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Spectral properties of inorganic materials of the alkali-earth metal fluoride group on the example of nanostructured MgF_2

© *P.V. Kuzhakov*[1–3], *N.V. Kamanina*[1–3]

[1] Vavilov State Optical Institute, St. Petersburg, Russia
[2] St. Petersburg Nuclear Physics Institute, National Research Center Kurchatov Institute, Gatchina, Russia
[3] St. Petersburg State Electrotechnical University „LETI", St. Petersburg, Russia
E-mail: kpv_2002@mail.ru

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New results are presented in the direction of improving the spectral properties of inorganic materials of the alkali-earth metal fluoride group by coating them with carbon nanotubes (using the example of MgF_2) optical material). Modeling and data analysis indicate that the resulting nanostructures can be used as modern transparent optical elements, such as nanostructured protective windows, plane-parallel plates, for devices in the UV range of the spectrum. The studied structured material can be used as a new structural material for optical emission and X-ray spectrometers.

Keywords: Protective windows, nanotubes, spectrometers.

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Magnesium fluoride (MgF_2) has unique optical properties, remaining transparent over a wide spectral range. The popularity of MgF_2 is constantly increasing as it became an ideal anti-reflective coating for laser devices, an important material for optical fiber communication due to its wide forbidden band, low refraction index, its mechanical properties and high resistance to laser damage [1–3]. The studied material is used in the vacuum ultraviolet region and often finds application in optical windows, lenses, etc. [4,5]. Note that a special place in studies is occupied by the process of nanostructuring of crystalline systems, and the emphasis is on the use of carbon nanotubes (CNTs) for this purpose, they exhibit high hardness and a unique system of energy levels [6,7]. In the present paper, the spectral properties of nanostructured magnesium fluoride and related features are studied in the UV wavelength band in order to reveal the effect of translucence of the nanostructured material. MgF_2 was used as an inorganic matrix, and nanoobjects in the form of single-walled nanotubes were considered as a coating. Mention that carbon nanotubes were deposited on the surface of the material using CO_2 laser with p-polarized radiation at a wavelength of $10.6\,\mu$m and a power of 30 W [8]. The proposed optical coating and optical element are a system consisting of a single CNT layer 100 nm thick, deposited in vacuum, and MgF_2 matrix substrate.

The carbon nanotubes were deposited in vacuum on substrates heated to a minimum temperature 80°C using directional deposition of the coating material from carbon nanotubes by laser radiation. As noted above, a quasi-cw slit CO_2 laser served as the radiation source. To orient the CNTs, a special mesh with the possibility of voltage supply was used, which made it possible to vary the electric field strength from 100 to 600 V/cm.

The spectral characteristics of the coating and the optical element were measured using a Perkin Elmer Lambda 9 spectrometer according to GOST R 54164−2010.

The use as an optical coating of a layer of carbon nanotubes oriented deposited in vacuum using radiation from a quasi-cw CO_2 laser made it possible to significantly increase the homogeneity of the coating, reducing the size of inhomogeneities from micro- to nanosize, and significantly expand the spectral range of the optical element operation due to work in the UV region of the spectrum. In addition, the deposition of nanotubes on substrates with a heating temperature of less than 80°C involves the coating deposition on solid materials. Improved homogeneity of the coating and the optical element, as well as increased light transmission (up to 87−90%) in a wide spectral range are necessary conditions for applications in optoelectronics, telecommunication systems, as well as in laser, display, and medical equipment.

It is important to emphasize once again that carbon nanotubes were oriented in vertical position in an electric field from 100 to 600 V/cm in order to form a possible covalent „binding" of nanoobjects to the surface layers of the matrix and to avoid material loss in a large solid angle. In the narrow spectral range from 200 to 205 nm, the effect of translucence is observed in the CNT/MgF_2 system, and this effect is confirmed by measurements of both the transmission spectrum and the reflection spectrum (Figs. 1 and 2). Moreover, nanostructured samples exhibit better microhardness. Indeed, after CNT deposition on the MgF_2 surface, the microhardness increases by 6% [8].

In the paper [8] the changes in the electronic properties caused by the presence of deposited CNTs were studied. It was established that the presence of adsorbed CNT leads

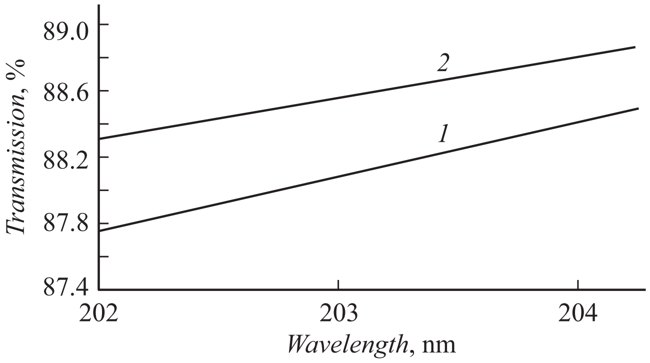

Figure 1. Transmission vs. wavelength for pure (*1*) and nanostructured (*2*) MgF_2 sample 5 mm thick.

