

B.A. Baitimbetova¹, K.S. Tolubayev², Yu.A. Ryabikin³,
D.O. Murzalinov³, B.A. Zhautikov¹, G.S. Dairbekova^{1,2}

¹Satbayev University, Almaty, Kazakhstan;

²Karaganda Industrial University, Temirtau, Kazakhstan;

³Institute of Physics and Technology, Almaty, Kazakhstan

(E-mail: baitim@physics.kz)

The study of carbon nanomaterials by IR-Fourier spectroscopy, obtained by the action of an ultrasonic field on graphite

In this work, the absorption lines corresponding to nanomaterials (nanotubes, nanofibers, graphene), as well as vibrational spectra in the studied samples of graphene structures obtained by processing an ultrasonic field on an aromatic hydrocarbon and pure graphite, are studied by IR-Fourier spectroscopy. With an increase in time in the studied spectra of ultrasonic treatment on pure graphite, absorption bands are observed in the frequency range of $\nu = 2967,7 \text{ cm}^{-1}$, $2926,1 \text{ cm}^{-1}$, 2853 cm^{-1} , 1449 cm^{-1} , related to stretching and deformation vibrations of the bond C-H of saturated aromatic hydrocarbons. The spectra of carbonyl (carbon) compounds of the C-C bond are also noted in the regions of the absorption bands: $1449,9 \text{ cm}^{-1}$ – $1652,6 \text{ cm}^{-1}$. This means that in the IR spectra, with an increase in the time of sonication, the carbon formations of asymmetric stretching vibrations of C-C bonds increase. In these frequency ranges, the absorption bands corresponding to adsorbed benzene are not observed. With an increase in the processing time of the samples, the absorption band of OH hydroxyl groups is not observed. In the samples under study, numerous aromatic carbon-carbon bonds are observed, due to the collective groups of vibrations of carbon nanomaterials (graphene structures, nanofibers, single-layer and multilayer carbon nanotubes, etc.).

Keywords: carbon nanosystems, polyaromatic condensed systems, aromatic hydrocarbon, carbonate-carboxylate compounds, absorption lines, by IR-Fourier spectroscopy, stretching and deformation vibrations, ultrasonic treatment.

Introduction

Carbon nanomaterials (fullerene, nanotubes, graphene) are topical materials in modern materials science. The introduction of small additives of carbon nanoparticles with a developed and active surface makes it possible to provide new properties of materials such as sorption capacity with respect to heavy metals [1].

Multilayer (technical) graphene is of great interest for studying its properties and applications in modern materials science. Such graphite nanoplanes are obtained as a result of its oxidation and subsequent destruction by ultrasound by the Hammer method [2].

Due to the fact that this method (Hammer method) is due to the release of toxic reaction products, the method of combined action of ultrasound and surfactant has received wide practical application. The advantage of the method is that the substances used are non-toxic, but the power and duration of ultrasonic interaction are increased [1].

The authors of [3] studied intense bands in the region of $1700\text{--}1450 \text{ cm}^{-1}$, which correspond to stretching vibrations of the carbon plane of graphene. In the region of $1450\text{--}1000 \text{ cm}^{-1}$ the most intense vibrations correspond to deformation vibrations of the graphene plane and deformation vibrations of terminal C–H bonds [3]. The most intense band (about 900 cm^{-1}) corresponds to the out-of-plane vibrations of C–H bonds [3]. It should be noted that the ratio of the intensities of carbon plane stretching vibrations C–H bonds out-of-plane vibrations can be used to estimate the size of graphene fragments [3, 4].

The spectra of the initial graphite powder and graphene are well described by the authors of [1]. Two absorption maxima were obtained by IR spectroscopy at 1273 and 2373 cm^{-1} , which we attributed to the C–O–C and C–O₂ bonds in accordance with the data of [5]. The formation of these bonds is due to the oxidation of graphite and the formation of broken carbon-carbon bonds, which increases the reactivity of the resulting graphene. Graphene which does not have OH groups on the surface is hydrophobic, which makes it difficult to introduce it into binders [1].

