

## Combination of BN Nanotubes with Diamond-like c-BN and Giant Nonlinearities in Dendritic Nanostructures

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(Received 18 June 2013; published online 31 August 2013)

The matching of the properties of carbon and BN based nanostructures has been carried out. It was studied a strong frequency shifts and changes of the intensities vibrational bands of BN dendritic nanostructures. It was demonstrated the simultaneous manifestation vibrations of nanotubes and diamond-like c-BN. The giant vibrational nonlinearity of BN nanostructures provides an effective nonlinear interaction of vibrational modes with the generation of high-frequency excitations. This fact finds its proof in observation of the glow in the bands of overtones and summary tones.

**Keywords:** BN nanostructures, Raman scattering, IR absorption spectra, Vibration band, Giant nonlinearities.

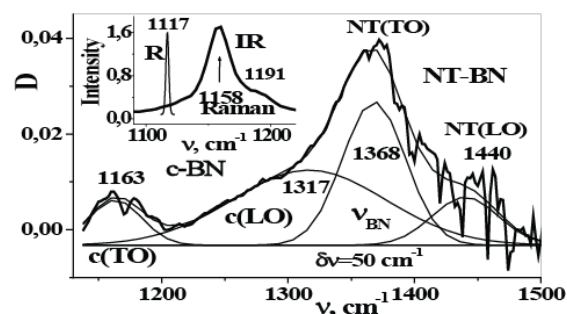
PACS numbers: 78.20.\_e, 78.30.\_j

### 1. POLICY OF THE PROCEEDINGS

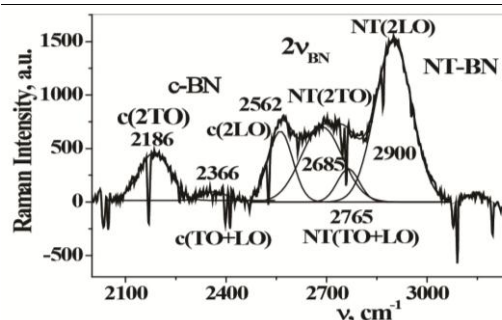
Boron nitride structures compare to carbon materials have an interesting feature. There is a much smaller frequency interval  $\Delta\nu$  between the vibrations of BN nanotubes (NTs) (1359  $\text{cm}^{-1}$ ) and diamond-like structures c-BN (1305  $\text{cm}^{-1}$ ) than between the vibrations of carbon NTs (1590  $\text{cm}^{-1}$ ) and diamond (1332  $\text{cm}^{-1}$ ). For carbon materials  $\Delta\nu = 258 \text{ cm}^{-1}$ , and for BN  $\Delta\nu \approx 54 \text{ cm}^{-1}$ . Due to this fact in the vibrational spectra of the BN dendritic structures and nanotubes joint variations of graphite-like and diamond-like structures appear. Since the substantial dipole oscillation of BN confirms by a significant LO-TO splitting [1], the BN materials are characterized by high nonlinear susceptibility in an oscillating field. This is supported by a strong vibrational anharmonicity BN and observation of anomalous (negative) thermal expansion ( $\alpha < 0$ ) in the 0-1040K [2] Vibrational nonlinearity BN NTs can become stronger in the formation of dendritic structures, which are formed from graphite-like h-BN in the focal zone of an optical furnace by heating 3 powerful xenon lamps and  $\text{Nd}^{3+}$ -laser radiation [3]. Raman scattering (RS) have been studied using a spectrometer Dilor (XY 800), and IR spectra - a Fourier spectrometer Nicolet FT-IR.

IR absorption spectra of planar vibrations  $E_{2g}$   $\nu_{\text{BN}} \approx 1360 \text{ cm}^{-1}$  BN NTs were shown in Figure 1. Together with the TO and LO components of BN NTs [1] with frequencies 1368 and 1440  $\text{cm}^{-1}$  were observed weaker frequencies 1163 and  $\sim 1317 \text{ cm}^{-1}$ , corresponding to the TO and LO modes of c-BN. The observed frequencies around 1300 – 1317  $\text{cm}^{-1}$  is close to the famous line of 1305  $\text{cm}^{-1}$  c-BN. There were significant changes in the oscillation frequencies of BN NTs and c-BN and as well as intensity change of the vibrational bands that characterize the variability of the dendritic structure of BN NTs. In the IR spectra, especially in the Raman spectra were observed very sharp bands in 1117 and 1158  $\text{cm}^{-1}$  with half-widths  $\delta\nu \approx 2,3 - 23 \text{ cm}^{-1}$ , which are shown in the inset in Fig. 1 and are TO

modes of c-BN. Sharp increase in the intensity of the Raman bands of c-BN confirms growth of  $\text{sp}^3$  hybridization and amplification of covalent bonds. Simultaneous manifestation of vibrations BN NTs and c-BN is also confidently observed in the region of overtones which demonstrate Raman spectra in Fig. 2. Besides 2TO and 2LO overtones with frequencies 2186, 2562  $\text{cm}^{-1}$  for c-BN and 2685, 2900  $\text{cm}^{-1}$  for BN NTs, weaker sum-frequency TO + LO are observed too.



