Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 18 July 2018 doi:10.20944/preprints201807.0333.v1

Peer-reviewed version available at *Sensors* **2018**, *18*, 3013; doi:10.3390/s18093013

Article

Advantages of the Surface Structuration of the KBr Materials for the Spectrometry and Sensors

Natalia V. Kamanina [1,2,*], Svetlana V. Likhomanova [1], Pavel V. Kuzhakov [1]

[1] Lab for Photophysics of media with nano-objects at Vavilov State Optical Institute, Kadetskaya Liniya V.O., dom 5/2, St.-Petersburg, 199053, Russia. *e-mail: nvkamanina@mail.ru

[2] St.-Petersburg Electrotechnical University ("LETI"), Ul.Prof.Popova, dom 5, St.-Petersburg, 197376, Russia

* Correspondence: e-mail: nvkamanina@mail.ru; Tel.: +7(812)328-4608

Abstract: A potassium bromide KBr material, which has been widely used as the key element in the Fourier spectrometers and as the output window of the IR-lasers, has been studied with good advantage via applying the carbon nanotubes in order to modify the potassium bromide surface. The laser oriented deposition method has been used to place the carbon nanotubes at the matrix material surface in the vertical position at the different electric field varied from 100 to 600 V×cm^{-1}. The main idea of the improvement of the spectral properties of the potassium bromide structure is connected with the fact that the refractive index of the carbon nanotubes is substantially less than the refractive index of the studied material, and the small diameter of the carbon nanotubes allows one to embed these nano-objects in the voids of the lattice of the model matrix systems. Moreover, the mechanical characteristics and wetting features of the potassium bromide structures have been investigated under the condition mentioned above. Analytical and quantum-chemical simulations have supported the experimental results.

Keywords: potassium bromide; carbon nanotubes; laser oriented deposition method; surface structuration; spectra; mechanical and wetting properties.

1. Introduction

At present time one of the main basic approaches to improve the properties of large group of the optical inorganic materials is regarded to the carbon nanotubes (CNTs) use in order to modify the materials surface. It is connected with the fact that the refractive index of the CNTs [1-3] is substantially less than the refractive index of the most inorganic materials, and the diameter of CNTs allows one to embed these nano-objects in the voids of the lattice of matrix systems. This contributes to the homogenization of the interfaces with a very small (air) and the relatively large (matrix materials, in which surfaces the CNTs are incorporated) refractive index, which causes a change in the range of the transmission, at least. Moreover these nano-objects have the strong hardness of their C—C bonds [4,5]. The Young's module of the CNTs is close to some units of TPa, which can increase the mechanical features of the optical inorganic materials as well.

In this consideration the potassium bromide KBr materials can be chosen as the good model matrix. These materials can apply with good advantage as the different optoelectronic elements, such as: as the output window of the IR-laser, as the electro-optical fibers, sensors, etc. KBr is transparent in the spectral range of 0,25-25 microns [6], that provokes its use not only in the optoelectronics area, but in the biomedicine as well. The refractive index of the KBr materials has changed from 1,594 (at the wavelength of ~0,391 microns) to 1,461 (at the wavelength of ~25,140 microns). Unfortunately the hydrophilicity of this material often creates a big problem. This material is soluble in water, acetone, methanol, ethanol, glycerin, and other solvents. Thus, the surface of the KBr crystals should be protected from the drops of the water. This problem can be solved via using the nanostructuration process, when CNTs can be placed on the KBr surface in the vertical position by the laser oriented deposition (LOD) technique [7].

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 18 July 2018 doi:10.20944/preprints201807.0333.v1

Peer-reviewed version available at Sensors 2018, 18, 3013; doi:10.3390/s18093013

In the current paper the spectral, mechanical and wetting properties of the potassium bromide materials are studied under the condition to apply the carbon nanotubes as the effective nano-objects and the laser oriented deposition technique as the perspective technical method.

2. Materials and Methods

To modify the properties of the potassium bromide KBr materials via their surface treatment, the single wall carbon nanotubes (SWCNTs) type #704121 with the diameter placed in the range of 0,7-1,1 nm purchased from Aldrich Co. have been used. The dimension of the nanotubes is important in order to combine the CNTs diameter directly with the elementary lattice of the model material. Moreover, the Russian CNTs and nanofibers type "Taunit-MD" from the Tambov Company "Nanotech-Center" production have been applied.