Experimental

In this work, samples obtained by ultrasonic treatment of pure graphite and aromatic carbon (benzene) were studied by the IR-Fourier spectroscopy. The absorption lines corresponding to carbon nanosystems (nanotubes, graphene structures, etc.) and carbonate-carboxylate compounds and polyaromatic condensed systems in the studied samples have been studied and analyzed. With an increase in the time of sonication, numerous single carbon-carbon bonds are formed due to the collective modes of carbon nanostructures, including carbon nanotubes [5, 6].

According to [1], during ultrasonic interaction with graphite and the preparation of graphene nanoplanes, two absorption maxima appear at 1273 and 2373 cm^{-1} . As mentioned above, such absorption peaks signify the formation of symmetrical C-O-C and C-O2 bonds [7]. These values allow us to conclude that the formation of bonds reflects the oxidation of graphite at broken C-C bonds. The presence of -OH groups chemically bonded on the surface confirms the value of the spectrum at 3414 cm^{-1} [1].

Results and Discussion

Carbonate-carboxylate compounds and polyaromatic condensed systems in the studied graphene-containing structures obtained by processing an ultrasonic field on an aromatic hydrocarbon (benzene) and pure graphite have been studied and interpreted by IR-Fourier spectroscopy.

In the IR spectrum of the original sample there are absorption bands of OH hydroxyl groups in the region of absorption bands $\nu=3440.6 \text{ cm}^{-1}$ (Figure 1).

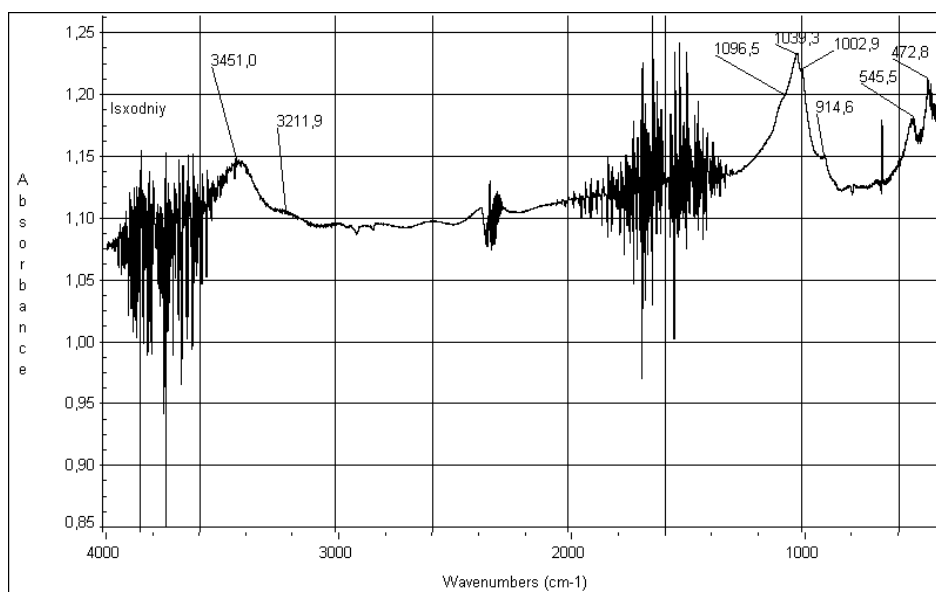


Figure 1. IR-Fourier spectrum of the original sample

In the range $\nu=2000-4000 \text{ cm}^{-1}$ there are intense absorption bands, $\nu=1075.7$ and 602.7 cm^{-1} . These ranges contain absorption bands related to the stretching and bending vibrations of silicon, aluminium, and iron oxide groups. According to the literature data [8], graphite contains ash containing oxides of silicon, aluminium, and iron with a content of 5–20%.

Since the absorption bands of metals in the IR spectra are in the range $\nu=700 - 50 \text{ cm}^{-1}$, the marked absorption bands belong to oxides of silicon, aluminium, and iron.