**Fig. 1** – Observation vibration bands BN NTs and c-BN and in the fundamental region of IR absorption of the BN structures



**Fig. 2** – Observation vibration bands BN NTs and c-BN and in the region of overtones and total tones of the Raman spectra of the BN dendritic structures

Due to a giant wave nonlinearity BN NTs and h-BN it is possible an efficient nonlinear interaction of vibrational modes with the generation of higher-frequency (HF) radiation [4-9]. This is proved by the discovery of own radiation of BN structures, as presented in Figure 3. The bands of nonlinear radiation 2492, 2679, 2738, 2852, 2920  $\text{cm}^{-1}$  and others were observed in the form of vibrational bands of negative polarity in the broad-band background of IR absorption spectra of BN. These frequencies are associated with the generation of radiation in the region of overtones and sum tones. For example, the radiation band 2738  $\text{cm}^{-1}$  is associated with an overtone  $2\nu_{\text{BN}}$  ( $\nu_{\text{BN}} = 1362 - 1368 \text{ cm}^{-1}$ ), and the total frequency of the TO and LO components of diamond-like BN  $\sim 1163 + 1317 \text{ cm}^{-1}$  causes the generation line 2492  $\text{cm}^{-1}$ . Total tone of the vibrations of BN NTs 1368  $\text{cm}^{-1}$  and c-BN 1317  $\text{cm}^{-1}$  gives the strongest line of radiation near 2679  $\text{cm}^{-1}$ .

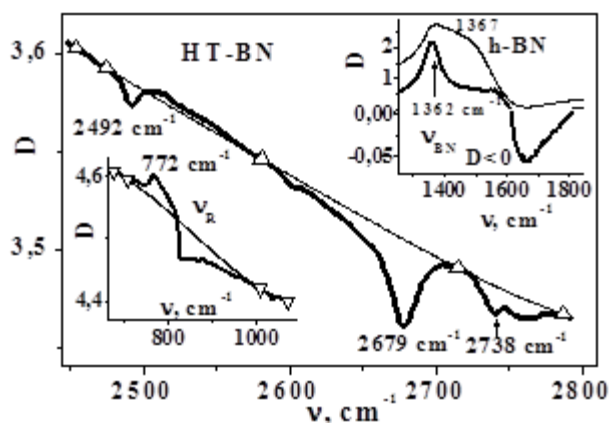


Fig. 3 – Observation of nonlinear radiation bands in the spectra of IR absorption and FTIR of dendritic structures of BN

Most strongly nonlinear radiation is observed in the HF region (1617 – 1808  $\text{cm}^{-1}$ ) because of characteristic strong line  $\nu_{\text{BN}}$  of FTIR spectrum, where there is the transmission  $T > 1$ , and the optical density  $D = -\ln T < 0$ , which are shown in the upper inset of Figure 3. Similar minima  $D$  are observed for h-BN, as well as in the HF

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region (825 – 958  $\text{cm}^{-1}$ ) of radial mode  $\nu_{\text{R}} = 772 - 813 \text{ cm}^{-1}$  BN NTs. The sharp bands of negative polarity were observed in the Raman spectra of the dendritic structures of BN NTs, which is clearly seen in Fig. 2. These spectral anomalies are associated with the nonlinear interaction of vibrations, generation of higher-frequency excitations and subsequent their parametric conversion [4-9]. The combination of  $\text{sp}^2$  and  $\text{sp}^3$  hybridization in synthesized dendritic structures BN NTs leads to increased sensitivity of the electronic states and to the growth of the nonlinear susceptibilities, which is similar to the states near the polymorphic transformations and melting of solids.

Giant increase of nonlinearity of BN NTs which leads to a high efficiency of nonlinear interactions of the vibrational modes is also associated with adsorbed water (AW). Fig. 4 shows selected OH bands of AW in frustrated total internal reflection (FTIR) spectra of BN NTs (bands 1,2), BN nanostructures (3) and also the infrared absorption of BN NTs (4). The band of a strongly bound of water  $\nu_{\text{OH1}} \sim 3215 \text{ cm}^{-1}$  (lane 1) dominates when a small amount of AW. With increasing AW content band  $\nu_{\text{OH2}} \sim 3450$  weakly bound water (2) increases. It is registered also bands of surface OH groups  $\nu'_{\text{OH}} \sim 2672$  and 2725  $\text{cm}^{-1}$ . OH vibrational states and their overtones are real intermediate levels, which contribute to increasing nonlinearity.

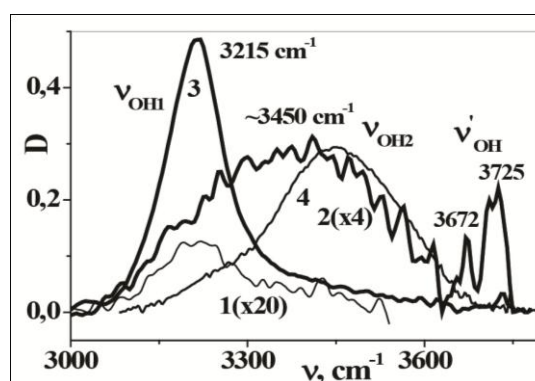


Fig. 4 – Comparison of selected OH valent bands of adsorbed water in the spectra of IR absorption and FTIR of dendritic structures of BN