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Original Research Paper

Photoluminescence optimization of BCNO phosphors synthesized using citric acid as a carbon source

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ABSTRACT

Citric acid was used as carbon source for the optimization of the photoluminescence (PL) performance of boron carbon oxynitride (BCNO) phosphor. Citric acid was chosen as an alternative carbon source because of its simple molecular structure, low decomposition temperature, relative inexpensiveness, and environmental friendliness. The prepared sample exhibited a single, homogeneous, and broad photoluminescence emission band whose peak varied from near-UV (400 nm) to yellow-visible (500 nm) upon excitation at 365 nm. The effects of varying the synthesis temperature, molar ratio of the carbon/boron and nitrogen/boron sources, and addition of SiO_2 nanoparticles on the PL properties were also studied. The optimized BCNO phosphors may find potential use in white LED applications.

1. Introduction

Recently, phosphor-converted white LEDs and multi-chip (RGB) LEDs have become commonplace in the fabrication of white light-emitting diodes (LEDs) [1,2]. The alternative method for fabrication of phosphor-converted white LEDs involves combining yellow-emitting oxynitride phosphors with blue (indium gallium nitride) LEDs [3,4]. Many oxynitride phosphors have been fabricated, and their photoluminescence (PL) properties have been studied. A few examples are Ca-α-SiAlON:Eu^{2+} [5], Ce^{3+} doped lanthanum silicon oxynitride [6] and $MSi_2O_2N_2$ with M = alkaline earth and boron carbon oxynitride (BCNO) phosphor [7,8].

The BCNO phosphor is a good candidate as a yellow emission phosphor that does not depend on rare-earth materials as the luminescence center [9]. BCNO phosphors have a wide excitation spectral window, from the short UV to blue, and the emission spectra can be tuned from violet, blue, greenish, yellow, to red with relatively high quantum efficiency [10–12]. The BCNO phosphor was synthesized using a facile heating method at low synthesis temperatures (below 900 °C) under atmospheric pressure [13,14]. To produce BCNO phosphor nanoparticles with 5 nm diameters, Lei et al. [15] synthesized BCNO phosphor materials in a salt melt matrix at 700 °C, the prepared samples have PL peaks in the 440–528 nm range. In addition, our group has synthesized a BCNO phosphor, with SiO_2 nanoparticles as an additive matrix, resulting in uniform and relatively high yellow luminescence intensities [16].

Some BCNO phosphor syntheses employ ethylene glycol, tetraethylene glycol, polyethylene glycol, polyallylamine, polyethyleneimine, guanidine hydrochloride, and glycerol as carbon sources [12,14,15,17]. However, the use of carbon sources with long hydrocarbon chains and high decomposition temperatures result in the formation of residual carbon due to incomplete combustion processes [13]. Additionally, carbon sources mentioned above are still relatively expensive for large-scale production.

Citric acid has a simple molecular structure, low thermal decomposition temperature, and high chemical reactivity. It is more economical, environmentally friendly, and has structural groups (C–OH) similar to other carbon sources that have been used in previous BCNO phosphor syntheses [17]. We assumed that citric acid could be used as a carbon source to synthesize BCNO phosphors. The use of citric acid was expected to reduce residual carbon formation, improve the PL properties, and allow for decreased synthesis temperatures.

In this study, we report, to the best of our knowledge, the first example of citric acid used as a carbon source in the synthesis of BCNO phosphors. In particular, we systematically investigated the influence of citric acid concentration in the precursor, synthesis temperature, and addition of SiO_2 nanoparticle on the PL properties of the BCNO phosphor material. The crystal structure formation and morphology of the BCNO phosphor is also discussed.

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2. Experimental

2.1. Materials and synthesis

BCNO phosphors were synthesized from the following precursors: boric acid ($B(OH)_3$), urea ($(NH_2)_2CO$), and citric acid ($C_6H_8O_7$), which were used as the boron, nitrogen, and carbon sources, respectively. All chemicals were purchased from Merck Co., Ltd., Germany, and were used without further purification. The detailed facile synthesis method is described in our previous paper [8]. Precursor solutions were prepared by mixing boric acid, urea, and citric acid in distilled water, followed by stirring at 500 rpm and 70 °C for 10 min to obtain homogeneous solutions. The molar ratio of the carbon/boron (C/B) source was varied from 0.1 to 0.7, and the molar ratio of the nitrogen/boron (N/B) source was adjusted from 5 to 15. To improve the PL properties of the BCNO phosphors, SiO_2 nanoparticles (Wacker Chemicals Fumed Silica Co., Ltd., China) were added at different mass fractions (0–5 wt%) to the precursor solutions [16]. The precursors were heated at 700–850 °C for 30 min in a ceramic crucible under ambient atmospheric pressure. The flow diagram for the synthesis of BCNO or BCNO/SiO_2 phosphor materials with a citric acid carbon source is shown in Fig. 1.

