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Original Research

Tunable and enhanced luminescence of $\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_{4-y}\text{N}_{2/3y}:\text{Eu}^{2+}$ phosphors for white light-emitting diodes

Xinglai Zhang, Baodan Liu*, Wenjin Yang, Xin Jiang*

Shenyang National Laboratory for Materials Science (SYNL), Institute of Metal Research (IMR), Chinese Academy of Sciences (CAS), No. 72 Wenhua Road, Shenyang 110016, China

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ABSTRACT

Color tuning and luminescence enhancement are predominant challenges for improving the performance of white light emitting diodes (LEDs) toward commercial application. In this paper, a novel promising $\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_{4-y}\text{N}_{2/3y}:\text{Eu}^{2+}$ phosphors with tunable and enhanced luminescence for phosphors converted LEDs (pc-LEDs) have been successfully synthesized by a direct gas-reduction nitridation method. The effects of Ca and N doping on the phase purity, morphology and optical properties of $\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_{4-y}\text{N}_{2/3y}:\text{Eu}^{2+}$ phosphors were also systematically investigated. The optical results show that $\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_{4-y}\text{N}_{2/3y}:\text{Eu}^{2+}$ phosphors can be actively excited over a broad range from 250 to 430 nm. With the adding of different concentrations of Ca^{2+} ions in phosphors, the emission color wavelength can be tailored from 501 to 441 nm by a 375 nm NUV LED excitation source. Furthermore, it has been found that the emission and absorption of $\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_4:\text{Eu}^{2+}$ phosphor can be significantly improved when N^{3-} ions were introduced into the host lattices. The intensity of $\text{Ba}_{1.5}\text{Ca}_{0.5}\text{SiO}_{4-y}\text{N}_{2/3y}:\text{Eu}^{2+}$ phosphor was 3.4 times higher than the phosphor without N doping. The fabrication and characterization of pc-LEDs using $\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_{4-y}\text{N}_{2/3y}:\text{Eu}^{2+}$ phosphors-silica gel as the coating layer onto 375 nm-emitting InGaN LED caps demonstrated the superior optical and current tolerant properties, making it a promising and competitive candidate for commercial utilization in white LED applications.

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1. Introduction

In recent years, white light emitting diodes (LEDs) are emerging as promising light sources to replace traditional fluorescent and incandescent bulbs due to their overwhelming advantages in energy savings, long life span, decent reliability and environment friendliness [1–5]. Phosphor converted LEDs (pc-LEDs) offer a number of merits over all-LED devices owing to their high color rendering index and the easy tenability of a wide range of color temperatures [6–8]. As the core component of the LED devices, the phosphor material plays a key role for its importance in governing the overall luminous efficacy, color temperature, and color rendition of the resulting white light [9–11]. To generate white light, an efficient way is to combine the blue InGaN LED chip with yellow emitting phosphor $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG: Ce^{3+}) [12,13]. However, this kind of white light has a rather low color render index (CRI, $R_a < 80$) due to the lacking of sufficient red components in its spectrum [14]. In order to enhance the white light quality, an

alternative approach to combine a near UV (NUV) LED chip with multi-phased (red, green and blue) phosphors is proposed to realize the white emission with higher CRI [15,16].

Recently, rare earth doped alkaline earth silicates have attracted extensive research interest due to their facile synthesis, excellent chemistry and thermal stabilities, and low cost of raw materials [17–19]. Especially, the Eu^{2+} activated alkaline earth orthosilicate $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ green phosphor has gained strong attention owing to its energy saving, high material stability, and long operation lifetime [20]. However, the poor luminescence efficiency of $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ is still far away from commercial application. To improve the photoluminescence characteristics of $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ phosphor, both rare earth and non-rare earth ion doping in its lattice have been carried out in the solid state reaction and it has been demonstrated quite useful [21–24]. For example, Hu et al. showed that the luminescence intensity of $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ phosphor was increased to 134% and 156%, respectively, after the co-doping of La or Y ions [25]. The slight adding of Gd^{3+} and Li^+ ions into the host lattices can also lead to a further 1.39 time enhancement of the emission intensity of $\text{Ba}_{1.95}\text{SiO}_4:0.04\text{Eu}^{2+}$ [26]. Additionally, He et al. reported that the substitution of 0.1 mol of Sr^{2+} with Mg^{2+} can induce the selective modulation of the two emission bands of $\text{Mg}_{0.1}\text{Sr}_{1.88}\text{SiO}_4:\text{Eu}_{0.02}$ in the blue (from 473 to 459 nm)

* Corresponding authors.

