Thermoluminescence Properties of BCNO Phosphors after X-ray Irradiation

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Amorphous solids composed of B, C, N, and O, which are called BCNO, were developed as thermoluminescent (TL) materials for dosimetry. On the basis of X-ray diffraction patterns, the amorphous phase of the samples was confirmed. Photoluminescence spectra had an emission peak attributed to the electronic transition of emission centers based on a N vacancy and a C atom. A glow peak in TL glow curves was observed at around 380 K after X-ray irradiation. The result indicates that BCNO can be applied as tissue-equivalent TL materials for dosimetry.

1. Introduction

Dosimetry based on optical materials has widely been used. From the viewpoint of sensitivity, the use of storage phosphors is advantageous.[1] Thermoluminescence (TL)[2,3] and optically stimulated luminescence (OSL)[4–7] have been used for personal dosimetry and radiation imaging. Also, radio-photoluminescence (RPL), which is defined as the photoluminescence of radiation centers produced by ionizing radiation, has been used for personal dosimetry and fluorescence track detection.[8,9] To achieve further sensitivity[10–16] or expand the applicability to thermal neutrons,[17–24] a large number of studies have been conducted and published. In general, storage phosphors that can be used for dosimetry are composed of inorganic crystals or glasses containing elements of relatively high atomic numbers.

In medical dosimetry, for example, for the radiation therapy of cancers, tissue equivalence is required for dosimeters. The tissue equivalence is the equivalence of the absorption characteristics of the energy of ionizing radiations to that of biological tissue. To achieve tissue equivalence, a limited number of elements (typically atomic numbers of 3–9) can be used. This imposes a severe limitation in the materials design based on inorganic compounds. An effective approach to achieve tissue equivalence is the use of organic materials or soft matters. Thus far, radiochromic dosimeters based on gels[25] or polymers[26–31] have been developed. Also, organic

materials exhibiting RPL have been developed.[32–34] However, it is difficult to achieve high sensitivity using organic materials or soft matters. Another approach is to use the limited number of elements in inorganic compounds.[35, 36]

In the present study, we aim to develop tissue-equivalent TL dosimeters based on the latter approach. Recently, amorphous solid materials based on B, C, N, and O have been developed as rare-earth-free phosphors.[37] They are called BCNO. Because of their elemental composition, BCNO can be used as tissue-equivalent dosimeters. Thus far, there is a report on the TL response of BCNO;[38] however, judged from the XRD pattern in the paper, the sample was crystalline. In this paper, we report on the photoluminescence (PL) and TL properties of amorphous BCNO phosphors synthesized with calcination at different temperatures.

2.   Materials and Methods

Samples were fabricated according to a previous paper.[39] Boric acid (99.5%, Aldrich), melamine (99%, Aldrich), and hexamethylenetetramine (99%, Wako) were used as raw materials without further purification. 0.1 mol of boric acid and melamine were dissolved in 200 g of distilled water. The solution was heated at 90 °C for 20 min with stirring. Subsequently, 0.01 mol of hexamethylenetetramine was dissolved in the solution and stirred at 90 °C for 20 min. The solution was dried at 80 °C in an oil bath overnight to obtain a dry gel, which was subsequently formed into pellets of 13 mmφ and ~3 mm thickness. The pellets were calcined at 550, 600, 625, or 650 °C for 12 h. Some samples were crushed and formed into pellets again and subsequently calcined at the same temperature for 3 h to obtain rigid samples. It is difficult to elucidate the chemical compositions of the samples in this study. The chemical compositions of BCNO phosphors have been reported in a limited number of previous papers. For example, the composition of B:C:N:O of 27:23:24:26 was estimated on the basis of the XPS spectrum of BCNO synthesized from boric acid, urea, and polyethylene glycol in a previous study.[40] As another example, the compositions of B:C:N:O of BCNO synthesized from trimethyl borate, melamine, and hexamethylenetetramine were 3.03:2.70:1:4.13 and 3.09:2.77:1:4.50 depending on the ratio of trimethyl borate and melamine.[41] Judged from the raw materials, the atomic compositions of the samples in the present study are close to the latter example.

The structural phase of the samples was analyzed for crushed powder using X-ray diffraction (XRD; Ultima II, Rigaku) at 10–80°. Thermogravimetry (TG) and differential thermal analysis (DTA) at 40–900 °C were performed for the samples before or after one calcination at 550 °C in ambient atmosphere using a TG/DTA instrument (DTG-60A, Shimadzu). The excitation and emission spectra were obtained as contour plots using a spectrofluorometer (Quantaurus-QY, C11347-01, Hamamatsu). Also, PL quantum yields (QYs) were estimated on the basis of contour plots.

The TL properties of the samples were analyzed after X-ray irradiation using an X-ray generator (Monoblock® XRB80N100, Spellman) operated at 80 kV and 1.2 mA. The dose rate was 1.0 Gy/min. The TL glow curves after X-ray irradiation were obtained using our original setup: the samples were heated at a rate of 1.0 K/s up to 400 °C using a ceramic heater (WALN-6H, Sakaguchi) and a programmable temperature controller (SCR-SHQ-A2, Sakaguchi). The TL

photons from the samples were detected using a photon counting unit (H11890-210, Hamamatsu). A thermal cut filter was placed in front of the photon counting unit to suppress the thermal radiation from the samples at high temperatures.

