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Study of Ice-Forming Properties of Zinc Oxide and Silver Iodide Nanoreagents

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***Abstract*—The article is devoted to the development of methods for dispersing nanoreagents based on zinc oxide and silver iodide and the study of their ice-forming properties. It is shown that nanotubes of zinc oxide and silver iodide have good ice-forming properties with a specific yield of ice-forming nuclei up to 1013г-1. Unlike traditional reagents, the activity of zinc oxide nanotubes is manifested when they are dispersed directly into the cloudy environment; the maximum specific yield is observed at higher temperatures (1013 ice crystals at temperatures of about 0°C).**

Keywords*—nanotubes, zinc oxide, silver iodide, carbon, specific yield of crystals, cloud environment, reagent, active influencing

I. INTRODUCTION

To control cloud processes (hail suppression, stimulation of sedimentation processes, fog dissipation, creation of zones of enlightenment in stratus clouds, and many others), chemicals with condensation and crystallization properties are used as a reagent. At the same time, the issues related to the formation of reagent particles remain open. The particle size of reagents, obtained by dispersion, ranges from 10 to 100 nm. In this region of particle sizes, the significance of surface phenomena increases greatly because of the large surface area of these particles, which has a significant influence on phase transitions of water and coagulation of reagent particles.

The modern period in the world of science is described by the intensive development of experimental and theoretical studies of the formation of a new phase in the nanoscale range. The results obtained can be used in the development of more efficient reagents to influence the atmospheric processes. One of the ways to increase the effectiveness of reagents is to create hollow particles, i.e. nanotubes of reagents, which is connected with the fact that only the surface of the particle is involved in the process of ice formation.

The number of dispersed particles with the same surface of one gram of substance nanoscale (10-9m) will be greater compared to the ordinary particles dispersing [1, 2].

The main goal of this work is to develop methods for dispersing nanoreagents based on zinc oxide and silver iodide, as well as to study their ice-forming properties.

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II. METHODS AND MATERIALS

In recent years, many methods have been developed for synthesizing nanoreagents [3-11]. The method of thermal sublimation is most suitable for active influencing on cloud processes. Currently, the introduction of regents into the cloud by thermal methods is widely used in practice of active influencing on the atmospheric processes and is considered as one of the main methods.

The authors have done a great deal of work on the synthesis of *ZnO* zinc oxide nanotubes and *AgI* silver iodide, as well as the study of their ice-forming properties [1,2]. For these purposes, a set of equipment (Fig. 1) and a method for reagent synthesizing in the form of nanotubes was developed.

1 - electron microscope EMMA-4, 2 - optical microscope MBI-15, 3 - vacuum unit, 4 - large cloud chamber, 5 - optical microscope Motic.
Fig. 1. Set of laboratory equipment, where the synthesis of nanotubes was carried out.

The set includes: optical microscope Motic, optical microscope MBI-15, electron microscope EMMA-4, vacuum unit, sublimation chamber, large cloud chamber and small cloud chamber, reagent sublimation chamber.

Synthesis of zinc oxide nanoparticles was carried out in the following way. A graphite boat with the length of 5-6 cm and the width of 1 cm was placed in a vacuum unit between the electrodes. When a constant voltage of 9V was applied, the boat was heated and the reagent was sublimated [1,2]. In order to prevent the spraying of the substance placed in the boat, the experiments were carried out with the glass cover of the vacuum unit closed. The maximum current passing through the boat reached approximately 100-150A, the sublimation temperature of composition ranged from 1000°C to 2500 °C. The synthesis lasted 3-4 minutes. The nanotubes were deposited on glass substrates that were installed at the bottom of the chamber of the exhaust cart. After exposure, the substrates were kept in a humid environment in Petri dish for 5–10 minutes, which have resulted in an increase in the diameter of tubes and made it possible to study them under the optical microscope. Fig. 2 shows zinc oxide nanotubes, which were captured on a substrate and were kept in humid environment.

The nanotubes of silver iodide were studied in a similar way; in this case, pyrotechnic composition from the rocket Alazan-6 was used as a reagent.

Fig. 3 shows photographs of silver iodide nanotubes obtained in the manner described above.

