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# Strong deep-blue photoluminescence of mesographite boron nitride

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## Abstract

Amorphous boron nitride (a-BN) powder was prepared by mechanical milling of hexagonal BN. Annealing the a-BN between 600 and 1200 °C produced turbostratic BN (t-BN) and mesographite BN (m-BN) with different degrees of three-dimensional order (DTDO). The photoluminescence (PL) of the BN samples was investigated using 325 nm laser excitation. The a-BN and t-BN emit continuums with a maximum near 340 nm. The m-BN samples that have three-dimensional order show deep blue PL bands. The positions of the bands change with lattice constants, while the PL intensity increases firstly with increasing DTDO then decreases after reaching a maximum. The strongest PL band is observed at 413 nm in one of the m-BNs prepared at an annealing temperature of 1100 °C. It is suggested that the bands are related to structural defects in the m-BNs.

## 1. Introduction

Photoluminescence (PL) of many III–V group semiconductors, such as InP, GaAs, GaN, etc, have been extensively studied recently, due to their important applications in optoelectronic devices [1–3]. Graphite-like hexagonal BN (h-BN) is a good III–V group electrical insulator with high thermal conductivity, good thermal stability and chemical stability, and has a wider energy band gap of about 4–6 eV [4–6]. When impurities or defects exist in h-BN, acceptor or donor energy levels may be formed in the band gap and luminescence can occur in the visible, in particular the blue and ultraviolet region, that makes h-BN have much wider potential applications in optoelectronics. Some research on the luminescence of h-BN has been carried out over the past few years [7–16]. Larach *et al* [7] reported first that they observed a PL spectrum with a fine structure throughout the 300–500 nm region in a purified h-BN and considered the fine structure emission to be inherent to the BN molecular layers. However, Katzir *et al* [8] and Andrey *et al* [9] only observed a blue PL continuum covering a range of

390–500 nm, with a maximum near 420 nm in Grad HP hot-pressed h-BN. They attributed the PL continuum to deep levels of carbon impurity. Bose and Hensch [10] observed very weak PL bands in hot-pressed h-BN. As reported in the previous literature, the PL spectra are different for h-BN produced by different methods, so that the luminescent mechanism of h-BN is still a problem that needs further investigation.

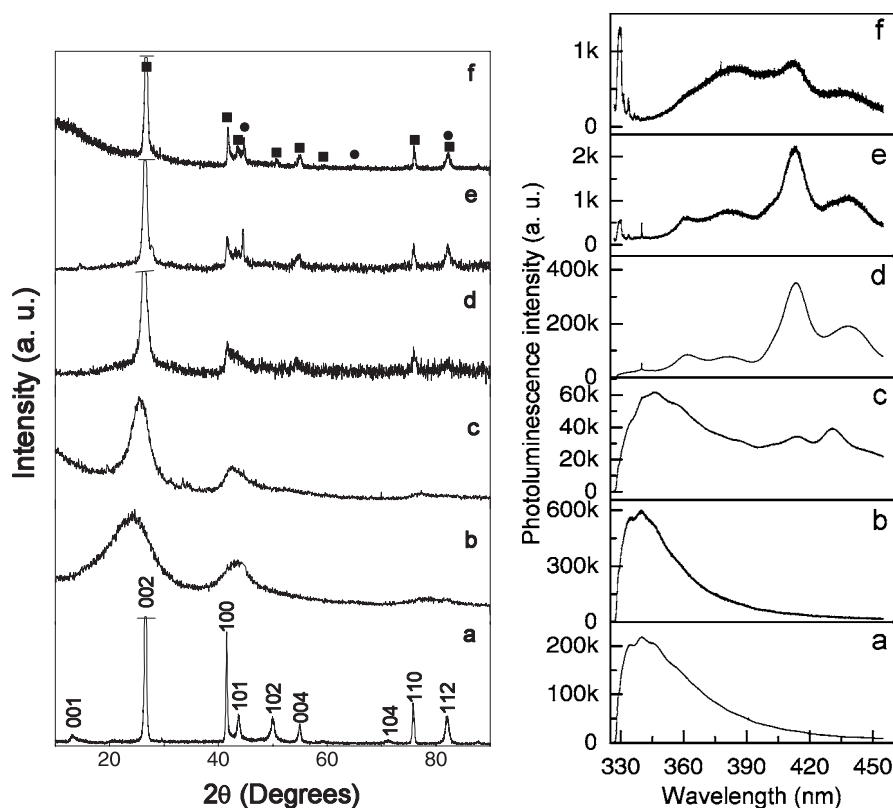
A h-BN with a fully ordered structure is normally synthesized by annealing an amorphous BN (a-BN) at a high temperature of about 2000 °C where it undergoes a series of intermediate phases with improved DTDO [17, 18]. Many kinds of structural defects will be formed in the intermediate phases and change with DTDO. The local levels formed by the impurities and defects may be different in the different intermediate phases and h-BN, resulting in different luminescent properties of BN. Therefore, it is very interesting to study the change of the luminescent properties with structure from amorphous BN to h-BN for researching the luminescent properties of BN systematically and understanding the luminescent mechanism correctly. However, no such research has been reported up to now, though the structure and phase transition of the intermediate phases have been studied extensively [17–22]. In the present paper, we study the PL properties of BN with various structures and DTDO and a correlation between the PL and the DTDO.

