OPTICAL
PROPERTIES

Interaction of Hydrofullerite $C_{60}H_{42}$ with Air

A. V. Bazhenov[a, *]**, I. O. Bashkin**[a]**, M. Yu. Maksimuk**[a]**, T. N. Fursova**[a, **]**,
L. V. Zorina**[a]**, and A. P. Moravskii**[b]

[a] *Institute of Solid State Physics, Russian Academy of Sciences,
ul. Akademika Ossipyana 2, Chernogolovka, Moscow oblast, 142432 Russia*
* *e-mail: bazhenov@issp.ac.ru*
** *e-mail: fursova@issp.ac.ru*
[b] *Materials and Electrochemical Research (MER) Corporation,
7960 South Kolb Road, Tucson, Arizona, AZ 85756 United States*
Received August 11, 2014

Abstract—The transmission and Raman spectra of $C_{60}H_{42}$ samples synthesized at a high hydrogen pressure and stored under different conditions have been measured. It has been found that, upon interaction of the compound with air, a part of $C_{60}-H$ chemical bonds are replaced by $C_{60}-O-H$ bonds. It has been experimentally shown that the observed changes in the vibrational and electronic properties of $C_{60}H_{42}$ are caused by the interaction of the compound with atmospheric oxygen and water vapor. The rate of oxidation of the studied samples is significantly less than the value previously published for the oxidation of the $C_{60}H_{36}$ compound synthesized by the reduction of fullerene C_{60} dissolved in different solvents with the use of Zn/HCl. This is explained by the fact that particles of the product of the hydrogenation at a high hydrogen pressure are polycrystals with relatively large sizes, unlike the fullerene hydrides synthesized by the reduction of C_{60} with Zn/HCl.

1. INTRODUCTION

Earlier, it was reported [1] that the $C_{60}H_{36}$ compound synthesized by the reduction of fullerene C_{60} with the use of Zn/HCl is chemically unstable in air. According to the later data [2], upon the interaction with air, the white color of the $C_{60}H_{36}$ compound synthesized in different solvents changes to orange and the complete oxidation occurs for less than 1 h. The exposure to the light significantly increases the oxidation rate.

For different states of the fullerene in the literature, there are terms such as fullerene, fullerite, fulleride, and fullerane. The last term refers to the hydrogenated fullerenes. In this paper, for hydrogenated fullerite, we prefer to use the term "hydrofullerite."

We synthesized hydrofullerites $C_{60}H_x$ with the hydrogen content from $x = 36$ to 60 [3] by the reaction of C_{60} with molecular hydrogen under a high pressure. It was found that, after extraction in air, their optical properties change with time at approximately the same rate independently of x. However, the rate of change in the properties proved to be extremely low in comparison with the data available in the literature [2]. In order to explain these differences, we have restricted ourselves to a detailed study of one type of hydrofullerite, namely, $C_{60}H_x$ with the hydrogen content $x \cong 42$. An attempt has also been made to understand what is the cause of changes in the properties of hydrofullerites $C_{60}H_x$ in air, i.e., whether it is oxygen or water vapor.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The fullerite C_{60} was hydrogenated at a hydrogen pressure of 30 ± 3 kbar and at a temperature of $450°C$ for 10 h. The initial material was fullerene C_{60} with a purity of 99.99%. After the vacuum sublimation at the final stage of purification, C_{60} had the form of a powder consisting of small single crystals and was thermally unstable under the AlH_3 pressure. Hydrogen was released upon the decomposition of AlH_3 under pressure and infiltrated through a palladium foil separating pellets of AlH_3 and C_{60}. This technique was described in detail in [4]. The resulting product was brittle and easily broken. After the removal from the reaction cell, it had the form of a white powder, the largest particles of which reached a few millimeters in size and were transparent. The hydrogen content in the samples was determined by the combustion in an oxygen flow and the subsequent weighing of the combustion products CO_2 and H_2O. In four tests, we obtained the hydrogen content $x = 41.7 \pm 1.0$.

