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A Facile Synthesis and Photoluminescence Properties of Boron Carbon Oxynitride (BCNO) Phosphor Materials for Security Ink Application

A Facile Synthesis and Photoluminescence Properties of Boron Carbon Oxynitride (BCNO) Phosphor Materials for Security Ink Application

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Abstract. A facile synthesis of rare-earth free using boron carbon oxynitride (BCNO) phosphor material for security ink has been investigate. BCNO were synthesize by low temperature microwave heating methods, with H_3BO_3, citric acid and urea to be used as boron, carbon and nitrogen source, respectively. Then, the BCNO nanocrystals were disperse in water-polymer based solution until they became evenly spreading and turn into security ink without rare earth metals. The photoluminescence (PL) and UV-Visible spectroscopy were use to characterize the optical properties of BCNO and the security ink. The characterization results showed that BCNO and the security ink had similar PL properties (PL Peak and PL Peak Intensity). In addition, the UV-Vis spectra proved that the security ink had electronic properties such as being semiconductors based phosphor materials. The results indicate that BCNO phosphor material can be potentially be developed as rare-earth free security inks, and other applications such as optoelectronic, white LED, lighting, etc.

1. Introduction

In recent years, there are many researches about the compounds of oxynitride and nitride as phosphorus materials due to their superior characteristics, such as being non-toxic, having good thermal and chemical stability, having wide excitation and emission wavelength, and also possessing high luminance efficiency when being activated by rare earth ions such as Ce3 +, Eu 2+, and Li + [1]. However, the aforementioned elements of rare earth ions, which act as the activator and the centres of luminescence, are expensive, scarce, and also becoming the sources of environmental pollution [2].

In 2008, Ogi et al did manage to synthesize boron carbon oxynitride (BCNO) phosphor materials without the use of rare earth metal ion doping at a relatively low heating temperature between 700-900 0C and at an atmospheric pressure condition. BCNO has a broad spectrum of excitation wavelength (from UV to blue ray) which causes luminescence in the visible light spectrum (400 nm - 585 nm). It also has half-life of luminescence (emission lifetime) from nano to milliseconds. The range of emission/luminescence colour of BCNO is from purple to near red and it can be adjust easily by

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varying the ratio of carbon source using an optimum heating temperature and reaction time [3]. The chemicals used to produce phosphorus material BCNO are economical and non-toxic. The chemicals used include H3BO3, (NH2)2CO, and polyethylene glycol (PEG) as the source of boron, nitrogen, and carbon, respectively. A continuous development of the manufacture of phosphor from BCNO have managed to generate new findings which include the knowledge on the luminescence mechanism of BCNO, a better synthesis method to adjust the amount of emissions [4], the selection of carbon sources [4, 5] addition of nanoparticles SiO2 [6], BCNO with red luminescence [7]. As well as possible applications in the field of optoelectronics [8].

In recent years, many study about phosphorescent have been published in regards of the development of non-colour ink [9, 10]. Non-color ink applied for security ink, which is an effective and low cost (efficient) method, for the protection of valuable documents and products against fraud, forgery, alteration, and unauthorized trading. Non-colour ink applied on the field of optoelectronics such as light-emitting diodes (LED). Non-colour inks can be customize with inkjet printing technology to print confidential documents. Inkjet printing process has a number of advantages such as the exact deposition of ink on the paper or substrate with a good layout, and low ink consumption hence it will therefore reduce the cost. Non-colour inks are generally develop from colloidal made from a mixture of polymers and phosphorescent materials.

To the best of our knowledge, there is still no existing study about the development of a non-colour security ink based on BCNO. This is due to the difficulty in dispersing the material of BCNO in a suitable solvent and the difficulty of producing BCNO in nanoparticle size. In this paper, we report on the research about the BCNO nanophosphor using microwave method. It were expected that the solution of BCNO nanoparticle can be applied as a non-colour security ink that can replace the use of phosphorescent materials, which based on rare earth metal ions so that the application non-colour security ink becomes more economical, applicable, and pollution-free to the environment.

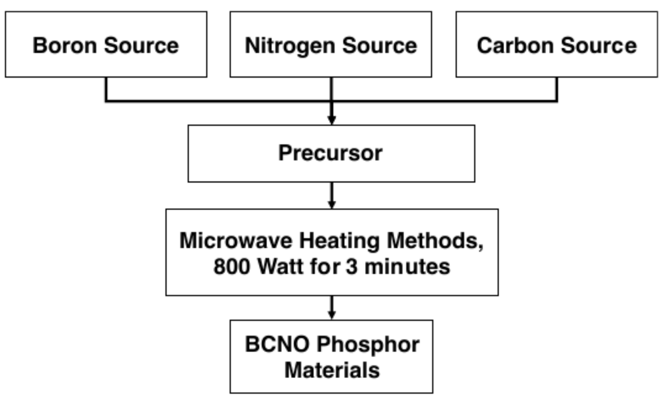

Figure 1. Flow diagram of the synthesis of BCNO nanoparticle using microwave-heating methods.