## 2. Experimental details

An a-BN powder was prepared by mechanical milling of h-BN under argon atmosphere for 30 h, using stainless steel balls and vial. The weight ratio of ball to powder was 10 to 1. In order to produce BN with various structures, the a-BN sample was annealed under high pure Ar atmosphere at temperatures between 630 and 1200 °C for periods of 60–1020 min. Compositions of samples were detected by energy dispersive x-ray spectroscopy (EDX) and x-ray photoelectron spectroscopy (XPS). Structures of the samples were examined by x-ray diffractometer (XRD) with Cu K $\alpha$  radiation and transmission electron microscopy (TEM). The thermal stability of the a-BN was studied using a differential scanning calorimeter (DSC) at a heating rate of 20 °C min<sup>-1</sup> under a flow of argon gas. The distribution and valence state of Fe in the BN were detected by XRD and Mössbauer spectrometry (MS). The PL spectra were excited by a 325 nm line of a He–Cd ultraviolet (UV) laser with an output power of 5 mW.

## 3. Experimental results and discussions

Figure 1(a) shows the XRD pattern of the starting material, which is a typical XRD profile of fully ordered h-BN [23]. After milling for 30 h, the h-BN was transformed into a-BN, as shown in figure 1(b). The amorphous nature of the a-BN was also confirmed by TEM. The crystallization temperature of the a-BN was measured to be about 600 °C. After annealing the a-BN at 630 °C for 500 min, a long trail was found on the high diffraction angle side of the peak indexed as (10) in the XRD pattern shown in figure 1(c), which is characteristic of the turbostratic BN phase (t-BN) [17]. Upon annealing the a-BN at 820 °C for 60 min, some weak diffraction peaks corresponding to (004), (110) and (112) diffraction peaks in h-BN were observed, as shown in figure 1(d), but the (10) peak did not change and (102) peak was absent, indicating an incompletely ordered h-BN structure. When the a-BN was annealed at 1100 °C for 1020 min, the (10) peak began to split into (100) and (101) peaks, as shown in figure 1(e). After annealing at 1200 °C for 1020 min, the (100) and (101) peaks further split, and the (102) peak also appeared, as shown in figure 1(f). But the relative intensity between (102) and (004) peaks in figure 1(f) is still different from that of the fully ordered h-BN shown in



