

Radiation Stability of Pigment ZnO Modified by Nanopowder

Chundong Li, V. V. Neshchimenko, M. M. Mikhailov

Abstract—The effect of the modification of ZnO powders by ZrO_2 , Al_2O_3 , TiO_2 , SiO_2 , CeO_2 and Y_2O_3 nanoparticles with a concentration of 1-30 wt % is investigated by diffuse reflectance spectra within the wavelength range 200 to 2500 nm before and after 100 keV proton and electron irradiation. It has been established that the introduction of nanoparticles ZrO_2 , Al_2O_3 enhances the optical stability of the pigments under proton irradiation, but reduces it under electron irradiation. Modifying with TiO_2 , SiO_2 , CeO_2 , Y_2O_3 nanopowders leads to decrease radiation stability in both types of irradiation. Samples modified by 5 wt. % of ZrO_2 nanoparticles have the highest stability of optical properties after proton exposure. The degradation of optical properties under electron irradiation is not high for this concentration of nanoparticles. A decrease in the absorption of pigments modified with nanoparticles proton exposure is determined by a decrease in the intensity of bands located in the UV and visible regions. After electron exposure the absorption bands have in the whole spectrum range.

Keywords—Irradiation, nanopowders, radiation stability, zinc oxide.

I. INTRODUCTION

SPACE vehicles are subjected to a number of factors causing changes in the properties and operating characteristics of the outer surface materials. In particular, an increase in the absorbency of thermal control coatings (TCCs) is observed. This is mostly concerned with TCCs of the solar reflector class, to which enamel and ceramic coatings, based on oxide white pigments with polymeric and inorganic binders, belong.

Among the pigments for the coatings of this class (ZnO , TiO_2 , Al_2O_3 , ZrO_2 , Zn_2TiO_4), zinc oxide powders have found the greatest application as the most stable to the effects of charged particles and solar ultraviolet radiation [1]. However, a rather large amount of defects and absorption centers is formed in these pigments during long-term orbital spacecraft flights, which results in a decrease in the spectral reflectance (ρ_λ) in the ultraviolet (UV), visible and near infrared (IR) spectral regions, and an increase in the solar absorptance (α_s).

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Therefore, it is relevant to search for methods of increasing the photo and radiation stability of zinc oxide powder pigments. One of the most promising methods is their modification by white oxide nanopowders, which has demonstrated a high efficiency for ZrO_2 [2] and TiO_2 [3]–[5] pigments. A study of the radiation stability of ZrO_2 [6] and Al_2O_3 nanoparticles themselves shows that unlike micropowders, a smaller number of defects absorbing in the near IR spectral range forms in them.

The aim of this work was to study the effect of additions of ZrO_2 , Al_2O_3 , TiO_2 , SiO_2 , CeO_2 and Y_2O_3 nanopowders in different concentrations to ZnO on the optical properties and radiation stability of a zinc oxide pigment under proton and electron irradiation.

II. EXPERIMENTAL

The research was carried out on commercial zinc oxide pigment and ZrO_2 , Al_2O_3 , TiO_2 , SiO_2 , CeO_2 , Y_2O_3 nanopowders purity 99.8%, purchased the company Aladdin Chemistry. Average particle size of ZnO micropowder was 500-800nm, nanopowders – 30-50nm.

The above nanopowders were dispersed in distilled water with the imposition of ultrasonic fluctuations (2min, 200 W) and followed by the addition of the ZnO powders into the solution. Then, the mixture was treated by ultrasonic exposure (3min, 200 W) and further was dried at $T = 250^\circ C$, ground in an agate mortar, and heated at $T = 800^\circ C$ for 3h in air. The rate of the temperature increase was on average 50 deg/min, and that of cooling was 9 deg/min. After cooling the powders were pressed into pellets with a diameter of 17 mm and a height of 4 mm, under a pressure of 1 MPa with a hold time of 2 min.

The samples were irradiated with protons and electrons under identical conditions: the particle energy was 100 keV, the fluence was $5 \times 10^{15} \text{ cm}^{-2}$, the flux density was $1 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$, and vacuum was maintained at $2.5 \times 10^{-4} \text{ Pa}$. The reflective spectra of the samples were measured using a Perkin Elmer Lambda 950 spectrophotometer with a scanning rate of 5 nm and a wavelength range from 250 to 2500nm. The value of solar absorptance of the samples was calculated in accordance with the American Society for Testing and Materials (E490 and E903-00a-96) for powders by the formula:

$$a_s = 1 - \rho_s = 1 - \frac{\int_{\lambda_1}^{\lambda_2} \rho_\lambda I_\lambda d\lambda}{\int_{\lambda_1}^{\lambda_2} I_\lambda d\lambda} \quad (1)$$

The ρ_λ is defined as an average of two experimental points.

