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Original Research Paper

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

Bebek W. Nuryadin^a, Tri Puspita Pratiwi^a, Ferry Iskandar^{a,*}, Mikrajuddin Abdullah^a, K. Khairurrijal^a, Takashi Ogi^b, Kikuo Okuyama^b^a Department of Physics, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, Jalan Ganesa 10, Bandung 40132, Indonesia^b Department of Chemical Engineering, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi Hiroshima 739-8527, Japan

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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 SiO₂ nanoparticles on the PL properties were also studied. The optimized BCNO phosphors may find potential use in white LED applications.

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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:Eu²⁺ [5], Ce³⁺ doped lanthanum silicon oxynitride [6] and MSi₂O₂N₂ 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 SiO₂ 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 SiO₂ nanoparticle on the PL properties of the BCNO phosphor material. The crystal structure formation and morphology of the BCNO phosphor is also discussed.

* Corresponding author. Tel.: +62 22 250 0834; fax: +62 22 250 8452.

E-mail address: ferry@fi.itb.ac.id (F. Iskandar).

2. Experimental

2.1. Materials and synthesis

BCNO phosphors were synthesized from the following precursors: boric acid ($\text{B}(\text{OH})_3$), urea ($(\text{NH}_2)_2\text{CO}$), and citric acid ($\text{C}_6\text{H}_8\text{O}_7$), 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.

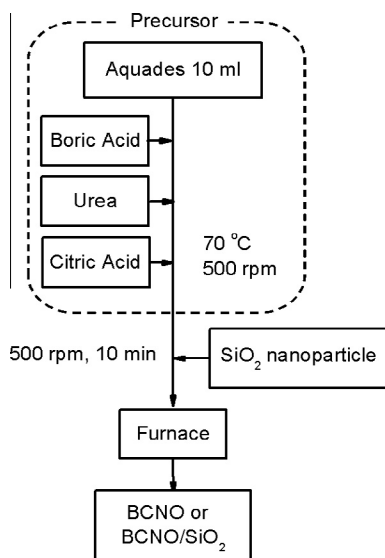


Fig. 1. Flow diagram for the synthesis of BCNO and BCNO/ SiO_2 phosphor.

2.2. Measurements and characterization

The crystal structure of the samples was analyzed using an X-ray diffractometer (RINT 2000V, Rigaku Denki, Japan) using $\text{Cu K}\alpha$ 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 ($<5 \mu\text{m}$) 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 $2.44 \mu\text{m}$ 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), $h\text{-BN}$ (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 $\text{B}(\text{OH})_3$ 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 $h\text{-BN}$ on BCNO phosphors are thought to originate from the exothermic reaction of urea with boric acid or B_2O_3 with NH_3 . The $h\text{-BN}$ 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

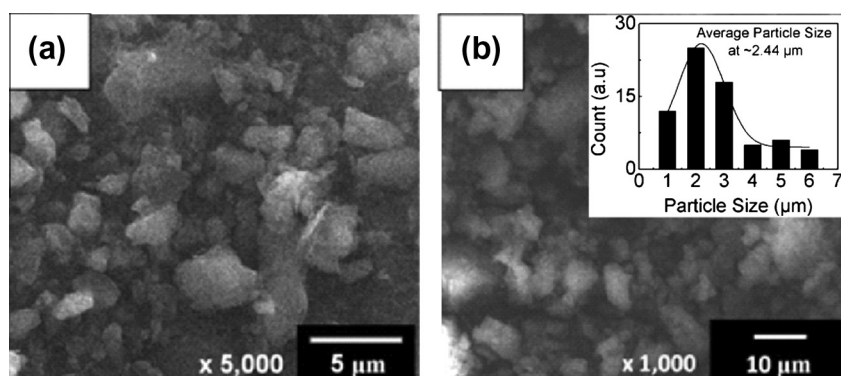


Fig. 2. SEM image of BCNO phosphors prepared with N/B = 10, C/B = 0.5, and synthesis at 750 °C for 30 min; (a) 5000 times and (b) 1000 times magnifications (inset: particle size distribution of BCNO phosphor material).

