# STUDY OF THE OPTICAL CERAMICS PROPERTIES: $MgF_2$

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**Abstract**

It is well known that the optical ceramics are important functional materials used in the different area of the optoelectronics applications. In the current paper the brief review of the basic properties of the optical ceramics based on magnesium fluoride ($MgF_2$ - KO1 optical ceramics) is presented and supported by the experimental results. Spectral and mechanical properties as well as the wetting phenomena will be discussed. The mentioned above characteristics of this type of the optical ceramics KO1 have been improved via application of the laser oriented deposition technique when the carbon nanotubes have been placed on the materials surface in the vertical position. Analytical and quantum chemical calculation supported the experimental results. It should be mentioned that this study continues the previous our experiments of this material partially presented before.

**Keywords:** optical ceramics, $MgF_2$ structures, carbon nanotubes, surface, spectra, mechanical hardness, wetting angle, laser-oriented deposition method.

**Introduction**

It is known that magnesium fluoride materials are widely used in the optoelectronics area due to the reason that these structures are transparent in the broad spectral range, namely: from 120 nm to ~ 8 micrometers [1]. The lens and prisms have been developed from this type of the optical materials. These materials are applied in the biomedicine as well. For example, UV-lamp windows, that are used in the processing of the medical facilities (hospitals, clinics, etc.), are made from the magnesium fluoride. Different techniques are used in order to improve the physical and chemical properties of these structures, such as: PVD, CVD, laser ablation approaches, etc. But the laser oriented deposition (LOD) method has some advantages, which permits to increase the transparency, the mechanical hardness and the wetting angle of the optical materials [2-4]. In this case the carbon nanotubes (CNTs) can be considered as the most efficient materials to reinforce the parameters of the different composites [5]. In the current paper the experimental and theoretical results are shown to support the idea of the effective nanostructuration process use to modify the surface of the optical materials. The results are presented in continuation of earlier revealed studies.

**Experimental condition**

It should be mentioned that to modify the properties of the magnesium fluoride materials via their surface treatment, the SWCNTs type #704121 with the diameter of 0.7 nm purchased from Aldrich Co. have been used. These nanotubes have been deposited on the material surface using the IR-$CO_2$-laser with the *p*-polarized irradiation at the wavelength of 10.6 μm and of the power of 30 W. Moreover, the CNTs have been placed at the materials interface from one and two their sides. The spectra of the nanotubes-treated materials have been obtained using the Furrier FSM-1202 instruments as well as using VIS SF-26 device operated in the range of 250-1200 nm. Surface mechanical hardness has been revealed using the micro-hardness device PMT-3M (produced by “LOMO”, Saint-Petersburg, Russia) with the ability to vary an indenter forces. The special accent has been given to observe the relief at the material surface via checking the wetting angle. The modified surface analysis has been made using Solver Next AFM (purchased from NT MDT Co., Zelenograd, Moscow region, Russia).

## Results and discussion

Partially, the spectral data for the magnesium fluoride $MgF_2$ substrates in the VIS and in the near and middle IR-range are shown in Fig.1, *a*,*b*. It should be noticed that in the case of the analysis of the spectra one take into account the change of the transmittance spectrum with the one-sided processing of the material and with the processing from two their sides. It should be mentioned that the substrate thickness was 5 cm. Moreover, it should be mentioned that when these substrates have been treated at the wavelength of 125 nm, the dramatic change of the transparency has been established. The change of the transmittance for the five randomly selected $MgF_2$ samples from pure to nanostructured material has been as follows shown in Table 1.

**Table 1.** Change of the transparency of the $MgF_2$ materials treated with the CNTs

| Number of the sample | Transmittance of the pure $MgF_2$, % | Transmittance of the nanostructured $MgF_2$, % |
|---|---|---|
| 1 | 61.8 | 66.6 |
| 2 | 63.6 | 69 |
| 3 | 54.5 | 65.8 |
| 4 | 58.1 | 67.5 |
| 5 | 50.9 | 65 |

One can testified that the nanostructured of the $MgF_2$ substrate can provoke the change of their spectral parameters.

