APPLICATION OF NUCLEAR METHODS

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PECULIARITIES OF RADIATION-INDUCED EFFECTS IN ZnO NANOPARTICLES

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Gamma activation of ZnO nanoparticles was carried out using the method of developing the features of identifying their radiation-induced effects for further development in applied directions. The methods of gamma spectrometry, X-ray spectrometry, photoluminescence and IR spectroscopy were used. A higher concentration of sour vacancies on the surface of gamma-activated nano-ZnO was shown.

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INTRODUCTION

Zinc oxides (ZnO) nanoparticles has been widely used in many applications such as transparent conductive films, resistors, solar cell window, bulk acoustic wave devices, lasers and diodes. One of the materials that has attacted great interest from a wide range of technological fields associated with nanotechnology is zinc oxide. The metal oxides show enchanced photocatalytic activity with the increase in electronic defects in the crystallites by introducing defects into the crystal lattice of ZnO nanoparticles [1–5].

The two principal factors cause the properties of nanomaterials to differ significantly from other materials: the increased surface to volume ratio and dominance of quantum effects. These factors can change or enhance chemical reactivity, electrical transport characteristics including properties such as ionization pitential, electron affinity, capillary forces, melting point, specific heat. That's why Zinc oxides nanoparticles have applications in luminescent devices, photocatalysis, photoelectrochemistry, and nonliner optical devices. Zinc oxides nanoparticles are widely used in cosmetics (sunscreens, foot care, oinments, and over-the-counter topical products), pigments and coatings protection (ultra-violet), fungicide in paints, electronic devices, and catalysts [6–9].

However, so far no work has been reported on the structure and phase composition, and element content of zinc oxide nanoparticles by irradiated bremsstrahlung. Therefore, in the present work, a study was carried out of the optimal conditions for the production of gamma-activated zinc oxide nanoparticles, suggesting their use to increase their reaction activity in various applied areas.

MATERIALS AND RESEARCH METHODS

In this work the nanoparticles of metal oxide ZnO were used, producer: firm Alta Aesar Sigma, USA. The size of nanoparticles was ~ 40 nm for ZnO. Samples of nanoparticles (1 g) were placed in aluminum foil and were irradiated by irradiated bremsstrahlung on LAE with E = 22 MeV and I = 500 μA. The nuclear reaction $^{66}Zn(\gamma,n)^{65}Zn$ was used. The maximum absorbed dose during γ-irradiation (Eγ ~ 1.5…2 MeV) accounted for ZnO – 20 MGy. The spectrum of gamma-activated nano-ZnO was recorded by a detector.

Using the methods of gamma spectroscopy, X-ray diffractometry, photoluminescence, and IR-spectroscopy, the elemental and structural-phase composition, crystallinity, and emission properties of nano-ZnO were studied.

The structural-phase composition of the nano-ZnO was controlled by the X- ray diffraction method using a DRON-2 diffractometer at a voltage of 30 kV and a current of 10 μA. Spectra were recorded in the range from 20 to 80° at a scanning speed of 1°/min. Diffraction reflection from the (200) plane of a single crystal NaCl was used as a standard when taking X-ray spectra.

The photoluminescent spectra of nano-ZnO, excited by UV-light with a wavelength of 300 nm, were recorded by luminescence intensity.

The structure and phase composition of samples were investigation by infrared (IR) spectroscopy (IRS-29, LOMO) in the frequency 400…4000 cm^{-1} with a measurement error of ± 2…7 cm^{-1}. For IR spectroscopy anlysis the samples were prepared in the form of transparently compressed tablets from a mixture of KBr and the test substance in an amount of 1% (100 mg sample). The pressing pressure was 9200 kg/cm^2. To eliminate matrix absorptio bands, a tablet of pure potassium bromide preliminarily dried at 180 °C for 10 h was placed in the comparison channel of the device. The powders were ground in agate mortars to a size of ~1…10 μm and mixed in a special closed box; pressing was carried out immediately before the spectra were recorded. Graduation in the range of 4000...700 cm^{-1} was carried out according to the spectrum of polystyrene with known frequencies of absorption maxima, and in the range of 700…400 cm^{-1}. The correction averaged 15…5 cm^{-1}.

RESULTS AND DISCUSSION

In Fig. 1 shows the nano-ZnO gamma spectrum with an exposure time of $5.0 \cdot 10^2$ min. In the gamma spectrum of nano-ZnO from the reaction $^{66}Zn(\gamma,n)^{65}Zn$, and ^{67}Cu lines from the reaction $^{68}Zn(\gamma,p)^{67}Cu$ are additionally observed.

