Synthesis and optical properties of P^{5+} co-doped Ba_3SiO_5:Eu^{2+} orange persistent phosphor

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A B S T R A C T

By co-doping the P^{5+} ions into Ba_3SiO_5:Eu^{2+}, we synthesized new orange persistent phosphor using cellulose assisted liquid phase precursor (LPP) method. The emission spectra showed a typically broad orange emission band centered at 575 nm attributed to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} ions under 400 nm excitation source. The persistent luminescence property of Eu^{2+} doped Ba_3SiO_5 orange phosphor was enhanced by co-doping non-equivalent phosphorus ions into silicon sites. This enhancement can be explained by formation of the trapping center due to the charge compenstation. Consequently, the afterglow decay exhibited an orange emission for more than 5 min after irradiation at under 365 nm for 1 min.

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1. Introduction

Persistent luminescence is a phenomenon in which long durations of luminescence are exhibited after removing the excitation light sources [1,2]. Recently, persistent phosphors have been rapidly reported since the $SrAl_2O_4$:Eu^{2+}, Dy^{3+} green persistent phosphors were discovered in 1996 [3] and are being widely used not only in night-vision applications such as security signs, emergency route signs, traffic signage, dials, paints, and displays but also in temperature sensors and medical diagnostics [4,5].

Up to now, $CaAl_2O_4$:Eu^{2+}, Nd^{3+} blue, and $SrAl_2O_4$:Eu^{2+}, Dy^{3+} green phosphors have been commercialized because of their sufficiently strong and long-lasting persistent luminescence and their ability to be excited by room light as well as sunlight [1,2]. In contrast, other yellow to red color commercialized phosphors which are based on sulfides and oxysulfides host materials have

poor chemical stability, low luminous intensity, and short life time [6,7]. In order to overcome these disadvantages, the design of oxide based persistent phosphors has been studied by co-doping non-equivalent ions and controlling the electron transfer via conduction band engineering [8—11]. Thus, it is also necessary to understand persistent luminescence mechanisms.

Persistent phosphors have two types of activate centers: emitting centers and trapping centers [2]. Emitting centers are capable of emitting radiation after being excited. Trapping centers usually store the excitation energy by trapping charge carriers and gradually releasing excitation energy to the emitting centers by thermal or other physical stimulations. Consequently, persistent luminescence results from the recombination of the stored energy and its intensity and lifetime depends on the trapping states (for example, trap type and distribution) [2]. Therefore, to promote persistent luminescence, it is important to select not only suitable emitting centers, but also proper trapping centers with the host lattice. In order to introduce appropriate trapping centers to the energy level structures, the general approach involves adding non-equivalent co-dopants as the trapping centers. For example, persistent luminescence was improved by co-doping In^{3+}, Mg^{2+}/Ti^{4+}, and Tm^{3+} in

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place of Ti^{4+} in $CaTiO_3:Pr^{3+}$, Y^{3+} in $Y_2O_2S:Eu^{3+}$, and Ca^{2+} in $Ca_2Si_5N_8:Eu^{2+}$ respectively [12—14]. Thus, we can improve the persistent luminescence properties by selecting the appropriate co-dopant.

In this study, P^{5+} ions were employed as the co-dopant and $Ba_3SiO_5:Eu^{2+}$, P^{5+} phosphors were prepared using the cellulose assisted liquid phase precursor (LPP) method which is a simple liquid state synthesis method developed by our group. Eu^{2+} activated silicate phosphors are very widely researched phosphor hosts due to their broad excitation spectra and tendency of controlling the emission wavelength. The orange persistent luminescence, attributed to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} ions, was improved by co-doping P^{5+} ions in place of the Si^{4+} site in $Ba_3SiO_5:Eu^{2+}$, P^{5+} phosphor. The different charged state between P^{5+} and Si^{4+} creates defects that act as the trap centers in the structure due to the charge compensation. The effects of the trap and activator concentration as well as the reduction temperature on the persistent luminescence properties are discussed.

2. Experimental

2.1. Preparation of the $Ba_3SiO_5:Eu^{2+},P^{5+}$ orange phosphors

Eu^{2+} and P^{5+} doped Ba_3SiO_5 orange phosphors were synthesized using the cellulose assisted liquid phase precursor (LPP) method. The procedure for the preparation of the raw material solution is as follows. $Ba(CH_3COO)_2$ (Sigma-Aldrich, 99%) and Eu_2O_3 (Sigma-Aldrich, 99.9%) were dissolved in deionized water and acetic acid, respectively. 85% phosphoric acid (Duksan) was diluted with deionized water to 30% solution. Then, each solution was stirred on a heating plate at 50 °C for 30 min. Propylene-glycol-modified silane (PGMS) was obtained by reacting tetraethoxysilane (TEOS) (Kanto Chemicals, 99.9%) with propylene glycol (Kanto Chemicals, 99.9%) at 80 °C in the presence of a small amount of hydrochloric acid (Kanto Chemicals) as a catalyst [15]. Raw materials were mixed with stoichiometric composition and stirred at room temperature for 5 min. This solution was impregnated on microcrystalline cellulose (MCC) powder (Asahi Kasei Corporation) with a ratio of 1:0.9 (solution:MCC). The impregnated MCC powder with solution was heat treated at 600 °C for 3 h and 800 °C for 2 h to remove the organic materials, after which the obtained powder was calcined at 950 °C for 3 h to obtain an oxide precursor. The oxide precursor was ground using an agate mortar and then reduced at 1000—1200 °C for 5 h in a tube furnace under a flow of an Ar (85%)-H_2 (15%) gaseous mixture at a rate of 800 mL/min.

