IR TRANSMISSION SPECTRA OF NANOSTRUCTURAL MATERIALS

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Introduction

Investigations into various properties of nanostructural materials (nanotubes, fullerenes etc.) attract great attention due to their outlook in many applications. We are interested in comparison of IR transmission spectra of carbon nanotubes (NT) with those of C_{60} and C_{70} fullerites as they belong to the same class of monomolecular compounds but with different electron structures of bands. Carbon NTs belong to the class of semimetals (like graphite), and fullerites belong to the class of semiconductors ($Eg \approx 1.2$-1.9 eV) [1-23]. Additionally, IR transmission spectra of highly dispersed NTs of silicon nitride have been studied. In the first time, we have prepared these NTs using nanostructural carbon forming in the fullerene synthesis.

Experimental

IR spectra of the three groups were recorded using Specord 75-IR two-beam spectrophotometer in the band of wave numbers 400-4000 cm^{-1} for carbon NTs and 400-1500 cm^{-1} - for silicon nitride NTs. The samples studied were prepared according to the typical technique for compaction of the substance with KBr. The weighed samples were 1:300 mg.

Fig.1 shows IR transmission spectra of carbon NTs (spectrum "a") and fullerite C_{60} (spectrum "c"). Fig.2 shows the spectra for Si_3N_4 NTs of α and β modifications.

Results and discussion

As seen in Fig.1, the IR spectrum of carbon NTs has no features. This is a monotonous curve with increasing transmission in the long wave region of the spectrum. Such an IR transmission spectrum is typical for the narrow band semiconductors ($Eg \approx 0.01$-0.1 eV) or semimetals.

The IR spectrum for fullerite C_{60} has other form (Fig.1c). Four strong narrow transmission lines are clearly seen in the spectrum. They are attributed to intramolecular oscillations of mode 4 F_{1u} active in the IR region. The lines are near ~526 cm^{-1}, ~578 cm^{-1}, ~1178 cm^{-1} and ~1426 cm^{-1}. The first two lines are due to radial vibrations of the carbon sphere, the other two are due to stretching vibrations. Vibrations tangentially to the sphere of single bond C-C are observed in the range of ~1178 cm^{-1}, double bond C=C (common side of hexagons) - in the range of ~1426 cm^{-1}. Insignificant number of absorption bands (AB) in the IR spectrum of C_{60} fullerite is resulted from high symmetry of this molecule. Spectral positions of ABs in the IR spectrum of fullerite C_{70} practically correspond to those for C_{60}. It should be noted that IR spectra of fullerites may contain additional ABs resulted from insufficiently careful purification of fullerite from solvent that was used to extract fullerite from the fullerene-containing soot (see Fig.1,c). As seen in Fig.1,c, the spectrum contains, besides ABs of C_{70} fullerite, additional ABs attributed to absorption by solvent, in particular, toluene.

The basic intensive AB in the range of 1050-830 cm^{-1} and the band of medium intensity in the range of 460-445 cm^{-1} are observed in IR spectra of Si_3N_4 NTs (Fig.2). In general, spectra differ by their structure and the shape of ABs in the range of 1050-830 cm^{-1}. This range may be due to stretching bridge vibrations. The absorption band is attributed to deformation vibrations of N-Si-N bond. It is positioned in the range of 460-445 cm^{-1} does not practically change.

It is known that the basic structural element of all silicon nitride modifications is SiN_4 tetrahedron with T_d symmetry.

According to [2], in IR absorption spectra of tetrahedral molecules one should expect two absorption bands to be present due to fundamental three times degenerated vibrations $\nu_3(F_2)$ and $\nu_4(F_2)$. Vibrations of SiN_4 tetrahedrons occur in the local crystalline field of Si_3N_4 that results in distortion of tetrahedrons. Therefore, one should expect the degeneration to be removed partially or completely, and inactive vibrations in IR spectra of an isolated tetrahedron to be excluded. In this case the rules of selection for α- and β-Si_3N_4 vibrations will be different as these modifications belong to different space groups (α- Si_3N_4 belongs to P 3/c ($C_{3\upsilon}^{4}$), group, β-Si_3N_4 belongs to P 6_3/m (C_{6h}^{2})), group, i.e. distortion of tetrahedrons will be different for α- and β-Si_3N_4. IR spectrum of β-Si_3N_4 must be simpler as distortion of tetrahedrons in it is weaker than that in α- Si_3N_4.

Theoretical ground of ABs in IR spectra for crystalline powder-like Si_3N_4 of both modifications may be applied to explain the nature of ABs in IR spectra of Si_3N_4 nanotubes. Apparently, ABs present in the range of ~1045 ~980 and ~910 cm^{-1}

in the spectrum for α- Si_3N_4 NTs may be attributed to removing degeneration from the $\nu_3(F_2)$ vibration.

