High Pressure Raman Spectroscopy of Double-Walled Carbon Nanotubes

Vikram Gadagkar,[1*] Surajit Saha,[1] D. V. S. Muthu,[1] P. Ramesh,[2] H. Shinohara,[2] R. O. Loutfy,[3] and A. K. Sood[1]
[1]Department of Physics, Indian Institute of Science, Bangalore 560012, India.
[2]CREST, Japan Science and Technology Agency,
c/o Department of Chemistry, Nagoya University, Nagoya 464-8602, Japan.
[3]Materials and Electrochemical Research Corporation, Tucson, AZ, USA.

Abstract

We have investigated the pressure dependence of the radial breathing (RBM) and tangential Raman modes of two different samples of double-walled carbon nanotubes (DWNT) up to 20 and 13 GPa. The Raman signatures of both the samples recovered to a remarkable degree on pressure release, indicating the high mechanical resilience of DWNT. The sample with the larger diameter outer tubes, inferred through the positions of the RBM, showed a higher pressure coefficient (dω/dp). The outer tube Raman modes of the two DWNT samples showed a higher pressure coefficient than those of single-walled carbon nanotubes (SWNT).
* Corresponding author. Email: gadagkar@physics.iisc.ernet.in

INTRODUCTION

While single-walled (SWNT) and multi-walled (MWNT) carbon nanotubes have been extensively investigated, double-walled carbon nanotubes (DWNT) have been observed [1] and synthesized [2] more recently. Being the simplest of the MWNT, they are ideal systems to study the evolution of various properties from the single to the multi-walled regime. High-pressure Raman experiments on SWNT [3] point to a structural phase transition at around 2 GPa. The current understanding is that the initially circular nanotube cross section is distorted to an oval shape under pressure. Molecular dynamics simulations [4-5] suggest that SWNT bundles collapse under hydrostatic pressure and that the collapse pressure varies as an inverse power law of the tube radius. More recently, [6-7] have used Raman spectroscopy to study bundles of DWNT under hydrostatic pressure. We report high pressure Raman results on two samples of DWNT with different diameters and compare with the recent results in the literature.

MATERIALS AND METHODS

One DWNT sample, called DWNT-A, was synthesized by catalytic chemical vapor deposition (CVD) of alcohol over Fe/Co loaded mesoporous silica [8]. DWNT-B was grown using high temperature CVD. The high-pressure Raman experiments were done at room temperature in a gasketed Mao-Bell-type Diamond-Anvil Cell with a mixture of methanol, ethanol, and water in the ratio 16:3:1 as the pressure transmitting medium. The ruby fluorescence technique [9] was used for the in-situ measurement of pressure. The samples were excited with an Ar^+ ion laser (Spectra Physics Model 165) lasing at 514.5 nm and the back-scattered light analyzed using the SPEX Ramalog 5 spectrometer, a double grating monochromator with a cooled photomultiplier tube. The behavior of the radial breathing (RBM) and tangential (TM) modes was followed as a function of pressure from atmospheric pressure to about 20 GPa for DWNT-A and 13 GPa for DWNT-B and back. The RBM were found to fit to two and the T modes to six Lorentzian curves.

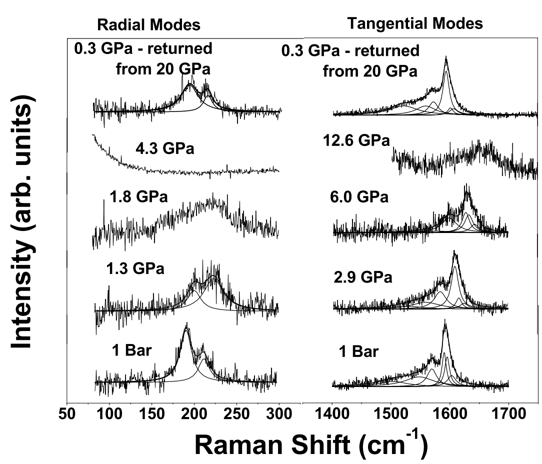

Fig. 1. A few representative radial and tangential modes for the DWNT-A as a function of pressure.

RESULTS

Fig. 1 shows typical RBM and TM spectra of DWNT-A. The spectra recorded at 0.3 GPa initially and after pressure release are similar. Similarly, for DWNT-B, the spectra recorded at 0.8 GPa before and after pressure release (data not shown) are similar, demonstrating that DWNT samples recover completely on decompression.

