UKRAINIAN JOURNAL OF MECHANICAL ENGINEERING AND MATERIALS SCIENCE

Vol. 1, No. 1, 2015

Ihor Virt[*,], Yuriy Pavlovskyy[*], Ivan Hadzaman[*]**
[*] Drogobych State Pedagogical University, Drogobych, Ukraine
[**]University of Rzeszow, Rzeszow, Poland

MICROMECHANICAL PROPERTIES AND THERMAL ANNEALING OF ZINC OXIDE BULK CERAMIC

Received: May 19, 2015 / Revised: August 12, 2015 / Accepted: September 16, 2015

Abstract. Zinc oxide has numerous commercial device applications. Polycrystalline ZnO varistors, for example, are widely used in high voltage and power-related applications in industries such as microelectronics. One of the ways to control the properties of ZnO is its annealing in various environments, including oxygen, which leads to increased hardness and fracture toughness of ceramics. Therefore, the study of micromechanical properties of materials for modern electronics is an important and vital issue, both in terms of technology for improving quality of the final product and from the point of view of prospect of its practical use.

The structural properties of the ceramic samples of ZnO have been studied. The average grain size has been defined. The micromechanical properties have been studied. The temperature conditions of increasing microhardness of ZnO have been defined after annealing in an oxygen atmosphere.

Introduction

Zinc Oxide due to its unique properties is one of the most promising semiconductor materials for electronics, optoelectronics, spintronics, for the application in nanotechnology and more etc. It is thermally and chemically stable material. He is characterized by enormous exciton binding energy (60 meV), which enables you to observe UV stimulated emission at room temperature. On the basis of ZnO one could provide for the establishment of light-emitting devices in short-range spectrum. In the case of magnetic impurities Co or Mn doping we observed ferromagnetic state. There is information that may help to create ultraviolet photoconductive detectors and Schottky diodes based on ZnO. Being transparent in a wide spectrum range, ZnO is resistant to exposure, malleable to chemical etching and relatively cheap, which makes it attractive for the application in microelectronics [1-5].

Single crystals of zinc oxide possess the unique physical and chemical properties: anisotropic crystal structure, non-stoichiometric composition of the compound semiconducting properties with a large bandgap, fluorescent properties, photoconductivity, photovoltaic and photochemical properties [6], high reflectivity in the visible spectrum and strong absorption in the ultraviolet region of the spectrum, catalytic activity, laser and electro-optical effect, strong piezoelectric and pyrotechnic effect, low coefficient of linear expansion and so on [7]. Among piezo- semiconductor materials used at present in acoustic electronics, zinc oxide is preferable because it has a high value of the electromechanical coupling coefficient that determines the efficiency of transformation of electromagnetic energy in elastic and vice versa. In many fundamental studies the zinc oxide was the "model" materials that allow understanding the various phenomena in physics and chemistry of solid states and its surface [8].

Most studies on zinc oxide are related to monocrystals or films obtained by different methods.

This work is devoted to obtaining pressed zinc oxide materials and investigation of their structural and micromechanical properties.

Polycrystalline materials obtained by powder sintering can be attributed to ceramic materials. Such studies have independent significance for a deeper understanding of physical processes in ceramic materials. Taking into account technological considerations it is supposed the use of such materials as targets for laser deposition of films [9].

Sintering of ZnO and the studied structures

Below, among other characteristics, the data on obtaining by uniaxial hot pressing ZnO ceramics has been shown. The method of uniaxial hot pressing, in which the process of obtaining the polycrystalline material is carried out at relatively low temperatures (Tm 0.5-0.7 K), makes high demands to the quality of the output powder: phase composition, morphology, and the dispersed particle composition.

ZnO-ceramics have been produced by the method of uniaxial hot pressing in a high vacuum furnace. We used commercial ZnO-powders of high purity, and also powders of the "Sigma-Aldrich" Company (the certified average grain size of 50-100 nm). In addition, the average grain size of ZnO of the "Sigma-Aldrich" Company has been evaluated by the CEM image (Fig. 1).

