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Synthesis of high efficient Ca_2SiO_4:Eu^{2+} green emitting phosphor by a liquid phase precursor method

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ABSTRACT

Green emitting Eu^{2+}-doped Ca_2SiO_4 phosphors were synthesized by three different methods (a conventional solid state reaction (SSR) method, a novel liquid phase precursor approach using SiO_2 sol (LPP-SiO_2(sol)) and water-soluble silicon compound (LPP-WSS)). The obtained phosphors exhibited a broad excitation spectrum ranging from 225 to 450 nm and a strong green emission peak at 502 nm due to the $4f^65d^1 \rightarrow 4f^7(^8S_{7/2})$ transition of Eu^{2+}. The highest luminescent intensity was obtained for the samples fired at 1100 °C. The dependence of luminescence properties on Eu^{2+} concentration for the phosphors synthesized using LPP-WSS method was also examined from 0.1 to 5.0 mol% and the maximum emission intensity was observed at 3.0 mol% Eu^{2+}. A detailed analysis using various characterizations revealed that phosphors produced by the LPP-WSS process exhibited more homogenous phase distribution and higher luminescence intensity than those from the other two processes, which suggested the potential application of Ca_2SiO_4:Eu^{2+} in white light-emitting diodes and fluorescence lamps.

1. Introduction

Rare earth doped silicate phosphors have been widely studied recently due to their potential application in white light emitting diodes (white-LEDs) and fluorescence lamps which are the promising candidates for the next generation solid state lighting materials. The broad photo-luminescent spectra, high chemical and thermal stability and low cost synthesis are the outstanding merits of silicate phosphors for these applications [1–4]. The divalent europium doped alkaline earth silicate phosphor is especially of great interest since the ion radii of alkaline earth ions are similar to that of divalent europium, such as [Eu^{2+}]=0.112 nm, [Ca^{2+}]=0.099 nm, [Sr^{2+}]=0.112 nm and [Ba^{2+}]=0.134 nm. Consequently divalent europium is more stable in an alkaline earth silicate host and more easily diffuses into the lattice sites [5–8].

Alkaline silicate phosphors are generally synthesized by a conventional solid state reaction method (SSR) at high temperature for long periods of time. However, the products obtained by the SSR method have some disadvantages, such as inhomogeneous phase distribution, bulky and non-uniform particle shape, which may degrade luminescence properties of the phosphors [9,10]. Hydrothermal synthesis for alkaline silicate phosphors has also been reported, but it seems difficult to obtain fine particle shape and homogeneous crystalline phase by common solution process [11]. Such problems have been overcome by a novel liquid phase precursor (LPP) approach. Considerable reduction of the synthesis temperature and time as well as improvement of the phase composition and homogeneity can be achieved by solution based synthesis when an extremely high degree of mixing on the atomic level is achieved by simply dissolving all the components together [10,12–15]. For the synthesis of silicate phosphor by LPP method, it is essential to select an appropriate silicon reagent which should not only be miscible in water but also can react easily. Most silicates are obtained using tetraethoxysilane (TEOS) or derivatives of TEOS, but they are incompatible and immiscible with pure water [10,16]. In our previous work, SiO_2 sol with a uniform 10 nm particle size was adopted for the synthesis of silicate phosphors by the LPP method, which was termed LPP-SiO_2(sol) method [12]. Recently, a novel water-soluble silicon compound (WSS) was developed by Kakihana et al. [10,17]. According to their experiment, TEOS and propylene glycol (PG) were mixed and stirred for 48 h at 80 °C, then they were blended with HCl solution for 1 h at 80 °C, and finally a transparent solution of a silicon compound was achieved. It was reported that this solution could be combined with pure water in any ratio without a trace of hydrolysis even

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after keeping it under ambient atmosphere for several weeks. It is expected that the use of WSS compound in the LPP method could improve the synthesis for silicate phosphors.

Therefore, in this work, the synthesis of $Ca_2SiO_4:Eu^{2+}$ phosphors were carried out using LPP-SiO_2(sol), LPP-WSS and SSR methods under different synthesis temperatures. Based on our analysis, LPP-WSS process was identified as the best one among these three different approaches. Additionally, the activator concentration dependent luminescence properties were also investigated in this study.

2. Experiment

2.1. Preparation of precursor by SSR method

$CaCO_3$ (99.99%, High purity Chemicals, Japan), Eu_2O_3 (99.9%, High purity chemicals, Japan) and SiO_2 (99.5%, Aldrich, America) solid powders were mixed in a stoichiometric ratio and ground adequately together in an agate with acetone solvent.

2.2. Preparation of precursor by LPP-SiO_2(sol) method

$CaCl_2$ (95.0%, Junsei chemical Co., Japan) and $EuCl_3$ (99.98%, Aldrich grade) were dissolved in deionized water in a mass fraction of 20.0% and 10.0%, and then mixed with SiO_2 sol (20.0%, particle size 10 nm, Nissan Kagaku Japan, SNOTEX-O) in a stoichiometric ratio. The mixed solutions (~pH 3.5) were impregnated into the partially crystallized cellulose powder ($(C_6H_{10}O_5)_n$, 20 μm) at a weight ratio of 2:1 (solution:cellulose) under vibration process for 20 min and dried in an oven at 100 °C for 24 h.