3.   Results and Discussion

The XRD patterns of the samples after twice calcination at different temperatures are presented in Fig. 1. Halo peaks were observed at around 26.6 and 43.6º, which are consistent with those in a previous study.[39] The halo peaks have similar peak angles to those of the (002), (100), and (101) reflections of t-BN. The results indicate the amorphous nature of the sample with short-range order similar to that of t-BN. The sample calcined at 600 °C had sharp peaks at 14.6 and 27.9º, which can be attributed to the BN impurity crystalline phase. From our experience with the development of BCNO phosphors, some samples had a BN impurity crystalline phase irrespective of the fabrication conditions used. Because of the small fraction of the impurity phase, the effects of the impurity phase on the PL and TL properties of the samples are minimal.

The TG-DTA curves of the sample before calcination are presented in Fig. 2(a). At 160 and 310 °C, significant weight loss and endothermic peaks were observed, indicating that pyrolysis occurred at these temperatures. The pyrolysis at 160 °C has been reported in a previous paper.[38] An additional weight loss occurred at 500–650 °C with an exothermic peak, indicating combustion. Because the sample experiences combustion in this temperature range, we calcined the samples at 550–650 °C to change continuously the composition through combustion. The TG-DTA curves of the sample after one calcination at 550 °C are shown in Fig. 2(b). Judged from the endothermic peak temperature with a slight decrease in mass, the peak at 120 °C can be attributed to the desorption of adsorbed water. The change in weight and the DTA signal were much smaller than those of the sample before calcination. Hence, the main effect of the second calcination is making the samples rigid.
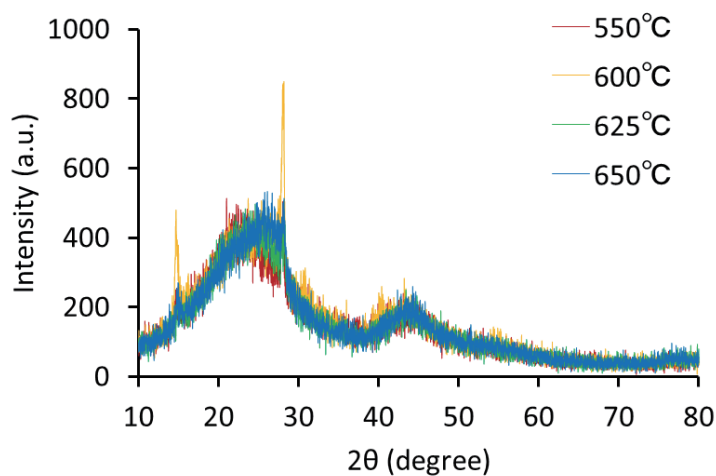

Fig. 1.   (Color online) XRD patterns of BCNO samples calcined twice at different temperatures.
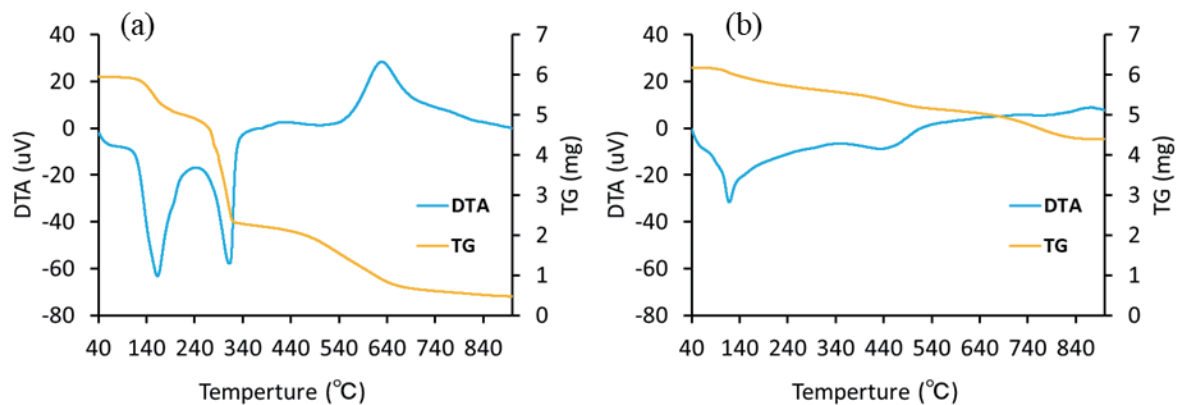
Fig. 2. (Color online) TG-DTA curves of BCNO samples (a) before and (b) after calcination at 550 ℃.