Solid solutions of ZnO and ZnMnO have been obtained by solid-phase reactions method, which is widely used in ceramic technology [10]. The powders were mixed with deionized water in Jasper drums of planetary mill SAND-1. Time of mixing and grinding was defined by the degree of homogenization and was 16 hours. The obtained mixture was dried at 120±5°C. The previous annealing mixture, which took place during its activation, has been conducted in air at the temperature of 700 ± 5°S for 4 hours. The press-blank with diameter of 11,5–15 mm and thickness of з 1–2,5 mm was formed by isostatic pressing with pressure of 40-60 MPa on the hydraulic press PG-10 without plasticizer. The mixtures have been sintered at temperatures close to 1000°C. The samples have been annealed in a chamber furnace batch VTP-06M1 in air (temperature control accuracy ± 5°S) for 3 hours. The maximum temperature annealing that matched isothermal curve area heating-cooling was 1110°C.

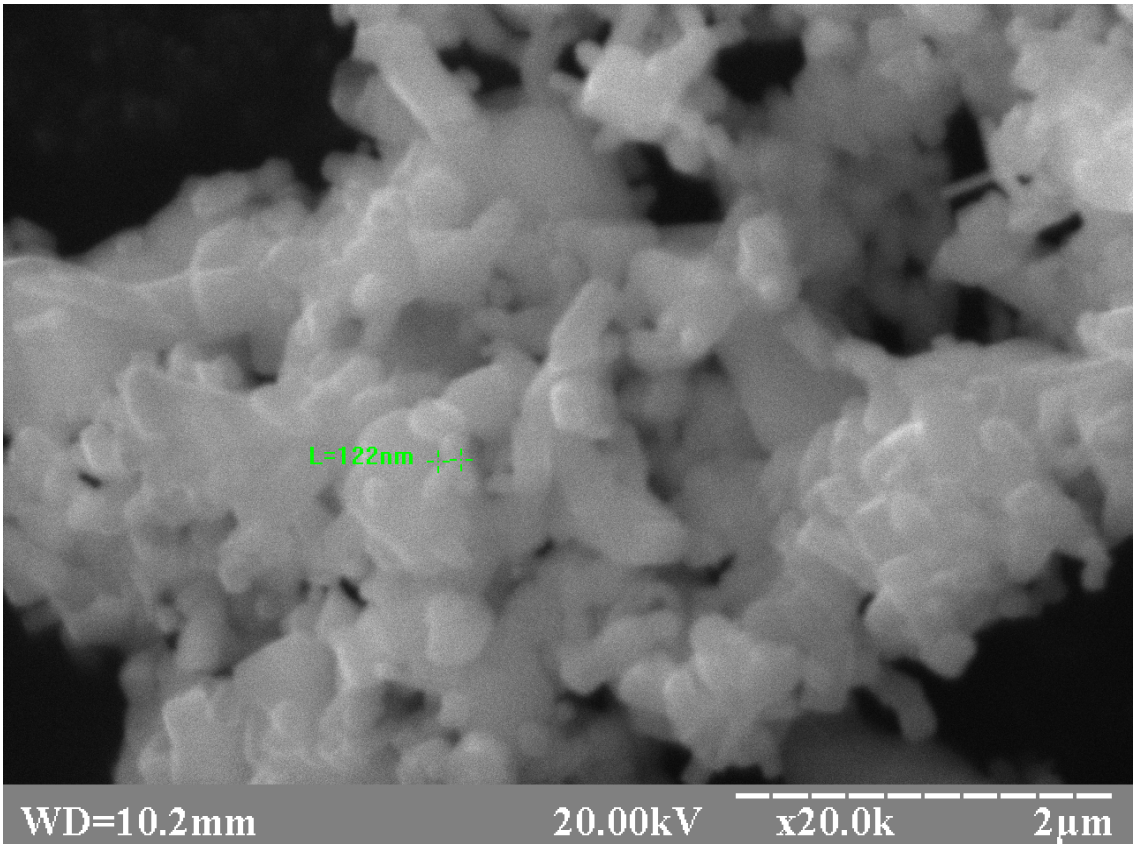


Fig. 1. CEM- micrograph of the "Sigma-Aldrich" Company powders

The temperature-hour reception mode of pressed ceramic material based on ZnO is shown in Fig. 2. The samples in the form of discs with a diameter of 15 mm after machining had a thickness of 1.5 to 2.0 mm. The morphology and the average grain size of powders were studied and the microstructure study of ceramic samples was carried out using an optical POLAM microscope. The obtained ceramic samples of ZnO and ZnMnO were shown in Fig. 3.

The phase analysis and the study of the structure were performed using X-ray diffraction (RD) in the configuration of θ-2θ. The determination of the average grain size of raw (source) zinc oxide powders and X-ray analysis of the elemental composition of pressed samples were performed using a scanning electron microscope-microanalyzer-REM-106Y.

