attained.

2. Experimental

Samples of $Ba_{9-3(m+n)/2}Bi_mEu_nY_2Si_6O_{24}$ and $Ba_9Y_{2-m-n}Bi_mEu_nSi_6O_{24}$ (m = 0.001–0.1, n = 0–0.1) were prepared by heating the appropriate stoichiometric amounts of $BaCO_3$ (Alfa 99.8%), Y_2O_3 (Alfa 99.9%), SiO_2 (Alfa 99.5%), Bi_2O_3 (Aldrich 99.99%), and Eu_2O_3 (Alfa 99.9%) at temperatures up to 1100 °C for 3 h in air. Likewise in previous studies, in each sample, 2.5 wt% Li_2CO_3 (Alfa 99%) was added as a flux [21–24]. Phase identification of phosphors was done using a Shimadzu XRD-6000 powder diffractometer using CoKα– radiations and the unit cell parameters were determined by using the Rietveld refinement program Rietica. Ultraviolet–visible spectroscopy with photos to measure the excitation and emission spectra of the Bi^{3+}, Eu^{3+}-doped $Ba_9Y_2Si_6O_{24}$ phosphor materials were done using spectrofluorometer (Sinco Fluromate FS-2, PMT 500 V, integration time 20 ms, response time 0.02 s) at room temperature.

3. Results and discussion

The $Ba_{9-3(m+n)/2}Bi_mEu_nY_2Si_6O_{24}$ and $Ba_9Y_{2-m-n}Bi_mEu_nSi_6O_{24}$ phase was identified by powder X-ray diffraction (XRD) analysis after Bi^{3+} (r = 1.03 Å for CN = 6, r = 1.17 Å for CN = 8) and Eu^{3+} (r = 0.947 Å for CN = 6, r = 1.12 Å for CN = 9) ions were substituted for Ba^{2+} (r = 1.47 Å for CN = 9, r = 1.52 Å for CN = 10, r = 1.75 Å for CN = 12) or Y^{3+} (r = 0.9 Å, CN = 6) ions in the barium yttrium orthosilicate host lattices. Fig. 2(a) depicts the calculated X-ray diffraction (XRD) patterns of the $Ba_9Sc_2Si_6O_{24}$ (ICSD 50736) lattice. Fig. 2 (b)–(f) and (g)–(j) show the XRD patterns of $Ba_{9-3(m+n)/2}Bi_mEu_nY_2Si_6O_{24}$ and $Ba_9Y_{2-m-n}Bi_mEu_nSi_6O_{24}$, respectively, wherein the corresponding m and n values are as follows: (b) (g) m = 0.025, n = 0, (c) (h) m = 0.1, n = 0, (d) (i) m = 0, n = 0.1, and (e) (j) m = 0.025, n = 0.1. Phase identification was performed by analyzing the powdered XRD patterns. Single-phase orthosilicate $Ba_9Y_2Si_6O_{24}$ phosphors co-doped with Bi^{3+} and Eu^{3+} were formed when m = 0.1 and n = 0.1 In both the $Ba_{9-3m/2}Bi_mY_2Si_6O_{24}$ and $Ba_9Y_{2-m}Bi_mSi_6O_{24}$ (m = 0.001–0.1) phosphors, the broad excitation spectra in the PL spectra occur from 300 to 380 nm centered around 332 and 373 nm caused by the $^1S_0 \rightarrow {}^3P_1$ transitions of the Bi^{3+} ions; moreover, the rest of the emission spectrum is attributed to the intense $^3P_1 \rightarrow {}^1S_0$ transitions of the Bi^{3+} ions that range broadly from 380 to 600 nm, as shown in Fig. 3 (a) and (b). The intensity of the emission bands centered near 409 and 490 nm were monitored as the Bi^{3+} concentration was increased. As shown in Fig. 3 (c), the relative luminescence intensity calculated from the integrated emission clearly reached a maximum when the Bi^{3+} content was m = 0.025 in both $Ba_{9-3m/2}Bi_mY_2Si_6O_{24}$ and $Ba_9Y_{2-m}Bi_mSi_6O_{24}$ phosphors. Any further increase in the Bi^{3+} content led to an apparent quenching of the blue and green emissions. Sodium salicylate powder, which emits blue light between 380 and 500 nm when excited with 355 nm radiation, can be used as a standard to approximate the QE by comparison with its absolute QE of 58 ± 1% [8,25,26]. Through a comparison with the QE of sodium salicylate, the relative QE of the $Ba_9Y_{2-m}Bi_mSi_6O_{24}$ (m = 0.025) phosphors subjected to excitation with 332 nm radiation was calculated to be 31.8% based on the integrated emission. At the Bi^{3+} concentration corresponding to the maximum emission intensity, the critical distance between the activators decreased with increasing energy transfer. A decrease in the emission intensity resulted in nonradiative energy transfer between the activators from the electric interaction. The critical distance (R_c) was calculated using the following formula:

$$R_c = 2[3V/4\pi m_c N]^{1/3} \quad (1)$$

where V is the volume of the unit cell, N is the number of available sites for the dopant in the unit cell, m_c is the critical concentration of Bi^{3+}, and R_c is the critical distance for energy transfer [8,20–22]. The lattice constants of $Ba_{8.9625}Bi_{0.025}Y_2Si_6O_{24}$ and $Ba_9Y_{1.975}Bi_{0.025}Si_6O_{24}$ obtained by using the Rietveld refinement were

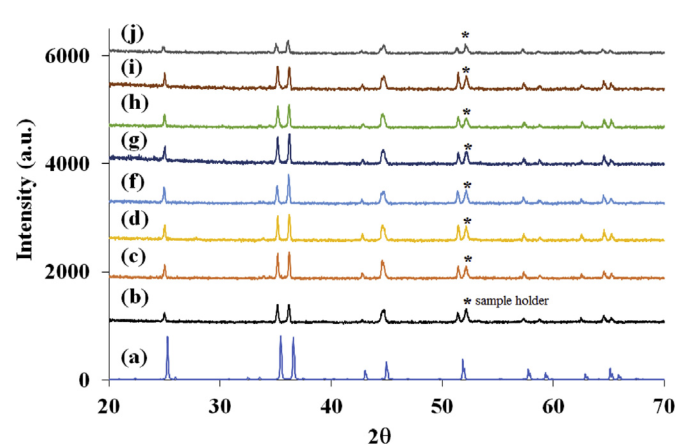

Fig. 2. XRD patterns of (a) $Ba_9Sc_2Si_6O_{24}$ (ICSD 50736) and $Ba_{9-3(m+n)/2}Bi_mEu_nY_2Si_6O_{24}$ and $Ba_9Y_{2-m-n}Bi_mEu_nSi_6O_{24}$ (b) (g) m = 0.01, n = 0, (c) (h) m = 0.1, n = 0, (d) (i) m = 0, n = 0.1, and (e) (j) m = 0.025, n = 0.1.