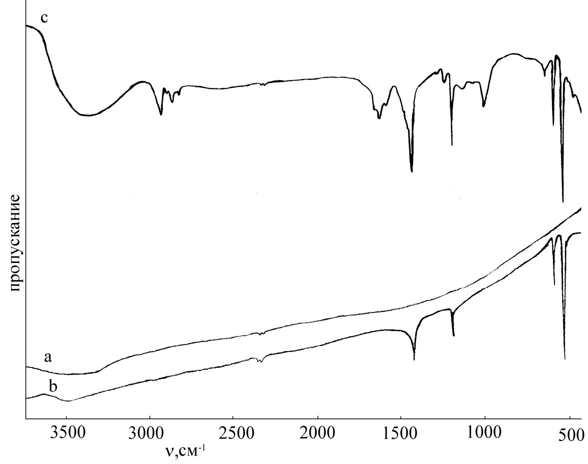

Fig. 1.

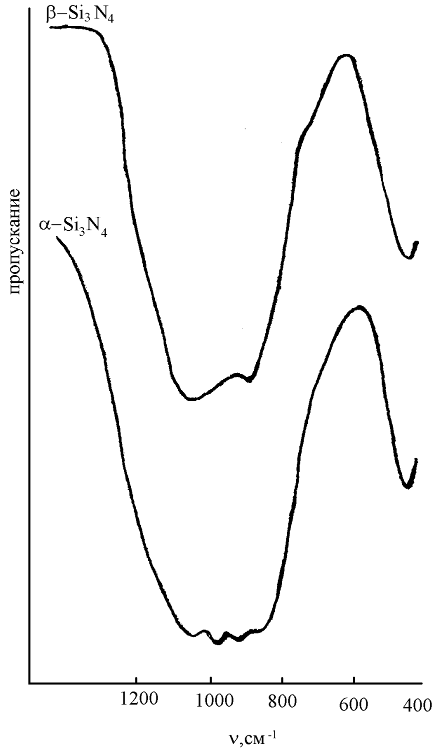

Fig. 2.

ABs present in the range of ~830 cm^{-1} are due to removing exclusion for the $\nu_1(A)$ vibration which is inactive in the isolated tetrahedron. In the IR spectrum of β-Si_3N_4 NTs the valence band splits into two ABs positioned in the range of ~1050 cm^{-1} and ~900 cm^{-1} what seems to be attributed to the partial removing of degeneration from the $\nu_3(F_2)$ vibration for this modification. Difference in IR spectra of crystalline powder-like Si_3N_4 and IR spectra for Si_3N_4 NTs consists in the absence of several additional bands with weak and medium intensities in the range of 800-500 cm^{-1} in the spectra for NTs of α and β modifications. This seems to be due to the features of their structure, shape and size.

Conclusions

1. IR spectra of carbon NTs and C_{60}, C_{70} fullerites have been recorded. IR spectra of fullerites may be used for qualitative control of the degree of fullerite purity after their extraction from the fullerene-containing soot.
2. In the first time, we have recorded IR spectra for Si_3N_4 NTs of both modifications. It has been found difference in IR spectra for α- and β- Si_3N_4. IR spectra of Si_3N_4 may be used as the additional (to X-ray phase analysis) method for determination of the phase composition of Si_3N_4 NTs, especially in the case when NTs are highly dispersed X-ray amorphous materials.

References

1. Matysina ZA, Zaginaichenko S Yu, Schur DV, Pishuk VK; Theoretical investigation of isopleths of hydrogen solubility in transition metals,Journal of alloys and compounds, 330,85-88,2002,Elsevier
2. Trefilov VI, Schur DV, Pishuk VK, Zaginaichenko S Yu, Choba AV, Nagornaya NR; The solar furnaces for scientific and technological investigation, Renewable energy, 16,1,757-760, 1999, Elsevier
3. Трефилов ВИ, Щур ДВ, Загинайченко СЮ; Фуллерены-основа материалов будущего, 2001, Laboratory 67
4. Schur Dmitry V, Zaginaichenko Svetlana Yu, Veziroğlu T Nejat, Javadov NF; The Peculiarities of Hydrogenation of Fullerene Molecules C60 and Their Transformation, Black Sea Energy Resource Development and Hydrogen Energy Problems,191-204,2013, Springer Netherlands
5. Schur DV, Dubovoi AG, Anikina NS, Zaginaichenko S Yu, Dobrovol’skij VD, Pishuk VK, Tarasov BP, Shul’ga Yu M, Meleshevich KA, Pomytkin AP; The production of utrafine powders of fullerites by the salting out method,Proceedings of VII International Conference “Hydrogen Material Science and Chemistry of Metal Hydrides”, Alushta-Cremia-Ukraine, September, 16-22, 2001,
6. Kharlamov AI, Loytchenko SV, Kirillova NV, Kaverina SN, Vasilev AD, Fomenko VV, Zolotarenko AD, Kazimirov VP; Tubular and filamentous nanostructures of hexagonal silicon carbide, Proceedings of VII International Conference “Hydrogen Material Science and Chemistry of Metal Hydrides”, Ukraine, 572-574,2001,
7. Slys IG, Berezanskaya VI, Schur DV, Zaginaychenko SYu, Rogozinskaya AA, Adejev VM, Zolotarenko AD; Making the point metal coatings on the particles of hydride-forming intermetallides, Proceedings of VII International Conference “Hydrogen Material Science and