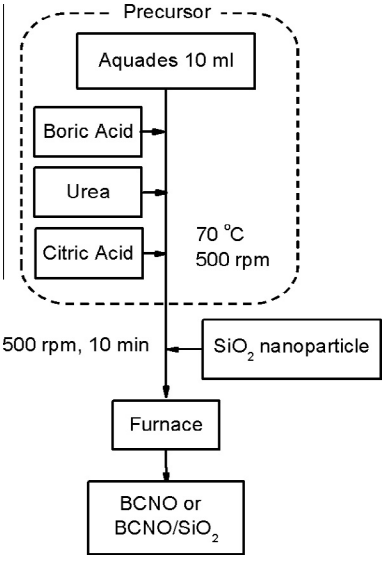

Fig. 1. Flow diagram for the synthesis of BCNO and BCNO/SiO_2 phosphor.

2.2. Measurements and characterization

The crystal structure of the samples was analyzed using an X-ray diffractometer (RINT 2000V, Rigaku Denki, Japan) using Cu Kα radiation. The morphology of the prepared samples was observed using a scanning electron microscope (SEM, Hitachi S-5000, Japan) at an operating voltage of 20 kV. The photoluminescence (PL) spectrum of each sample was measured at room temperature using a spectrofluorophotometer (RF-5300PC, Shimadzu Corp., Japan) equipped with a xenon laser source. All PL analyses were performed at room temperature with 365 nm excitation.

3. Results and discussion

3.1. SEM images and XRD pattern of BCNO phosphor

The phosphor particle size distribution significantly influences the luminescence quality of the phosphor material. A uniform particle size distribution and fine particles (<5 μm) are required to obtain high-quality phosphor materials [18]. Fig. 2(a) shows SEM micro-photographs of the BCNO phosphor. The average particles size are approximately 2.44 μm as shown in Fig. 2(b), which are much smaller than previously reported BCNO phosphors [8]. These physical dimensions should be favorable for yellow-emitting oxynitride phosphors for use in white LEDs [10]. Possible explanations for the small BCNO phosphor particle size are the low thermal decomposition temperature, the use of a small molecule precursor, and the lack of a molecular weight distribution in this precursor compared with carbon sources used in previous studies.

To determine the crystallite structure of the BCNO phosphor, XRD measurements were performed for the BCNO phosphor particles prepared at a synthesis temperature of 750 °C. The X-ray diffraction (XRD) patterns of BCNO phosphors are shown in Fig. 3. The diffraction peaks indicate the presence of crystalline B_2O_3 (JCPDS No. 06-0297), *h*-BN (JCPDS No. 34-0421), and carbon (JCPDS No. 41-1487). These results are similar to a previous study of BCNO phosphors by our group [8–10]. The high B_2O_3 intensity is due to byproduct formation from $B(OH)_3$ decomposition during the synthesis process. Kaihatsu et al. [13] explained that the B_2O_3 intensity can be reduced by increasing the synthesis temperature (above 900 °C). Meanwhile, according to Liu et al. [19], B_2O_3 can be removed from BCNO phosphors by dissolving in water. However, the loss of B_2O_3 content there is no effect on the PL properties of the BCNO phosphor [19]. The *h*-BN on BCNO phosphors are thought to originate from the exothermic reaction of urea with boric acid or B_2O_3 with NH_3. The *h*-BN is a semiconductor material and has a band gap of approximately 3.395 eV, and can produce luminescence when irradiated by UV light. The presence of low-intensity

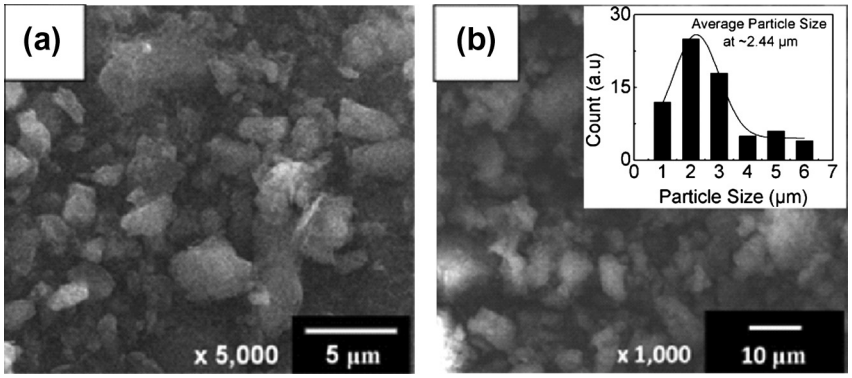

Fig. 2. SEM image of BCNO phosphors prepared with N/B = 10, C/B = 0.5, and synthesis at 750 °C for 30 min; (a) 5000 times and (b) 1000 times magnifications (inset: particle size distribution of BCNO phosphor material).