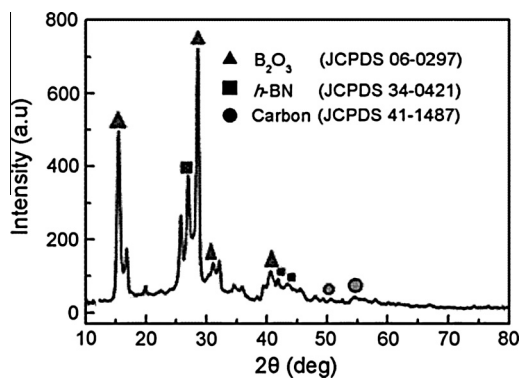


Fig. 3. XRD pattern of BCNO phosphors prepared with N/B = 10, C/B = 0.5, and synthesis at 750 °C for 30 min.

carbon peaks in the XRD pattern indicates carbon impurities within the crystal structure of the BCNO phosphor.

3.2. Effect of C/B and N/B molar ratio on the PL properties of BCNO phosphor

While maintaining a N/B molar ratio of 10, we systematically investigated the effect of the carbon/boron source (C/B) molar ratio on the PL properties of the BCNO phosphor prepared at 750 °C. The PL properties of the BCNO phosphor were observed under excitation at 365 nm. Fig. 4(a) shows PL spectra from samples derived from the 0.1, 0.3, 0.5, and 0.7 of C/B molar ratio precursors. The prepared samples were observed to have a single-peak emission, which is good for blue to yellow emissions. Upon increasing the C/B molar ratio in the precursor solution, the BCNO phosphor PL peak red-shifted from 444 to 520 nm. This phenomenon is consistent with the previous studies which stated that increasing the

carbon concentration would red-shift the PL peak wavelength, because the presence of carbon impurities in the crystal structure result in a decreased energy band gap for the BCNO phosphor [8,12,16].

This is caused by the emission energy being absorbed by carbon impurities, so that the emission wavelength will be red-shifted ($1/E \approx \lambda$) according to the following equation:

$$E_g = \frac{hc}{\lambda}, \quad (1)$$

where E_g is the emission energy (eV), h is Planck's constant (6.63×10^{-34} J s), c is speed of light (3×10^8 m s $^{-1}$), and λ is the emission wavelength (m).

However, increasing carbon impurities lead to a decrease in PL intensity. This can be seen with the C/B molar ratio of 0.7, where the PL intensity of the synthesized BCNO phosphor materials was 5-fold lower than the PL intensity of BCNO phosphors made with a C/B molar ratio of 0.1. The carbon particle residue acts to absorb both the incident UV light and emitted luminescence from the BCNO phosphors, thus reducing the BCNO phosphor PL intensity. The PL properties of BCNO phosphors prepared with various C/B molar ratios are shown in Fig. 4(b).

Fig. 5(a) displays PL spectra of BCNO phosphors made with various N/B molar ratios. Urea and boric acid precursors were used as the nitrogen and boron sources, respectively. The PL spectra show that increasing nitrogen concentration causes a blue-shift of the sample PL peak from 508 nm (yellow) toward 440 nm (blue). The shift of the BCNO phosphor PL peak to the blue luminescence region is consistent with previous studies [8,9,12,13]. The BCNO phosphor with N/B = 15 had the highest PL intensity, 3-fold higher than the sample prepared with N/B = 10. This demonstrates that increasing of N/B molar ratio leads to a good nitriding process and reduces carbon impurities, which blue-shifts the PL peak and increases the PL intensity. The PL properties of BCNO phosphors prepared with various N/B molar ratios are shown in Fig. 5(b).

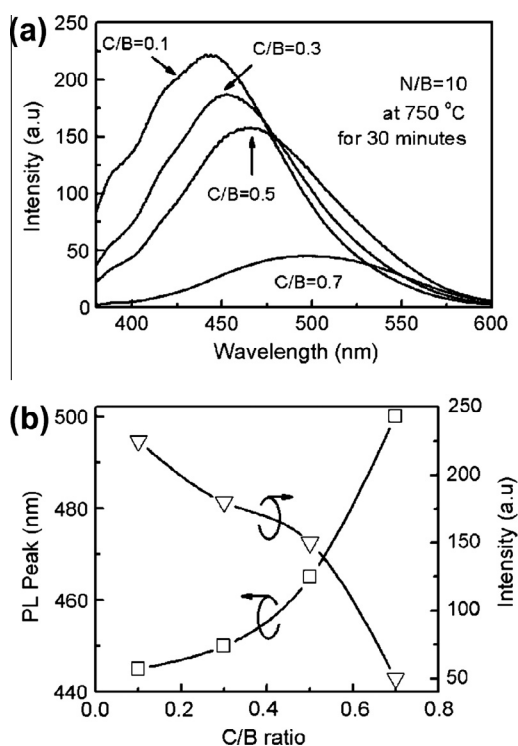


Fig. 4. (a) PL emission spectra and (b) PL properties of BCNO phosphors prepared using various C/B molar ratios.