**Figure 1.** XRD patterns of h-BN (a), a-BN (b), t-BN (c), lm-BN (d), mm-BN (e) and pm-BN (f). ■—BN, ●— $\alpha$ -Fe.

**Figure 2.** Photoluminescence spectra of a-BN (a), t-BN (b), lm-BN (c), mm-BN (d), hm-BN (e) and pm-BN (f).

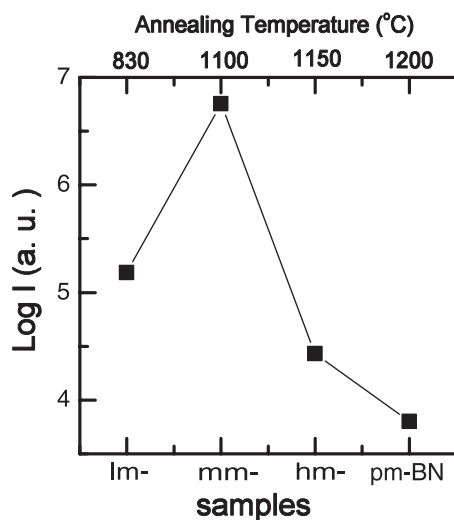
figure 1(a). This implies that the sample is still an incompletely ordered h-BN phase, though its XRD profile is very similar to that of fully ordered h-BN. In the present paper, the BN phases obtained at annealing temperatures of 820, 1100, 1150 and 1200 °C are all referred to as mesographite BN (m-BN) [17], and are denoted with signs lm-, mm-, hm- and pm-BN in an order of temperature from low to high. Apparently, the m-BN is an incompletely ordered h-BN phase with three-dimensional order, and its DTDO is higher than that of t-BN and increases with a rise in annealing temperature, but lower than that of h-BN. The structure of BN obtained by crystallization of the a-BN is affected mainly by the annealing temperature and is almost independent of annealing time, in agreement with previous results [17, 18]. However, the DTDO of the m-BN is related to annealing time.

Figures 2(a) and (b) show the PL spectrum of the a-BN and t-BN, respectively; both are strong continuums with a maximum near 340 nm. However, in the PL spectrum of the lm-BN the intensity of the continuum decreases greatly, and two additional weak PL bands appear at 413 and 431 nm, respectively, as shown in figure 2(c). When the BN is in mm-BN status, as figure 2(d) shows, the continuum disappears completely, while the intensities of the bands increase sharply and the position of the band at 431 nm in figure 2(c) moves to the lower energy position of 439 nm. For hm- and pm-BN, the positions of the bands do not change, but the PL intensity decreases greatly, as shown in figures 2(e) and (f). The above results indicate that the nature of the PL spectrum of the BN is related to its structure. It is known that the

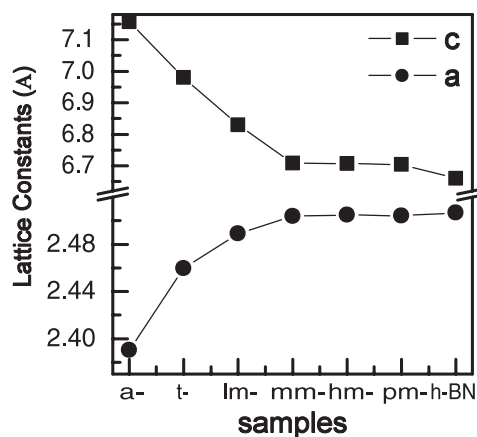
t-BN is ordered within the two-dimensional (2D) graphite-like layers but still lacks ordering among the layers, however, some three-dimensional order is established in the m-BN. So, only two-dimensional order cannot make the BN emit a separate band, and the appearance of the PL bands is related to the formation of three-dimensional order in the m-BN. The intensity of the bands is related to the DTDO of m-BN. It increases firstly with increasing DTDO, and then decreases greatly after reaching a maximum at mm-BN. Since fully ordered h-BN has the highest DTDO in the BN series, it is expected from results of figure 2 that the bands will disappear in the PL spectrum of h-BN and its PL spectrum becomes a weak continuum, as observed in Grad HP h-BN [8, 9]. Comparing figure 2 with previous results, the PL spectra obtained by Larach [8] and Bose [10] are similar to those of mm-BN and pm-BN. Therefore, it can be deduced that the difference in the PL spectra obtained by Larach, Katzir and Bose is attributed to the difference in the DTDO of the BNs they used.

From figures 1(e) and (f) it is found that there exists Fe contamination in the sample, which is produced by collision between the steel balls and the vial during milling. That is also confirmed by Mössbauer measurement. However, an emission spectrum similar to figure 2(d) was also observed previously in a purified h-BN, where no Fe existed [7]. Bose also demonstrated that no correlation between Fe content and luminescence was found [10]. These facts indicate that the bands are not related to Fe contamination. In addition to the Fe contamination, XPS and EDX measurements show that there are also Ca and B<sub>2</sub>O<sub>3</sub> impurities in the BN samples. Ca content is almost the same in the all samples, but B<sub>2</sub>O<sub>3</sub> content changes with annealing temperature and time. Carbon content is not clear, for it could not be detected by EDX and could not be distinguished from carbon contamination in the XPS instrument. However, it should be tiny and almost a constant in all the samples. In the present experiment, photoluminescence of the BN samples with different B<sub>2</sub>O<sub>3</sub> content were measured and no correlation between PL and B<sub>2</sub>O<sub>3</sub> was found, in agreement with previous results [10]. Since the PL intensity of a sample is directly proportional to impurity content, and Ca and C impurities contents are constants in the BN samples, the PL intensities of the bands should have been the same for the samples from mm-BN to pm-BN if the PL was related to the Ca and C impurities. However, the PL intensities decrease with increasing DTDO. Therefore, it is deduced that the bands are not related to Ca and C impurities.