Fig. 2 shows the diffraction patterns of nano-ZnO before and after irradiation. The appearance of these

diffraction patterns – the nature of the location of the interference maxima, their width and intensity – indicate the high crystallinity of the samples under study. Analyzing the X-ray diffraction patterns of nano-ZnO before and after γ-activation, the fact of their close similarity should be especially noted. When comparing the spectra, no shifts of the maxima or distortions of their shape were detected. Upon closer analysis, minor differences were noticed in the presented X-ray patterns associated with changes in the intensity of the lines of some basic reflections. These changes are more clearly observed in fragments of X-ray photographs in the angle range from 20 to 80°.

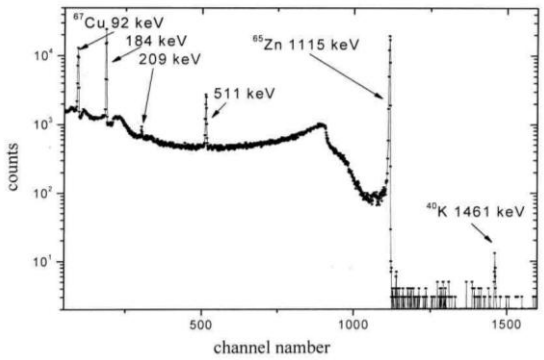

Fig. 1. Gamma spectrum of nanoparticles of metal oxide ZnO

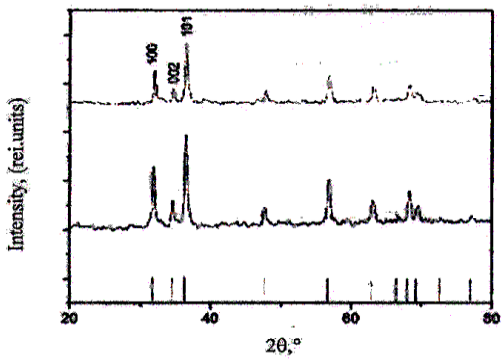

Fig. 2. Diffraction patterns of nanoparticles in the initial state and after irradiation to an absorbed dose of 20 MGy

No peaks attributed to any other nano or impurity phase were observed, indicating the high purity of the sample studied. The presence of metallic zinc was not detected in the nano-ZnO the peak corresponds to diffraction on the crystalline structure of zinc at $2\theta = 44.5^{o}$.

The content of the crystalline form in the nano-ZnO is 99%.

After irradiation of ZnO nanoparticles, a slight decrease in the intensities of three peaks is observed: 2θ = 31.7; 34.4; 36.2° and a peak at 2θ = 47.6°. The most significant decrease in intensity - almost 1.3 times – is observed at the maximum at 2θ = 34.4°. Based on the nature of the changes noted, it can be argued that a noticeable decrease in the intensity of the interference lines may be a consequence of partial distortion of the ZnO crystal lattice, in particular, as a result of the displacement of atoms from ideal positions.

Comparison of peaks at 2θ = 31.7; 34.4; 36.2° before and after gamma activation indicates their slight narrowing, and indicates a slight decrease in the dispersion of nano-ZnO after irradiation. This can be explained by the fact that during irradiation, local microstresses may arise and, as a consequence, deformation of the crystals. At the same time, it can be argued that irradiation of nano-ZnO, although it introduces some defects into the structure of nano-ZnO, does not lead to either a change in the phase composition or destruction of the crystal structure of the samples.

The studied nano-ZnO exhibit a strong and broad PhL signal in the range of 385…600 nm with two PhL peaks at 465 and 485 nm, which correspond to the edge of the bands of free and bound excitons, respectively (Fig. 3, curve a). A series of emission bands in the UV-blue region of the spectrum include several weak peaks at 388, 390, 410, and 485, and a strong band at 465 nm, as well as a green band at 510…550 nm and an extremely small yellow-orange band at 560…620 nm in the visible region of the spectrum.