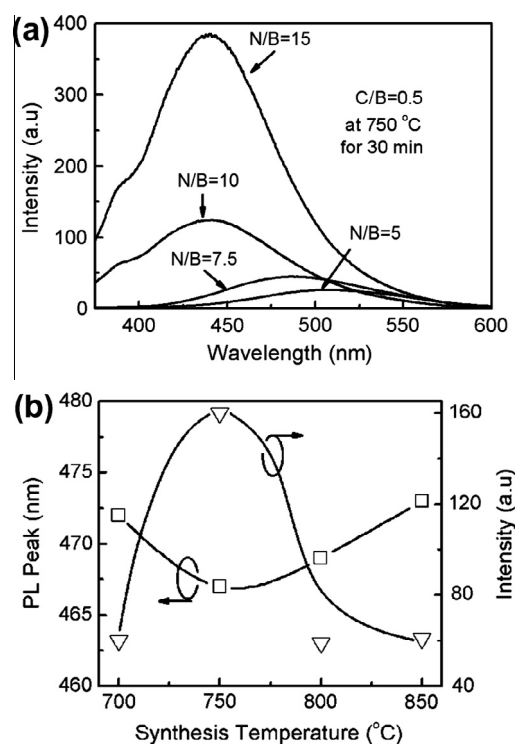


Fig. 5. (a) PL emission spectra and (b) PL properties of BCNO phosphors prepared using various N/B molar ratios.

3.3. Effect of synthesis temperature on BCNO phosphor PL properties

To investigate the effect of synthesis temperature on the PL properties, BCNO phosphors were synthesized at different synthesis temperatures. Fig. 6(a) shows the PL spectra of the prepared samples with synthesis temperatures ranging from 700 to 850 °C. The sample prepared at 750 °C had the highest PL intensity. The PL properties for the BCNO phosphors prepared at various synthesis temperatures are shown in Fig. 6(b). The low PL intensity for the 700 °C sample can be rationalized by incomplete formation of the BCNO phosphor crystal structure, such that the effect of impurities still dominates. For the sample prepared at 750 °C, the crystal structure of BCNO phosphors has completely formed and impurities have been completely decomposed. However, upon increasing the synthesis temperature to 800–850 °C, the PL intensity decreased. These results are consistent with recent research by Kaihatsu et al. [10] and Ogi et al. [14]. This phenomenon might be considered a possibility that the increasing temperature lead to a decrease in the concentration of carbon and nitrogen compounds in the sample due to a decomposition process [10,14]. Thus, it changes the chemical composition of the prepared sample and lead to the decrease of PL intensity.

3.4. Effect of SiO₂ nanoparticle addition on the PL properties of BCNO phosphor

The addition of SiO₂ nanoparticles within the BCNO phosphors was expected to improve the PL performance, based on findings in previous research [8,16]. To determine the effect of adding SiO₂ nanoparticles on the PL performance of the BCNO phosphor, varied mass fractions (0–5 wt%) of SiO₂ were added to the precursor with N/B = 10 and C/B = 0.5. Then, the precursors were heated at 750 °C for 30 min. The PL spectra of the prepared samples with different SiO₂ mass fractions are shown in Fig. 7(a). All prepared samples exhibit an excitation peak at 356 nm, and their emission