To modify the potassium bromide surface the IR CO_2-laser with *p*-polarized irradiation at the wavelength of 10.6 μm and with the power of 30 W has been used. The general view of the block scheme is shown in Figure 1. It is seen that the laser system is connected with a vacuum hood, which contains the fixing unit samples and the device for placing substances deposited on the substrate.

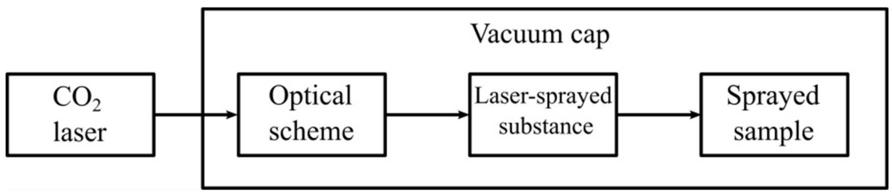


Figure 1. Principle scheme of laser-deposition technique

Moreover, the CNTs have been placed at the materials interface under the conditions when an additional electric field of 100-600 V×cm^{-1} has been applied in order to orient the nanotubes in the vertical position during the deposition process. Thus, the laser oriented deposition method [7] has been realized. The above indicated approach permits to vary the velocity of the CNTs and to form the covalent bonding between the carbon atoms and the surface matrix materials ones with good advantage. It should be noticed that the LOD method does not require the creation of any additional conditions for heating of the substrates and the composition of the gas reagents, which favorably differs from the classical methods based on the CVD and PVD processes.

The spectra of the nano-object-treated materials have been obtained using the Perkin-Elmer Lambda 9 and the Furrier FSM-1202 instruments as well as using the VIS SP-26 spectrophotometer operated in the spectral range of 250-1200 nm. POLAM-P312 microscope has been applied to make the image of the materials treated. The microhardness has been measured via using the PMT-3M device produced by "LOMO" Co. (Saint-Petersburg, Russia) with the ability to vary an indenter forces as well. The special accent has been given to observe the relief at the material surface via checking the wetting angle. In this case the OCA 15EC device has been purchased from LabTech Co. (Saint-Petersburg-Moscow, Russia) and has been used to carefully control the wetting angle change. As an additional, the analysis of the modified surface has been made using the Solver Next atomic force microscope AFM (purchased from NT MDT Co., Zelenograd, Moscow region, Russia). It should be mentioned that it permits to register the homogeneity of the surfaces and to estimate their roughness under the condition to use the nanostructuring prosess as well.

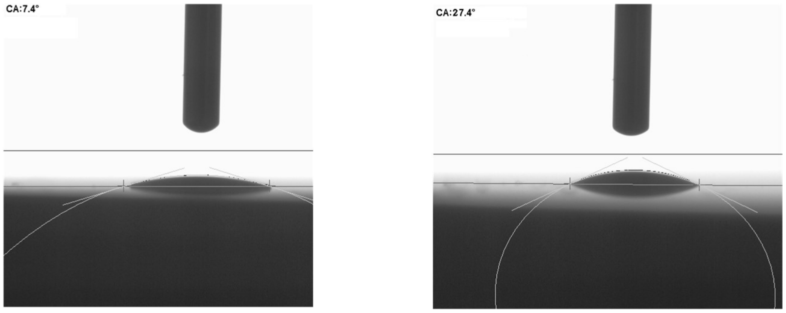
3. Results and Discussion

Some results which testified the wetting angle change for the potassium bromide KBr materials via their surface nanostructuration are shown in Figure 2. The sample has been chosen from 12

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 18 July 2018 doi:10.20944/preprints201807.0333.v1

Peer-reviewed version available at *Sensors* **2018**, *18*, 3013; doi:10.3390/s18093013

randomly selected samples with the similar parameters. One can see that the wetting angle has been increased from ~7 degrees up to 27 degrease after the CNTs oriented laser deposition technique application. It permits to provoke the better properties in order to protect the drops of the water, when the KBr material can be used in the Furrier spectrometers devices or in the specific sensitive electro-optical sensors.



(a) **(b)**

Figure 2. The value of the wetting angle of the KBr crystal before **(a)** and after **(b)** the nanostructuring process

Furthermore, the transmittance of the KBr materials can be increased after the use of the LOD procedure. The data for the UV-VIS spectral range are shown in Figure 3.

