The 1DTbBrx@SWCNT meta-nanotubes are obtained using a capillary technique and investigated by HRTEM and HAADF STEM in JEOL ARM 200F at 80 kV. Raman spectroscopy is performed in Renishaw Invia Raman microscope. Four versions of 1D TbBrx crystal structure are proposed.

The first type of the structure is characterized by a rhombic unit cell (Pmmm). An <001> crystal axis coincides with the nanotube axis. In this case a Br/Tb ratio is 3.25. A HRTEM image, the model and corresponding image simulation in a (110) projection were shown in Fig. 1.

The second type of the structure is characterized by “rhomboid” defects observed in the (110) projection of 1D crystal when a set of micrographs was taken (Fig. 2). It is suggested that due to electron beam heating Br atoms located in a center of Br (Tb) tetrahedrons are lost. As a result covalent bonds of Tb-Br atoms were replaced by Tb-Tb metallic bonds. This is accompanied by a displacement of Tb atoms towards the center of the tetrahedrons. The Br/Tb ratio is 2.66.

The third type of structure is observed in the HAADF STEM images (Fig. 3). In this case the “rhomboid” defect is observed in each unit cell and the Br/Tb ratio is 2.5.

The fourth structure resemble the third one, but in it additionally four bromide atoms are lost. The Br/Tb ratio is 2 in this case.

The existence of a structural variety for 1D TbBrx crystals can be explained by different oxidation degree of Tb atoms.

In a G-region of Raman spectra of metananotubes a significant peaks shift towards higher frequencies spectrum area is observed in the range from 4 to 7 cm⁻¹ for s-SWCNTs and from 7 to 17 cm⁻¹ for m-SWCNTs. This effect can indicate a higher influence of intercalated nanocrystals on the electronic structure of metallic nanotubes. Furthermore a value of the observed G-mode shift depends on a chemical nature of intercalated halogenide and appears to have maximum values for bromides. According to literature data the G-mode shift towards the region of high oscillation energies can correspond to an electron charge transfer from the SWCNT walls to the nanocrystals (acceptor doping of SWCNTs).

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Fig. 1: HRTEM image of 1DTbBr.@SWCNT. A model of a first type of structure in a (110) projection and a corresponding image simulation ($d_1=3.4$ Å and $d_2=3.8$ Å).

Fig. 2: HRTEM image of a second type of 1DTbBr.@SWCNT structure. The “rhomboid” defects are arrowed.

Fig. 3: STEM HAADF image of a third type of 1DTbBr.@SWCNT structure and its image simulation.