Boron–oxygen luminescence centres in boron–nitrogen systems†

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Received (in Cambridge, UK) 2nd August 2007, Accepted 28th August 2007
First published as an Advance Article on the web 4th September 2007
DOI: 10.1039/b711807d

Closed-shell BO_2^- and BO^- anions are proposed as high-efficiency luminescence centres in boron–nitrogen systems, which makes the anions localized and leads to a radiation transition.

Experimental and theoretical interest in the optical spectra of boron–oxygen molecules and ions has persisted for almost a century since Jevons first identified the emission bands of the BO radical in the early years of molecular spectroscopy.[1] Subsequently, initial studies focused on the theoretical molecule spectra in prototypes provided by various boron–oxygen systems: BO_2 is a linear Renner–Teller molecule with the characteristic combination of spin–orbit splitting and Renner distortion.[2] Mulliken experimentally established the vibrational isotope effect and demonstrated the existence of zero-point energy by virtue of a BO spectrum.[3] The applications investigated include BO- (or BO_2)-based chemical lasers and high-power white emitters.[4]

Over the years our attention has been focused on the preparation, characterization, property evaluation and applications of boron nitride (BN) nanotubes,[5] which are boron–nitrogen semiconductors with a band gap nearly independent of diameter and chirality. The large and stable gap makes BN nanotubes promising candidates for various luminescence applications.[6,7] One of the most important challenges at the present stage is to explore the possible luminescence centres in this system. However, the reported optical data display a notable scatter strongly dependent on the preparation method.[7,8] Considering the expected insensitivity of luminescence response to the geometry of BN nanotubes,[7] impurities or defects generated during the nanotube syntheses should be responsible for this. It is worth noting that the oxygen-substituted BN nanotubes are structurally stable[9] and nitrogen–boron–oxygen (oxynitride) solid solutions are the commonly observed intermediates in typical syntheses using boron oxide as the BN precursor.[10] Therefore, it is feasible to form novel luminescence centres by introducing the B–O acceptor or donor optical levels in the BN band gap.

In the present research we first develop a strategy for the creation of luminescence centres of boron–oxygen species in the boron–nitrogen systems and then verify it experimentally through studies of luminescence centres in various samples.

It is worth noting that we have frequently observed UV and blue emission from high-purity BN nanotubes synthesized through an oxide-assisted carbon-free CVD route.[11] Fig. 1a shows a typical liquid-helium-temperature cathodoluminescence (CL) spectrum for the pure BN nanotubes (free from carbon or metal impurities). This exhibits two sharp bands at deep UV 228 nm (5.44 eV) and UV 338 nm (3.67 eV), and two broad bands at blue 455–467 nm (2.66–2.73 eV) and red ~690 nm (~1.80 eV). This spectrum is obviously different from that previously reported by us and measured at room temperature.[8] This is possibly due to a temperature effect or a different preparation method. In view of the theoretical band gap of ~5.5 eV for BN nanotubes,[6] the deep UV emission at 228 nm could be unambiguously assigned to band-to-band optical transition or phonon-assisted band-edge emission. The broad red emission should relate to the sp^3 bonding possible in nanotube structures due to interlinked layers. In fact, such emission has frequently been observed in cubic-, whisker- and nanorod-structured BN materials.[12] Nevertheless, the blue and UV (338 nm) emissions with relatively high intensity could hardly be assigned to any well-known phenomena; to the best of our knowledge they have never been observed in the literature. Further CL investigations indicate that the peak position of the UV emission red-shifts and its intensity decreases with increasing specimen temperature. This may imply a possible defect-induced origin of such emission (shallow donor–deep acceptor pair). However, the temperature-dependent effect does not rule out the possibility of an exciton origin of the two emissions.

During the exploration of the luminescence defects we observed B–O luminescence centres in the BN system for the first time. In order to do so, we first oxidized the BN nanotubes by heating at 700 °C in oxygen and then checked the CL spectrum, shown in Fig. 1b. All CL peaks mentioned above are nearly unchanged with respect to intensity and position. This shows that the thermal