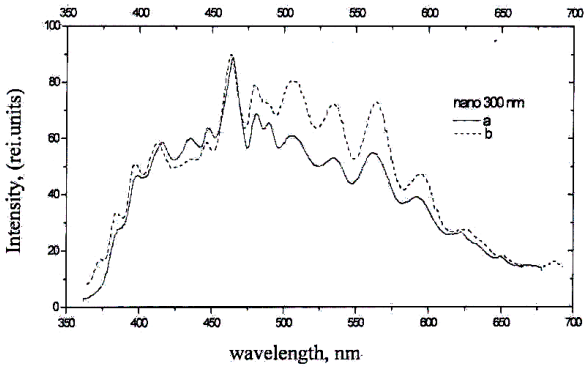

Fig. 3. Photoluminescence spectra nano-ZnO before and after irradiation at 300 nm photoexcitation mode

Gamma activation of nano-ZnO leads to some changes in their PL spectra at an excitation wavelength of 300 nm. The intensity of all small peaks of the green and yellow-orange band in the visible region of the spectrum 510…595 nm increased slightly, but the maxima of the UV-peaks remained practically unchanged (see Fig. 3, curve b). The emission of the green band corresponds to a singly ionized oxygen vacancy in the nano-ZnO, i.e. F^{+}-center.

Consequently, the higher the intensity of the green PhL region, the more singly ionized oxygen vacancies there are. Oxygen vacancies represent an active center that easily interacts with other active groups for stabilization, and which turns out to be responsible for the presence of a certain amount of adsorbed oxygen on the surface of nanoparticles. Responsible for the complex orange band is precisely the local excess of oxygen due to the high adsorption capacity of nano-ZnO, which can be caused by an increase in the concentration of free electrons due to the ionization of small donors.

The mutual enhancement of the action of two factors – a high concentration of active centers on the surface of the nano and large ionization losses of Auger electrons in the gamma-activated nano – can be widely used for various catalytic processes.

It is known that the decay is accompanied by the emission of Auger electrons with energy 0.92 (I = 126.7%), and 7.03 (I = 47.5%), which have a high stopping power (10…27 keV/μm) and a range of 76 and 2000 nm, respectively. These ranges, comparable to the sizes of nanoparticles, are the determining factors in the formation of high concentrations of surface defects and providing increased reactivity of the oxide.

Large ionization losses of Auger electrons lead to the formation of high concentrations of hydrated electrons (e-aq), hydroxide radicals (OH°), peroxides (H_2O_2), and, due to chemical reactions, radicals (HO_2°). It is obvious that the effect of nano-ZnO surface electronegativity and the presence of highly reactive centers are stimulating factors that ensure the directed development of the dehydration process. This fact is confirmed by the results of IR spectroscopy (Table).

Judging by the type of the IR-spectrum and the frequencies of the main maxima in the spectrum given in Table. This sample is a zinc oxide nanopowder. The presence of absorption bands at 1580 and 3430 cm-1 in the spectrum in the original sample indicates the content of adsorbed water. In the irradiated sample, these bands disappear, which indicates the decomposition of the water molecule with the formation of highly reactive forms OH°, H_2O_2, HO_2.

Characteristics of the intensity of absorption bands in the original and irradiated nano-ZnO in the IR-spectrum

Assigment of band, ν, cm^{-1}	Intensity of absorption bands	
	the original nano-ZnO	irradiated nano-ZnO
450	v.s.	v.s.
500	a	a
540	w	w
1300	w	w
1580	a	–
3400…5340	a, wide	–

List of abbreviations used to characterize the intensity of absorption bands: w – weak; a – average; v.s – very strong; wide – wide band.

CONCLUSIONS

The possibility of using electron beams for gamma activation nano-ZnO by bremsstrahlung at an electron accelerator has been demonstrated.

A comparative analysis of the phase composition and state of the nano-ZnO structure before and after gamma activation showed that the nano-ZnO samples are polycrystalline monophase zinc oxide and contain diffraction peaks characteristic of crystalline planes of zinc oxide with a hexagonal structure.

A comparative analysis of photoluminescent nano-ZnO showed a higher concentration of oxygen vacancies on the surface of gamma- activated nano-ZnO.

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ОСОБЛИВОСТІ РАДІАЦІЙНО-ІНДУКОВАНИХ ЕФЕКТІВ У НАНОЧАСТИНКАХ ZnO

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Проведено гамма-активацію наночастинок ZnO з метою вивчення особливостей виявлення їх радіаційно-індукованих ефектів для подальшого використання у прикладних напрямках. Було використано методи гамма-спектрометрії, рентгенівської спектрометрії, фотолюмінесценції та ІЧ-спектроскопії. Показано більш висока концентрація кисневих вакансій на поверхні гамма-активованих нано-ZnO.