

# Cathodoluminescence of Boron Nitride Nanotubes Doped by Europium

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## Abstract

Boron nitride (BN) nanotubes are wide-band-gap semiconductors, which make them an ideal host material for doping with rare-earth ions. Special luminescent properties are expected in doped BN nanotubes for applications in nanosized lighting and display devices. Europium (Eu) doped BN nanotubes have been synthesized by using a ball-milling and annealing method. A broad visible light emission, excited by electrons, from the Eu<sup>2+</sup> doped BN nanotubes has been realized. The Eu element content in the nanotubes has been determined by electron probe microanalysis. The mechanism of visible light emission from the Eu-doped BN nanotubes is discussed.

**Keywords:** Boron Nitride, Nanotube, Europium, Doping, Cathodoluminescence.

## INTRODUCTION

Nano luminescent materials are vital for nanosized light sources and display devices. Luminescent nanotubes have a potential application in drug delivery because they combine drug container and luminescent marker properties. Many studies on carbon nanotubes (CNTs) have been carried out. For example, Eu-contained organic compound was chemically bonded with multi-walled CNTs so as to functionalize the CNT surface[1], Eu-doped Y<sub>2</sub>O<sub>3</sub> was coated onto multi-walled CNTs[2] to promote luminescent emission. In these cases, the light emission mostly arises from the bonded organic compounds or coating materials that contain Eu or Eu compounds. The luminescence of boron nitride nanotubes (BNNTs) should have many advantages over CNTs as theoretical and experimental studies[3-5] demonstrate that the band-gap of BNNTs is wide, stable, and independent of tube radius, chirality and the number of tubular shells when the tube diameter is larger than 0.8 nm[4]. BNNTs are extremely temperature-stable up to 700°C in air[6]. This makes BNNTs' superior as a host of nano luminescent material.

There are also some reports on visible emission[7] and intrinsic luminescence[8] from BN thin films and pure BNNTs[9,10]. In this paper, we report the cathodoluminescence (CL) of BNNTs doped with europium.

## METHODS AND PROCEDURES

The synthesis of Eu doped BNNTs was carried out using a ball milling and annealing approach with a mixture of boron and europium powders as starting materials. After ball milling for 50 hours, the milled sample was heated at 1200°C in N<sub>2</sub> and H<sub>2</sub> (5 vol%) mixed gas for 2 hours. Transmission electron microscopy (Philips CM300) was used to investigate the structure of the BNNT. A Hitachi 4300 scanning electron microscopy was used to observe the morphology of the as-synthesized BNNTs. An electron probe microanalyser (EPMA) attached to a JEOL 6400 scanning electron microscope was also employed to determine the average doping content of the Eu in BNNTs.

The CL was studied at room temperature using a fiber optic spectrometer (SD2000, Ocean Optics, Inc.) attached to a Hitachi S2250-N SEM instrument.

### RESULTS AND DISCUSSION

Figure 1a presents a SEM image of Eu-doped BNNTs showing the uniform nanotubes. The TEM image in Fig. 1b shows the BNNTs with a bamboo like structure. The Eu content is determined by EPMA and the typical EPMA spectrum is displayed in Fig. 2. The Eu peak is clearly seen in the spectrum. The ratio of B to N is very close to 1:1, and the average Eu content is 0.5 at%. The Fe peak is from the metal catalyst used for growing the BNNTs, and the Au peak is from the conducting coating for the EMPA measurement.

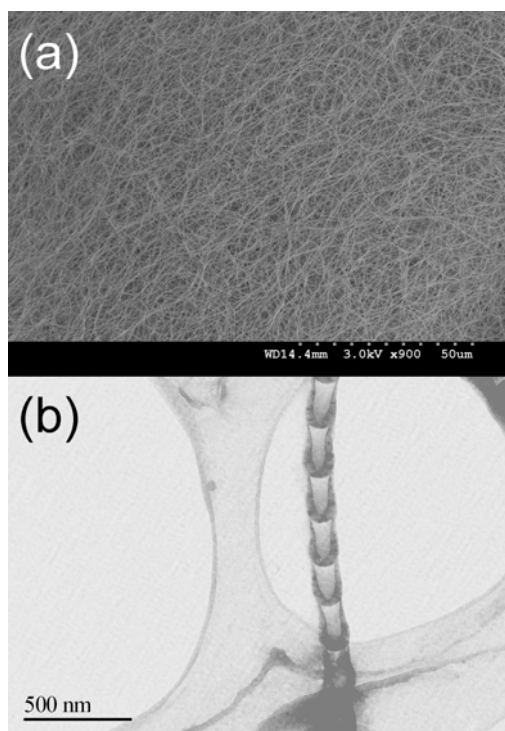


Fig. 1: (a) SEM image of Eu-doped BNNTs; (b) TEM image of Eu-doped BNNT.