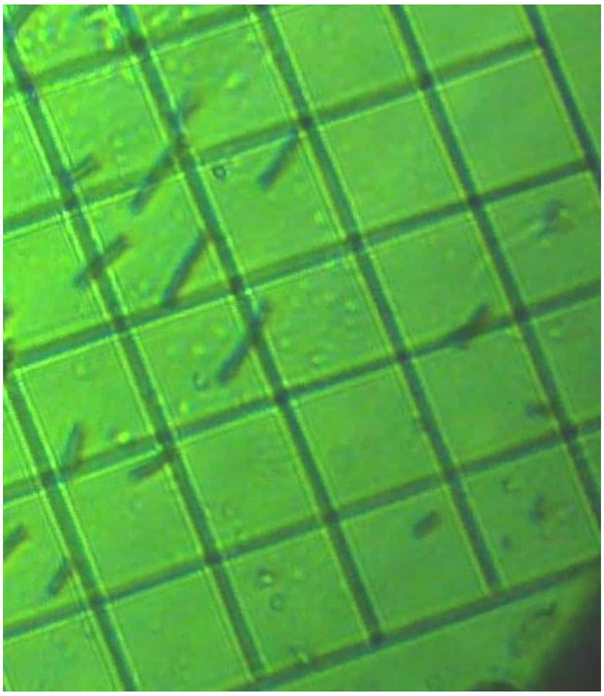

Fig. 2. Photograph of zinc oxide nanotubes under the optical microscope MBI-15 (mesh size 15 μm)

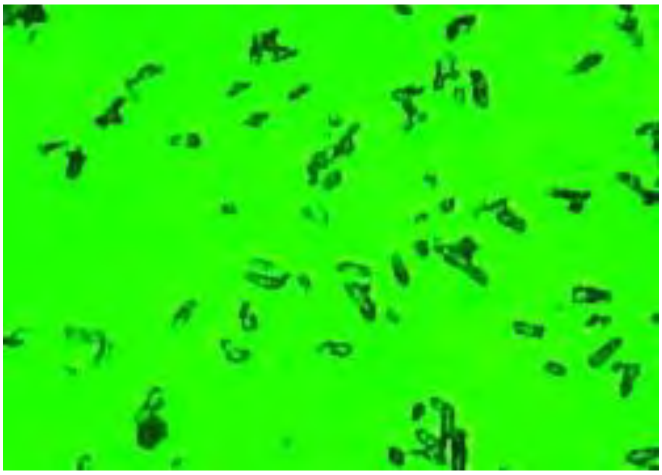

Fig. 3. Photograph of silver iodide nanotubes under optical microscope MBI-15

To study the ice-forming properties of reagents, large and small cloud chambers and a reagent sublimation chamber were used. The crystal was captured on special mirror substrates. The number of crystals was counted on the PC screen to which the image was transferred from the table of a digital microscope Motic.

The experiments on the study of the ice-forming properties of *ZnO* nanotubes under various thermodynamic conditions were carried out in a large cloud chamber of High-Mountain Geophysical Institute (HMGI). The large cloud chamber is a cube made of galvanized iron with the volume of V=8m^3 with heat-insulated walls cooled with the help of three refrigeration units. The temperature of the chamber is regulated and maintained in the range from 0°C to -17°C. To mix the air in the chamber four fans were installed.

The reagent sublimation was carried out from a graphite boat as described above.

The studies of the ice-forming properties of *AgI* and the pyrotechnic composition of AD-1 with the carbon catalyst of nanotubes were carried out in a small cloudy chamber of HMGI with a smaller volume of 0.081 m^3 and with an operating temperature from 0° to –25°C.

First, the reagent was sublimated in the sublimation chamber, then a certain volume of air with the reagent particles was transferred from the chamber to a small cloud chamber. The counting of the crystals was carried out as described above. The synthesized *ZnO* nanotubes, used as a reagent, were studied for their ice-forming properties in various temperature ranges.

To determine the specific yield of crystals, two methods were used. The method in which the sublimation of the reagent was carried out directly in a cooled medium in a large cloud chamber, crystals were also formed there, and the standard method when the sublimation of the reagent was carried out in the sublimation chamber and a known volume of air with the reagent was transferred to the cooled cloud environment.

At the beginning of the experiment, in the first method, the steam was introdused into a large cloud chamber and the reagent was burned. The crystals formed were deposited on the substrates that were removed from the camera and photographed under the microscope Motic. Then, the number of crystals on the substrate was counted, after that the number of crystals over the entire chamber area and an average number of crystals per 1 µm2 were determined.