The excitation–emission contour plots of the samples calcined twice at different temperatures are presented in Fig. 3. The excitation peak wavelength was around 370 nm and slightly shifted to the short wavelength side with the calcination temperature. The emission peak wavelength also shifted to the short wavelength side from 420 to 395 nm with the calcination temperature. On the basis of the excitation and emission wavelengths consistent with the previous result, the emission is attributed to the electronic transition of emission centers based on a N vacancy and a C atom.[42] The shift in peak wavelength to the short wavelength side with the calcination temperature is consistent with that in a previous result and is attributed to the decrease in C content in BCNO.[42] The PL QYs of the samples after being calcined twice at 550, 600, 625, and 650 ℃ were 54, 64, 61, and 56%, respectively.

The TL glow curves of the BCNO samples after being calcined twice at different temperatures and TLD-100 after X-ray irradiation at 1 Gy are presented in Fig. 4. For all the BCNO samples, a TL glow peak was observed at around 380 K. This result indicates that the BCNO phosphors exhibit TL without dopants. The integral TL intensities of the samples were 91, 48, 24, and 60% of the TL intensity of TLD-100. The masses of the samples were within ±20%. Note that the TL intensity was higher for the sample with a lower PL QY. A possible reason for this anticorrelation is similar to that proposed by Prof. Yanagida[43], i.e., the anticorrelation of the scintillation light yield and intensity of storage-type luminescence including TL. In the case of BCNO, the PL QYs were recorded under host excitation. The low PL QY may be partly attributable to the trapping of electrons and holes at different sites. If this trapping is one of the main causes for the low PL QY, the anticorrelation of PL QY and TL intensity in BCNO can be explained. The weights of the samples were larger than that of TLD-100 by an order of magnitude, which indicates that the TL intensity for the same weight or size is much lower than that of TLD-100. Hence, for the practical use of BCNO, it is necessary to significantly increase the TL intensity.
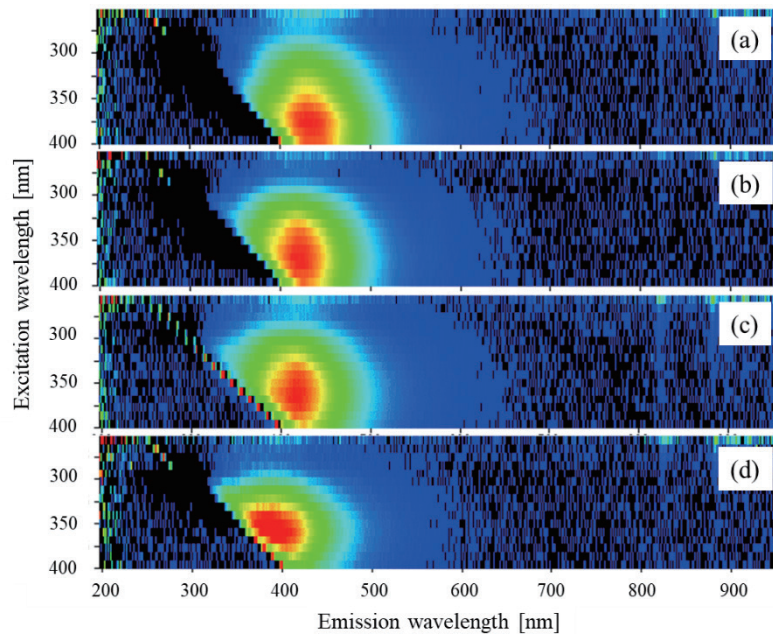
Fig. 3.   (Color online) Excitation–emission contour plots of BCNO samples calcined at (a) 550, (b) 600, (c) 625, and (d) 650 ℃.
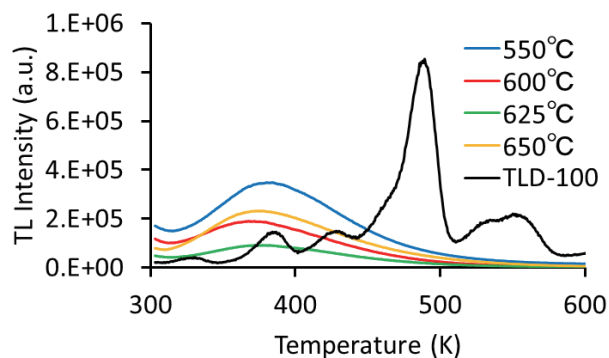

Fig. 4.   (Color online) TL glow curves of BCNO samples after being calcined twice at different temperatures and TLD-100 after X-ray irradiation at 1 Gy.

4.   Conclusions

The PL and TL properties of BCNO phosphors have been analyzed. The BCNO samples were fabricated by calcinating them twice at different temperatures. XRD patterns indicate the amorphous phase of the samples. The PL and PLE spectra had an emission peak and an excitation peak, respectively. The origin of the emission is attributed to the electronic transition of emission centers based on a N vacancy and a C atom. The shift in excitation or emission peak wavelength

to the short wavelength side was observed with the calcination temperature. TL glow curves had a peak at around 380 K. The result indicates that BCNO can be used as tissue-equivalent TL dosimeters.

Acknowledgments

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