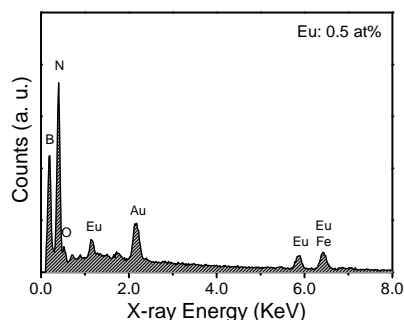


Fig. 2: EPMA spectrum of Eu-doped BNNTs clearly shows the presence of Eu.

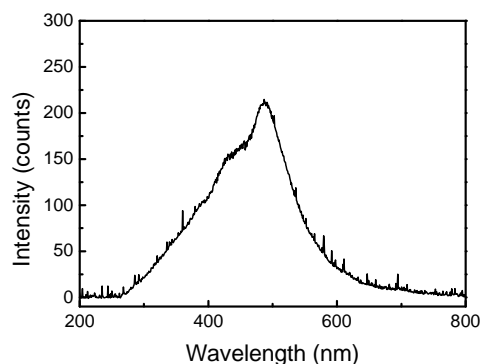


Fig.3: CL spectrum of Eu-doped BNNTs

Zhi[9] reported that the main peak of BNNTs in CL is located at 3.3 eV ( 373 nm) and there is a long tail in the low energy side. It has also been reported that pure BNNTs have a very broad absorption from 620 nm to an intrinsic absorption edge[5], probably arising from various defects ( e.g. B or N vacancies), excitons and lattice distortion during the formation of the nanotubes, that may all contribute to energy shifts in light excitation. Detailed light emission of the pure BNNTs needs to be further explored.

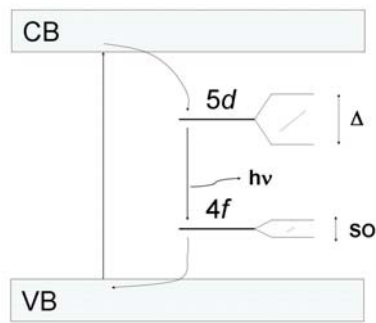


Fig. 4: Sketch of 5d-4f emission of  $\text{Eu}^{2+}$ -doped BNNTs

Figure 3 presents the CL spectrum of Eu-doped BNNTs recorded at the accelerating voltage of 15kV. It is noteworthy that the dominant CL peak (373 nm) in pure BNNTs is significantly weakened and a strong new emission peaked around 491 nm is found in the Eu-doped BNNTs. The strong broad light emission peak at 491 nm exhibits a strong blue emission. Such a band emission can be ascribed to the transitions between  $4f^65d^1$  and  $4f^7$  configurations of divalent  $\text{Eu}^{2+}$  ions, consistent with the luminescent emission of  $\text{Eu}^{2+}$  ions in  $\text{Eu}:\text{SrB}_4\text{O}_7$ [11]. We expect that the Eu exists in BNNTs in the divalent state rather than trivalent state as a result of the reducing atmosphere used during nanotube formation. We believe that the broad emission spectral feature is due to the complexity in the 5d-4f emission (see sketch in Fig. 4). The emitting level contains octets and sextets, whereas the ground state level ( $^8S$  from  $4f^7$ ) is an octet. As a result, the spectral position of the emission band strongly relies on the structural environment of  $\text{Eu}^{2+}$  ions, which alters the crystal field splitting of the 5d configuration. It is noteworthy that the Eu:BNNTs show a broad blue-light emission with an emission maximum around 490 nm, which is compatible with the requirement of some lighting applications of a very high color rendering index (CRI), normally obtained by using a phosphor with an emission peaked at 490 nm[12]. The observed light emission is so strong that the Eu-doped BNNTs might be expected to have direct application for illumination.

## CONCLUSION

Eu doped BN nanotubes have been synthesized using a ball-milling and annealing method and the structure of these nanotubes has been analyzed by TEM. The Eu element with content of 0.5 at% in the nanotubes has been identified by EPMA. A broad visible light emission (in the blue region) from  $\text{Eu}^{2+}$  doped BN nanotubes has been realized in CL.

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