2. Experiment

The BCNO nanophosphors for security ink application were synthesized using boric acid ($B(OH)_3$), urea ((NH2)2CO) and citric acid (C6H8O7) as the boron, nitrogen and carbon sources, respectively. All chemicals were purchase from Merck Co., Ltd., Germany without further purification. Precursor solutions were prepared by mixing boric acid, urea, and citric acid in distilled water, followed by stirring with high rotational speed and at room temperature for 10 min to obtain homogeneous solutions. The citric acid/boric acid (C/B) mass ratio was varied at 0.2 (Sample B), 0.4 (Sample C), 0.8 (Sample D), 1.2 (Sample E), 1.6 (Sample F) and 2 (Sample G), and the urea/boric acid (N/B) mass ratio for all samples was prepared at 4. The precursors were heated using microwave at 800 watt for 3 min under ambient atmospheric pressure. Then, the BCNO nanocrystals dispersed in water-polymer based solution until they evenly spread and disperse. The flow diagram to describe the synthesis process of BCNO phosphor materials using microwave-heating method shown in Figure 1. The photoluminescence (PL), photoluminescence excitation (PLE) and UV-Visible spectra of each sample measured at room temperature using a spectrofluorophotometer (Cary Eclipse Spectrophotometer, Agilent, Australia) equipped with a xenon laser source and Homemade UV-Visible spectroscopy (LD Didactic, Leybold, Germany). All PL, PLE and UV-Vis spectra analyses were performs at room temperature with 365 nm excitation.

3. Results and Discussion

Figure 2 shows the samples of BCNO phosphor solution synthesized using a microwave with variation in carbon concentration, without being exposed to UV light (a) and during irradiation process by UV light (b). From Figure 2 (a) it appears that the increase of carbon concentration caused the phosphoric solution of BCNO became brownish. The color of the solution turned darker when the concentration of the carbon increased which was possibly due to the formation of free carbon in the sample. The phosphoric solution of BCNO that was irradiated by UV light produced blue luminescence as can be seen in figure 2 (b). The amount of carbon content was very influential to the photoluminescence of BCNO in which the blue color became brighter as the content of carbon increased.

The influence of the amount of carbon content on the photoluminescence of BCNO can be seen from the characterization results of Photoluminescence (PL) spectrofluoro-photometer in Figure 3 (a). The luminescence emission of BCNO was within the range of wavelength from 461 to 475 nm which showed that the luminescence of the sample was in blue region. The wavelength shifted toward larger number as the concentration of carbon in the solution increased. The shift of peak wavelength of the BCNO luminescence due to the addition of carbon concentration has been reported by Ogi, et al., in the manufacture of BCNO with simple heating method [3].

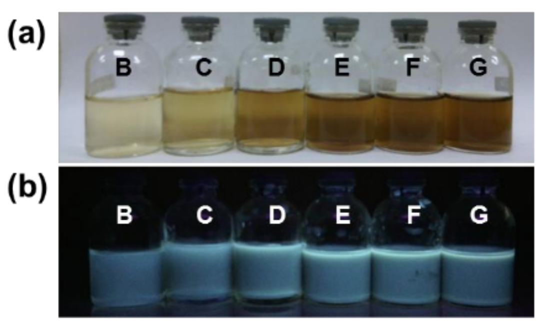

Figure 2. Digital image of BCNO nanoparticles on water for various carbon concentrations, under (a) visible light, and (b) UV light.

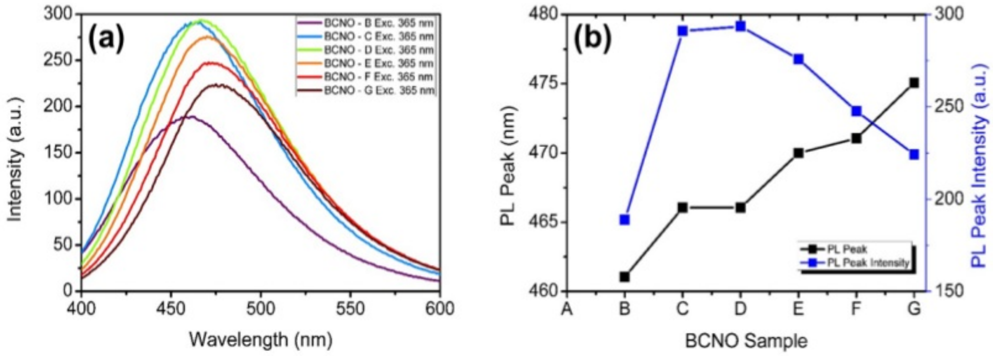

Figure 3. Effect of carbon concentration on the Photoluminescence properties of BCNO nanoparticle: (a) PL Spectra and (b) PL Properties.