Figure 2 shows the IR spectrum of a sample treated for 10 minutes. This spectrum contains very weak absorption bands at 1039 and 1008 cm^{-1} of silicon, aluminium, and iron oxides; this is due to the washing out of ash impurities from graphite during sonication. There are no signs of benzene adsorption, since there are no absorption bands in the range $\nu=3100 - 3000 \text{ cm}^{-1}$, as well as at $\nu=1600$ and 685 cm^{-1} .

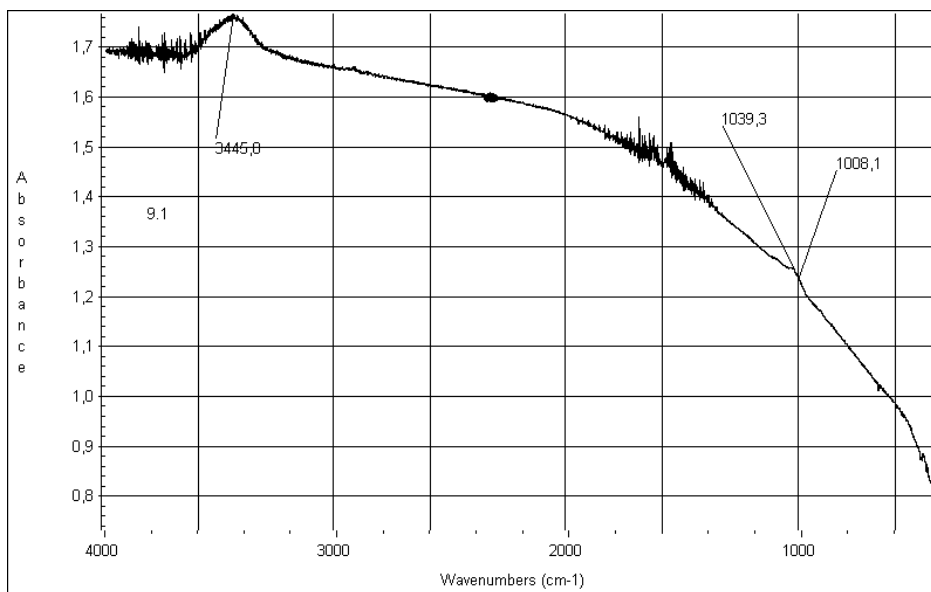


Figure 2. IR-Fourier spectrum of a sample treated for 10 minutes

Stretching vibrations of the C-C bond are present in the ranges of absorption bands $\nu=1100 - 900 \text{ cm}^{-1}$.

Figure 3 illustrates the IR spectrum of a sample treated for 20 minutes. The spectrum shows stretching vibrations of the C-C bond in the range $\nu=1100 - 900 \text{ cm}^{-1}$, as well as stretching and deformation vibrations of the C-H group in the region of absorption bands $\nu=1449 \text{ cm}^{-1}$, 2967, 2926, 2853. Benzene adsorption is not observed.