2.3. Preparation of precursor by LPP-WSS method

$CaCl_2$ (95.0%, Junsei chemical Co., Japan) and $EuCl_3$ (99.98%, Aldrich grade) were dissolved in deionized water in a mass fraction of 20.0% and 10.0%, and then mixed with WSS (from Kakihana's group) in a stoichiometric ratio. The mixed solutions (~pH 3.5) were impregnated into the partially crystallized cellulose powder ($(C_6H_{10}O_5)_n$, 20 μm). The impregnation process was similar to the process used in the LPP-SiO_2(sol) method.

2.4. Synthesis of $Ca_2SiO_4:Eu^{2+}$ phosphors from the precursors

All of the prepared precursors were heated at 225 °C for 6 h, and then at 700 °C for 2 h, subsequently at 1000 °C for 2 h in air. Finally, the $Ca_2SiO_4:Eu^{2+}$ phosphor powders were synthesized at a series of temperatures ranging from 1000 °C to 1200 °C for 3 h in a 95%N_2–5%H_2 (reducing atmosphere in order to investigate temperature dependence of the phosphors with various techniques). The main processes of these three synthesis methods are briefly illustrated in Fig. 1. Furthermore, $Ca_2SiO_4:Eu^{2+}$ with different dopant concentrations (0.1–5.0 mol%) were synthesized by LPP-WSS methods in order to examine the effect of Eu^{2+} concentration.

2.5. Characterization of the obtained phosphor powders

Energy dispersive spectroscopy (EDS) mapping of the impregnated precursor was analyzed using field emission scanning electron microscopy (FE-SEM, 7600, JEOL) at 15 kV with a magnification rate of ×6.0k and a 10 μm bar. Double scanning powder X-ray diffraction (XRD, Cu $K\alpha$, $\lambda=1.5406$, 40 kV, 20 mA, Rigaku) with a step size of 0.02° (2θ) and scan speed of 6°/min was used to determine the crystalline phases of the synthesized samples. The morphology of the obtained phosphors was observed by the same

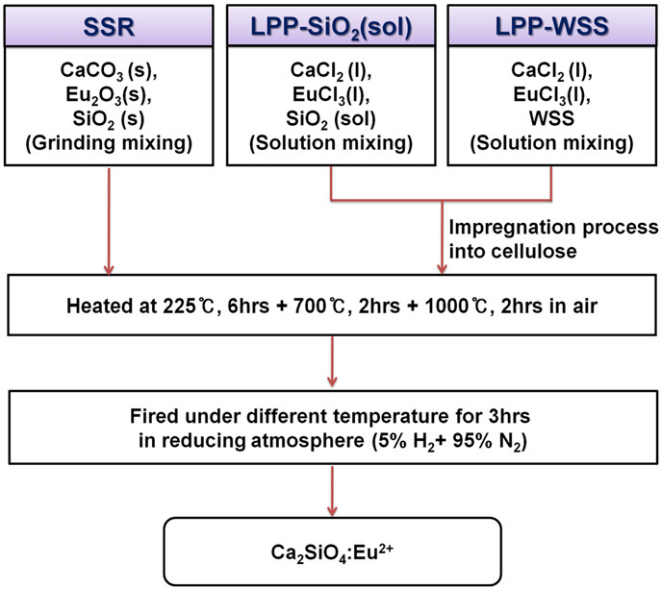

Fig. 1. Three different synthesis routes for $Ca_2SiO_4:Eu^{2+}$ phosphor.

FE-SEM device with a magnification rate of ×3.0k. The luminescence properties were obtained using a xenon lamp (SCINCO FS-2, 350 W, Korea) operating with 5 nm slits. An optical microscope (Olympus GX41, ×50 objective lens, 0.5 in. CCD camera, 20 in. LCD) was used to observe the emission from particles under 365 nm UV radiation. All the measurements were carried out at room temperature. The thermal degradation profiles of the as-prepared precursors were examined by thermogravimetric analysis and differential thermal analysis (TG/DTA, Seiko Exstar, Japan) at a heating rate of 20 °C/min from 50 °C to 1300 °C in air atmosphere.

3. Results and discussion

3.1. Role of cellulose, SiO_2(sol) and WSS in precursor

Partially crystallized 20 μm cellulose powder was used in the LPP methods. The cellulose is composed of crystalline and amorphous domains. The reactant solution penetrated into the amorphous area and the reaction took place in the amorphous area or on the surface of the cellulose crystallites [18]. Moreover, it was confirmed that crystalline cellulose was transformed into amorphous cellulose during the impregnation process above 100 °C. The cellulose powder has two major functions in the synthesis procedure. First one is that when the solution was impregnated into the cellulose under vibration process, the particles in solution were expected to be closely connected and homogeneously distributed in the porous network structure. Second, the heat released from the decomposition of cellulose could promote the reaction and lower the firing temperature required for reaction compared with SSR method [18,19].

In order to study the elemental distribution in the impregnated cellulose, the EDS mapping of LPP-SiO_2(sol) and LPP-WSS precursors were evaluated as shown in Fig. 2. It was found that all the reactant elements were uniformly distributed in both the precursors except the silicon element. The distribution of SiO_2 sol was not as homogeneous as WSS, which could be assigned to the structural difference between these two silicon sources. It was reported that the stability of SiO_2 sol particles decreases with the decrease of pH; and especially when the pH is below 7, the