Chemistry of Metal Hydrides”, Ukraine,404-405,2001,

8. Schur DV, Matysina ZA, Zaginaichenko S Yu; Theoretical study of interstitial atoms distribution in the bulk and at the surface of crystal. Surface segregation,Journal of alloys and compounds,330,81-84,2002,Elsevier
9. Lavriv LV, Anikina NS, Simanovskij AP, Zolotarenko AD, Schur DV; Features of fullerene extraction wth toluene, Proceedings of VII International Conference “Hydrogen Material Science and Chemistry of Metal Hydrides”, Ukraine,596,2001
10. Schur DV, Zaginaichenko S Yu, Adejev VM, Voitovich VB, Lyashenko AA, Trefilov VI; Phase transformations in titanium hydrides, International journal of hydrogen energy, 21,11,1121-1124,1996, Pergamon
11. Schur DV, Tarasov BP, Zaginaichenko S Yu, Pishuk VK, Veziroglu TN, Shul'ga Yu M, Dubovoi AG, Anikina NS, Pomytkin AP, Zolotarenko AD; The prospects for using of carbon nanomaterials as hydrogen storage systems,International journal of hydrogen energy,27,10,1063-1069,2002,Pergamon
12. Shul’ga Yu M, Martynenko VM, Tarasov BP, Fokin VN, Rubtsov VI, Shul’ga N Yu, Krasochka GA, Chapysheva NV, Shevchenko VV, Schur DV; On the thermal decomposition of the C60D19 deuterium fullerite,Physics of the Solid State,44,3,545-547,2002, Nauka/ Interperiodica
13. Schur DV, Matysina ZA, Zaginaichenko S Yu; Study of physico-chemical processes on catalyst in the course of synthesis of carbon nanomaterials,Hydrogen Materials Science and Chemistry of Metal Hydrides: Proceedings of the NATO Advanced Research Workshop on. Alushta Crimea, Ukraine, 16-22 September 2001,235,2002,Kluwer Academic Pub
14. Tarasov BP, Shul’ga Yu M, Fokin VN, Vasilets VN, Shul’ga N Yu, Schur DV, Yartys VA; Deuterofullerene C 60 D 24 studied by XRD, IR and XPS,Journal of alloys and compounds, 314,1,296-300,2001,Elsevier
15. Tarasov BP, Fokin VN, Moravsky AP, Shul'ga Yu M, Yartys VA, Schur DV; Promotion of fullerene hydride synthesis by intermetallic compounds, Hydrogen energy progress, 2, 1221-1230,1998,
16. Schur DV, Zaginaichenko S Yu, Matysina ZA, Smityukh I, Pishuk VK; Hydrogen in lanthan–nickel storage alloys,Journal of alloys and compounds,330,70-75,2002,Elsevier
17. Schur DV, Tarasov BP, Shul'ga Yu M, Zaginaichenko S Yu, Matysina ZA; Research of Fullerites Hydrogen Capacity,Hydrogen Materials Science and Chemistry of Metal Hydrides: Proceedings of the NATO Advanced Research Workshop on. Alushta Crimea, Ukraine, 16-22 September 2001,1,2002, Kluwer Academic Pub
18. Muratov VB, Meleshevich KA, Bolgar AS, Zolotarenko AD; Application of dynamic c-calorimetry method for investigation of enthalpy at hydride dissociation,Proceedings of VII International Conference “Hydrogen Material Science and Chemistry of Metal Hydrides”, Ukraine,342-343,2001,
19. Anikina NS, Schur DV, Simanovskiy AP, Zolotarenko AD, Dubovoy AG, Ivanchenko NV; Problem on fullerene production by electric arc method, Proceedings of VII International Conference “Hydrogen Material Science and Chemistry of Metal Hydrides”, Ukraine,590-591, 2001,
20. Matysina ZA, Schur DV; Hydrogen and solid phase transformations in metals, alloys and fullerites, Dnepropetrovsk: Nauka i obrazovanie, 420p (in Russian),2002,
21. Matysina ZA, Pogorelova OS, Zaginaichenko S Yu, Schur DV; The surface energy of crystalline CuZn and FeAl alloys,Journal of Physics and Chemistry of Solids,56,1,9-14, 1995,Elsevier
22. Schur DV, Lavrenko VA, Adejev VM, Kirjakova IE; Studies of the hydride formation mechanism in metals,International journal of hydrogen energy,19,3,265-268,1994,Elsevier
23. Pishuk VK, Schur DV, Bogolepov VA, Savenko AF, Zaginaichenko SYu, Zolotarenko AD, Mar'yanchuk IV, Prikhod'ko AB; Problem on production of highly dispersed extra pure powders, Proceedings of VII International Conference “Hydrogen Material Science and Chemistry of Metal Hydrides”, Ukraine,586-587,2001,