In order to measure IR transmission spectra of powder samples, they were uniformly distributed using a plastic spatula on a KBr or CaF_2 substrate. The

transmission spectra $T(\nu)$ at room temperature in the spectral range of 600–5000 cm^{-1} were measured using an IR microscope of the Fourier spectrometer with a spatial resolution of 80 μm. Then, the optical density D was calculated according to the formula $D = -\ln T$. From these spectra, we subtracted the monotonic baseline determined by the reflection and scattering of the light. For the measurement of IR transmission spectra of water, it was placed between CaF$_2$ plates separated by a gap of approximately 5 μm. These spectra were recorded in the region of optical transparency of CaF$_2$ at a frequency $\nu > 800$ cm^{-1}.

For the measurement of transmission spectra in the visible range, we dissolved samples in toluene and measured optical transmission spectra of a thin layer of the powder deposited on the walls of the cuvette after evaporation of the toluene from it. The cuvette was placed under a microscope objective and illuminated from below with an incandescent lamp. The image from the focal plane of the microscope was focused via a system of mirrors onto the slit of the prism spectrograph. The relative aperture of the spectrograph was 1 : 3, and its dispersion varied from 24 nm/mm in the blue region to 110 nm/mm in the red region.

In the visible and IR ranges, we obtained not the true transmission, but a combination of the transmission and scattering of the light. Therefore, we were interested only in qualitative differences in the properties of the samples.

Raman scattering was measured on a Dilor Microdil spectrometer in backscattering geometry at room temperature. The sample was placed in the focal plane of the microscope, onto which the radiation from a continuous wave He–Ne laser (wavelength 632.8 nm, power 1 mW) was focused into a spot with a diameter of ~5 μm. The characteristic time of the measurement of one spectrum was 1 h. The wavenumber was known to within ±2 cm^{-1}, and the spectral resolution—to within 7 cm^{-1}.

The X-ray diffraction measurements were carried out on a Siemens D-500 diffractometer (CuK_α radiation). The reference point on the C$_{60}$H$_{42}$ sample was obtained by applying a small amount of the Al powder.

3. EXPERIMENTAL RESULTS

Figure 1 shows the optical density spectra: spectrum *1* corresponds to the C$_{60}$H$_{42}$ initial sample of white color, and spectrum *2*, to the sample yellowed after the storage in the open air for six months. Spectra *1* and *2* are normalized so that the lines in the range of 1100–1500 cm^{-1} would have approximately the same intensity. It can be seen that the coloring of the samples is accompanied by the appearance of an intense broad absorption band with a maximum at approximately 3400 cm^{-1} and absorption lines with maxima at 1700 and 1010 cm^{-1} (indicated by arrows in Fig. 1). In
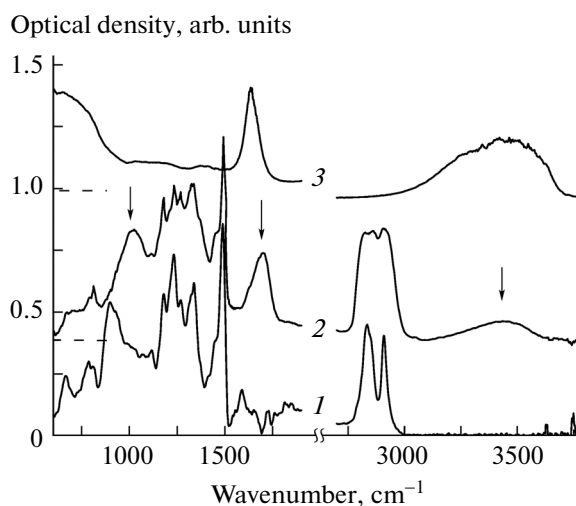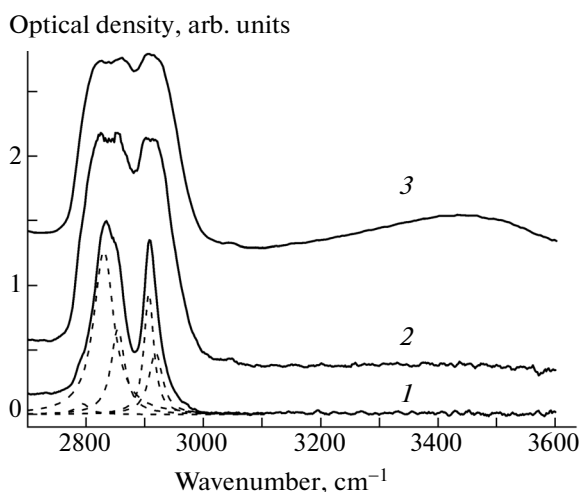