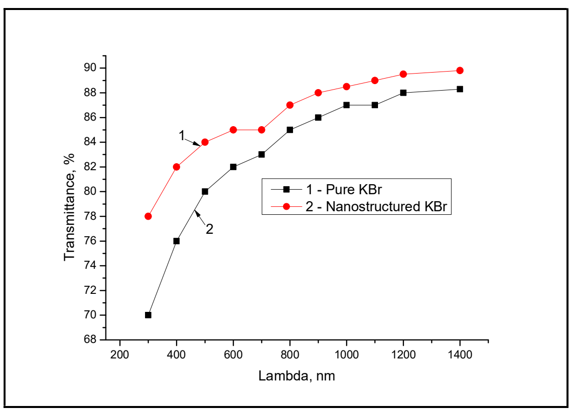


Figure 3. KBr sample transmittance in the UV-VIS spectral range

It should be mentioned that KBr materials have shown the increase of the transparence from 70% to 78% at the wavelength of 350-400 nm and from 87% to 89% in the range of 1000-1300 nm. The increase of the tested transparency has been from 88,3% to 89,8% in the spectral range of 1400-2400 nm. It should be noticed that in order to study the structuration process influence on the physical-chemical characteristics of the KBr materials the substrates with the polished surfaces and with the thickness of 5 mm and the diameters of 30-35 mm have been used. Figure 4 shows the KBr substrate and the CNTs mixture in the vial.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 18 July 2018 doi:10.20944/preprints201807.0333.v1

Peer-reviewed version available at *Sensors* **2018**, *18*, 3013; doi:10.3390/s18093013

(a) **(b)**

Figure 4. KBr substrates **(a)** and CNTs mixture type #704121 **(b)**

In order to support the transmittance spectra increase the analytical consideration based on the Fresnel losses decrease can be made. For example, as the good evidences, that the Fresnel losses can be changed under the nanostructuration process, it can be easy shown based on the model glass substrate. Really, using the classical method in order to reduce the losses at the reflection process and thus to improve the light transmission (aperture ratio) of the optics, the surface of the glass can be subjected to special treatment, which is called "enlightenment of optics." On the surface of the matrix materials (glass) the thin film should be placed, the refractive index of which should be less than the refractive index of glass, namely: $n_{\text{film}} = \sqrt{n_{\text{glass}}}$. In order to make the minimal reflection losses, the film must have a certain thickness, which can be calculated by the formula: $h = \frac{d}{n_{\text{film}}}$, there h – the geometric thickness of the film, d – the optical thickness of the film obtained as $d = \frac{\lambda}{4}$, λ - the wavelength of the light in that part of the spectrum, where it is necessary to obtain the maximum of the transmittance. It is well known that the film with the thickness of $\frac{\lambda}{4}$ from the substance with the refractive index of $\sqrt{n_{\text{glass}}}$ decreases the reflective coefficient dramatically. If one considers the interface such as the air-glass with the reflective index of the glass material closed to 1.5, the reflection from one surface of the substrate is approximately 4%, and from two surfaces it is approximately 8%.

According the interface of CNT/KBr it should be remarked that using the innovative structuration LOD approach and forming the covalent bonding between the nano-objects (carbon nanotubes) with the little refractive index n of ~1.1 and the larger refractive index of the studied matrix substrate (n of the KBr material can be placed in the range of 1.46-1.59 depended on the wavelength), the Fresnel loses via the reflection can be changed in one order of magnitude, at least. It can provoke the change of the transmittance with good advantage.

The correlation between spectral change and mechanical parameters improvement has been found as well. One can testify that the microhardness of the KBr structure can be increased substantially via the placement of the CNT at the vertical position on the KBr surface under the LOD procedure. The corresponding results are shown in Table 1. One can see that the microhardness has been increased up to ~6% after the LOD technique application. This result has been obtained when only one KBr surface has been treated. But, this value can be increased even more if not one but two surfaces of the KBr model material have been nanostructured.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 18 July 2018 doi:10.20944/preprints201807.0333.v1

Peer-reviewed version available at Sensors 2018, 18, 3013; doi:10.3390/s18093013

Table 1. Comparative data of the KBr microhardness change (Indentor was 10 g)

Material studied	Middle value of the microhardness, Pa×10^9	Increasing coefficient of the microhardness change, %
Pure KBr	0.00865	~6%
KBr structured with CNTs	0.00918	

In order to support the experimentally obtained results and to visualize the influence of the CNTs on the KBr surfaces, the quantum-chemical calculation has been made using the approach proposed in the papers [8-10] based on the density functional theory, implemented in VASP package with the projector augmented wave method. For the considered interfaces, the density of the electronic states has been calculated. The interface based on the CNT and the KBr substrate (namely CNT/KBr) has been carried out. The atomic structure of the considered interfaces is presented in Figure 5. According the data shown in Figure 5, the CNT has been adsorbed on the (111) KBr surface with two possible types of the termination: with K (red) and Br (blue) atoms, respectively. It has been found that the CNT adsorption leads to the changing of the surface of KBr structure caused by the strong interaction between the substrate atoms and the carbon atoms in the CNTs.

