Thermal conductivity of B–C–N and BN nanotubes

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We have measured the temperature-dependent thermal conductivity $\kappa(T)$ of boron–carbon–nitride (B–C–N) and boron nitride (BN) nanotube mats between room temperature and 20 K. For both materials, $\kappa(T)$ increases with increasing temperature, with no sign of saturation. We employ an analysis method to estimate the intrinsic $\kappa(T)$ of BN nanotubes converted from B–C–N nanotubes, and find that at room temperature $\kappa(T)$ of a multiwalled BN nanotube can be comparable to that of a multiwalled carbon nanotube and may exceed it if made isotopically pure. At low temperature, the functional form of $\kappa(T)$ reflects dimensional confinement. © *2005 American Institute of Physics.*
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Boron nitride (BN) nanotubes have been shown to exhibit many interesting properties.[1,2] BN tubes can be viewed as geometrically derived by rolling a hexagonal BN sheet into a cylinder, much like carbon nanotubes can be viewed as rolling a graphene sheet into a cylinder. Both single-walled and multiwalled BN nanotubes have been synthesized in recent years.[3] Because of the low-dimensional effects, carbon and BN nanotubes have been predicted to exhibit unusual thermal properties.[4,5] The temperature-dependent thermal conductivity $\kappa(T)$ of an isolated multiwalled carbon nanotube has been measured by using a microfabricated device and its room temperature value exceeds 3000 W/m K.[6] Molecular dynamics simulations suggest an even higher value ($\sim$6600 W/m K) at room temperature for a (10, 10) carbon nanotube.[7] Comparison with the $\kappa(290\text{ K})\sim 400$ W/m K of graphite indicates a large enhancement of a phonon mean free path in carbon nanotubes. Although the experimentally measured in-plane $\kappa(290\text{ K})$ of hexagonal BN varies from 200 to 500 W/m K,[8–10] the thermal conductivity of BN nanotubes has been predicted to be comparable to that of carbon nanotubes.[5] Hence it is interesting to ask whether BN nanotubes also exhibit high thermal conductivity like carbon nanotubes.

Boron–carbon–nitride (B–C–N) nanotubes were synthesized by a substitution reaction using multiwalled carbon nanotubes as a template.[11] B_2O_3 powder was placed in a crucible covered with carbon nanotubes. The crucible was held in a flowing nitrogen atmosphere at 1600 °C for 30 min. The mats of B–C–N nanotubes were made by first pressing the samples, followed by annealing at 150 °C in air. B–C–N nanotubes were transformed into BN nanotubes by a subsequent oxidation treatment at 650 °C.[12] The microstructure of the nanotubes was characterized by high-resolution transmission electron microscopy. B–C–N or BN nanotubes made by this method are predominantly multiwalled with an average diameter of 6–8 nm. Recent Raman and electron energy loss spectroscopy studies indicate that B–C–N nanotubes have strong phase separation between the BN layers and carbon layers along the radial direction.[11,13]

Thermal conductivity was measured by a comparative method. A constantan rod whose $\kappa(T)$ had been measured was mounted in series with the sample. A chip resistor was attached to the end of the constantan rod to provide heat. Type E thermocouples were used for determining the temperature difference, typically 0.8–1.2 K across the sample. The sample size was generally $4\times 1.5\times 0.7$ mm^3. In some measurements we employed two constantan rods, one before and one after the sample to estimate the heat loss through radiation and the thermocouples. The whole measurement process was as follows: First, we measured the $\kappa(T)$ of mats of B–C–N nanotubes. Next, to estimate the carbon concentration in each sample, we used thermogravimetric analysis (TGA) to monitor the weight loss while heating the sample in oxygen at 650 °C for $\sim$30 min. This process had been demonstrated to completely remove the carbon nanotubes and transform the B–C–N nanotubes to pure BN nanotubes.[12] We found that this heating process did not affect the macroscopic geometry of the sample after burning. Finally, converted samples were mounted back to the thermal conductivity probe with the same thermocouple locations to minimize the geometrical uncertainties. The $\kappa(T)$ of the mats of BN nanotubes was then measured.