The micro hardness results reveal the increase of these parameters as well. Thus, for the $MgF_2$ materials the micro hardness has been increased up to 6 percent. It should be mentioned that the indenter with the forces of 40 g has been used to treat this type of the optical ceramics. The data presented in Table 2 can support the microhardness improvement. It can be connected with the results obtained by other scientific teams [6-10] for the materials.

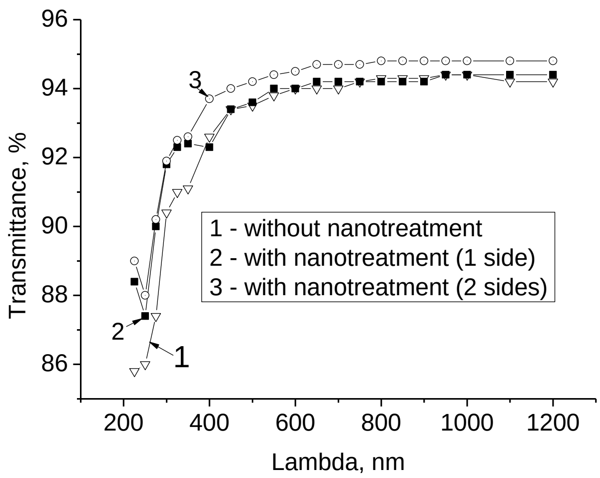
In the study [6] it has been shown the deposition on the surface of the diamond-like carbon coatings from the separated plasmatic arcing discharge. To analyze the subsidence on the surface the authors used an approach based on the different combinations of the following three effects: the multiphase hardening, the size effect of the grains and the boundary displacement suppression effect by forming the strong contacts. As a result, the microhardness has increased two times.

Highly transparent yttric ceramics [7] has been manufactured by pressing of 1 at.% $ZrO_2$ or 12 at.% $La_2O_3$ as the fussing additive. Mechanical properties have been strengthened due to their dense and thin microstructures created by means of hot pressing. Thermal shock resistance has been increased by means of the additives.

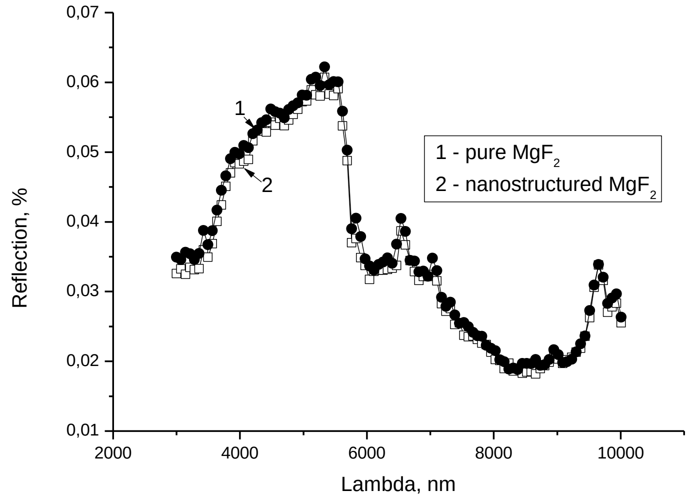
Influence of CNT on the $Si_2BC_3N$ ceramics has been studied in [8]. Judging by the interphase characteristics the hardening and toughening mechanisms of MWCNT in the $Si_2BC_3N$ ceramics can be classified as the “opening of cracks”, “extrusion” and “crack deflection”.

The material hardening has been achieved by Nd, Y-codoped $CaF_2$. The study [9] has addressed the research of the deformation speed on the polycrystalline ceramics achieved by the ceramificating individual crystals. It has been found that the Nd,Y-codoped $CaF_2$ ceramic ($\Delta a$= 62%) shows the most optimal performances among other ceramics with the different deformation rates ($\Delta a$= 34%, 40%, 50%, and 75%).

Moreover, the tendency to slightly increase the wetting angle for the $MgF_2$ structure after the nanostructuration from 86-87 degrees to 88-89 degrees has been established.