A specific output *A* was determined by the following formula:

$$A = \frac{n_{кр}}{m_{реаг}} \quad (1)$$

where, m_{reag} is the mass of the reagent introduced, g; n_{cr} is the number of crystals in chamber, m^{-3}.

In the experiments carried out according to the method described above, the ice-forming properties of the following compositions were investigated: zinc oxide nanotubes obtained using a catalyst of graphite, nanotubes with a graphite catalyst, silver iodide nanotubes obtained with a catalyst of carbon nanotubes. The results of these studies are presented below.

The ice-forming properties of the reagent based on nanotubes of silver iodide were studied in the following way: the reagent AD-1 with the carbon additive was burned in the sublimation chamber, after that the air with the reagent (0.4x10-3 ml) was taken out with the help of a syringe and introduced into the small cloudy chamber of HMGI. The specific yield was determined as described above.

III. RESEARCH RESULTS

3.1. The results of the study of ice-forming properties of zinc oxide nanotubes

Table 1 shows the evaluation results of specific yield of ice-forming nuclei when using the reagent in the form of *ZnO* nanotubes at different temperatures.

TABLE I. SPECIFIC YIELD OF ZNO NANOTUBE CRYSTALS

n/n	Temperature in the cloud chamber, °C	Specific yield 0f crystals, r^{-1}	n/n	Temperature in the cloud chamber, °C	Specific yield 0f crystals, r^{-1}
1	-9.0	$1.5 \cdot 10^{8}$	12	-5.6	$4.2 \cdot 10^{10}$
2	-7.5	$1.4 \cdot 10^{9}$	13	-4.6	$1.6 \cdot 10^{11}$
3	-7.2	$5.0 \cdot 10^{8}$	14	-4.5	$1.7 \cdot 10^{11}$
4	-6.6	$2.2 \cdot 10^{9}$	15	-0.2	$1.7 \cdot 10^{13}$
5	-7.3	$6.1 \cdot 10^{9}$	16	-4.2	$1.4 \cdot 10^{12}$
6	-7.1	$5.2 \cdot 10^{9}$	17	-4.6	$6.5 \cdot 10^{11}$
7	-9.5	$5.3 \cdot 10^{9}$	18	-2.0	$1.8 \cdot 10^{13}$
8	-5.7	$5.9 \cdot 10^{9}$	19	-1.6	$2.2 \cdot 10^{13}$
9	-5.8	$2.1 \cdot 10^{9}$	20	-1.1	$1.1 \cdot 10^{13}$
10	-5.1	$1.4 \cdot 10^{10}$	21	-3.2	$4.8 \cdot 10^{12}$
11	-4.9	$1.8 \cdot 10^{10}$	22	-1.5	$1.9 \cdot 10^{12}$

The scatter plot with two linear trends in the “cold” temperature range (-10 ° C -: - -5.5 ° C) and in the “warm” temperature range (-5.5 ° C -: - 0 ° C) is presented in Fig. 4.

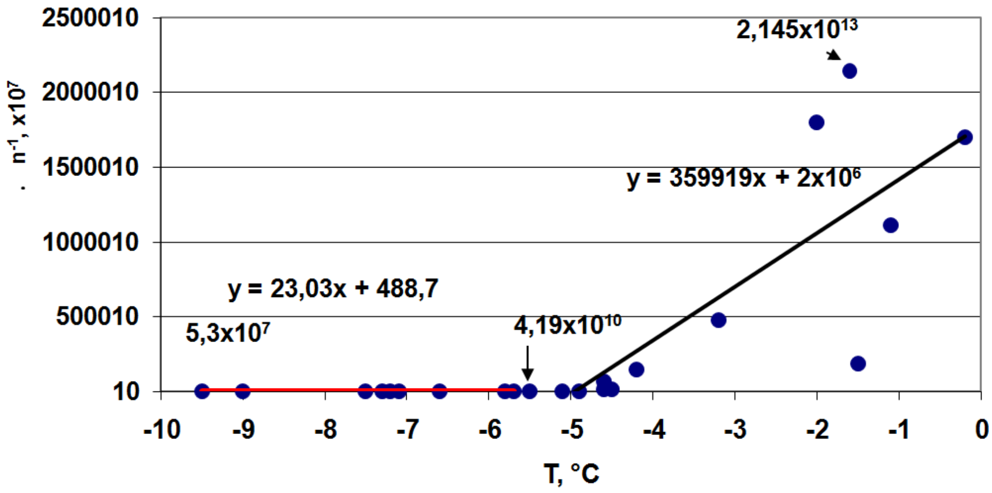

Fig. 4. Dependence diagram of specific yield of crystals when using ZnO nanotubes on the temperature T within two ranges (with linear trends).