E-mail addresses: baodanliu@hotmail.com (B. Liu), xjiang@imr.ac.cn (X. Jiang).

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and yellow (from 535 to 564 nm) regions [27]. Moreover, the enhanced bluish-green long-lasting phosphorescence of N contained $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ was reported by Wang et al. They found that the long-lasting phosphorescence of $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ by introducing N were observed to be enhanced continuously with increasing Si_3N_4 content. These findings indicate that the doping approach is an effective strategy for the tailoring of the emission color and efficiency increase in silicates phosphor. However, the influence of Ca^{2+} ions and N^{3-} ions co-doping into $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ phosphor on the optical properties and their application to LEDs have not been investigated.

In this work, the co-doping of Ca^{2+} and N^{3-} in $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ phosphor lattice with aim to tailor the luminous wavelength is investigated and their influence on the photoluminescence property is systemically studied. The luminescent characterization of $\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_{4-y}\text{N}_{2/3y}:\text{Eu}^{2+}$ phosphors demonstrates that the emission wavelength can be artificially tuned by incorporating Ca^{2+} ions into the $\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_{4-y}\text{N}_{2/3y}:\text{Eu}^{2+}$ phosphor, while a remarkable enhancement of photoluminescence is observed through N^{3-} ions co-doping. In addition, the fabrication and test of pc-LED devices using the $\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_{4-y}\text{N}_{2/3y}:\text{Eu}^{2+}$ phosphors excited by NUV LEDs demonstrate the capability of cation/anion co-doping technique in enhancing the luminescence properties of silicates phosphor and will open up more opportunities to their potential applications in promising color conversion materials.

2. Experimental

2.1. Synthesis of $\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_{4-y}\text{N}_{2/3y}:\text{Eu}^{2+}$ and $\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_4:\text{Eu}^{2+}$ phosphors

$\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_{4-y}\text{N}_{2/3y}:\text{Eu}^{2+}$ phosphors were synthesized using a gas-reduction-nitridation (GRN) method. In a typical synthesis process, BaCO_3 (A.R.), CaCO_3 (A.R.), SiO_2 (G.R.) were used as the starting precursors. And high purity Eu_2O_3 (99.99%) powder was utilized as the activator. The appropriate amounts of Li_2CO_3 (A.R.), Na_2CO_3 (A.R.) and K_2CO_3 (A.R.) powders were added as the charge compensator for the phosphors. The stoichiometric raw materials with a small amount of ethanol were mixed thoroughly in an agate mortar by grinding for 12 h, and then dried in an oven under 90°C for 24 h. The dried mixture powders were loaded in a high purity alumina boat and inserted into a tubular furnace. The furnace was then heated to the temperature of 1150°C with a constant heating rate of $600^\circ\text{C}/\text{h}$ in an NH_3 gas with a flowing rate of $300\text{ mL}/\text{min}$. After 6 h sintering, the phosphors were furnace-cooled to room temperature in an NH_3 atmosphere.

In order to study the effect of N dopant on $\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_{4-y}\text{N}_{2/3y}:\text{Eu}^{2+}$ phosphors, we prepared $\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_4:\text{Eu}^{2+}$ phosphors without N dopant using a conventional solid-state reaction method. The preparation process is similar with GRN method, and the only difference is that the reaction gas is the mixture of 5% H_2 , 95% Ar rather than NH_3 .

2.2. Structure, morphology and photoluminescence characterizations

The crystallinity of the as-obtained samples is examined by a conventional X-ray diffraction (XRD, Bruker AXS D8 Discover) using $\text{Cu-K}\alpha$ ($\lambda=0.15405\text{ nm}$). The morphology and size of the phosphors were measured by a field emission scanning electron microscopy (FESEM, HTACHI; S-4800). The elemental compositions of the phosphor were studied by energy dispersive spectroscopy (EDS; HORIBA; 7593-H). The excitation and emission spectra were recorded on a PL3-211-P spectrometer (HORIBA JobinYvon, America) and a 450 W xenon lamp was used as the excitation source. The luminescence decay curve was collected on a

Horiba Jobin-Yvon Fluorolog3-TCSPC spectrofluorometer using a 388 nm Nano LED laser (pulse width=1.2 ns, repetition rate=100 kHz) as the excitation source. The test of pc-LED was evaluated by a spectrometer (Ocean Optics; USB2000+) with an integrating sphere under forward DC bias conditions.