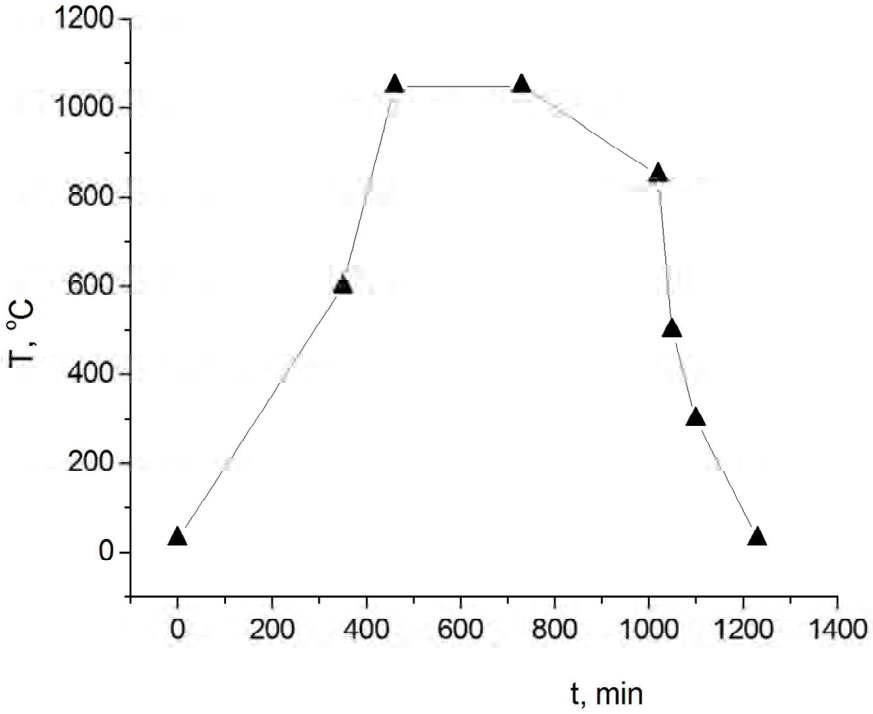


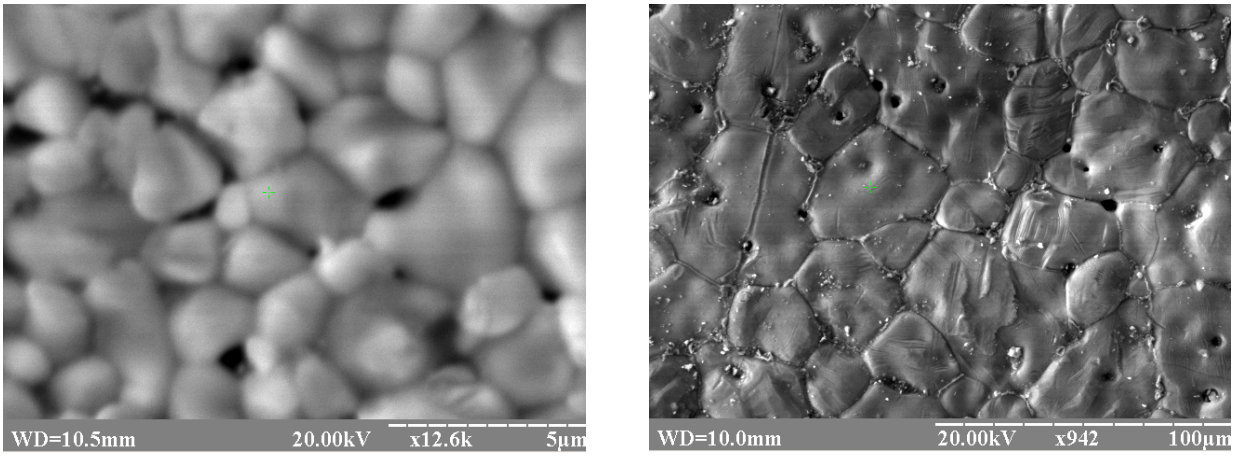
Fig. 2. The temperature-hour mode of the high-temperature annealing of the pressed ceramic materials based on ZnO

a) *b)*

Fig. 3. Ceramic samples of ZnO (*a*) and ZnMnO (*b*)

The resistivity of the samples was measured by two-probe electrometric method using thermocouples of the Keitheley Company. The average grain size of pressed samples was evaluated by analyzing SEM micrographs (Fig. 4). The results are shown in Table. 1. The data confirm the general tendency of increasing the size of crystallites (grains) of pressed powdered materials during long-term high-temperature annealing. The obtained in these conditions ceramic samples have a density of about 98%, this is the reason of their significant light scattering. These data confirm the general tendency of

increasing the size of crystallites (grains) of pressed powdered materials during long-term high-temperature annealing. It is well evident in the case of pure ZnO. The addition of impurities of different materials promotes or inhibits the growth of grains. In case of Mn addition, the formation of the largest grains in the sample matrix is observed.



a) *b)*

Fig. 4. CEM- micrograph of the pressed ZnO (*a*) and $Zn_{0,96}Mn_{0,04}O$ (*b*) samples

Table 1

Grain size of the pressed samples based on ZnO

samples	Grain size, nm
ZnO	775-848 (811)
$Zn_{0,96}Mn_{0,04}O$	$(2\text{-}4)\times10^4$ (30 mkm)

Micromechanical properties of ZnO