III. RESULTS AND DISCUSSION

The modification makes nanoparticles come out onto the surface of the pigment grains, with the formation of a single or double layer thick shell (Fig. 1), or a structure consisting of four or more nanoparticles on the edges of zinc oxide crystallites or in the spaces between pigment grains.

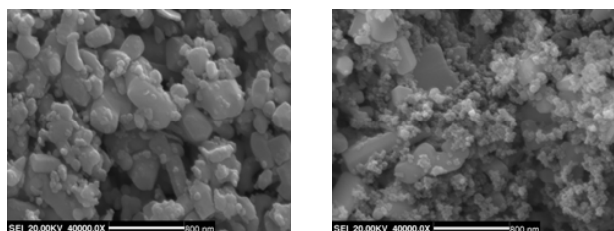


Fig. 1 Microphotograph of zinc oxide pigment modified with 5 wt. % ZrO₂ (A) and SiO₂ (B) nanopowder

Since the reflectance of modified and nanomodified samples reaches 90% in UV and visible regions (Fig. 2). The optical edge of the main absorption corresponds to 380 nm and during the modification it shifts to the UV region. In the near IR region, a decrease in the reflectance is observed, which is due to absorption by chemisorbed gases (CO, CO₂, O₂) and OH groups [7] and free electrons [8]. Modification with ZrO₂, TiO₂, SiO₂, CeO₂, Y₂O₃ in an increase of 3-15 % in the reflectance in the near IR region; the introduction of Al₂O₃ nanopowders results in a decrease by 4-10 % in comparison with the unmodified powder. For samples containing TiO₂ nanopowder at concentrations of 15-30 wt. % characterized by increased in the reflectance at the fundamental absorption edge of zinc oxide, which may be an occurrence of additional phases (ZnTiO₄) formed between ZnO and TiO₂ during modification.

Since the introduction of nanopowders leads to changes in diffuse reflectance spectra in the whole spectral region. Then as a parameter characterizing the ability of a material to absorb incident radiation, it is advisable to choose the solar absorptance (a_s).

It is follow from dependence of solar absorptance vs concentration of modifying additives (Fig. 3) that have the highest reflectance of zinc oxide powders modified by SiO₂ nanopowders. The a_s values reach 0.102 at C = 15 wt.%, whereas the value of the original non-modified zinc oxide is 0.14. Thus, improvement of reflectance at the introduction SiO₂ is 37% of the original.

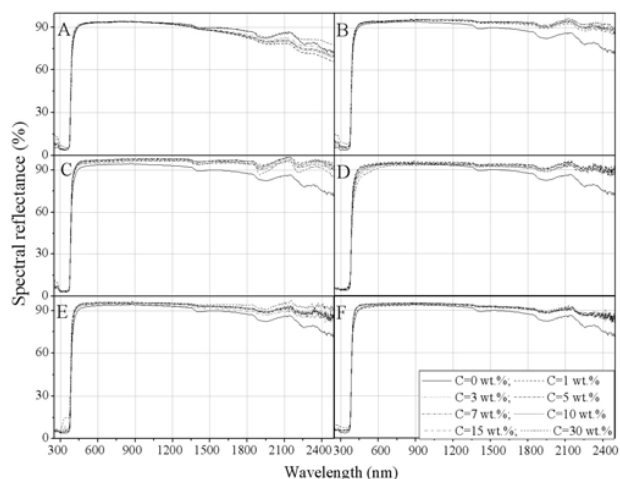


Fig. 2 Reflective spectra of zinc oxide pigment modified by Al₂O₃ (A), ZrO₂ (B), SiO₂ (C), CeO₂ (D), TiO₂ (E), Y₂O₃ (F) nanopowders

Introduction as the modifier additives large concentrations (15-30 wt.%) CeO₂ nanopowders increases of as to 4-7% compared with the original, whereas the addition of small concentration of nanopowders as reduced by 12% and as =0.124.

Modification with the Al₂O₃ nanopowder causes degradation of the reflectance of the ZnO pigment: the solar absorptance as increases to 4% at the concentration C = 3 wt. % in comparison with the unmodified sample. The solar absorptance as decreases with a further increase in the nanopowder concentration, and at C = 30 wt % it is 8% lower than the initial value (Fig. 3).