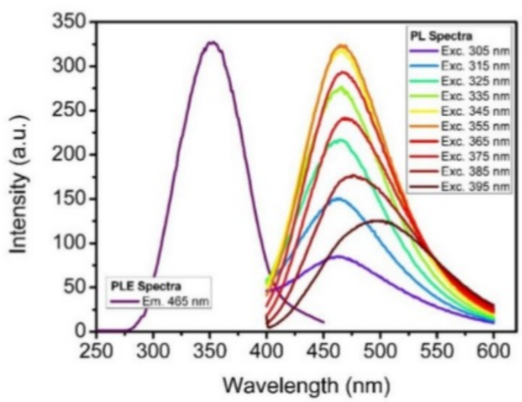

Figure 4. PLE spectra of BCNO phosphor material (Sample D) under UV light excitation.

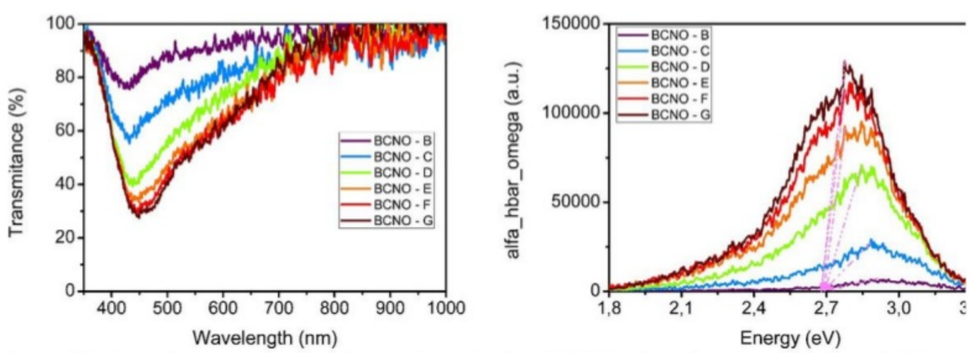

Figure 5. Transmitance spectra and tauc plot analysis of BCNO phosphor material (Sample D).

The intensity of luminescence produced was also highly dependent on the concentration of carbon as shown in Figure 3 (a) and (b). The addition of carbon in samples B, C and D caused the luminescence intensity to increase. However, the luminescence intensity in samples E, F, G decreased which was possibly due to the excessive carbon content in the solutions so that the carbon did absorb the excitation light and dim the light emission of BCNO phosphor. The lowest intensity was generated by sample B, which was allegedly happen to occur due to low carbon reaction so BCNO had not been formed. Meanwhile, the optimum intensity was obtained by sample D.

To complete the PL data, sample D was characterized using Photoluminescence Exciation (PLE) to determine the effect of the excitation wavelength on the emission color intensity of the photoluminescence material of BCNO at the wavelength of 465 nm. The excitation wavelength used was varied from 305 to 395 nm. The highest emission color intensity was produced at the excitation wavelength of 365 nm (Fig. 4).

To determine the energy gap of BCNO which had been successfully created, a characterization by UVVIS spectrometer was conducted. The measurement results are shown in Figure 4 which shows the transmittance spectrum of BCNO phosphor material synthesized by a microwave. From the graph, it was proven that the large amount of carbon concentration in the solution resulted in larger absorbance at the wavelength of 450 nm.

The optical band gap in a semiconductor can be evaluated by observing the absorption coefficient as a function of the photon energy using Tauc's law [11]:

$$\alpha = \frac{B(E-E_g)^P}{E}$$

where B is a constant, Eg is the optical energy gap and p is a constant which determines the type of the optical transition (p = 2 and 1/2 for direct allowed transition and indirect allowed transition, respectively). Therefore, the optical energy gap of the prepared BCNO was determined by assuming direct transition and interpolating the linear portion of the plot of $(\alpha E)^2$ *vs*. E. The value of the optical energy gap was about 2.7 eV which is well within 2.25-3.19 eV as reported by Wang *et al*. [12] for BCNO phosphors.

4. Conclusions

We have successfully synthesized rare-earth free security ink using carbon boron oxynitride (BCNO) phosphor material by microwave heating method. The BCNO was synthesized by low temperature microwave heating methods, with H3BO3, citric acid and urea to be used as boron, carbon and nitrogen source, respectively. Then, the BCNO nanocrystals were dispersed in water-polymer based solution until they became evenly spread and turn into security ink without rare earth metals. The photoluminescence (PL) and UV-Visible spectroscopy were used to characterize the optical properties of BCNO and the security ink. The characterization results showed that BCNO and the security ink had similar PL properties (PL Peak and PL Peak Intensity). In addition, the UV-Vis spectra proved that the security ink had electronic properties such as being semiconductors based phosphor materials.

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