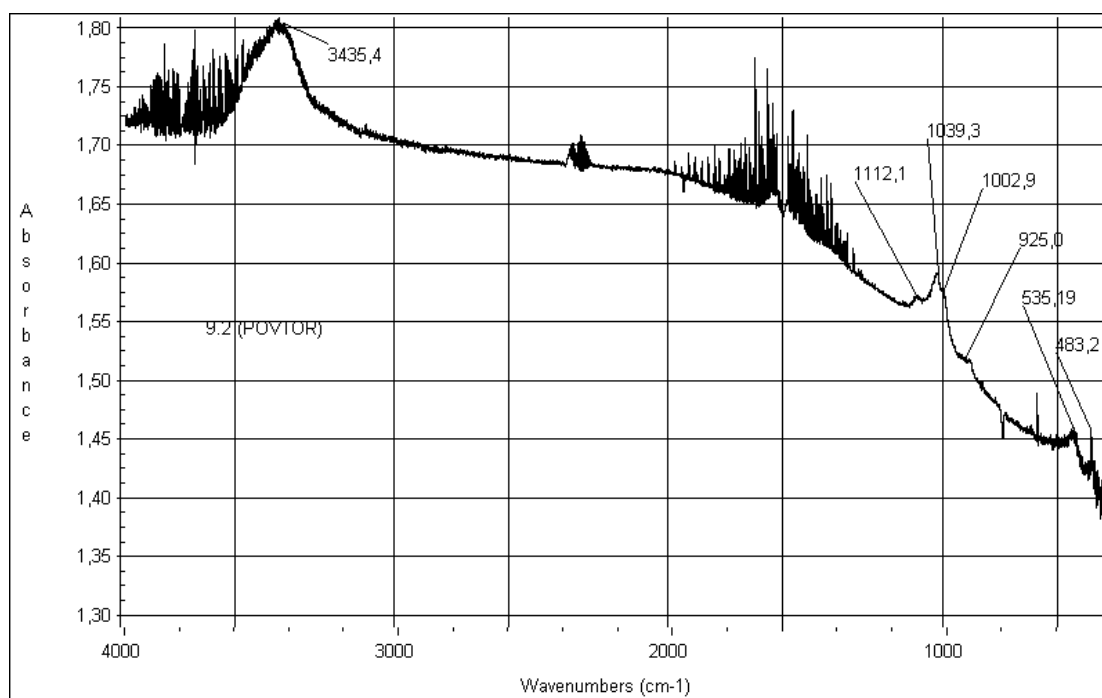


Figure 3. IR-Fourier spectrum of a sample treated for 20 minutes

In the IR spectrum of the sample treated with ultrasound for 120 minutes, there are new absorption bands $\nu=2967.7$, 2926.1, 2853, 1449 cm^{-1} , related to the stretching and deformation vibrations of the C-H bond of saturated aromatic hydrocarbons (Figure 4).

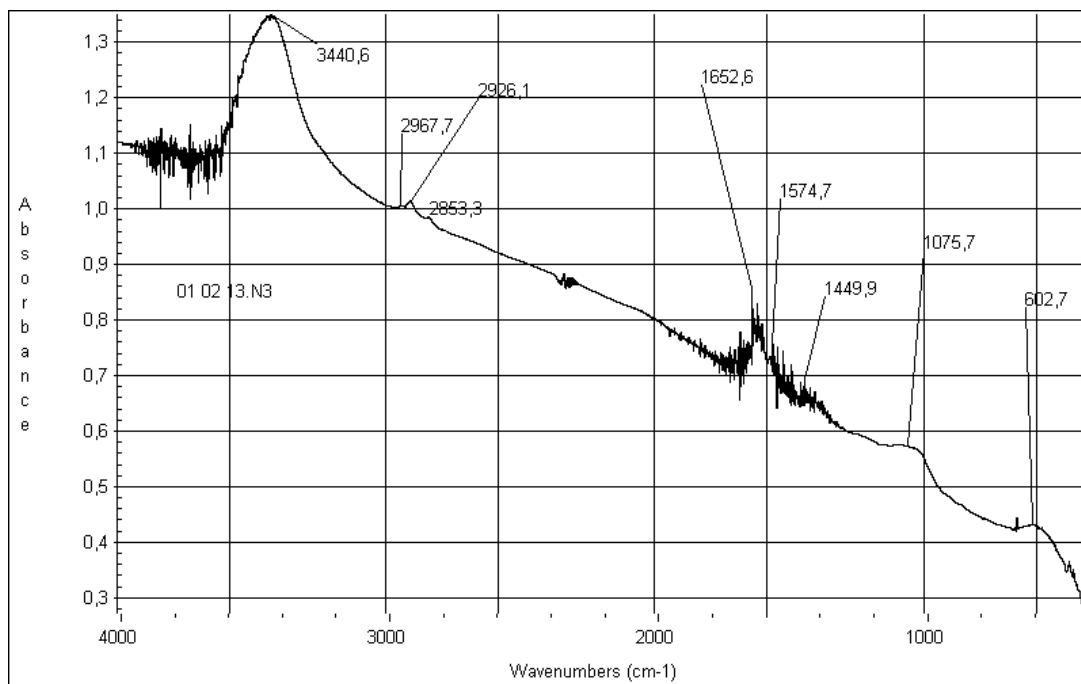


Figure 4. IR-Fourier spectrum of a sample sonicated for 120 minutes

There are also stretching vibrations of the C-C bond in the region of the absorption bands 1449.9 - 1652.6 cm^{-1} .