One of the methods to control the properties ZnO is its annealing in various environments in particular in oxygen, which leads to increase of hardness and fracture toughness of ceramics. Therefore, the study of micromechanical properties of materials for modern radioelectronics is an important and actual problem, both for improving technologies of quality of final product and the perspective of its practical use.

In measuring of microhardness the load in indenter from 0.1 H to 2.0 H has been used. It was found that the size of prints and their clarity at the load at less than 100 g is not sufficient to determine the microhardness within the limits of acceptable error (3.4%). Therefore, in the future in all samples the load of 150 g has been used. The structure of surface of ZnO sample was fine granular, so basically there were distinct prints of indenter that made it possible to determine the size of the diagonals with the error ~ 3%.

Annealing of the samples was held in an atmosphere of oxygen (Fig. 4) at temperatures 550°C, 700°C and 800°C during 7 hours followed by cooling in the same atmosphere.

At each sample the measuring at least 20 prints of indenter has been hold. The microhardness was determined by formula

$$H_\mu = \frac{P}{F_{\text{ind}}} = 2\frac{P}{d_c^2}\sin\frac{\alpha}{2} = 1{,}854\frac{P}{d_c^2}, \text{ [GPa]} \quad (1)$$

where P is the load on the indenter, *N;* a = 136° is the angle at the top of the diamond pyramid; d – the size of the indentation diagonal, averaged horizontal and vertical, *mm.*

Graphic dependence of microhardness ZnO sample temperature of annealing in an oxygen atmosphere is shown in Fig. 5. As one can see, the maximum strengthening of the samples occurs after annealing at 700°C. We will try explain it.