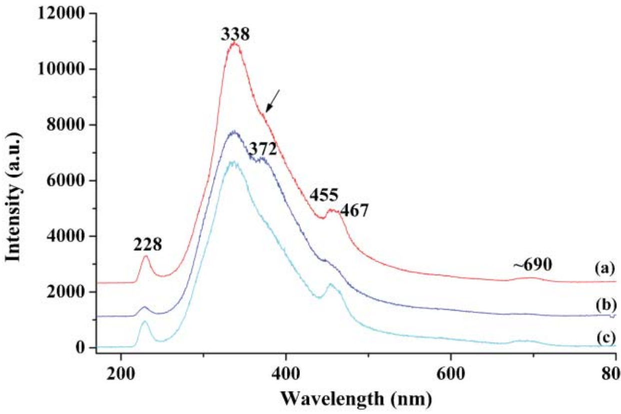

Fig. 1 Cathodoluminescence spectra of BN nanotubes: (a) a high-purity product synthesized *via* a carbon-free route; (b) an oxidized sample post-heat-treated at 700 °C in oxygen and (c) the oxidized BN nanotubes reduced in hydrogen at 1000 °C. The arrow points to luminescence of BO^- species.

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† Electronic supplementary information (ESI) available: Further experimental and characterization details. See DOI: 10.1039/b711807d

treatment does not strongly affect the luminescence defects or exciton emission. However, a new emission peak located at 372 nm emerges into the UV band. Further microscopy examinations on oxidized BN samples display some BO^- species randomly distributed on the nanotube surface. The 372 nm peak can thus be assigned to the BO^- emission, because it disappears again from the CL spectrum when the BO^- species are removed by reducing the oxidized samples in a hydrogen flow (Fig. 1c).

The BO^- centres discovered in the BN nanotubes provide a useful prototype for studying impurity-induced luminescence in the boron–nitrogen system as a whole. However, it is noted that in the case of BN tubular structure the luminescence profile from the randomly-generated centres on the surfaces is rather weak. Keeping the luminescence of B–O species in mind, we monitor the photoluminescence changes during processing stages of bulk BN synthesized by pyrolysis of an oxygen-containing precursor, *i.e.*, boric-diethanolamine-based complex, $NH(C_2H_4O)_2BOH$ (**1**). The basic complex **1** is coordinated in OH^- and is easily transferred to NH_2^- and N^{3-} ligands by a simple condensation reaction, in ethylenediamine and trioctylamine, respectively.[13]

As shown in Fig. 2, all BO_2^- species in the selected ligands exhibit a single-peak blue emission and a double-peak excitation. Both N-coordinated BO_2^- species (Fig. 2b and 2c) possess similar excitation spectra with a sharp high-wavelength peak and a low-wavelength shoulder, which is different from a OH^- ligand (Fig. 2a). This suggests that the low-wavelength excitation arises from the energy transfer between ligand and luminescence centre, and the sharp high-wavelength excitation arises from the configuration transition of BO_2^-. The BO_2^- is a closed-shell species with a linear ground state ($^1\Sigma_g^+$).[14,15] The ground state is basically characterized by a degenerate π_g orbital. The first excitation state is the ground state ($^2\Pi_g$) of BO_2 with a spin–orbital splitting too small ($\sim$150 cm^{-1})[16] to be resolved in the room-temperature PL measurements. Therefore, the radiation transition from $^2\Pi_g \rightarrow {}^1\Sigma_g^+$ observed here is basically a single-peak emission.

Another distinct spectral difference between the OH- and N-coordinated BO_2^- species is related to the Stokes shift. The shift of **1** with the OH-ligand is 5400 cm^{-1}, which is larger than for N-coordinated species (3700 cm^{-1} for NH_2^-, 4100 cm^{-1} for N^{3-}). If the calculated vibrational frequencies[14] of the ground states for BO_2^- (1100 cm^{-1}) and BO_2 (1080 cm^{-1}) species are applicable for the present system, the Huang–Rhys parameter S[17] can be estimated as 2.5 for OH^-, 1.7 for NH_2^- and 1.8 for N^{3-} ligands. The lower S values in the N-coordinated BO_2^- species are close to the electron–phonon coupling constant of some traditional rare-earth luminescence ions ($S < 3.5$ for energy levels belonging to the excited $4f^{N-1}5d$ configuration[18]), suggesting a local and weak ion-lattice coupling luminescence centre of BO_2^- species in the boron–nitrogen system. This is in agreement with the theoretical or photoelectron spectroscopy experiments for BO_2^- species in gas or embedded in rare gas solid,[15,19] and indicates no vibrational progress for the ground state transition of BO_2^- and BO_2.