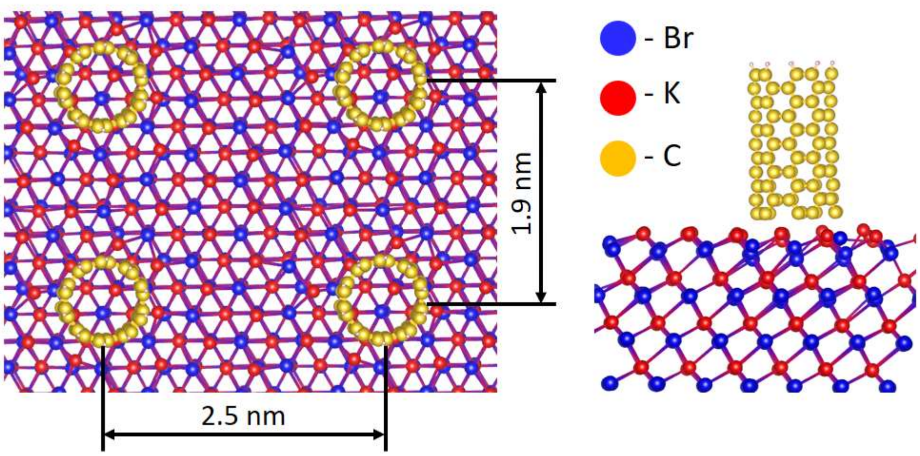


Figure 5. Atomic structure of the considered KBr/CNTs interfaces

For all considered interfaces the density of the electronic states has been calculated, which is shown in Figure 6. The red line indicates the CNT/K interface, the blue line regards to the CNT/Br interface and the black line shows the density of the states for the pure non-treated KBr substrate. It has been found that the presence of the carbon nanotubes on the KBr surface leads to the formation of the additional energy levels. For example, in case of the K termination, formation of the additional peaks in the energy range from -1.5 eV to -0.5 eV took place, while in the absence of the carbon nanotubes there have been no found peaks in this energy range. The same calculations have been carried out in the case of Br termination (the blue lines).

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 18 July 2018 doi:10.20944/preprints201807.0333.v1

Peer-reviewed version available at Sensors 2018, 18, 3013; doi:10.3390/s18093013

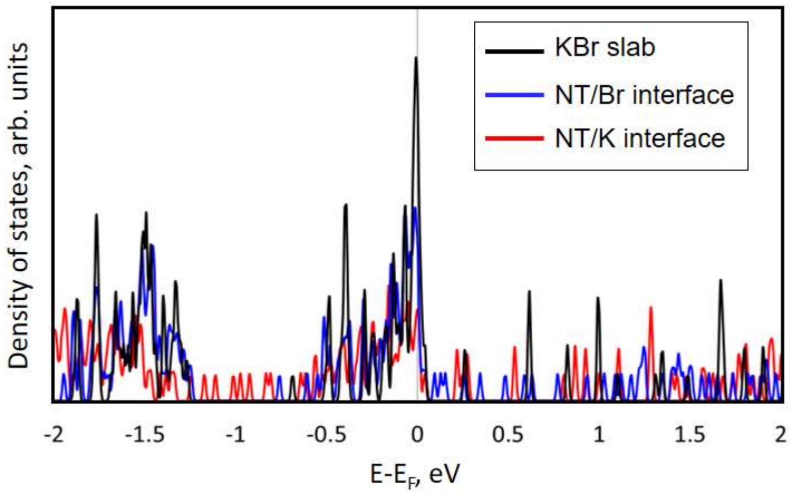


Figure 6. The density of the electronic states for all considered interfaces

Moreover, the calculation of the electron density distribution for the considered interfaces has been carried out, which is presented in Figure 7. The blue and yellow colors depicted the increasing and the decreasing of the negative charge. The obtained results have confirmed the data received from the calculations of the density of the states. Based on these data it could be testified that the redistribution of the electron density directly on the KBr/CNT interface have to change the electronic properties of the whole structure by means of the formation of the additional electronic levels.