The Zinc Oxide, which was obtained by the method of ceramic technology, belongs to a class of Non-Stoichiometric compounds. The main type of defects in it there power stoichiometric cation Zn in interstices of crystal lattice. Chemical equilibrium metal-oxygen is rather unstable and disruptes by small external factors that cause changes in the physical properties of the material (conductivity, microhardness, etc.). Concentration of defects in ZnO depends strongly on the temperature, the nature of the gas environment, prior heat treatment and other technological factors.

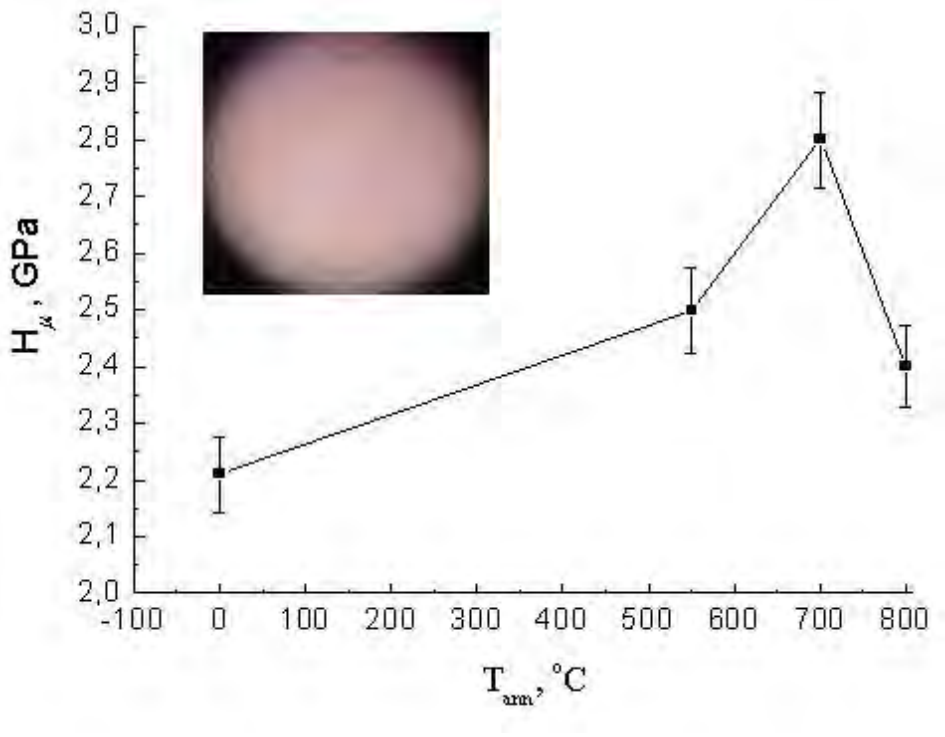


Fig. 5. Dependence on temperature microhardness ZnO arson in an oxygen atmosphere (insert - image of an indent)

After annealing of the samples at temperatures near 300°C in an oxygen atmosphere improvement of crystal lattice ZnO (wurtzite hexagonal lattice type), reduction of of interstitial atoms Zn according to to the equation has been observed:

$$Zn_i^+ + e + \frac{1}{2}O^{2-} \rightarrow ZnO,$$

where *i* is the index of interstitial ions.

During the annealing of the samples at temperatures above 700°C in an oxygen atmosphere the penetration of anions O_2 in ZnO is blocked by the thermal vibrations of the atoms of the crystal lattice of ZnO, and at temperatures near or higher than 800°C there are the sublimation and dissociation processes (formation of ZnO-gas). In such temperatures there is a balance in the gas phase above the crystal $ZnO \Leftrightarrow \frac{1}{2}O_2$.