Figure 3 shows the change of the PL intensity of the band at 413 nm with annealing temperature. Combining figures 1(d) and 2(c), it is concluded that only a small amount of the a-BN was transformed to lm-BN, and most of the a-BN crystallized to t-BN when the a-BN was annealed at 830 °C for 60 min, so the PL spectrum of lm-BN sample consists of a continuum and two weak bands. Upon annealing at 1100 °C, all the a-BN is transformed into mm-BN, so that no continuum but two strong bands appear in the PL spectrum of mm-BN, as shown in figures 1(e) and 2(d). Obviously, the PL intensities of the two bands increase greatly with increasing annealing temperature in the temperature range 820–1100 °C, that is due to the increase in the amount of m-BN phase produced by crystallization of the a-BN with increasing annealing temperature. Since the m-BN samples from lm-BN to mm-BN (obtained at annealing temperatures between 820 and 1100 °C) have lower DTDO, there exist many more structural defects. The increase in the amount of m-BN implies a rise in the number of structural defects, resulting in an increase of PL intensity of the emission bands related to the defects. However, when the a-BN is annealed above 1100 °C, all a-BN crystallizes to m-BNs (from mm-BN to pm-BN), and the m-BNs change towards a more ordered structure with increasing annealing temperature and time by thermal diffusion, leading to an improvement of the DTDO of the m-BN and a decrease in the number of structural defects, so that the PL intensity of the bands related to the defects decreases with increasing DTDO (or annealing temperature). In addition, the change of the PL intensity with annealing temperature shown in figure 3 is very



**Figure 3.** Plot of the logarithm of the PL intensity of the band at 413 nm ( $\log I$ ) in the m-BN as a function of DTDO or annealing temperature.



**Figure 4.** Lattice constants  $a$  and  $c$  for BN with various structures and DTDO.

similar to that of the band at 950.2 nm observed in electron-irradiated InP, which is attributed to the change in the number of InP antisite defects with annealing temperature [24]. Based on the above analysis and comparison, it is deduced that the bands are related to some structural defects in the m-BN, each of which can produce a certain local level in the bandgap. But the nature of the defects is not yet clear. For the a-BN, it is disorder in the structure and it has many kinds of defect. These defects distribute randomly and generate quasi-continuous local levels in the bandgap, resulting in a weak continuum. In the t-BN the atomic arrangement in  $sp^2$  layers is periodic, but the  $sp^2$  layers are stacked roughly parallel to each other and show random rotation and translation about the layers' normal. This random stacking leads to the existence of many kinds of defect in the t-BN and makes the t-BN show a similar PL spectrum to the a-BN. However, when (004), (110) and (112) peaks appear in the x-ray diffraction pattern of lm-BN, it implies that  $sp^2$  layers begin to stack periodically along the  $c$ -axis and three-dimensional order is established. The species and number of defects in the lm-BN will decrease greatly, and there only exist a few kinds of defect. These defects will form several separate local levels in the bandgap, resulting in the appearance of PL bands in the lm-BN spectrum. These results indicate that the emission bands cannot be only attributed to inherence of the  $sp^2$  layer, as Larach said [8], but to a whole BN crystal. The local levels of the structural defects of BN are affected not only by the crystal field formed by atoms in a  $sp^2$  layer, but also by the field formed by atoms in other  $sp^2$  layers. With increasing annealing temperature, the DTDO of the m-BN increases greatly and reaches the highest value in fully ordered h-BN, while the defects decrease with increasing DTDO and there are only a few defects in the fully ordered h-BN. So no PL bands but a weak continuum are observed in the PL spectrum of a fully ordered h-BN.