2.2. Characterization

In order to determine the crystallinity of the phase, powder X-ray diffraction (PXRD, Bruker D8 FOCUS) was carried out using Ni-filtered Cu Kα radiation with a tube voltage of 40 kV and tube current of 40 mA. The XRD pattern was recorded in the 2θ range of 15—70°. The Chemical bonding analysis of the samples was measured using the Fourier transform infrared (FTIR) spectroscopy (Bruker IFS-66/S, TENSOR27). The energy dispersive spectroscopy (EDS) mapping was carried out using high resolution transmission electron microscopy (HRTEM, JEM2100F). The photoluminescence (PL) and afterglow decay time were examined using a spectrometer (SCINCO, FS-2, Korea) with a xenon lamp excitation source (150 W) in the range of 300—700 nm. The afterglow decay times were measured for 300 s after 1 min exposure under 365 nm. All the measurements were performed at room temperature.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the $Ba_{2.98}Si_{1-y}O_5:Eu_{0.02},P_y$ orange phosphors with different phosphorus concentrations reduced at 1000 °C. As shown in Fig. 1(a), all the $Ba_{2.98}Si_{1-y}O_5:Eu_{0.02},P_y$ samples matched well with the tetragonal Ba_3SiO_5 (JCPDS no. 70-0667, space group of $I4/mcm$) and a small quantity of orthorhombic Ba_2SiO_4 which can easily coexistent with Ba_3SiO_5 [16—18]. No significant differences or peak shift were observed between without and with 0.006 mol phosphorus co-doping. This result indicates that the incorporation of P^{5+} ions did not affect the crystal structure of the Ba_3SiO_5 host lattice.

Fig. 1(b) presents the FT-IR spectra of the $Ba_{2.98}Si_{1-y}O_5:Eu_{0.02},P_y$ phosphors with various phosphorus concentrations reduced at 1000 °C. The broad absorption bands around 3400 cm^{-1} and 1630 cm^{-1} correspond to the surface adsorbed moisture. The peak at 1386 cm^{-1} was assigned to the Ba/Eu-O bond and 1100-400 cm^{-1} was attributed to the Si-O tetrahedron vibrations [19,20]. A weak peak at ~1035 cm^{-1} was only observed in the P doped samples (Fig. 1(b) inset). This peak can be characterized as PO_4^{3-}, indicating that phosphorus ions seem to be well diffused in the structure [21,22]. Fig. 1(c) and (d) also show an even distribution of phosphorus in the material along with other host elements (Ba,Si,O,Eu).

Fig. 2 shows the photoluminescence and persistent luminescence properties of the $Ba_{2.98}Si_{1-y}O_5:Eu_{0.02},P_y$ phosphors with different phosphorus concentrations reduced at 1000 °C. $Ba_3SiO_5:Eu^{2+},P^{5+}$ showed a broad band excitation spectrum in a range from UV to the blue region as well as a broad orange emission band with a maximum peak wavelength at 575 nm under an excitation light source of 400 nm attributed to the $4f^65d^1 \rightarrow 4f^7$ transition of the Eu^{2+} ion, as shown in Fig. 2(a) [23]. The Ba_3SiO_5 crystal structure has two Ba (tenfold for Ba(1) and eightfold for Ba(2)). The orange emission is owing to the Eu^{2+} in the Ba(1) site which have the larger crystal field due to the larger tenfold coordination number(CN) than Ba(2) site [24]. $Ba_{2.98}Si_{0.994}O_5:Eu_{0.02},P_{0.006}$ has the highest emission intensity, although a greater amount of doping could cause degradation of the luminescence property.

Fig. 2(b) and the inset show the persistent luminescence intensity and photographs as a function of time, respectively. The phosphorous co-doped sample exhibits more intense orange persistent luminescence. The existence of phosphorus in the structure improved the persistent luminescence property. The Ba_3SiO_5 crystal structure has two Ba (tenfold for Ba(1) and eightfold for Ba(2)) and one Si (fourfold) cation crystallographic sites that can be substituted by phosphorus ions [16]. The ionic radius percentage difference between the dopant (P^{5+}) and the possible substituted ions (Ba^{2+}, Si^{4+}) in Ba_3SiO_5 was calculated based on equation (1): [25]

$$D_r = 100 \times [R_m(CN) - R_d(CN)]/R_m(CN), \qquad (1)$$

where D_r is the radius percentage difference, CN is the coordination number, $R_m(CN)$ is the radius of the host cation, and $R_d(CN)$ is the radius of the dopant. The value D_r between P^{5+} and the four-coordinated Si^{4+} site is 34.62%, while D_r between P^{5+} and Ba^{2+} on the ten- and eight-coordinated sites are 88.82% and 88.03%, respectively. Therefore, P^{5+} ions are more appropriate for substituting the Si^{4+} site than the Ba^{2+} sites. Replacing Si^{4+} sites with P^{5+} ions having a different charge state can introduce lattice defects due to the charge compensation. As shown in equation (2), four P^{5+} ions substituted five Si^{4+} ions and introduce four $P_{Si}^{\cdot}$ positive and a V_{Si}'''' negative defects. Captured charges by this defects can be thermally released from the trap centers to luminescence centers.