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Analysis of Structure and Relaxation Mechanism of Boron Nitride Nanotubes

Jae Kap Jung*, Kwon-Sang Ryu, Yong-Il Kim, Seung Hoon Nahm, Young Tae Park, and Jeon Hong Kang

Korea Research Institute of Standards and Science, P. O. Box 102, Yuseong, Daejeon, 305-600, KOREA

1. Introduction

Chopra *et al.* were the first to synthesize pure boron nitride nanotubes (BNNTs) using an arc-discharge method in 1995[1]. BNNTs have semiconducting properties, with a large, near-constant band gap of 5.5 eV, which is independent of the diameter and chirality of the nanotube[2]. A material such as this, with a high structural stability that is also energetically stable, is of interest for many different technological applications, which can exploit its special physical and chemical properties. Recently, using X-ray diffraction (XRD) and transmission electron microscopy (TEM), BNNTs contain two undissolved mixed phases: a hexagonal and a rhombohedral phase[3].

In this work, ^{11}B nuclear magnetic resonance (NMR) and the spin lattice relaxation times (T_1) in BNNTs samples have been measured for the first time in the temperature range 180 - 430K. We anticipate that the results provide the information on the phase and relaxation mechanism in BNNTs.

2. Experimental

A mixture of boron and magnesium oxide located in a BN-made reaction tube was heated to 1,300 °C. At this temperature, the boron reacted with the MgO to form B_2O_2 and Mg vapour. The vapours were argon-transported into a reaction chamber maintained at a temperature of *ca.* 1,100 °C, and a flow of ammonia gas was then introduced into the chamber. BN was synthesized from the reaction of the B_2O_2 and ammonia vapours. After fully evaporating the mixture, the white product could be collected from the BN wall of the chamber[3].

The ^{11}B NMR spectra were obtained using two different NMR spectrometers operating at Larmor frequencies of 192.493 MHz (B_0 = 14.1 T, Varian, Unity NOVA 600) and 64.164 MHz (B_0 = 4.7 T, Varian, Unity INFINITY plus 200). The spectra were obtained using a solid echo ($\pi/2-\tau-\pi/2$) or a Hahn echo ($\pi/2-\tau-\pi$) sequence, where the $\pi/2$ and π pulse lengths were 2.5 μs and 5 μs, respectively. The repetition delay time was 50 s. All the NMR spectra were referenced to an aqueous saturated H_3BO_3 solution. The T_1 of ^{11}B NMR was measured using the same spectrometers in the temperature range 180 - 430 K. The temperature stability was kept within ± 0.05 K for the T_1 measurement times. The T_1 pulse sequence was an inversion recovery pulse sequence using solid echo, $\pi-t-(\pi/2-\tau-\pi/2)$. The pulse separation between the solid echo was 25 μs.

3. Results and discussion

Fig. 1 shows TEM micrographs of BN nanotubes, where its diameter was 30 nm. The ^{11}B NMR spectra of BNNTs in two magnetic fields at 297 K are shown in Fig. 2. The dotted and dashed lines of the two peaks shown in Figs. 2(a) and 2(b) represent the resolved spectra fitted to a Gaussian lines. The narrow peaks on the left-hand side(dotted lines) and the broad peaks on the right-hand side(dashed lines) arise from the hexagonal BNNTs (h-BNNTs) and rhombohedral BNNTs(r-BNNTs) phases, respectively. *a* and *b* are used to denote the fractions of the h-BNNTs and r-BNNTs phases in BNNTs, respectively. The values of *a* and *b* were estimated to be 0.67 and 0.33 for 14.1 T, and 0.71 and 0.29 for 4.7 T, respectively, from the fit to the NMR line intensity. The fractions *a* and *b* at other temperatures investigated, were almost the same as those estimated at 297 K.