The proposed local luminescence centres of BO_2^- in boron–nitrogen systems will naturally result in a high efficiency and a high quenching temperature. Therefore, we further obtained the solid boron–nitrogen system with BO_2^- species by treating the boric acid complex in a trioctylamine solution up to a high temperature of 600 K in a N_2-filled autoclave. Fig. 3a shows the XRD pattern displaying a broad hump centred at $\sim$20° (2θ). This pattern has been frequently observed in B–N-containing polymers,[20] and can be attributed to a semi-crystallization process. The FTIR spectrum, shown in Fig. 3b, clearly indicates the existence of a B–N linkage in the polymer structure (1377 cm^{-1} for B–N and 780 cm^{-1} for B–N–B vibrations[21]) and an OBO bending vibration at 474 cm^{-1}.[22] The solid polymer with the BO_2^- species again provides local $^2\Pi_g \rightarrow {}^1\Sigma_g^+$ luminescence with similar spectral characterization (Fig. 3c). However, the ionic excitation and emission peaks are red-shifted to 487 and 553 nm, respectively, compared with the luminescence in the liquid environment mentioned above. The Stokes shift is $\sim$1500 cm^{-1} with the coupling constant S of $\sim$0.7.

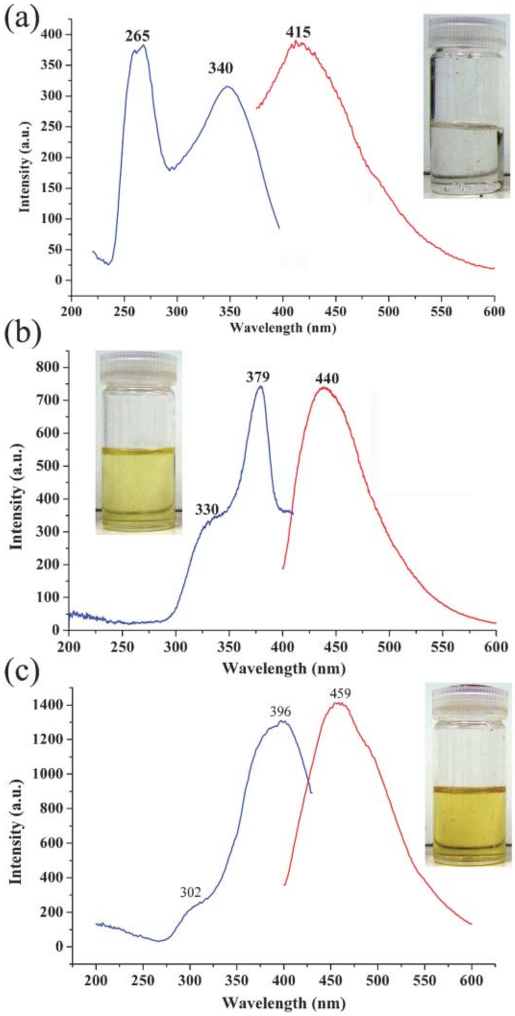

Fig. 2 Excitation (blue) and emission (red) spectra of **1** with BO_2^- species coordinated with different atmospheres: (a) OH^- ligand in diethanolamine (excited wavelength λ_{ex} = 340 nm; monitored wavelength λ_{em} = 415 nm); (b) with NH_2^- ligand in ethylenediamine (λ_{ex} = 379 nm; λ_{em} = 440 nm); (c) with N^{3-} ligand in trioctylamine (λ_{ex} = 396 nm; λ_{em} = 459 nm).

The polymer was vacuum pyrolysed to a black mixture of BN, B_2O_3, B_4C with remnant graphite,[13] and no photoluminescence was found in the visible region. However, a yellow powder could be obtained when ammonia was introduced during the pyrolysis at a low reaction temperature of 900 °C. The present route markedly reduced the amount of BO_2^- species, as evidenced from FTIR