These sublimation processes determine the reducing of microhardness of samples which were annealed at temperatures 800°C because actually ZnO sublimate from intercrystalline layers primarily –the contact between grains is less strong.

In the second stage of experimental research the microhardness of ZnMnO samples has been determined.

It was found that the additive of manganese leads to an increase in microhardness of ceramics ZnMnO from 2.21 to 2.55 GPa. The next heat treatment in an oxygen atmosphere leads also to a further

increase approximately 3.3 GPa. It should be noted that in this case the temperature of annealing has practically no effect on the value of the microhardness (Fig. 6).

Discussion of the results

This is due to the fact that the introduction of additive MnO to ZnO in small quantities, namely 0,4%, essentially influences on the overall picture of the physical and chemical transformations. It was known that impurity MnO in the molar quantity of about 0.5% dissolves in crystalline lattice MnO. In such correlations in binary system MnO-MnO the solid solutions (base ZnO) have been formed. The distribution of impurity MnO by volume of crystallites is heterogeneous and usually MnO concentration is higher in the intercrystalline region [11]. At annealing of the samples at temperatures lower 500°C in an oxygen atmosphere, the quantity of interstitial cations Zn reduces, similarly as is the case of undoped ZnO, and also MnO diffusion inside the crystallites which causes the improvement of crystal lattice and a is accompanied by increasing of microhardness of material.

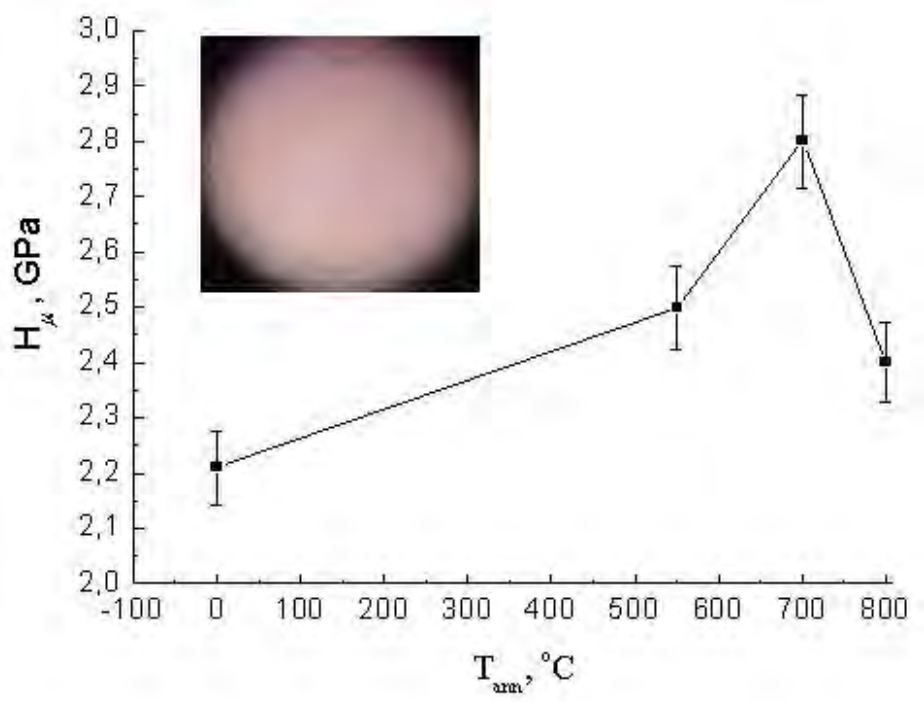


Fig. 6. Dependence on temperature microhardness ZnMnO arson in an oxygen atmosphere (insert - image of an indent)

At annealing of samples at temperatures above 500°C in an oxygen atmosphere, impurity MnO interferes with the passage of sublimation processes in intercrystallite layers (formation of gas phase ZnO), due to the formation of a solid solution ZnO-MnO. The pressure of ZnO vapor is significantly reduced due to the formation of phases with the structure of pyrochlore and spinel. It actually determines the fact that microhardness of samples, which were annealed in oxygen atmosphere at temperatures 500-800°C, virtually unchanged [12].