Due to the large size of the considered system the electronic density of states has been calculated only for the small area. Thus, the considered structures consisted of 96 Br atoms, of 96 K atoms and 110 carbon and 10 hydrogen atoms in the CNT.

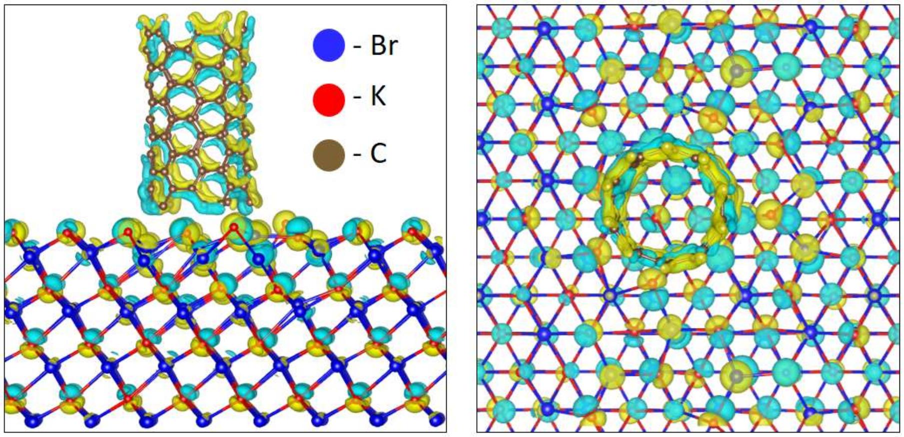


Figure 7. Electron density distribution on the KBr/CNT interface

Thus, the calculation really reveals the change of the electronic levels of the KBr materials under the conditions when CNTs have been deposited at the matrix surfaces using the oriented laser deposition technique. Thus, the appearance of the additional energy levels directly shows the change of the refractive parameters. But, the refractive index change naturally provokes the change of the spectral parameters as well. This interrelation is revealed by means of the carried-out calculations based on the experimental data. It should be remarked once again that based on these data one could testify that the redistribution of the electron density directly on the KBr/CNT interface have to change the electronic properties of the whole structure by means of the formation of the additional electronic levels. It connected with the spectral and mechanical properties improvement obtained by experiments and coincided with the results obtained before for other materials [11,12], for example, based on the ITO coatings structured by CNTs [13].

Thus, the KBr materials properties can be dramatically improved via use of the innovative LOD technique and CNTs as the perspective nano-objects.

Conclusions

To summarize the obtained experimental and theoretical results one can conclude the following:

1. The KBr materials can be considered as the perspective model matrix to obtain the correlation between spectral, mechanical and wetting properties change via nanostructuration of their surfaces by LOD technique.
2. The tendency to form the bonding between carbon atoms and model materials surface atoms has been supported experimentally and theoretically via extending the consideration on the KBr matrix.
3. The transmittance, the mechanical and the wetting characteristics of the KBr materials can be increased, which extends the area of the application in the Furrier spectroscopy, in the modulation and sensors schemes, in the IR-laser use and in the biomedicine as well.
4. The data presented can extend the range of the functional materials, which basic properties can be successfully varied and optimized namely via structuration of their surfaces.
5. The data observed can be used in the education process with good advantage due to the reason that the basic parameters change can be easy visualized.

Acknowledgments: The authors would like to thank their Russian colleagues: Prof. E.F.Sheka (University of Peoples' Friendship, Moscow, Russia), Prof.P.B.Sorokin and Dr.D.G.Kvashnin (MISiS, Moscow, Russia), as well as their colleagues from Vavilov State Optical Institute for their helpful discussions. The presented results are correlated with the work partially supported by the FP7 Program, Marie Curie International Researchers Exchange Proposal "BIOMOLEC" (2012-2015), by the Russian Project "Nanocoating-GOI" (2012-2015), as well as by the International Russian-Israel Project "Adaptatsiya" (2017).

Author Contributions: Dr.Kuzhakov P.V. is the researcher from the Lab for Photophysics of media with nanoobjects at Vavilov State Optical Institute. He has defended his PhD thesis on May, 2018. Scopus Author ID: 54909204100, *h* index is 2 He has the experience in the spectral and wetting angle measurements as well as in the quantum chemical simulation. He has published ~ 20 scientific papers in the International and Russian journals.

Dr.Likhomanova S.V. is the researcher from the Lab for Photophysics of media with nanoobjects at Vavilov State Optical Institute. She has defended her PhD thesis on May, 2017. Scopus Author ID: 36179855800, *h* index is 3. She has the experience in the spectral and wetting angle measurements as well as in the refractive characteristics study. She has published more than 25 scientific papers in the International and Russian journals.