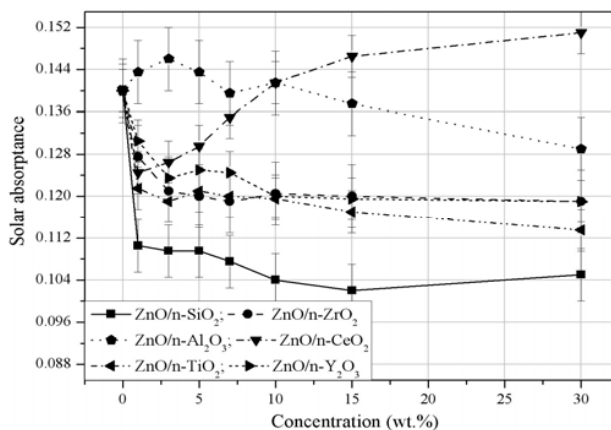


Fig. 3 Concentration dependence of solar absorptance of the ZnO powder modified by Al₂O₃, ZrO₂, SiO₂, CeO₂, TiO₂, Y₂O₃ nanopowders

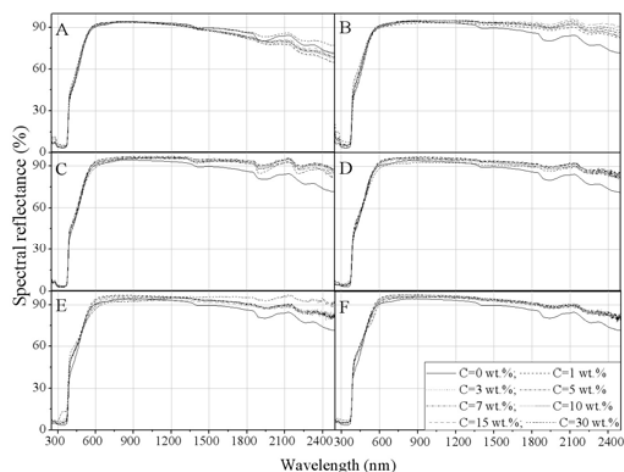


Fig. 4 Reflective spectra of zinc oxide pigment modified by Al_2O_3 (A), ZrO_2 (B), SiO_2 (C), CeO_2 (D), TiO_2 (E), Y_2O_3 (F) nanopowders after irradiation by protons $E_p=100$ keV, $F=5 \times 10^{15} \text{ cm}^{-2}$

When added ZrO_2 , TiO_2 and Y_2O_3 nanopowders there is increase in reflectance for a similar range of a_s values from 0.115 to 0.125.

Proton irradiation causes a decrease in the reflectance from 90 to 40% in the region from the main absorption edge to 600 nm (Fig. 4). The reflectance increases in this region with an increasing nanoparticle concentration, while in the near IR region, it changes insignificantly (by 1-5%).

The difference in the absorption spectra causes the corresponding difference in the values of the solar absorptance of the irradiated powders, specified by $\Delta a_s = a_{s1} - a_{s0}$, where a_{s0} , a_{s1} - solar absorptance before and after irradiation, respectively.

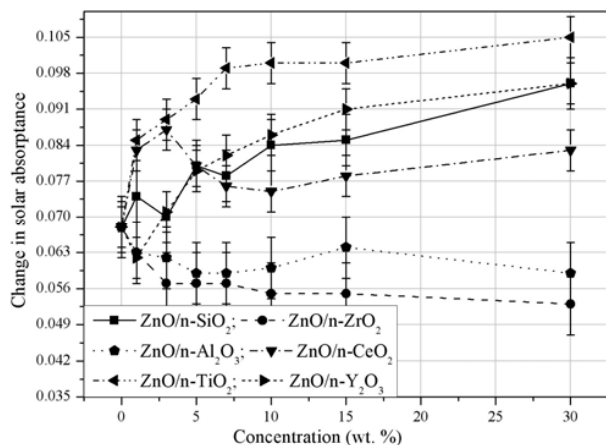


Fig. 5 Concentration dependence of change in solar absorptance of the ZnO powder modified by Al_2O_3 , ZrO_2 , SiO_2 , CeO_2 , TiO_2 and Y_2O_3 nanopowders after irradiation by protons $E_p=100$ keV, $F=5 \times 10^{15} \text{ cm}^{-2}$

From concentration dependence of change in solar absorptance of the ZnO modified pigment follows (Fig. 5) that the introduction of Al_2O_3 and ZrO_2 nanoparticles leads to an

increase in the radiation stability, whereas modification of the zinc oxide by SiO_2 , CeO_2 , TiO_2 and Y_2O_3 nanopowders increases the radiation-induced defects in the zinc oxide.