3. Results and discussions

To investigate the influence of Ca ion on the crystalline phase, morphology, composition and optical properties, $\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_{4-y}\text{N}_{2/3y}:\text{Eu}^{2+}$ phosphors with a wide range of Ca contents are synthesized. Fig. 1 presents the powder XRD patterns of $\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_{4-y}\text{N}_{2/3y}:\text{Eu}^{2+}$ phosphors with different Ca contents. It can be seen that the XRD pattern of pure $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ phosphor matches well with the standard data of orthorhombic Ba_2SiO_4 phase (JCPDS no. 26-1403). The adding of Ca ions into $\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_{4-y}\text{N}_{2/3y}:\text{Eu}^{2+}$ ($x=0.5, 0.8$ and 1.0) will lead to an obvious phase transition and the products can be identified as a single T-phase with a space group $P3m1$ and a hexagonal unit cell ($a=b=0.5749\text{ nm}$ and $c=1.465\text{ nm}$ for $\text{Ba}_{1.3}\text{Ca}_{0.7}\text{SiO}_4$, JCPDS no. 36-1449), which is made of five Ba/Ca sites [one $\text{M}(2)\text{O}_6$ ring, and four $\text{M}(1, 3, 4, 5)\text{O}_{10}$ or $\text{M}(1, 3, 4, 5)\text{O}_{12}$ polyhedra] and two SiO_4 tetrahedral sites [28]. As is well known to all, the substitution of host ions with dopants normally meets the requirement of energy minimization and the matching of geometrical size. As a result, it is speculated that the Ca^{2+} favors to replace the Ba^{2+} sites, while the Eu^{2+} ions with a coordination number higher than 6 prefer to occupy the Ca^{2+} sites [29]. Additionally, all the $\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_{4-y}\text{N}_{2/3y}:\text{Eu}^{2+}$ phosphor samples show extremely high phase purity and no secondary phases can be detected. The doping of Ca^{2+} only induces the structural transition of pure $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ from orthorhombic to T-phase. However, the adding of Ca^{2+} into $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ host lattice indeed causes the red-shift of the XRD peaks to higher values of the diffraction angle, indicating that the lattice constants are monotonically decreased due to the substitution of Ba^{2+} (149 pm) with smaller Ca^{2+} (114 pm) [30].

Fig. 2 shows the typical morphology of $\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_{4-y}\text{N}_{2/3y}:\text{Eu}^{2+}$ phosphors with various x values ranging from 0 to 1.0. Without Ca doping ($x=0$), the $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ phosphor exhibits a relatively uniform morphology in particle shape and size, and the particles have an average diameter of $1\ \mu\text{m}$. After doping with Ca ions, the particle size is drastically increased from 1 to $4\ \mu\text{m}$ as the Ca concentration increases from $x=0$ to 1.0, and the particles are more agglomerated with irregular morphologies due to Ca incorporation. Fig. 2e and f depict the corresponding EDS spectra of $\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_{4-y}\text{N}_{2/3y}:\text{Eu}^{2+}$ phosphors with $x=0$ and 1.0, respectively. It can be seen that only the Ba, Si, O, N and Eu peaks are observed in the EDS spectrum of $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ phosphor (in Fig. 2e), while an additional Ca peak with strong intensity is detected after Ca doping, confirming the invasion of Ca^{2+} ions in $\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_{4-y}\text{N}_{2/3y}:\text{Eu}^{2+}$ phosphors. Detailed composition analyses of all elements in $\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_{4-y}\text{N}_{2/3y}:\text{Eu}^{2+}$ phosphors are listed in Table 1.

Previous studies have demonstrated the possibilities of tuning the emission color of phosphor. An efficient way is to modify the host lattice with various dopants. For example, the luminescence of Eu^{2+} can be adjusted with a various crystal field splitting of the 5d band. Another approach is to control the active dopant concentrations. This can be attained through an energy transfer between different sites of the active ions. Here, the Ca dopant is utilized to modify the host lattice and a new single T-phase $\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_{4-y}\text{N}_{2/3y}:\text{Eu}^{2+}$ phosphor has been obtained. It has been found that the Ca substitution has a significant effect on the photoluminescence (PL) properties of $\text{Ba}_{2-x}\text{Ca}_x\text{SiO}_{4-y}\text{N}_{2/3y}:\text{Eu}^{2+}$ phosphors. Fig. 3a shows the photoluminescence excitation (PLE)

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