The equation of the linear trend of specific yield of crystals in the "cold" temperature range is as follows:

$$Y = (Y_1 t_1 + C_1)K \qquad (2)$$

where, Y_1 is the specific yield of crystals [g^{-1}]; A_1 is the angular coefficient, $A1$ = 23.03 [$°C^{-1} \cdot g^{-1}$]; t_1 is the temperature range (-10 ° C -: - -5.5°C); C_1 is the free term, C_1 = 488.7 [g^{-1}]; K is the coefficient, K=107 [g^{-1}].

In the "warm" temperature range, the linear trend equation for the specific yield of crystals is as follows:

$$Y = (Y_2 t_2 + C_2)K \qquad (3)$$

where Y_2 is the specific yield of crystals [g^{-1}]; A_2 is the angular coefficient, A_2 = 359919 [$°C^{-1} \cdot g^{-1}$]; t_2 is the temperature range (-5.5 ° C -: - 0°C); C_2 is the free term, C_2 = $2 \cdot 10^6$ [g^{-1}]; K is the coefficient, K = 107 [g^{-1}].

As a result of a series of experiments, it was obtained that the specific yield of crystals increases "by a jump" by several orders of magnitude when the temperature changes from the "cold" range (-10°C -: - -5.5°C) to the "warm" range (-5 , 5°C -: - 0°C). In the "warm" temperature range, with an increase of 1°C, the specific yield (g^{-1}) of crystals increases from several tens to several hundred thousand.

3.2. The results of the study of the ice-forming properties of AgI silver iodide nanotubes

To study the ice-forming component AD-1 of the anti-hail rocket Alazan-6 in its pure form and with carbon additive in the form of graphite, a series of experiments were conducted.

It was assumed that the introduction of graphite leads to the formation of *AgI* nanotubes.

The results of the experiments are shown in Table 2 and in Fig. 5.

TABLE II. RESULTS OF STUDY OF ICE-FORMING COMPONENT AD-1 OF THE ROCKETS ALAZAN-6

n/n	Temperature in the cloud chamber, °C	Specific yield 0f crystals, r^{-1}	n/n	Temperature in the cloud chamber, °C	Specific yield 0f crystals, r^{-1}
1	-9.6	$2.7 \cdot 10^{12}$	11	-9.8	$2.3 \cdot 10^{12}$
2	-5.9	$1.1 \cdot 10^{12}$	12	-10.2	$1.2 \cdot 10^{12}$
3	-8.2	$3.3 \cdot 10^{12}$	13	-9.9	$6.4 \cdot 10^{11}$
4	-10.4	$1.2 \cdot 10^{12}$	14	-9.1	$6.2 \cdot 10^{12}$
5	-6.8	$6.5 \cdot 10^{11}$	15	-7.7	$1.2 \cdot 10^{11}$
6	-8.7	$1.3 \cdot 10^{12}$	16	-12.3	$6.5 \cdot 10^{11}$
7	-11.9	$5.7 \cdot 10^{12}$	17	-9.4	$1.6 \cdot 10^{12}$
8	-10.1	$8.8 \cdot 10^{11}$	18	-9.3	$2.9 \cdot 10^{11}$
9	-9.6	$5.0 \cdot 10^{12}$	19	-9.6	$1.2 \cdot 10^{12}$
10	-13.4	$4.4 \cdot 10^{12}$			