Optical density, arb. units

Fig. 1. Optical density spectra of C$_{60}$H$_{42}$: (*1*) initial sample, (*2*) sample after the storage in the open air for six months, and (*3*) optical density spectrum of the H$_2$O film with a thickness of ~5 μm. The horizontal dashed lines indicate the zero values on the ordinate axis for spectra *2* and *3*.

the range from 1900 to 2700 cm^{-1}, there is no absorption line.

For comparison, we observed the appearance of absorption lines with maxima at 3400 and 1705 cm^{-1} in the spectrum of hydrogenated carbon nanotubes stored in air for a few months. In the spectra of the initial nonhydrogenated carbon nanotubes stored in air under the same conditions, these lines did not appear. After annealing of the hydrogenated nanotubes at 120°C under vacuum at a residual pressure of approximately 10^{-4} Pa for 1 h, the absorption lines previously observed at 3400 and 1705 cm^{-1} disappeared. This indicated that the hydrogenated carbon nanotubes simply adsorbed water without the formation of new chemical bonds.

By assuming that the water is also absorbed in the hydrofullerite C$_{60}$H$_{42}$, we attempted to remove it by vacuum thermal annealing. However, the annealing at 120°C for 1 h did not lead to changes in the spectra. The absorption lines observed at 3400 and 1705 cm^{-1} did not disappear even after the subsequent annealing at 200°C for 2 h. Moreover, the samples, being yellow in color before annealings, became brown, and the intensities of the lines at 3400, 1700, and 1010 cm^{-1} increased. This result indicates that, in the case of the hydrofullerite, the annealing leads not to the physisorption of water but to the formation of C$_{60}$–O–H chemical bonds.

A comparison of the absorption spectrum of water (spectrum *3* in Fig. 1) with the spectrum of the C$_{60}$H$_{42}$ sample stored in the open air for six months (spectrum *2* in Fig. 1) demonstrates that, in both spectra, there is

Optical density, arb. units

Fig. 2. Optical density spectra of $C_{60}H_{42}$: (*1*) initial sample, (*2*) sample with the surface yellowed after the storage in a desiccator for one year, and (*3*) sample after the storage in the open air for six months.

an absorption line with a maximum at 3400 cm^{-1} due to the stretching vibrations of the O−H bonds. The half-width of this line in the spectrum of the $C_{60}H_{42}$ sample (150 cm^{-1}) is somewhat less than that in the spectrum of the water (200−250 cm^{-1}). The absorption line at 1700 cm^{-1} is attributed to the bending vibrations of the O−H bonds. A similar line in the spectrum of the water is located at approximately 1635 cm^{-1}. Moreover, in the spectrum of the water, there is an intense broad absorption band (spectrum *3* in Fig. 1) with a maximum at approximately 600 cm^{-1}, which is assigned to librational vibrations of water molecules [5]. Librational vibrations are different types of motions of water molecules with respect to each other. The spectrum of the hydrofullerite, in which the C−O−H bonds were revealed after the storage in the open air, does not contain lines corresponding to librational vibrations of water; i.e., in our sample, there are no aggregates of water molecules. Moreover, in the spectrum of the $C_{60}H_{42}$ sample after the storage in the open air, there appeared an absorption line at 1010 cm^{-1}. In our opinion, this band corresponds to stretching vibrations of the OH groups with respect to C_{60}. This assignment is confirmed, for example, by the spectrum of methanol [6].