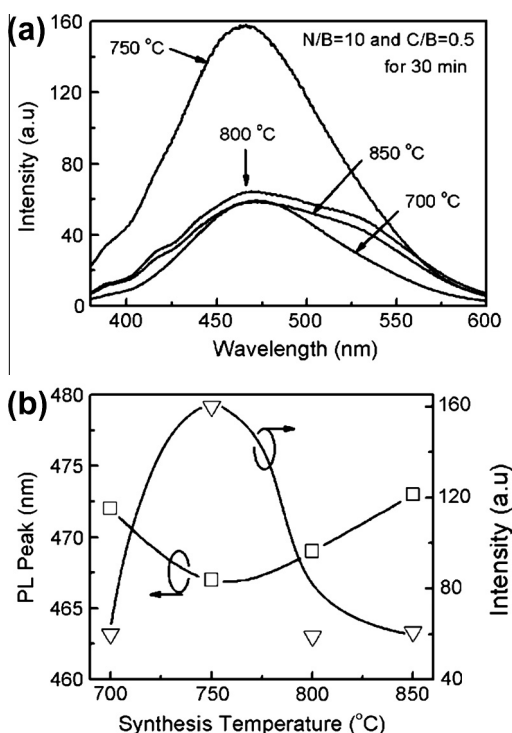


Fig. 6. (a) PL emission spectra and (b) PL properties of BCNO phosphors prepared at various synthesis temperatures.

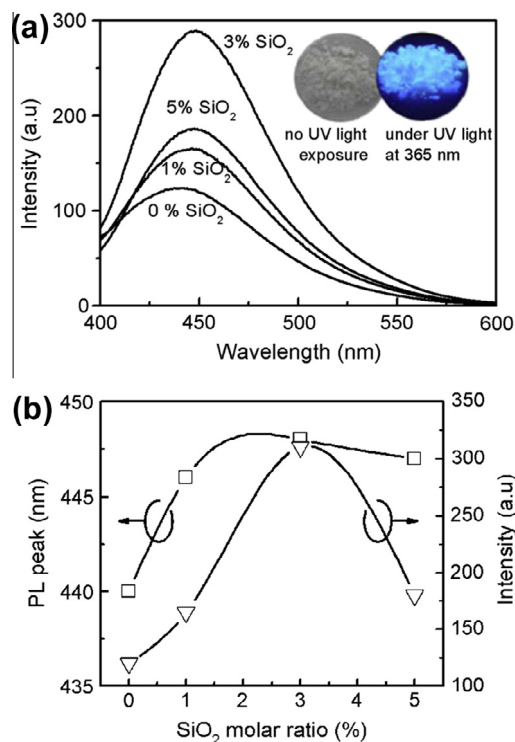


Fig. 7. (a) PL emission spectra and (b) PL properties of BCNO phosphors prepared with various mass fractions of SiO₂ nanoparticles.

peaks range from 440 to 449 nm. Under direct observation by the naked eye, the color of the sample containing 1 wt% SiO₂ was indicative of blue luminescence. The PL intensity of the BCNO phosphors with 1 wt% SiO₂ was increased significantly compared with samples prepared without SiO₂ nanoparticles. Samples containing 3 wt% SiO₂ showed the highest intensity. Their PL intensities were nearly 3-fold larger than samples without SiO₂ nanoparticles. Addition of 5 wt% SiO₂ resulted in decreased PL intensity, and produced BCNO phosphors with coarser textures. The decrease in PL intensity was ascribed to the agglomeration of the SiO₂ nanoparticles, which forms larger particles that dominate the surface and reduce the PL intensity of the BCNO phosphors. All the PL properties of BCNO phosphors prepared with various SiO₂ mass fractions are shown in Fig. 7(b). High amounts of SiO₂ also scatter light through the Tyndall effect, which can also reduce the emission intensity of the BCNO phosphors [16]. The added SiO₂ nanoparticles act as a matrix that distributes heat more evenly, which helps reduce carbon impurities and yields BCNO phosphors with uniform luminescence characteristics.

4. Conclusion

In summary, we have studied how precursor concentration, synthesis temperature, and SiO₂ additive concentration affect the crystal structure and PL performance of BCNO phosphors. Using citric acid as a carbon source, we observe that the PL peak red-shifts as the carbon concentration in the precursor increases. The overall PL peak emission of the BCNO phosphors was close to “yellow emission” within the visible spectrum. The BCNO phosphor prepared with 3 wt% SiO₂ a synthesis temperature of 750 °C displayed the highest PL intensity. Based on crystal structure and PL property analyses, we have clarified the luminescent behavior of BCNO phosphors. The phosphors reported here are promising candidates for developing white LEDs.

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