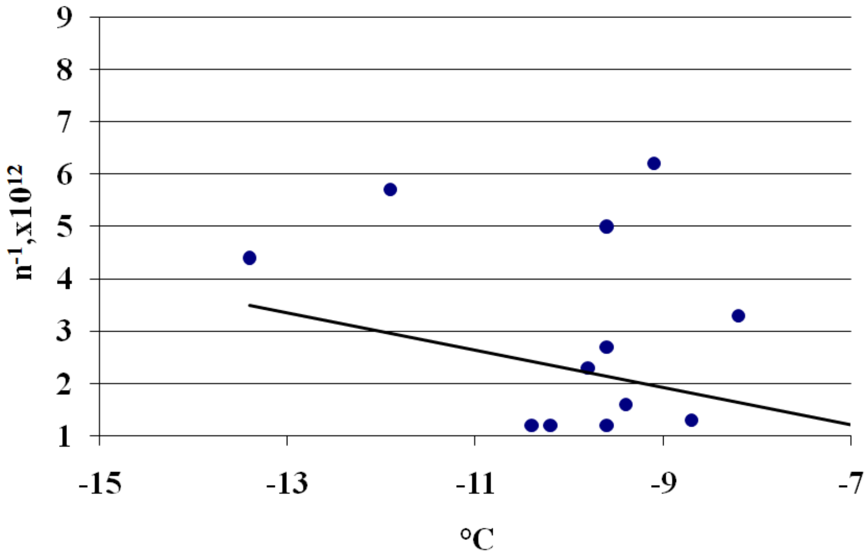

Fig. 5. Specific yield dependence of crystals when using the reagent AD-1 on temperature

The results of the experiments are shown in Table 3.

TABLE III. STUDY RESULTS OF THE ICE FORMING COMPONENT AD-1OF THE ROCKET ALAZAN-6 WITH CARBON ADDITIVE

n/n	Temperature in the cloud chamber, °C	Specific yield 0f crystals, r^{-1}	n/n	Temperature in the cloud chamber, °C	Specific yield 0f crystals, r^{-1}
1	-12.7	$14.0 \cdot 10^{13}$	13	-12.7	$3.9 \cdot 10^{13}$
2	-12.9	$12.0 \cdot 10^{13}$	14	-12.0	$1.3 \cdot 10^{13}$
3	-13.2	$5.0 \cdot 10^{13}$	15	-8.9	$2.3 \cdot 10^{13}$
4	-13.3	$2.6 \cdot 10^{13}$	16	-9.1	$1.1 \cdot 10^{13}$
5	-12.6	$1.4 \cdot 10^{13}$	17	-12.5	$0.5 \cdot 10^{13}$
6	-11.0	$1.2 \cdot 10^{13}$	18	-13.2	$5.1 \cdot 10^{13}$
7	-11.6	$0.6 \cdot 10^{13}$	19	-14.4	$2.6 \cdot 10^{13}$
8	-11.2	$2.3 \cdot 10^{13}$	20	-13.3	$2.5 \cdot 10^{13}$
9	-11.8	$0.9 \cdot 10^{13}$	21	-12.8	$1.4 \cdot 10^{13}$
10	-12.2	$0.6 \cdot 10^{13}$	22	-13.6	$3.0 \cdot 10^{13}$
11	-11.2	$0.1 \cdot 10^{13}$	23	-13.2	$2.9 \cdot 10^{13}$
12	-12.5	$3.6 \cdot 10^{13}$			

Fig.6 shows a combined diagram of the specific yield of ice-forming particles of the reagent AD-1 and AD-1 with the carbon additive. The Y-axis is represented as a logarithmic scale.

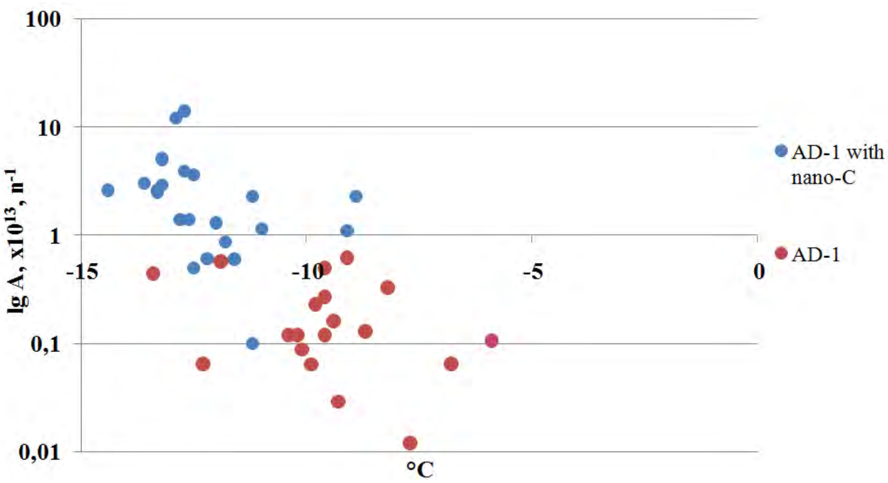

Fig. 6. Specific yield of ice-forming particles of the reagent AD-1 and AD-1 with carbon additive

IV. CONCLUSION

The results of experiments conducted in the laboratory of cloud microphysics of High-Mountain Geophysical Institute showed the following:

- during the reagent sublimation based on the nanotubes of zinc oxide directly in a cloudy environment its ice-forming properties were increased;

- during the experiments on the sublimation of the reagent in the temperature range from 0°C to -10°C, the highest specific yield of ice-forming nuclei (3 · 1013 g-1) was observed in the temperature range from 0°C to -2°C.