Figures 1(a) and 1(b) show the $\kappa(T)$ of two samples before (B–C–N) and after (BN) the oxidation treatment.[14] Both $\kappa(T)$'s of the B–C–N and BN nanotubes show increasing thermal conductivity with increasing temperature. Note that the value $\kappa(T)$ shown here is the measured thermal conductivity without any density correction adapted in Refs. 15 and 16. A small slope change can be seen at $\sim$100 K for BN nanotubes. The umklapp processes for hexagonal BN occurs at $T_U\sim 100$ K,[9] which indicates that the slope change of the $\kappa(T)$ of BN nanotubes may be due to the umklapp processes in the mats. Since each nanotube has different chirality, the nonuniformity of the unit cell from one nanotube to another is expected to lead to a wide distribution of T_U in the mats. This would result in a somewhat smeared umklapp signature in the $\kappa(T)$ data. Similar observations have been reported for the $\kappa(T)$ of mats of carbon nanotubes.[15,16]

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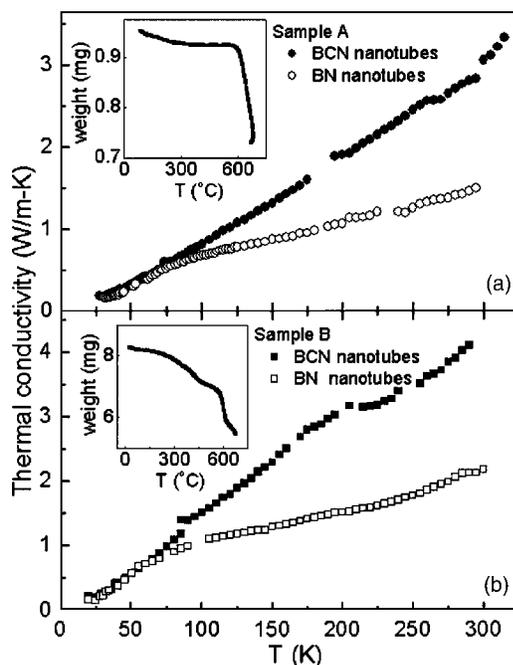
FIG. 1. (a) and (b) Thermal conductivity (uncorrected for geometry) vs temperature for two different samples of nanotubes before (solid symbols, B–C–N) and after (open symbols, BN) the oxidation treatment. The insets show the corresponding weight vs temperature for each sample during the oxidation treatment. The weight ratio of carbon to BN is 0.30 and 0.50 in (a) and (b), respectively.

The insets of Figs. 1(a) and 1(b) show the weight versus temperature monitored by TGA. Samples of Figs. 1(a) and 1(b) have a carbon to BN weight ratio 0.30 and 0.50, respectively. Since the difference between the molecular weight of C_2 and BN is small, the weight ratio can be approximated to the number ratio of carbon layers to BN layers in each B–C–N nanotube.

Figure 2 shows the low-temperature behavior of $\kappa(T)$ of B–C–N and BN nanotubes. All the curves are normalized and can be fitted to a $T^{1.6}$ dependent curve for $T < 70$ K. Since at low temperature $\kappa(T)$ is dominated by the heat capacity, the fact that the $\kappa(T)$ deviates from a linear temperature-dependent behavior reflects the intrinsic dimensionality of most large diameter nanotubes. Similar dimensionality effects on the low-temperature $\kappa(T)$ have been ob-
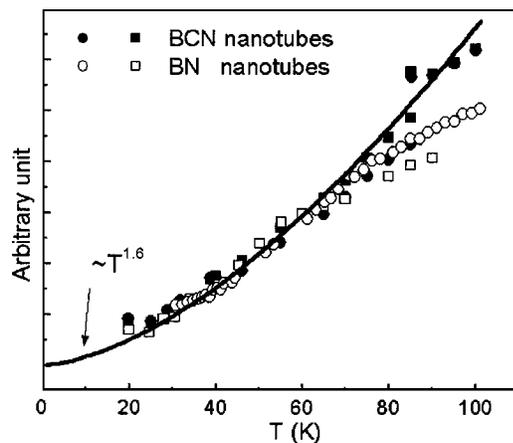
FIG. 2. Low-temperature behavior of $\kappa(T)$ for B–C–N and BN nanotubes shown in Fig. 1. All the curves are normalized and can be fitted to a $T^{1.6}$ curve (solid line) below 70 K.

served for single-walled and multiwalled carbon nanotubes.[15,16]

Of prime interest is the magnitude of the intrinsic thermal conductivity of BN nanotubes. Although previous experimental results on the $\kappa(T)$ of mats of carbon nanotubes reflect the intrinsic dimensionality of nanotubes at low temperature, the value of the magnitude of the intrinsic $\kappa(T)$ deduced from the mat data is highly uncertain due to the difficulty in determining the density correction factor. For example, the uncorrected $\kappa(290$ K) of single-walled carbon nanotube mats is 0.7 W/m K, which is believed to be lower than the intrinsic value by a factor of 2500–8300.[16] Even if the measured $\kappa(T)$'s of mats are corrected for the theoretical density of a close-packed bundle,[15–17] they are still one to two orders of magnitudes smaller than those of an isolated multiwalled carbon nanotube measured by a microfabricated device (3000 W/m K).[6] Moreover, the electrical conductivity assumption used in Ref. 16 does not apply for insulating BN nanotubes.