Figure 2 shows the region of C−H and O−H stretching vibrations in the IR absorption spectra of the initial samples (spectrum *1*) and the samples stored in a desiccator for about one year and yellowed from the surface (spectrum *2*). Spectrum *3* was measured on the $C_{60}H_{42}$ sample yellowed after the storage in the open air for six months.

It is essential that, after grinding in an agate mortar, the yellowed samples transformed into a white powder. Therefore, their main volume did not react with air.

The rate of propagation of this reaction deep into the sample can be visually estimated as 2 μm per year.

The absorption lines of C−H vibrations in spectrum *1* are relatively narrow. These lines are well approximated by five Lorentzians (shown by dashed lines in Fig. 2). They have the following positions of the maxima and the half-widths (given in parentheses): 2791 (11), 2831 (40), 2855 (25), 2908 (20), and 2918 (30) cm^{-1}.

The yellowing of the surface led only to a broadening of the lines and to a change in the intensity of their components (spectrum *2* in Fig. 2). In spectrum *2* of the sample stored in the desiccator, we did not reveal new absorption lines or the disappearance of lines typical of the $C_{60}H_{42}$ initial sample. In contrast to spectrum *3* of the sample stored in the open air for six months, spectrum *2* does not contain the absorption line at 3400 cm^{-1}, which corresponds to the O−H vibrations. Although the O−H vibrations did not manifest themselves in spectrum *2* in Fig. 2, the yellow color of the $C_{60}H_{42}$ sample indicated that the $C_{60}H_{42}$ compound was also oxidized in a dry air (the silica gel of the desiccator absorbed water vapor). However, the oxidation is more efficient in air due to the presence of water vapor (spectrum *3* in Fig. 2).

The Raman spectra (Fig. 3) changed more significantly than the IR spectra. After the storage in the open air for one month, the color of the $C_{60}H_{42}$ sample remained white, but the intensity of the pedestal, against the background of which we observed lines of molecular vibrations (see inset in Fig. 3), increased by one order of magnitude. After the storage for six months, the intensity of the pedestal further increased by one order of magnitude and, on this background, we already could not reveal vibrations of C−H bonds. As in the IR spectra, the Raman lines corresponding to C−H stretching vibrations become broadened with an increase in the time of storage of the sample in the open air. After one month of storage, the broadening of the lines was approximately 30%.
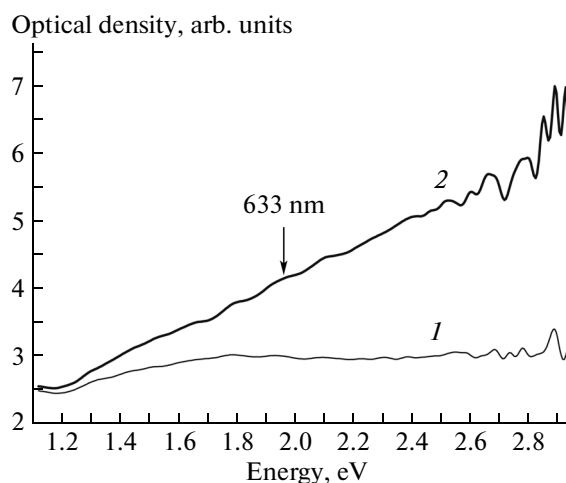
Undoubtedly, the increase in the intensity of the pedestal was caused by the luminescence on the background of which the Raman spectrum was measured. A necessary condition for the appearance of luminescence is the occurrence of electronic transitions in the region which there is radiation from the exciting laser (in our case, it is the He−Ne laser with λ = 632.8 nm). Therefore, we measured the light transmission spectra (*T*) in the visible range. These spectra are presented in Fig. 4 in the form of spectra of the optical density $D = -\ln T$. The spectrum of the fullerite C_{60} (see, for example, [7]) differs from the spectrum of the $C_{60}H_{42}$ initial sample, which in this spectral range is also transparent (spectrum *1* in Fig. 4). This is consistent with the results obtained in [2], where it was shown that, in the visible range, the absorption lines typical of the spectrum of the fullerite C_{60} completely disappear in the
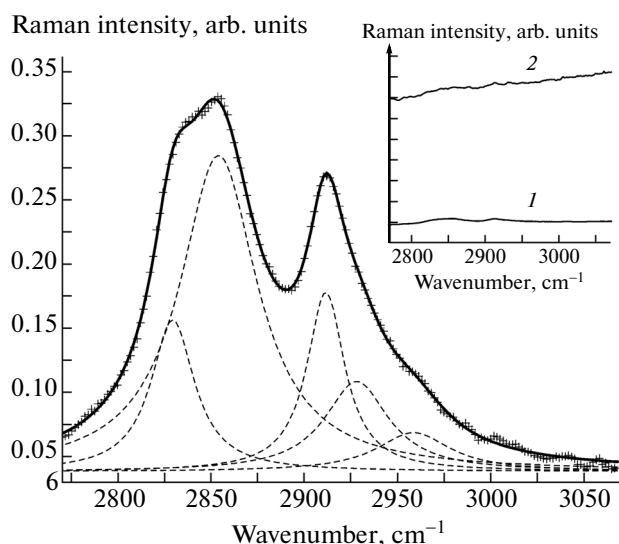
Fig. 3. Raman spectra of the $C_{60}H_{42}$ compound. Crosses indicate the spectrum of the $C_{60}H_{42}$ initial sample in the region of C−H stretching vibrations. The solid line represents the result of fitting this spectrum by five Lorentzians (dashed lines). The inset shows the Raman spectra with luminescence for the initial sample (spectrum *1*) and the sample stored in air for one month (spectrum *2*).