Prof.,Dr. Sci., PhD Kamanina N.V. is the Leader of the team, Head of the Laboratory for Photophysics of media with nanoobjects at Vavilov State Optical Institute. She coordinates the job of the team, participate at all experiments and analyze the theoretical and the experimental data. Scopus Author ID: 55980751700. *h*-index in Scopus is 18. She has been an adviser of 5 PhD-students, which have successfully defended their PhD-thesis. Kamanina N.V. has current interest in the areas of investigations of the inorganic optical materials operated in the UV-IR spectral range; new coatings; in the organic conjugated materials; liquid crystals; fullerenes; nanotubes; quantum dots; DNA, etc.; laser-matter interaction process via four wave mixing technique. She has published more than 200 scientific papers in the International and Russian journals and has edited 3 InTech volumes in the Display, Nonlinear Optics and Fullerenes study areas. She has published 2 own books about surface and materials body structuring in Nova Science Publishers, Inc., New York. Moreover, she has lecturing from 2003 year in Saint-Petersburg Electrotechnical University "LETI".

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Fa, W.; Yang, X.; Chen, J.; Dong, J. Optical properties of the semiconductor carbon nanotube intramolecular junctions. *Phys. Lett*. **2004**, Vol.A323, pp.122–131, www.elsevier.com/ locate/pla
2. Yang, Z.-P.; Ci, L.; Bur, J.A.; Lin, S.-Y.; Ajayan, P.M. Experimental observation of an extremely dark material made by a low-density nanotube array. *Nano Letters*. **2008**, Vol.8, No.2, pp. 446–451. Published on Web 01/09/2008. DOI: 10.1021/nl072369t
3. Taherpour, A.A.; Aghagolnezhad-Gerdroudbari, A.; Rafiei, S. Theoretical and quantitative structural relationship studies of reorganization energies of [SWCNT(5,5)-Armchair-CnH20] (*n* = 20-310) nanostructures by neural network CFFBP method. *Int. J.Electrochem. Sci.* **2012**, Vol.7, pp.2468–2486. www.electrochemsci.org
4. Robertson,J. Realistic applications of CNTs. *Materialstoday*. October **2004**, pp.46-52.
5. Namilae, S.; Chandra, N.; Shet, C. Mechanical behavior of functionalized nanotubes. *Chemical Physics Lett.* **2004**, Vol.387, pp.247–252.
6. Rabinovich, V.A.; Khavin, Z.Ya. Brief chemical Handbook; Publisher: Leningrad, "Chemistry", 1978, 316 p. [in Russia].
7. Kamanina, N.V.; Kuzhakov, P.V.; Vasilyev P.Ya. RU Patent No.2013118962 (RU (11) 2013 118 962(13) A). A protective coating for hygroscopic optical materials based on laser-deposited carbon nanotubes for the purpose of optoelectronics and medical equipment. Priority on 23.04.2013, registered in RF State register on 27.10.2014, Bul.No.30.
8. Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys Rev B*. **1996**, Vol.54, pp.11169−11186.
9. Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci*. **1996**, Vol.6, pp.15–50.
10. Blöchl, P.E. Projector augmented-wave method. *Phys. Rev. B*. **1994**, Vol.50, pp.17953–17979.
11. Kamanina, Natalia V. Features of Optical Materials Modified with Effective Nanoobjects: Bulk Properties and Interface. New York, Physics Research and Technology, “Novinka”, Published by Nova Science Publishers, Inc., New York, 2014, 116 p. ISBN: 978-1-62948-033-6.
12. Kamanina, N.V.; Bogdanov, K.Yu.; Vasilyev, P.Ya.; Studeonov, V.I. Enhancing the mechanical surface strength of “soft” materials for the UV and IR ranges and increasing their transmission spectrum: Model MgF_2-nanotube system. *J. Opt. Technol*. **2010**, Vol.77, No.2, pp.145-147.
13. Kamanina, N.V.; Zubtcova, Yu.A.; Kukharchik, A.A.; Lazar, C.; Rau, I. Control of the IR-spectral shift via modification of the surface relief between the liquid crystal matrixes doped with the lanthanide nanoparticles and the solid substrate. *OPTICS EXPRESS.* **2016**, Vol.24, No.2, 6 pages, DOI:10.1364/OE.24.00A270 | OPTICS EXPRESS A270.