For samples modified with the Al_2O_3 nanopowder Δa_s values have a minimum near the concentration 5-7 wt %, where it is 0.059. When the concentration increases to 15 wt %, Δa_s increases to 0.064, and at $C=30$ wt % it again becomes 0.059. Samples modified with the ZrO_2 nanopowder have a similar degradation region near $C = 3, 5, \text{ and } 7$ wt %, where $\Delta a_s = 0.057$. At $C = 30$ wt % Δa_s is 0.053, which is the best result obtained in these experiments.

Electron irradiation resulted in a slight increase in reflectance of the unmodified powder (Fig. 6). This effect earlier in [9] associated with the cleaning of the polycrystalline surface in vacuum and radiation annealing of defects.

The greatest changes occurred in the pigment zinc oxide modified by nanopowders Al_2O_3 and SiO_2 under electrons exposure. For these samples reflectance is reduce in the visible region to values of 85%. The smallest changes were zinc oxide powders with addition of nano- Y_2O_3 .

Calculation of the change in solar absorptance has shown (Fig. 7) that increasing the concentration of nanoparticles in zinc oxide leads to the deterioration of radiation stability. Most degradation occurs in samples of zinc oxide with the addition of nano-silica at a concentration of 30 wt.%, the value Δa_s is 0.034. Obtained by proton irradiation high radiation stability for sample ZnO/nano- ZrO_2 is also having not high degradation in comparison with other samples. It is typical for all samples that most radiation stability of the modified samples have the lowest concentration ($C = 1$ wt. %).

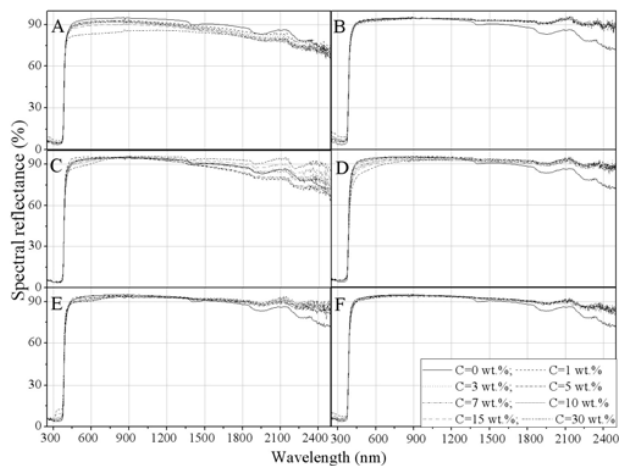


Fig. 6 Reflective spectra of zinc oxide pigment modified by Al_2O_3 (A), ZrO_2 (B), SiO_2 (C), CeO_2 (D), TiO_2 (E), Y_2O_3 (F) nanopowders after irradiation by electrons $E_c=100$ keV, $F=5 \times 10^{15} \text{ cm}^{-2}$

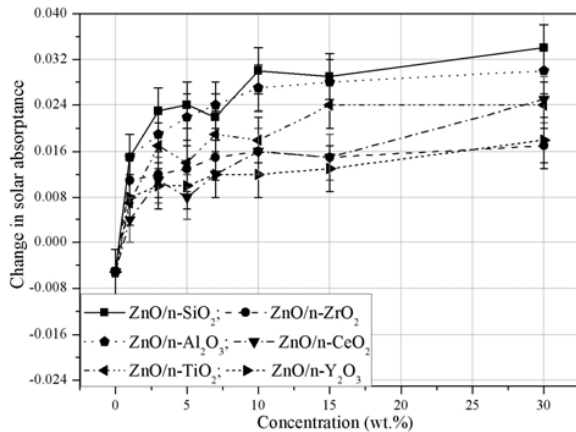


Fig. 7 Concentration dependence of change in solar absorbance of the ZnO powder modified by Al_2O_3 , ZrO_2 , SiO_2 , CeO_2 , TiO_2 and Y_2O_3 nanopowders after irradiation by electrons $E_e=100$ keV, $F=5 \times 10^{15} \text{ cm}^{-2}$

Thus, the pigments modified with the ZrO_2 nanopowder have the highest stability of the optical properties to proton and electron irradiation among all studied modes and concentrations. The nanoparticle concentration of about 5 wt %, at which the largest increase in the radiation stability under proton radiation and its lowest decrease under electron irradiation are observed, can be recommended.