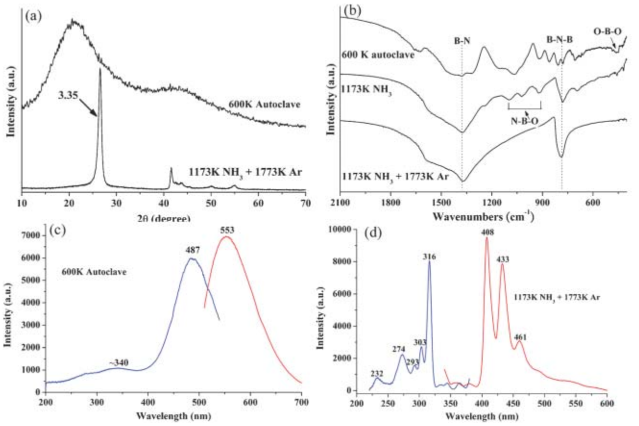

Fig. 3 Structural and spectral characterization of the boron–oxygen systems in a solid boron–oxygen–carbon polymer (marked in 600 K autoclave) and BO^--doped BN crystal (marked in 1173 K NH_3 + 1773 K Ar): (a) XRD pattern; (b) FTIR analyses; (c) and (d) excitation (blue) and emission (red) photoluminescence spectra ($\lambda_{ex} = 487$ nm and $\lambda_{em} = 553$ nm for the polymer; $\lambda_{ex} = 316$ nm and $\lambda_{em} = 408$ nm for BN crystal).

measurements (also shown in Fig. 3b). The bands observed in BN (1372 and 777 cm^{-1}) and boron oxynitride (in 1100–900 cm^{-1} N–B–O stretching region[23]) vibrations clearly indicate the transfer from BO_2^- to BO^- species. The concentration of the BO^- species can be further decreased to less than 10% after high-temperature annealing. This can be confirmed from the XRD (Fig. 3a) and FTIR (Fig. 3b) characterizations of a product after carbon removal and annealing at 1500 °C in an argon flow. Chemical composition analyses indicate a ~7.1 wt% O remnant, which uniformly distributes into the hexagonal BN crystal because the d value of (002) diffraction increases to 0.335 nm from 0.333 nm of a standard pure BN. Such doping obviously differs from the post-oxidation of the above BN nanotubes, during which surface oxidation forms a BO dangling bond and does not change the crystalline parameter.

The luminescence of the BO^--doped BN crystals is also markedly different from the BO^- species surface-attached in BN nanotubes or BO_2^- in polymers. The room-temperature photoluminescence spectrum of the BN crystals (Fig. 3d) is dominated by three periodic emission bands centred at 408, 433 and 461 nm, exhibiting a well-resolved vibrational progression with the spacing of ~1400 cm^{-1}. The BO^- ion is also a closed-shell molecule with a ground state ($^1\Sigma^+$) and first excited state ($^2\Sigma^+$).[15] Compared with the BO_2^- anion, the ground state is basically a B 2s lone pair with a slight BO antibonding character. The consequent $^2\Sigma^+ \rightarrow {}^1\Sigma^+$ radiation transition exhibits a triplet-transition pattern, which is in good agreement with the photoelectron spectrum measurement for BO^- anion. The excitation spectrum contains five UV peaks. The 232 nm peak can be assigned to band-gap excitation, excitations at 293, 303, and 316 nm result from the deep-level transitions from the ground state to the first excited state $^2\Sigma^+$. The 274 nm excitation might be related to the second excited state.

Although the Stokes shift for BO^- in BN crystal is ~7100 cm^{-1} larger than ~1500 cm^{-1} of BO_2^- species, the S value is still ~2.1 due to the relatively larger vibrational frequency.[15,24] This again suggests a local luminescence in the hexagonal BN crystals.

In conclusion, the existence of boron–oxygen luminescence centres in boron–nitrogen systems has been proposed and demonstrated in BN nanotubes, B–N–C–O polymer and highly B–O doped BN crystals for the first time. The luminescence must be highly useful to spectrally check the purity of any BN nanomaterials. More importantly, the local luminescence centres in boron–nitrogen systems can find smart applications in various lighting fields, such as green fluorescence sources for blue emitting InGaN-based white light-diodes, and blue sources for plasma display panels.[25]