Figs. 2 and 3 show the variation of mode peak position with pressure for DWNT-A and B respectively. The two lowest frequency TM of DWNT-A were very weak modes and could not be clearly resolved after 4.0 GPa. The points beyond 4.0 GPa shown in Fig. 2 for these two modes were fixed by extrapolating from the lower pressure values to facilitate fitting of the other four strong modes.

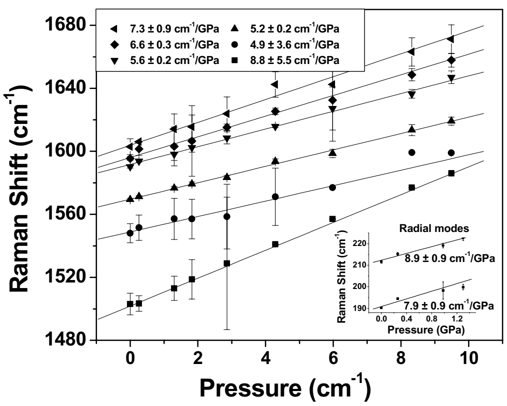

Fig. 2. DWNT-A. Phonon frequency as a function of pressure for the T and RBM (Inset).

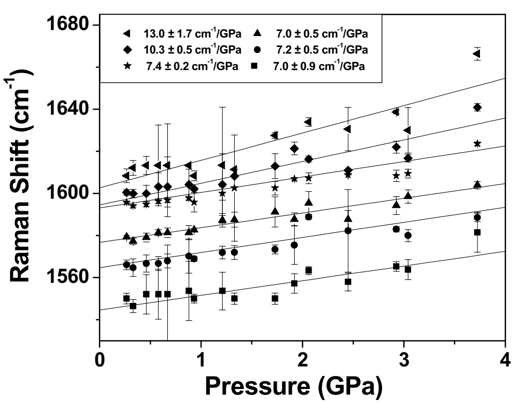

Fig. 3. DWNT-B. Phonon frequency as a function of pressure for the T modes.

Figs. 2 and 3 show that apart from the very weak first mode, DWNT-B has a higher pressure coefficient (*dω/dp*) than DWNT-A. One clear difference between the two samples is the diameter of the outer tubes, which were estimated [10], using the average value of the two RBM peaks, to be 1.3 nm for DWNT-A and 1.8 nm for DWNT-B. Larger diameter tubes are relatively easy to compress and deform compared to smaller ones.

The *dω/dp* of the SWNT RBM under hydrostatic pressure have been reported to be 7-10 cm^{-1}/GPa. We find that the radial modes of DWNT-A (8.9 and 7.9 cm^{-1}/GPa) show similar pressure coefficients to that of SWNT. While the strongest TM *dω/dp* values of DWNT-A (5.6 cm^{-1}/GPa) are similar to those of SWNT (4.7-6.1 cm^{-1}/GPa), that of DWNT-B is much higher (7.4 cm^{-1}/GPa). This is in contrast to the results of [6] who report very small pressure coefficients for their DWNT samples (2.1-6.1 cm^{-1}/GPa) They assign the tangential modes to the inner and outer tubes based on their differing behavior of the pressure coefficient and the linewidth. We do not observe such differences and thus cannot unambiguously assign some modes to the outer and other modes to the inner tubes. The *dω/dp* of both samples are much larger than that of MWNT (3.7-4.3 cm^{-1}/GPa).

We do not observe a change in the slope of the *ω* versus *p* plot which often indicates a phase transition, such as one around 2 GPa for SWNT [3]. This observation suggests that it is relatively more difficult to cause a collapse of DWNT as compared to SWNT.

CONCLUSION

We have investigated the pressure dependence of the RBM and T Raman modes of two different DWNT samples up to 20 and 13 GPa. The modes of both samples recovered to a remarkable degree on pressure release indicating their high mechanical resilience. The sample with the larger diameter outer tubes, inferred through the positions of the RBM, showed a higher pressure coefficient (*dω/dp*), which shows that larger diameter tubes are easier to compress or deform than smaller ones. The outer tube TM of the two DWNT samples showed a significantly higher *dω/dp* than those of SWNT, in contrast to what has been reported by other workers. Further, the *dω/dp* curve did not show a change in slope as has been reported for SWNT.

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