Conclusions

By the method of solid-phase reactions, which are widely used in ceramic technology, the pressed materials of ZnO were obtained. Using scanning electron microscopy and X-ray microanalysis of the elemental composition, the average size of the grains which forms the pressed materials and their elemental composition was determined. The increasing size of crystallites (grains) of the pressed powdered materials during long-term high-temperature annealing was revealed.

It has been found that annealing ZnO in an oxygen atmosphere leads to a significant increase in their microhardness, whereby the maximum strengthening occurs after annealing at 700°C. Adding manganese leads to an increase in microhardness of ZnMnO ceramics from 2.21 to 2.55 GPa, and subsequent heat treatment in an oxygen atmosphere to its further growth of about 3.3 GPa. In this case, the annealing temperature does not affect the microhardness.

References

[1] Ozgur U., Alivov Ya. I., Liu C., Teke A., Reshchikov M.A., Doğan S., Avrutin V., Cho S.-J., Morkoc H. A comprehensive review of ZnO materials and devices // J. Appl. Phys. – 2005. – Vol. 98. – P. 041301–041310.

[2] Pan F., Song C., Liu X. J., Yang Y. C., Zeng F. Ferromagnetism and possible application in spintronics of transition-metal-doped ZnO films // Materials Science and Engineering. –2008. – R. 62. – P. 1–35.

[3] Dutta Sreetama, Chattopadhyay S., Sarkar A., Chakrabarti Mahuya, Sanyal D., Jana D. Role of defects in tailoring structural, electrical and optical properties of ZnO // Progress in Materials Science. – 2009. – № 54. – P. 89–136.

[4] Cheng H., Xu X. J., Hng H. H., Ma J. Characterization of Al-doped ZnO thermoelectric materials prepared by RF plasma powder processing and hot press sintering // Science Direct. – 2009. – № 35. – P. 3067–3072.

[5] Orton J. W., Powell M. T. The Hall Effect in Polycrystalline and Powdered Semiconductors // Repts. Prog. Phys. –1980. – Vol. 43, № 11. – P. 1263–1307.

[6] Chaari M., Matoussi A., Fakhfakh Z. Structural and Dielectric Properties of Sintering Zinc Oxide Bulk Ceramic // Materials Sciences and Application, 2011, 2, 765–770.

[7] Abdullin Kh. A., Bakranov N. B., Ismailov D. V., Kalkozova J. K., Kumekov S. E., Podrezova L. V., Cicero G. Composite materials based on nanostructured zinc oxide // Semiconductor, 2014, V 48, № 4 487–491.

[8] Pinckney L. R. Transparent glass-ceramics based on ZnO crystals // Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B, 2006, 47 (2), 127–130.

[9] Virt I. S., Hadzaman I. V., Bilyk I. S., Rudyi I. O., Kurilo I. V., Frugynskyi M. S., Potera P. Properties of ZnO and ZnMnO thin films obtained by pulsed laser ablation // Acta Physica Polonica. – 2010. – Vol. 117, № 1. – P. 34–37.

[10] Joint Committee on Powder Diffraction Standards (JCPDS) diffraction data card, published by American Society for Testing and Materials (ASTM).

[11] Tae-Bong Hur, Dae-Hwang Yoo, Gwang Soo Jeen, Yoon-Hwae Hwang and Hyung-Kook Kim_The Efects of Thermal Annealing of ZnO Ceramics // Journal of the Korean Physical Society. – 2003. – Vol. 42. – pp. S1283-S1286.

[12] Electrical characterization of ZnO ceramics by scanning tunneling spectroscopy and beam-induced current in the scanning tunneling microscope / C. Dıaz-Guerra and J. Piquerasa // Journal of applied physics, 1999. – Vol. 86, № 4, 1874–1877.