In the region of absorption of bonds (metal – oxygen) Me–O ($700 - 50 \text{ cm}^{-1}$), one band is observed at 602.7 cm^{-1} , with an increase in the time of ultrasonic treatment of benzene and graphite. No absorption bands corresponding to adsorbed benzene (in the range of absorption bands $\nu=3440.6-2967.7 \text{ cm}^{-1}$, 1547.7 cm^{-1} and 602.7 cm^{-1}) were found. As a result of studies carried out on an IR-Fourier spectrometer, a decrease in the ash content of graphite with the time of sonication was established. It is noted that an increase in carbon formations of stretching vibrations of C-C bonds.

Conclusions

As a result of the studies carried out by the method of IR spectroscopy, a decrease in the ash content of graphite with the time of sonication was established. It is shown that an increase in carbon formation of stretching vibrations of carbon-carbon bonds with an increase in the processing of the ultrasonic field.

Based on these data, it can be concluded that vibrations of single carbon-carbon bonds of carbon nano-systems are observed in the ranges of $1320-1652.2 \text{ cm}^{-1}$ [5, 6].

IR-Fourier studies show that the absorption bands in the ranges of 1652.2 , 1574.7 and 1449.9 cm^{-1} are due to the absorption of collective modes of carbon nanosystems (multilayer nanotubes, graphenes, fullerenes and nanofibers). In terms of their structure, carbon nanosystems can be considered three-dimensional analogues of aromatic compounds [4, 5]. Thus, IR spectroscopic studies confirm the formation of carbon nanosystems in the samples under study, which is in good agreement with literature data [5, 6, 9, 10].

References

- 1 Денисюк И.Ю. FT-IR-спектры многослойного графена и его композиции с поверхностно-активным веществом / И.Ю. Денисюк, К.Ю. Логущова, М.И. Фокина, М.В. Успенская // Оптика и спектроскопия. — 2019. — № 2 (126). — С. 177–179.
- 2 Hirata M. Thin-Film Particles of Graphite Oxide I: High Yield Synthesis and Flexibility of the Particles / M. Hirata, T. Gotou, S. Horiuchi, M. Fujiwara, M. Ohba // Carbon. — 2004. — No. 42. — P. 2929–2937.
- 3 Степаньян С.Г. Влияние кислородсодержащих групп на колебательные спектры оксида графена / С.Г. Степаньян, А.Ю. Иванов, Л. Адамович, В.А. Карачевцев // Наносистемы, наноматериалы, нанотехнологии. — 2016. — № 4 (14). — С. 513–526.
- 4 Si Y. Synthesis of Water Soluble Graphene / Si Y., E.T. Samulski // Nano Letters. — 2008. — No. 6(8). — P. 1679–1682.

- 5 Baitimbetova B.A. The study by spectroscopy method of carbon nanostructure in carbonized ferrochromic spinel / Baitimbetova B.A., Yu. F.Ryabikin, Oksana V.Zashkvara // An International Journal for Rapid Communication, Spectroscopy Letters, London. — 2008. — No. 41. — P. 9–14.
- 6 Рябикин Ю.А. Изучение углеродных нанотрубок методом ИК-Фурье спектроскопии, полученных при каталитическом разложении углеводородов / Ю.А. Рябикин // Вестн. Казах. нац. техн. ун-та. — 2015. — № 3. — С. 456–432.
- 7 Yongchao Si. Samulski Synthesis of Water Soluble Graphene / Si Yongchao, T. Edward // Nano Letters. — 2008. — No. 6(8). — P. 1679–1682.
- 8 Бетехтин А.Г. Курс минералогии: учеб. пос. / А.Г. Бетехтин. — М.: КДУ, 2007. — С. 715.
- 9 Péter Szirmai, Gábor Fábíán, Balázs Dóra. Density of states deduced from ESR measurements on low-dimensional nanostructures; benchmarks to identify the ESR signals of graphene and SWCNTs // Phys. Status Solidi B. — 2009. — No. 246. — P. 2558.
- 10 Cataldo F. The impact of a fullerene-like concept in carbon black science / F. Cataldo // Carbon. — 2002. — No. 40. — P. 157–162.