To give a better estimation of the $\kappa(T)$ of a single BN nanotube, we therefore adapt here an analysis method that allows us to estimate the intrinsic $\kappa(T)$ of individual BN nanotubes more reliably. We assume that for a single B–C–N nanotube, the BN layers and carbon layers have parallel contributions to the total thermal conductance. This assumption can be justified by the highly anisotropic thermal conductivity of graphite or hexagonal BN (c axis vs ab plane). The weak van der Waals force implies that the intratube or intertube interactions have negligible contributions to the total thermal conductivity of the B–C–N nanotubes in the axial direction. Comparing the thermal *conductance* (λ) of B–C–N nanotubes to that of BN nanotubes converted from B–C–N nanotubes, we have the following relation:

$$r \equiv \frac{\lambda_{BCN}}{\lambda_{BN}} = \frac{\kappa_{BN} + x\kappa_C}{\kappa_{BN}} \Rightarrow \kappa_{BN} = \frac{x\kappa_C}{r - 1}, \qquad (1)$$

where λ_{BCN} and λ_{BN} are the measured thermal conductance of the B–C–N and BN nanotube mats, respectively, and κ_{BN} and κ_C are the axial thermal conductivities of BN and carbon nanotubes, respectively. x denotes the number ratio of carbon layers to BN layers in each B–C–N nanotube. Since our nanotubes have large diameters, the ratio of the cross-sectional area of carbon to BN layers in each B–C–N nanotube is approximately x. We emphasize that κ_{BN} and κ_C represent the ensemble-averaged thermal conductivity of an individual multiwalled nanotube, not the mats of the BN and carbon nanotube, respectively.

There are several factors limiting the measured thermal conductivity value of mats and thus underestimate the κ_{BN} in Eq. (1). For example, we neglect the contributions of the thermal conductance across nanotube junctions, the inhomogeneous length and radius distribution of nanotubes in the sample, the possible microscopic geometry change after the oxidation treatment, the junction interaction possibly becoming weaker after removing the carbon layer of a B–C–N nanotube, the difficulty of thermally contacting the inner walls of nanotubes, and an extremely low concentration of carbon impurities or other defects. Moreover, the lack of clear umklapp processes in our B–C–N and BN nanotube mats indicates that factors other than phonon mean free path of an individual nanotube may lower the measured thermal conductivity of the material.

From Eq. (1), we determine the *lower bound* of κ_{BN} at 290 K to be $\kappa_{BN} \sim 0.32\kappa_C$ and $\kappa_{BN} \sim 0.54\kappa_C$ for samples *A* and *B*, respectively. Since multiwalled carbon nanotubes have been shown to exhibit very high thermal conductivity ($\sim$3000 W/m K at 290 K),[6] our result suggests that κ(290 K) of an individual BN nanotube to be at least 1620 W/m K. Thus, not unexpectedly, the $\kappa(T)$ of an individual BN nanotube appears to be three orders of magnitudes larger than that of the mat samples. We are currently measuring the thermal conductivity of an isolated BN nanotube to verify the result.

The total thermal conductivity of a nanotube can be written as $\kappa(T) = \Sigma C \upsilon \mathit{l}$, where C, υ, and l are, respectively, the specific heat, group velocity, and phonon mean free path, and the sum is over all phonon states. Since currently there are no available data for the heat capacity of BN nanotubes, we assume the ratio of heat capacity of hexagonal BN to graphite to be the same as that of BN nanotubes to carbon nanotubes.[5] Choosing $\upsilon = 10$ km/s estimated by theory,[18,19] we have $\mathit{l} = 320$ nm for BN nanotubes, which is comparable to $\mathit{l} \sim 500$ nm estimated for an isolated multiwalled carbon nanotube, and is only a fraction of the average length ($\sim$2 μm) of our BN nanotubes.

Since the natural abundance of boron is 19.9% ^{10}B and 80.1% ^{11}B, in contrast with that of carbon (98.9% ^{12}C, 1.1% ^{13}C), the effect of isotope disorder is much more severe for BN nanotubes than for carbon nanotubes. Theoretical calculations have suggested a larger enhancement factor of thermal conductivity $[\kappa(\text{isotopically pure})/\kappa(\text{naturalabundance})]$ for cubic BN (125%) than that of diamond (23%).[20] Because the disorder-induced localization effect is more pronounced in one dimension, we would expect that such an enhancement factor to be much higher for BN nanotubes. Therefore, BN nanotubes might be better thermal conductors than carbon nanotubes if made isotopically pure.

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