Fig. 4. Transmission spectra of $C_{60}H_{42}$ in the visible range: (*1*) as-prepared sample and (*2*) sample after the storage in the open air for one year.

spectrum of $C_{60}H_{36}$. There remains only the absorption line at 217 nm, whose tail extends into the visible range of the spectrum. We assume that the absence of absorption in the $C_{60}H_{36}$ initial samples and the $C_{60}H_{42}$ samples studied in our work is associated with the filling of the lower unoccupied molecular orbitals (LUMO) due to the partial electron transfer from hydrogen to C_{60}. The interaction of $C_{60}H_{42}$ with atmospheric air leads to the appearance of structureless absorption, which increases monotonically with an increase in the photon energy (spectrum *2* in Fig. 4). It is this absorption that is responsible for the change of the white color of the $C_{60}H_{42}$ samples to yellow during the storage in air, as well as for the appearance of luminescence of these samples in the Raman spectra. The luminescence intensity correlates with the reacted fraction of the sample.

By comparing the spectra of the $C_{60}H_x$ samples stored in the open air and in the desiccator (Fig. 2), we assumed that the observed changes in their properties are due to the reaction of the samples both with atmospheric oxygen and with water vapor. In order to verify this hypothesis, we divided the initial sample into two parts. One part was placed in distilled water, whereas the other part was left in air. Under these conditions, the samples were kept at room temperature for one month. As a result, both parts of the sample remained white. However, the measurement of the Raman spectrum showed that the ratio of the integrated intensity of C−H vibrations to the intensity level of the pedestal I/I_{bg} decreased by a factor of five ($\pm 10\%$) in both sam-

ples due to the increase in the luminescence intensity by approximately one order of magnitude. The rate of "aging" of the sample placed in the water ($I/I_{bg} = 4.6 \pm 0.4$) was slightly less than that of the sample exposed to air ($I/I_{bg} = 4.9 \pm 0.3$), but the difference did not exceed the measurement error.

It is known that the properties of the water differ from the properties of the water vapor. At room temperature, water molecules are joined by hydrogen bonds into clusters. Moreover, there is a small amount of water molecules dissociated into H^+ and OH^- ions. In water vapor, there are individual H_2O molecules and very small clusters. That is why the IR spectrum of the water exhibits a broad structureless line corresponding to O−H vibrations, in contrast to the set of narrow lines of the water vapor. The experiment with the sample placed in water demonstrated that the changes in the properties of the $C_{60}H_{42}$ compound stored in air are caused by the surface adsorption and diffusion of both the oxygen and water molecules deep into the $C_{60}H_{42}$ particles. The diffusing molecules enter into the chemical reaction with hydrofullerite molecules. The rate of diffusion of the molecules into the studied samples is very low.