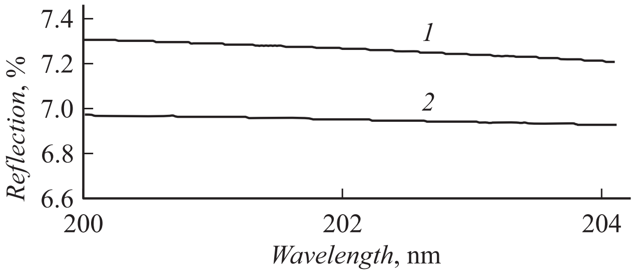

Figure 2. Reflection vs. wavelength for pure (*1*) and nanostructured (*2*) MgF_2 sample 5 mm thick.

to the formation of additional electronic bands within the forbidden band of the MgF_2 substrate. These data indicate the effect of CNTs adsorbed on the surface on the optical properties of the new composite.

We continue our earlier modeling of the CNT/MgF_2 system. In the present paper, we used the DFT (density functional theory) method with the exchange-correlation functions LSDA (local spin density approximation) in the 3-21*G basis and the Hartree−Fock calculation method with the HF/STO-3G SP atomic basis set. The calculations were performed using the Gaussian 09W program. The results visualization of the quantum chemical modeling was carried out using the GaussView 5.0 program.

In the studied atomic structure of the CNT/MgF_2 interface (Fig. 3) CNTs were deposited on the MgF_2 surface. It was found that the presence of CNTs on the MgF_2 surface leads to charge redistribution directly at the interface, which will undoubtedly lead to the electronic properties change. To characterize the chemical bond, the standard Mulliken population analysis for effective atomic charges Q and bond populations [9,10] was used. The calculated effective charges are $1.294e$ for Mg_{ion} and $0.278e$ for F_{ion}. The population of the bond between Mg and F ions is negligible and is $0.042e$. The population of the F−F bond is negative (at the level of $-0.024e$), which indicates repulsion between the F ions.

When considering bond of the CNT/MgF_2 structure, the calculated effective charges are $1.294e$ for Mg_{ion} and $-0.826e$ for C_{ion}. Bond length is 1.6 Å. The resulting bond is single. The charge redistribution forms new energy levels, which significantly affects the optical properties of the material. This does not contradict the simulation data obtained in [8].

Due to the large number of atoms for the lattice cell under consideration, the CNT model consisted of a small cluster of CNTs, the upper end of which was passivated by hydrogen atoms. Since, after deposition, the main changes in the atomic structure occur directly at the interface, the chosen CNT length is sufficient to qualitatively describe also the electronic properties change. The system under consideration consisted of 56 fluorine atoms, 62 magnesium atoms, as well as 60 carbon atoms and 11 hydrogen atoms that make up the CNT cluster.

As a practical application of the CNT/MgF_2 structured system, it is possible to propose the use of protective windows made of MgF_2 material in optical emission spectrometers. During such devices operation, for example, deterioration of the quality of optical glasses of lenses is possible, caused mainly by contamination from spark action, the protection from it is special protective windows installed in the lighting unit [11].

After analyzing the system nanostructured by carbon nanotubes using the example of MgF_2 and the studied optical characteristics, and then comparing them with the results of papers [8–11], we can make the following conclusions.

1. The application of the laser-oriented method of the carbon nanotubes deposition on the surface of MgF_2 materials leads to noticeable spectral shifts in the UV region, to the effect of translucence. This effect tends to spread to the shorter wavelength region of the spectrum.

2. Using the methods of quantum chemistry, we demonstrated that the neutral and polar surfaces of the MgF_2 substrate itself are ionic and bulk, revealing a near-surface chemical bond, while the MgF_2 bond with CNTs significantly affects the optical properties of the substrate material.

3. According to the results of comparative studies, the processed materials can be used in optoelectronics and laser optics (for example, for gas storage and solar energy

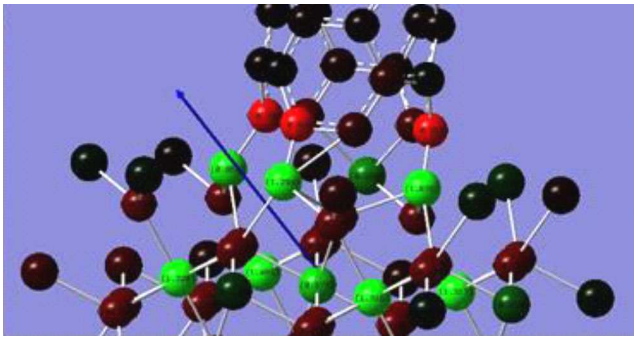

Figure 3. Image of the atomic charges distribution of the CNT/MgF_2 structure.

storage), etc. The obtained results are useful for hardening and translucence of the output windows of UV lamps used for disinfection of hospitals and polyclinics, as well as in general in optoelectronics, telecommunications and display systems.

4. Due to the translucence effect in the working region of the UV spectral range, the studied nanostructured material can be used as a new structural material for spectroscopy in optical emission spectrometers.

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Conflict of interest

The authors declare that they have no conflict of interest.

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