The change in spectra reflectance $\Delta\rho_E$ represents the radiation induced absorption spectra (Fig. 8), which is obtained by subtraction of the spectra after irradiation from the spectra of the unirradiated samples, whereas the transmission and the scattering under such conditions is not changed. After proton irradiation, the highest absorption is registered in the region 1.9 to 3.3 eV. After electron irradiation forms a small absorption peak at 2.8 eV. The absorption bands of the other defects are absent; the change in spectral reflectance has the opposite sign this indicating the recovery of these defects during electron irradiation.

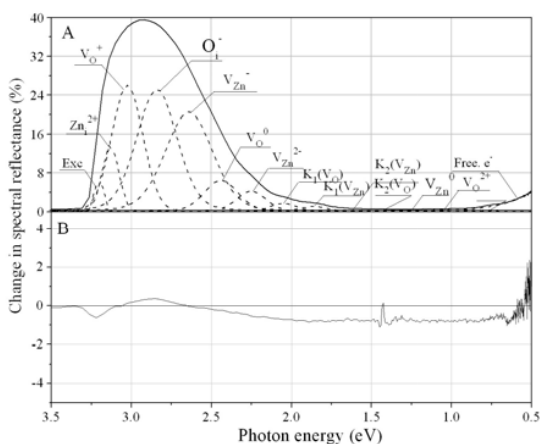


Fig. 8 Change in spectral reflectance ($\Delta\rho_E$) of zinc oxide after proton (A) and electron (B) exposure with energy 100 keV and fluence $5 \times 10^{15} \text{ cm}^{-2}$. Their decomposition into subband absorption

In order to elucidate the nature of the bands and to qualitatively analyze the effect of nanopowders on the accumulation of absorption centers, the $\Delta\rho_\lambda$ spectra were decomposed into elementary bands. The expansion function consisted of the Gaussian dependence (80%) and the Lorentz dependence (20%).

The peak positions and their full widths at half maximum (FWHMs) of the bands were obtained as reported in [10]-[13]: $A(\text{exciton}) - 3.2$, $\text{Zn}_i^{2+} - 3.13$; $\text{V}_O^+ - 3.03$; $\text{O}_i^- - 2.83$; $\text{V}_{\text{Zn}}^- - 2.64$; $\text{V}_O^0 - 2.44$ eV; $\text{V}_{\text{Zn}}^{2-} - 2.25$; complex of $\text{V}_O - 2.05$; complex of $\text{V}_{\text{Zn}} - 1.86$; complex of $\text{V}_{\text{Zn}} - 1.64$; complex of $\text{V}_O - 1.44$; $\text{V}_{\text{Zn}}^0 - 1.25$; $\text{V}_O^{2+} - 1.05$ eV.

The decomposition results show (Fig. 8) that under electron irradiation the main contribution to the absorption of the unmodified powder is made by interstitial oxygen O_i^- . Proton irradiation leads to an increase in the concentration of oxygen vacancies V_O^0 and V_O^+ , interstitial oxygen O_i^- , zinc vacancies V_{Zn}^- .

Mechanisms of defect formation in zinc oxide modified by nanoparticles under protons and electrons exposure proposed in [13]. The main idea is that, during the modification, a layer of nanoparticles bound to each other is formed on the pigment surface. The diffusion of nanopowder oxide cations into the grain bulk leads to a crystal lattice distortion, due to the formation of inclusion or substitution impurities. With regard to the ionic radius of zinc (0.74 Å), silicon (0.39 Å), alumina (0.50 Å), titanium (0.69 Å), zirconium (0.80 Å), yttrium (0.97 Å), cerium (0.97 Å) it is possible to conclude that aluminum, titanium and silicon ions generate substitution defects, whereas zirconium, yttrium, cerium ions generate such defects with a lower probability because their radius is close to the radius of zinc ions, and, in this case, defects of both types are possible. Therefore, the concentration of interstitial zinc ions can be higher during modification with oxide of aluminum, titanium and silicon than during modification with zirconium dioxide and yttrium oxide.