Figure 4 shows lattice constants of  $a$  and  $c$  of the BN with various structures and DTDO (the  $a$  and  $c$  for the a-BN and t-BN are calculated based on correlation between  $d$ -space, Miller's index and lattice constants of h-BN. They can be approximately considered as average lattice constants here). The  $c$  decreases while the  $a$  increases from t-BN to mm-BN, but the  $a$  and  $c$  do not change basically from mm-BN to pm-BN. Combining this with the results of figure 2,

the shift of the position of the band from 431 nm for 1m-BN to 439 nm for mm-BN is due to their different lattice constants.

#### 4. Conclusions

An a-BN was prepared by mechanical milling of h-BN. Annealing the a-BN in the temperature range between 630 and 1200 °C produced t-BN and m-BN with different DTDO. The t-BN and a-BN emit strong continuums with a maximum near 340 nm, whereas m-BNs that have three-dimensional order emit deep-blue emission bands. The position of the bands changes with lattice constants, while the PL intensity first increases with increasing DTDO and then decreases after reaching a maximum until the PL bands disappear in fully ordered h-BN. The bands are related to structural defects in the m-BN samples.

#### References

- [1] Zhao Y W, Dong H W, Chen Y H, Zhang Y H, Jiao J H, Zhao J Q, Lin L Y and Fung S 2002 *Appl. Phys. Lett.* **80** 2878
- [2] Pal B, Gopal A V, Prabhu S S and Vengurlekar A S 2002 *Phys. Rev. B* **65** 054312
- [3] Huang H Y, Chuang C H, Shu C K, Pan Y C, Lee W H, Chen W K, Chen W H and Lee M C 2002 *Appl. Phys. Lett.* **80** 3349
- [4] Zunger A, Katzir A and Halperin A 1976 *Phys. Rev. B* **13** 5560
- [5] Hoffman D M, Doll G L and Eklund P C 1984 *Phys. Rev. B* **30** 6051
- [6] Solozhenko V L, Lazarenko A G, Petitot J-P and Kanaev A V 2001 *J. Phys. Chem. Solids* **62** 1331
- [7] Larach S and Shrader R E 1956 *Phys. Rev.* **104** 68
- [8] Katzir A, Suss J T, Zunger A and Halperin A 1975 *Phys. Rev. B* **11** 2370
- [9] Andrey E J, Katzir A and Suss J T 1976 *Phys. Rev. B* **13** 2831
- [10] Bose D N and Hensch H K 1970 *J. Am. Ceram. Soc.* **53** 281
- [11] Era K, Minami F and Kuzuba T 1981 *J. Lumin.* **24/25** 71
- [12] Moore A W and Singer L S 1972 *J. Phys. Chem. Solids* **33** 343
- [13] Kawaguchi M, Nozaki K, Kita Y and Doi M 1991 *J. Mater. Sci.* **26** 3926
- [14] Lopatin V V and Konusov F V 1992 *J. Phys. Chem. Solids* **53** 847
- [15] Kobayashi H, Shibata H and Tagawa S 1994 *Nucl. Instrum. Methods B* **90** 556
- [16] Taylor C A II, Brown S W, Subramaniam V, Kidner S, Rand S C and Clarke R 1994 *Appl. Phys. Lett.* **65** 1251
- [17] Thomas J Jr, Weston N E and O'Conner T E 1963 *J. Am. Chem. Soc.* **84** 4619
- [18] Alkoy S, Toy C, Gönül T and Tekin A 1997 *J. Eur. Ceram. Soc.* **17** 1415
- [19] Hamilton E J M, Dolan S E, Mann C M, Colijn H O, Mcdonald C A and Shore S G 1993 *Science* **260** 659
- [20] Hamilton E J M, Dolan S E, Mann C M, Colijn H O, Mcdonald C A and Shore S G 1995 *Chem. Mater.* **7** 111
- [21] Kobayashi T, Tashiro S, Sekine T and Sato T 1997 *Chem. Mater.* **9** 233
- [22] Huang J Y, Yashuda H and Mori H 2000 *J. Am. Ceram. Soc.* **83** 403
- [23] Joint Committee of Powder Diffraction Standard (JCPDS)—International Center for Diffraction Data, No. 73-2095
- [24] Radautsan S I, Tiginyanu I M, Ursaki V V, Korshunov F P, Sobolev N A and Kudryavtseva E A 1993 *Solid State Commun.* **85** 525