*a*




*b*

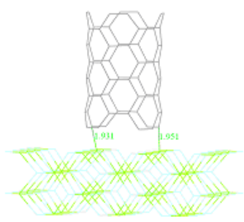
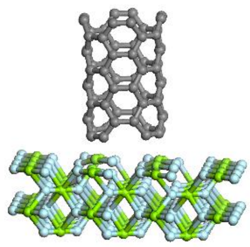
**Figure 1.** Spectral parameters of the pure and of the nanostructured $MgF_2$ sample: the transmittance spectra in the VIS (*a*) and the reflectance spectra in the IR spectral range (*b*)

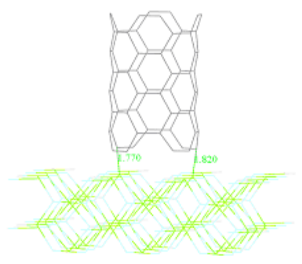
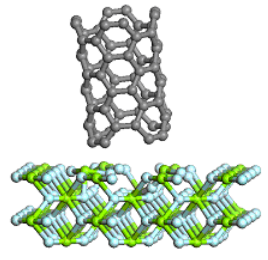
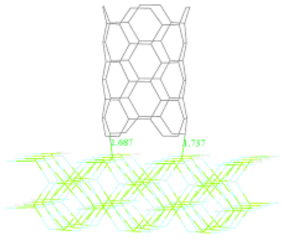
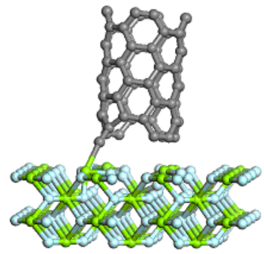
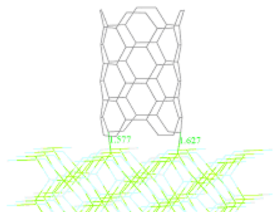
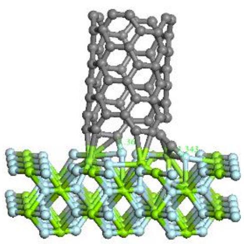
Table 2. The results of the microhardness of the $MgF_2$ materials

| Material studied | Middle value of the microhardness, Pa×$10^9$ | Increasing coefficient of the microhardness change, % |
|---|---|---|
| Pure $MgF_2$ | 0.3143 | ~6% |
| $MgF_2$ nanostructured | 0.3322 | |

To explain the results connected with the change of the spectral, mechanical and wetting properties the idea of the covalent bonding between Mg atoms and carbon ones has been used once again as has been before proposed in the framework of the analytical calculation [4]. It should be remarked that the quantum chemical simulation for $MgF_2$ structure has been performed using the semi-empirical ZAVA program with the PM3 parametrization [10-13]. Table 3 presents the results and supports the formation of the covalent bonding between the CNT and the $MgF_2$ system with good advantage.

**Table 3**. Results of the simulation of the bond between $MgF_2$ and the carbon nanotube: The initial and the optimized structure of the MgF2-CNT

| R start (min), Å | The initial structures | The optimized structures |
|---|---|---|
| 1,9 |  |  |

| | | |
|---|---|---|
| 1,8 |  |  |
| 1,7 |  |  |
| 1,6 |  |  |

As can be seen from Table 3, the different starting distances between the surface of magnesium fluoride structure and the CNT is considered, such as: 1,6; 1,7; 1,8; 1,9 Å. In all cases, the carbon nanotube is connected to the surface of the magnesium fluoride, in the last two cases it is provoked the formation of the chemical bonds. Thus, the analytical calculation and the quantum-chemical modeling have supported the evidences to improve the hardness of the $MgF_2$ surfaces with good advantage. Moreover, these results support that the LOD technique can be considered as the innovative method to form the new perspective coatings for the magnesium fluoride materials and other optical crystals as well.

## Conclusion

The optical ceramics based on the $MgF_2$ structures has been studied to reveal the advantage of their surface structuration using the CNTs and LOD approach. The spectral and mechanical parameters, as well as the wetting phenomena features have been slightly or drastically improved. The area of the use of this type of the optical ceramics can be extended in the practical optoelectronics and in the biomedicine.

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