IV. CONCLUSION

Our studies show that the stability of the optical properties under proton and electron exposure at same condition of the zinc oxide pigment modified by ZrO_2 , Al_2O_3 , TiO_2 , SiO_2 , CeO_2 and Y_2O_3 nanopowders, is higher under the action of accelerated electrons than under the action of protons. Pigments modified with the ZrO_2 nanoparticles have the highest stability. A nanopowder concentration of about 5 wt % may be optimal. At this concentration there is no significant degradation during electron irradiation, and at the same time, an increase in the radiation stability is observed during proton irradiation.

An analysis of the induced absorption spectra after proton irradiation reveals that a considerable decrease in the integral absorption band intensity during modification with ZrO_2 and Al_2O_3 nanopowders occurs because of a decrease in the concentration of defects relating to zinc and oxygen vacancies and interstitial oxygen whose bands are located in the visible and UV spectral regions. Electron irradiation causes an

increase in the absorption band intensity in comparison with the unmodified powder. As the nanoparticle concentration increases, the absorption first increases in the visible and UV regions and then in the near IR spectral region.

REFERENCES

- [1] A. C. Tribble, R. Lukins, E. Watts, V. A. Borisov, S. A. Demidov, V. A. Denisenko, A. A. Gorodetskiy, V. K. Grishin, S. F. Nauma, V. K. Sergeev, S. P. Sokolova, "United States and Russian Thermal Control Coating Results in LowEarth Orbit," *Journal of Spacecraft and Rockets*, vol. 33, no. 1, pp. 160-166, 1996.
- [2] M. M. Mikhailov, A. S. Verevkin, "Optical properties and radiation stability of thermal control coatings based on doped zirconium dioxide powders," *Journal of Material Research*, vol. 19, no. 2, pp.535-541, 2004.
- [3] M. M. Mikhailov, V. A. Vlasov, "A size effect in the optical properties of powdered TiO₂," *Russian Physics Journal*, V. 41, pp 1222-1228, 1998.
- [4] M. M. Mikhailov, A. N. Sokolovskii, "Efficiency of treating white pigments with aluminum oxide nanopowders" *Russian Physics Journal*, vol. 50, no. 7, pp.733-736, 2007.
- [5] M. M. Mikhailov, N. V. Dedov, A. N. Sokolovskii, V. V. Sharafutdinova, "Special features of point defect accumulation in coatings based on titanium dioxide doped with Al₂O₃ nanopowders," *Russian Physics Journal*, V. 50, pp 737-740, 2007.
- [6] M. M. Mikhailov, V. V. Neshchimenko, "Comparative analysis of diffuse reflection spectra and induced absorption spectra of ZrO₂ micro- and nanopowders after irradiation with 100 keV electrons and protons," *Journal of Surface Investigation X-ray Synchrotron and Neutron Techniques*, vol.3, no. 6, pp.950-955, 2009.
- [7] D. A. Burns, E.W. Ciurczak, *Handbook of Near-Infrared Analysis*. CRC Press Taylor and Francis group 2008.
- [8] Pidgeon C. R. *In Handbook on Semiconductors*: Balkanski M. Eds.: North-Holland: Amsterdam, 1980: Vol. 2, pp. 223-328.
- [9] Mikhailov, M.M., *Predicting the optical degradation of thermal control coatings for spacecrafts*. Nauka. Sib. Publ. Company, RAN, Novosibirsk, 1999, p. 192.
- [10] M.M. Mikhailov, V.V. Neshchimenko, Chundong Li, "Comparative analysis of emission and absorption spectra of zinc oxide powders," *Journal of Surface Investigation*, V. 5, pp. 775-779, 2011.
- [11] M.M. Mikhailov, V.V. Sharafutdinova, "Changes in optical properties of the spacecraft thermal control coatings under the influence of solar wind protons," *Russian Physics Journal*, No. 6, pp. 83-88, 1998.
- [12] M. M. Mikhailov, V. V. Neshchimenko, Shiyu He, Chundong Li, "Proton irradiation effects on ZnO pigments modified by ZrO₂ nanopowders" *Journal of Spacecraft and Rockets*, V 48, pp. 891-896, 2011.
- [13] M. M. Mikhailov, V. V. Neshchimenko, N. V. Dedov, Chundong Li, Shiyu He, "Proton and Electron Irradiation Induced Changes in the Optical Properties of ZnO Pigments Modified with ZrO₂ and Al₂O₃ Nanopowders" *Journal of Surface Investigation. X-ray, Synchrotron and Neutron Techniques*, vol. 5, no. 6, pp. 1152-1161, 2011.