The T_1 was measured in the temperature range 180 - 430 K in two magnetic fields of 4.7 T and 14.1 T. From a recovery function for the central line, It was shown that the dominant relaxation mechanism is due to quadrupole relaxation[4]. Fig. 3 shows the temperature dependence of $1/T_1$ for the two phases in two different magnetic fields. The experimental results show that the temperature dependence of $1/T_1$ for r-BNNTs phase is proportional to T^2, which is shown by the fitted solid line in Fig. 3, although the data fluctuation is quite large. An exponential recovery and no Larmor frequencies dependence of $1/T_1$(see Fig. 3) for r-BNNTs phase was also observed. These features indicate that the relaxation process of r-BNNTs phase in BNNTs is characteristic of a Raman relaxation mechanism driven by lattice vibration[5]. In summary, ^{11}B NMR technique was successfully employed to resolve the two local phases existed in BNNTs by line intensity analysis and T_1 data fit, unlikely XRD technique. Furthermore, the ^{11}B

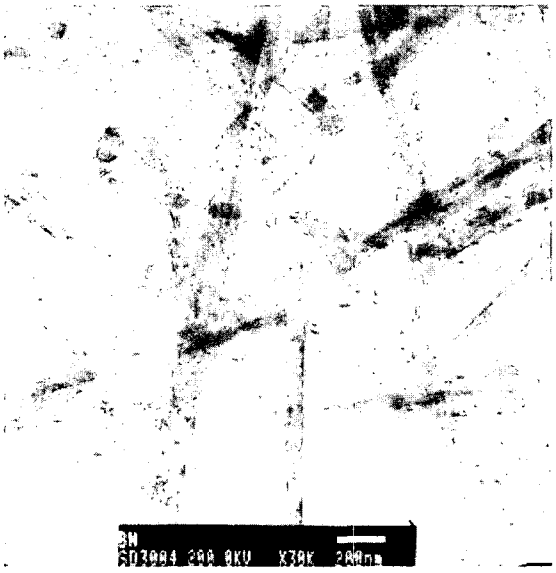

Fig. 1. TEM micrographs of BN nanotubes.

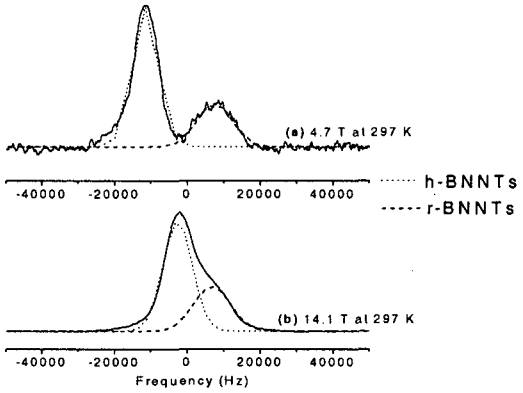

Fig. 2. The ^{11}B NMR spectra of BNNTs at 297 K in a magnetic field of: (a) 4.7 T and (b) 14.1 T. The dotted and dashed lines at two magnetic fields represent the decomposed fitted Gaussian lines for h-BNNTs and r-BNNTs, respectively.

relaxation mechanism was discovered by temperature dependence of $1/T_1$. Consequently, solid-state NMR technique is very powerful to study the local structure and the relaxation mechanism.

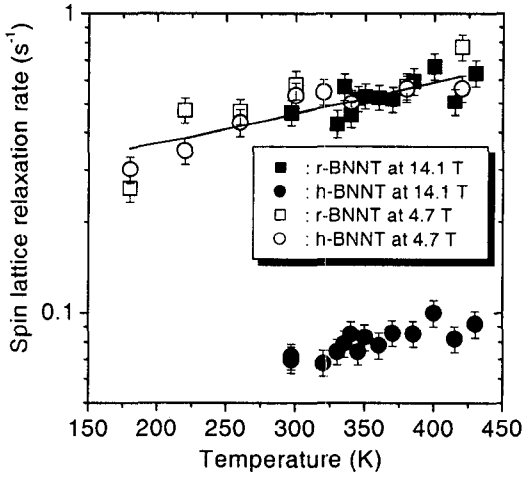

Fig. 3. The temperature dependence at two different magnetic fields, 4.7 T and 14.1 T, for h-BNNTs and r-BNNTs. The solid line is fitted using the relationship, $1/T_1 \propto T^2$.

Acknowledgement

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