The X-ray diffraction pattern of $C_{60}H_{42}$ (Fig. 5) is indexed in terms of the body-centered cubic lattice of the C_{60} molecules. Since the intensity and, consequently, the position and shape of the reflections are affected by the form factor of the C_{60} cage, we did not perform the profile analysis of the X-ray diffraction pattern, but estimated the unit cell parameter from the positions of the strongest peaks (110) and (211): $a_0 = 11.95 \pm 0.05$ Å. The transparency of $C_{60}H_{42}$ particles made it possible to measure the Laue pattern of a separate plate with sizes of approximately 0.5 mm. The obtained X-ray diffraction pattern represented an ideal
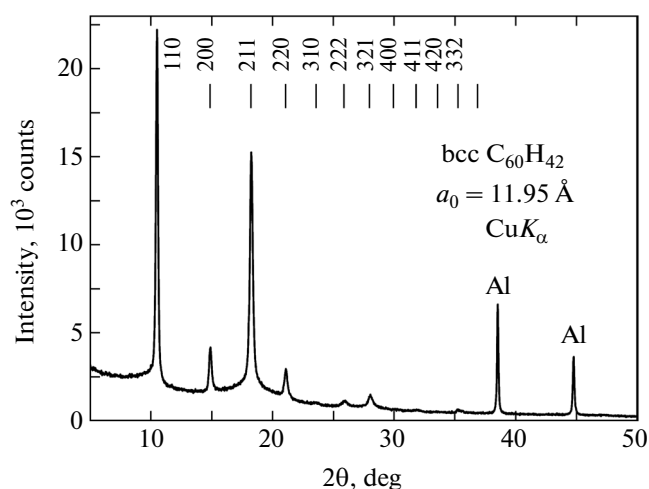
Fig. 5. X-ray diffraction pattern of $C_{60}H_{42}$ with reference reflections of the Al powder. CuK_α radiation. Shown also is the X-ray diffraction diagram of the body-centered cubic lattice with the unit cell parameter $a_0 = 11.95$ Å.

powder diffraction pattern with a uniform distribution of the intensity along the diffraction rings; i.e., the synthesized hydrofullerite appeared to be an isotropic fine-grained polycrystal.

4. DISCUSSION OF THE RESULTS

We have undertaken the investigation of the "aging" of $C_{60}H_x$ compounds during their storage in air due to the fact that there are published works dealing with the study of as if the hydrofullerite, but, actually $C_{60}H_xO_y$. For example, in the IR spectra [8], there is an absorption line at approximately 1700 cm^{-1} (corresponding to the O–H bending vibrations), whose intensity does not correlate with the hydrogen content in the sample, but correlates with an increase in the absorption near 3200 cm^{-1}, which, in our opinion, is the low-energy wing of the absorption line associated with the O–H stretching vibrations at 3400 cm^{-1}.

We studied hydrofullerites that are fine-grained polycrystals without discontinuities. This makes it possible to explain the significant differences in the processes of oxidation of the $C_{60}H_{36}$ compound, which was synthesized by the reduction of C_{60} with Zn/HCl [1, 2] (the oxidation time was less than 1 h), and the $C_{60}H_x$ compounds hydrogenated under a high hydrogen pressure (the oxidation rate was approximately 2 μm per year). Cataldo [2] investigated the interaction of air or ozone with $C_{60}H_{36}$ hydrofullerene molecules in a solution or in the form of a dried powder, actually a powder with a large ratio of the surface area to the volume. Naturally, the interaction of $C_{60}H_{36}$ in the form of molecules or a fine powder with air components is much more efficient than the interaction with polycrystals without discontinuities, when the

diffusion of O_2 or H_2O molecules into the crystal is hindered. It has long been known that diffusion of molecules into fullerite is possible. The octahedral pores of fullerite C_{60} with a face-centered cubic lattice can accommodate molecules whose sizes do not exceed 4.1 Å [9].