- at a sublimation temperature of 0°C to -2°C the specific yield of ice-forming nuclei was 3 · 1013 g^{-1}; at a sublimation temperature of -5.5°C to -10°C the specific yield was $1.2 \cdot 10^{11}$ g^{-1}.

The synthesized reagent based on nanotubes of zinc oxide, as well as carbon additives to the pyrotechnic composition AD-1 can be recommended for the application in case of active influences on the cloud processes as a complex composition. Such complex compositions will allow to expand the temperature range of the effective use of traditional reagents and increase the number of objects of active influence, to increase the efficiency on precipitation. However, for more specific recommendations, additional studies are required in order to increase the specific yield of complex compositions with the introduction of nanoreagents in a wider temperature range.

References

[1] I.N. Tapaskhanov, B.M. Khuchunayev, M.I. Tlisov, A.B. Khuchunayev, G.V. Kupovykh, “Preliminary Results of Study of Condensation Ice-Forming Properties of AgI Nanotubes and Zinc Oxide” Izvestiya HMGI. North Caucasus region, No. 6, 2014, pp. 40-43.

[2] V.O. Tapaskhanov, B.M. Khuchunaev, A.B. Khuchunaev, V.P. Panaetov, “Preliminary Results of Study of Ice Forming Properties of Zinc Oxide and AgI” Reports of the All-Russian Open Conference on Cloud Physics and Active Impacts on Hydrometeorological Processes October 7-9, 2014, Part 2., pp. 190-194.

[3] A.N. Gruzintsev, A.N. Redkin, Z.I. Makoviy, E.E. Yakimov, K. Barthou “Random lasing of vertical ZnO nanorods” Physics and semiconductor technology, Vol. 41, issue. 6, 2007, pp. 730-734

[4] N.S. Nikolaeva, V.V. Ivanov, A.A. Shubin, "Synthesis of highly dispersed forms of zinc oxide: chemical precipitation and thermolysis" Journal of the Siberian Federal University. Series: Chemistry, Vol. 3, No. 2, 2010, pp. 153-173.

[5] V.S. Burakov, N.V. Tarasenko, E.A. Nevar, M.I. Nedelko, “Morphology and Optical Properties of Zinc Oxide Nanostructures Synthesized by Thermal and Electric Discharge Sputtering” Journal of Technical Physics, Vol. 81, Issue. 2, 2011, pp. 89-93.

[6] V. Haupt M. A. Ladenburger, R. Sauer, and K. Thonke. "Ultraviolet-emitting ZnO nanowhiskers by self-assembled polymers", J. Appl. Phys., Vol. 93, N 10, 2003, pp. 6252-6257.

[7] Y.M. Heo, V. Varadarajan, M. Kaufman, K. Kim, and D. P. Norton, "Site-specific growth of zno nanorods using catalysis-driven molecular-beam epitaxy" Appl. Phys. Lett .. V. 81, N 16, 2002, pp. 3046-3048.

[8] V.S. Burakov, N.V. Tarasenko, E.A. Nevar, M.I. Nedelko, “Morphology and optical properties of zinc oxide nanostructures synthesized by thermal and electric discharge spraying” Journal of Theoretical Physics, issue. 2, Vol. 81, 2011, pp. 88-97.

[9] V.V. Pokropivny, MM Kasumov, “Production and Growth of Nanostructures from Zinc Oxide in an Arc Discharge”, Letters to the Journal of Theoretical Physics, issue 1, Vol. 33, 2007, pp. 88-94.

[10] Li Yana, Cha Kyongho, He Qinghui, "Advanced Materials Research", Vol. 174, 2011, pp. 450-453.

[11] E.Tang, G.Cheng and X.Ma, “Preparation of nano-ZnO / PMMA composite particles through the nanoparticles” Powder Technology Vol. 161, 2006, pp. 209-214.