Б.А. Байтимбетова, К.С. Толубаев, Ю.А. Рябикин,
Д.О. Мурзалинов, Б.А. Жаутиков, Г.С. Даирбекова

Графитке ультрадыбыстық өріс әсер еткен кезде алынатын көміртікті наноматериалдарды ИК-Фурье спектроскоп әдісімен зерттеу

Жұмыста спектроскопияның ИК-Фурье әдісімен тиісті наноматериалдардың (нанотүтікшелер, наноталшық, графен) жұтылу сызықтары, сонымен қатар ультрадыбыстық өрісті хош иісті көмірсутек пен таза графитке өңдеу кезінде алынған графен құрылымдарының зерттелетін үлгілеріндегі тербелмелі спектрлері зерттелген. Зерттелетін ультрадыбыстық өңдеу спектрлерінде таза графитке уақыттың жоғарылауымен қаныққан хош иісті көмірсутектердің С-Н байланысының валенттік және деформациялық ауытқуларына жататын $\nu=2967,7 \text{ см}^{-1}$, $2926,1 \text{ см}^{-1}$, 2853 см^{-1} , 1449 см^{-1} жиіліктер аймағында сіңіру жолақтары байқалады. Сондай-ақ, $1449,9 \text{ см}^{-1}$ – $1652,6 \text{ см}^{-1}$ сіңіру жолақтары аймағында С-С байланысының карбонилді (көміртекті) қосылыстарының спектрлері көрінді. Бұл ИК спектрлерінде ультрадыбыспен уақыт жоғарылаған сайын С-С байланыстарының асимметриялық валентті тербелістерінің көміртегі түзілімдері артады дегенді білдіреді. Осы жиілік диапазондарында адсорбцияланған бензолға сәйкес келетін сіңіру жолақтары байқалмайды. Үлгілерді өңдеу уақытының ұлғаюымен ОН гидроксил топтарының сіңіру жолақтары белгіленбейді. Зерттелетін үлгілерде көміртекті наноматериалдардың (графен құрылымдары, наноталшықтар, бірқабатты және көпқабатты көміртекті нанотүтікшелер және т.б.) тербелістерінің ұжымдық топтарына байланысты көптеген хош иісті көміртегі-көміртекті байланыстары көрсетілген.

Кілт сөздер: көміртекті наножүйелер, полиароматикалық конденсатты жүйелер, хош иісті көмірсутектер, карбонат-карбоксилат қосылыстары, сіңіру желілері, ИК-Фурье-спектроскопия әдісі, валенттік-деформациялық тербелістер, ультрадыбыстық өңдеу.

Б.А. Байтимбетова, К.С. Толубаев, Ю.А. Рябикин,
Д.О. Мурзалинов, Б.А. Жаутиков, Г.С. Даирбекова

Изучение углеродных наноматериалов методом ИК-Фурье спектроскопии, полученных при воздействии ультразвукового поля на графит