The data presented in this paper suggest that the diffusion of oxygen and, apparently, water vapor into $C_{60}H_{42}$ single crystals is the cause of changes in their vibrational and electronic properties. The efficiency of the interaction of air components with $C_{60}H_{42}$ polycrystals without discontinuities is many orders of magnitude less than that with molecules or a loose powder of $C_{60}H_{36}$ studied in [2].

5. CONCLUSIONS

The hydrofullerite $C_{60}H_{42}$ was synthesized at high hydrogen pressures. The product of the synthesis is a colorless or transparent isotropic fine-grained polycrystal with the body-centered cubic lattice and the unit cell parameter $a_0 = 11.95 \pm 0.05$ Å.

Under ambient conditions, the hydrofullerite $C_{60}H_{42}$ and other $C_{60}H_x$ compounds with $36 \leq x \leq 60$ are oxidized and transform into $C_{60}H_xO_y$. This causes the appearance of absorption lines that are characteristic of O–H bond vibrations in the IR and Raman spectra and structureless absorption bands in the visible spectral range. As a result, the samples become yellow in color at the initial stage. The oxidation of $C_{60}H_x$ hydrofullerites synthesized at a high hydrogen pressure is many orders of magnitude slower than the oxidation of $C_{60}H_{36}$ molecules synthesized by the reduction with Zn/HCl [2]. This is explained by the fact that the hydrogenation at a high hydrogen pressure results in the formation of polycrystals without discontinuities in contrast to the method used in [2]. The rate of diffusion of air components deep into the crystal and, accordingly, the oxidation of $C_{60}H_x$ is approximately equal to 2 μm per year in contrast to 1 h for the molecular hydrofullerite $C_{60}H_{36}$ or its fine powder produced using chemical reactions [2].

The results of the performed experiments demonstrated that the oxidation of $C_{60}H_x$ under ambient conditions is caused by the molecular oxygen and water vapor.

It should be noted that the Raman method proved to be more sensitive to the oxidation of $C_{60}H_x$ than the IR absorption method: the pedestal in the Raman spectrum, which is determined by luminescence, indicates variations in the properties of $C_{60}H_x$ upon the interaction with air already in the initial stage of the oxidation.

REFERENCES

1. A. D. Darwish, A. K. Abdul-Sada, G. J. Langley, H. W. Kroto, R. Taylor, and D. R. M. Walton, J. Chem. Soc., Perkin Trans. 2, No. 6, 2359 (1995).
2. F. Cataldo, Fullerenes, Nanotubes Carbon Nanostruct. **11** (4), 295 (2003).
3. I. O. Bashkin, A. V. Bazhenov, T. N. Fursova, A. P. Moravsky, O. G. Rybchenko, V. V. Shestakov, Yu. M. Shulga, and V. E. Antonov, in *Proceedings of the International Symposium on Metal−Hydrogen Systems (MH 2006), Lahaina, Maui, Hawaii, United States, October 1−6, 2006.*
4. V. E. Antonov, I. O. Bashkin, S. S. Khasanov, A. P. Moravsky, Yu. G. Morozov, Yu. M. Shulga, Yu. A. Ossipyan, and E. G. Ponyatovsky, J. Alloys Compd. **330−332,** 365 (2002).
5. G. V. Yukhnevich, *Infrared Spectroscopy of Water* (Nauka, Moscow, 1973) [in Russian].
6. Bernhard Schrader, *Raman/Infrared Atlas of Organic Compounds* (Wiley, New York, 1989).
7. A. V. Bazhenov, A. V. Gorbunov, and K. G. Volkodav, JETP Lett. **60** (5), 331 (1994).
8. A. V. Talyzin, A. Dzwilewski, B. Sundqvist, Y. O. Tsybin, J. M. Purcell, A. G. Marshall, Y. Shulga, C. McCammon, and L. Dubrovinsky, Chem. Phys. **325,** 445 (2006).
9. R. A. Assink, J. E. Schirber, D. A. Loy, B. Morosin, and G. A. Carlson, J. Mater. Res. **7**, 2136 (1992).

Translated by O. Borovik-Romanova