Notes and references

1 W. Jevons, *Proc. R. Soc. London, Ser. A*, 1914, **91**, 120.
2 K. Kawaguchi, E. Hirota and C. Yamada, *Mol. Phys.*, 1981, **44**, 509.
3 R. S. Mulliken, *Phys. Rev.*, 1925, **25**, 259.
4 M. A. A. Clyne and M. C. Heaven, *Chem. Phys.*, 1980, **51**, 299; M. S. Wang, G. C. Guo, W. T. Chen, G. Xu, W. W. Zhou, K. J. Wu and J. S. Huang, *Angew. Chem., Int. Ed.*, 2007, **46**, 3909.
5 C. C. Tang, M. Lamy de la Chapelle, S. S. Fan, P. Li and Y. M. Liu, *Chem. Phys. Lett.*, 2001, **324**, 492; C. C. Tang, Y. Bando, T. Sato and K. Kurashima, *Adv. Mater.*, 2002, **14**, 1046; C. C. Tang, Y. Bando, X. X. Ding, S. R. Qi and D. Golberg, *J. Am. Chem. Soc.*, 2002, **124**, 14550; C. C. Tang and Y. Bando, *Appl. Phys. Lett.*, 2003, **83**, 659; C. C. Tang, Y. Bando, D. Golberg, M. Mitome, X. X. Ding and S. R. Qi, *Appl. Phys. Lett.*, 2004, **85**, 106; C. C. Tang, Y. Bando, Y. Huang, S. L. Yue, C. Z. Gu, F. F. Xu and D. Golberg, *J. Am. Chem. Soc.*, 2005, **127**, 6552; C. C. Tang, Y. Bando, C. H. Liu, S. S. Fan, J. Zhang, X. X. Ding and D. Golberg, *J. Phys. Chem. B*, 2006, **110**, 10354.
6 X. Blase, A. Rubio, S. G. Louie and M. L. Cohen, *Phys. Rev. B*, 1995, **51**, 6868.
7 J. S. Lauret, R. Arenal, F. Ducastelle, A. Loiseau, M. Cau, B. Attal-Tretout, E. Rosencher and L. Goux-Capes, *Phys. Rev. Lett.*, 2005, **94**, 037405; R. Arenal, O. Stephan, M. Kociak, D. Taverna, A. Loiseau and C. Colliex, *Phys. Rev. Lett.*, 2005, **95**, 127601; L. Wirtz, A. Marini and A. Rubio, *Phys. Rev. Lett.*, 2006, **96**, 126104; C. H. Park, C. D. Spataru and S. G. Louie, *Phys. Rev. Lett.*, 2006, **96**, 126105; B. Berzina, L. Trinkler, V. Korsak, R. Krutohvostov, D. L. Carroll, K. B. Ucer and R. T. Williams, *Phys. Status Solidi B*, 2006, **243**, 3840.
8 C. Y. Zhi, Y. Bando, C. C. Tang, D. Golberg, R. G. Xie and T. Sekiguchi, *Appl. Phys. Lett.*, 2005, **86**, 213110.
9 L. De A. Silva, S. C. Guerini, V. Lemos and J. M. Filho, *IEEE Trans. Nanotechnol.*, 2006, **5**, 517.
10 R. T. Paine and C. K. Narula, *Chem. Rev.*, 1990, **90**, 73.
11 C. Tang, Y. Bando, T. Sato and K. Kurashima, *Chem. Commun.*, 2002, 1290.
12 Y. C. Zhu, Y. Bando, D. F. Xue, T. Sekiguchi, D. Golberg, F. F. Xu and Q. L. Liu, *J. Phys. Chem. B*, 2004, **108**, 6193.
13 H. Wada, K. Nojima, K. Kuroda and C. Kato, *Yogyo Kyokaishi*, 1987, **95**, 140.
14 J. V. Ortiz, *J. Chem. Phys.*, 1993, **99**, 6727; V. G. Zakrzewski and A. I. Boldyrev, *J. Chem. Phys.*, 1990, **93**, 657.
15 H. J. Zhai, L. M. Wang, S. D. Li and L. S. Wang, *J. Phys. Chem. A*, 2007, **111**, 1030.
16 J. Agreiter, M. Lorenz, A. M. Smith and V. E. Bondybey, *Chem. Phys.*, 1997, **224**, 301.
17 K. Huang and A. Rhys, *Proc. R. Soc. London, Ser. A*, 1950, **204**, 404.
18 B. Z. Malkin, O. V. Solovyev, A. Yu. Malishev and S. K. Saikin, *J. Lumin.*, 2007, **125**, 175.
19 R. Boucher, Y. Wang and K. J. Klabunde, *High Temp. Sci.*, 1991, **31**, 87.
20 D. P. Kim, K. T. Moon, J. G. Kho, J. Economy, C. Gervais and F. Babonneau, *Polym. Adv. Technol.*, 1999, **10**, 702.
21 A. S. Rozenberg, Y. A. Sinenko and N. V. Chukanov, *J. Mater. Sci.*, 1993, **28**, 5675.
22 T. R. Burkholder and L. Andrews, *J. Chem. Phys.*, 1991, **95**, 8697.
23 M. Hubacek, T. Sato and T. lshii, *J. Solid State Chem.*, 1994, **109**, 384.
24 F. Melen, I. Dubois and H. Bredohl, *J. Phys. B: At. Mol. Phys.*, 1985, **18**, 2423.