В работе методом ИК-Фурье спектроскопии исследованы линии поглощения соответствующих наноматериалов (нанотрубок, нановолокна, графен), а также колебательные спектры в исследуемых образцах графеновых структур, полученных при обработке ультразвукового поля на ароматический углеводород и чистый графит. С повышением времени в исследуемых спектрах ультразвуковой обработки на чистый графит наблюдаются полосы поглощения в области частот $\nu=2967,7 \text{ см}^{-1}$, $2926,1 \text{ см}^{-1}$, 2853 см^{-1} , 1449 см^{-1} , относящиеся к валентным и деформационным колебаниям связи С–Н насыщенных ароматических углеводородов. Также отмечаются спектры карбонильных (углеродных) соединений С–С связи в областях полос поглощения $1449,9 \text{ см}^{-1}$ – $1652,6 \text{ см}^{-1}$. Это означает, что в ИК спектрах с повышением времени обработки ультразвуком увеличиваются углеродные образования асимметричных валентных колебаний С–С связей. В этих диапазонах частот полос поглощения, соответствующих адсорбированному бензолу, не наблюдается. С увеличением времени обработки образцов полосы поглощения гидроксильных групп ОН не намечаются. В исследуемых образцах образуются многочисленные ароматические углерод-углеродные связи, обусловленные коллективными группами колеба-

ний углеродных наноматериалов (графеновых структуры, нановолокна, однослойные и многослойные углеродные нанотрубки и др.).

Ключевые слова: углеродные наносистемы, полиароматические конденсированные системы, ароматический углеводород, карбонатно-карбоксилатные соединения, линии поглощения, метод ИК-Фурье спектроскопии, валентно-деформационные колебания, ультразвуковая обработка.

References

- 1 Denisjuk, I.Yu., Logushkova, K.Yu, Fokina, M.I., & Uspenskaya, M.V. (2019). FT-IR-spektry mnogosloinogo grafena i ego kompozitsii s poverkhnostno-aktivnym veshchestvom [FT-IR spectra of multilayer graphene and its composition with explosively active radiation]. *Optika i spektroskopiiia — Optics and Spectroscopy*, 2(126), 177–179 [in Russian].
- 2 Hirata, M., Gotou, T., Horiuchi, S., Fujiwara, M., & Ohba, M. (2004). Thin-Film Particles of Graphite Oxide 1: High Yield Synthesis and Flexibility of the Particles. *Carbon*, 42, 2929–2937.
- 3 Stepanyan, S.G., Ivanov, A.Yu., Adamovich, L., & Karachevcev, V.A. Vliianie kislorodsoderzhashchikh grupp na kolebatelnye spektry oksida grafena [Effect of Oxygen-Containing Groups on the Vibrational Spectra of Graphene Oxide]. *Nanosistemy, nanomaterialy, nanotekhnologii — Nanosystems, nanomaterials, nanotechnologies*, 4(14), 513–526 [in Russian].
- 4 Si Y., Samulski E.T. (2008). Synthesis of Water Soluble Graphene. *Nano Letters*, 6(8), 1679–1682.
- 5 Baitimbetova B.A., Yu. F.Ryabikin, & Oksana V. Zashkvara (2008). The study by spectroscopy method of carbon nanostructure in carbonized ferrochromic spinel. *An International Journal for Rapid Communication, Spectroscopy Letters, London*, 41, 9–14.
- 6 Ryabikin, Yu.A. (2015). Izuchenie uglerodnykh nanotrubok metodom IK-Fure spektroskopii, poluchennykh pri kataliticheskom razlozhenii uglevodorodov [Study of carbon nanotubes by IR-Fourier spectroscopy, obtained by catalytic decomposition of hydrocarbons]. *Vestnik Kazakhskogo natsionalnogo tekhnicheskogo universiteta — Bulletin KazNTU*, 3, 456–432 [in Russian].
- 7 Yongchao, Si, & Edward, T. (2008). Samulski Synthesis of Water Soluble Graphene. *Nano Letters*, 6(8), 1679–1682.
- 8 Betehtin, A.G. (2007). *Kurs mineralogii [Course of mineralogy]*. Moscow: KDU [in Russian].
- 9 Péter Szirmai, Gábor Fábrián, & Balázs Dóra (2009). Density of states deduced from ESR measurements on low-dimensional nanostructures; benchmarks to identify the ESR signals of graphene and SWCNTs. *Phys. Status Solidi B*, 246, 2558.
- 10 Cataldo, F. (2002). The impact of a fullerene-like concept in carbon black science. *Carbon*, 40, 157–162.