A.S. FEDOTOV[1], A.V. PASHKEVICH[1], L.A. BLIZNYUK[2], J. KASIUK[3], A.K. FEDOTOV[1], N.A. BASOV[3], I.A. SVITO[1], M. BUDZYŃSKI[4], M. WIERTEŁ[4], P. ŻUKOWSKI[5]

Belarusian State University, Minsk, Belarus (1), Scientific-Practical Materials Research Center of NAS of Belarus, Minsk. Belarus (2), Research Institute for Nuclear Problems of BSU, Minsk, Belarus (3), Department of Mathematics, Physics and Informatics, Maria Curie-Skłodowska University, Lublin, Poland (4), Department of Electrical Devices and High Voltage Technology, Lublin University of Technology, Lublin, Poland (5)

doi:10.15199/48.2018.03.39

Electric properties of composite ZnO-based ceramics doped with Fe

Abstract. *This work is focused on the analysis of phase structure and temperature dependences of electric resistivity $\rho(T)$ in ZnO-based composite ceramics $(ZnO)_{90}(Fe_xO_y)_{10}$, doped with Fe by the addition of 10 wt.% of one of the iron oxides Fe_xO_y.*

Streszczenie. *Praca koncentruje się na analizie struktury fazowej oraz zależności temperaturowych rezystywności elektrycznej $\rho(T)$ kompozytów ceramicznych $(ZnO)_{90}(FexOy)_{10}$ opartych o ZnO, domieszkowanych Fe poprzez dodanie 10% wag. jednego z tlenków żelaza Fe_xO_y.* ***(Własności elektryczne ceramiki kompozytowej na bazie ZnO domieszkowanej Fe)***

Keywords: Electronic transport, electrical properties, ceramics.
Słowa kluczowe: Transport elektronowy, właściwości elektryczne, ceramiki.

Introduction

Nowadays special attention is paid to the search for new ceramic materials based on wide-gap oxides, as well as to the study of their structure and properties for the purpose of their application in various areas of the radioengineering, electronic and optoelectronic industries [1]. Analysis of the literature indicates that single crystals, polycrystalline films, nanostructured powders and wires based on ZnO have been studied in sufficient detail. At the same time, ZnO-based compositions, obtained by ceramic technologies, have not been studied so well. In particular, there is no many research dedicated to the effects of ZnO ceramics doping with magnetic impurities as well as influence synthesis technology and subsequent heat treatments on the chemical and phase compositions (including the magnetic states of phases and also the type of self-defects and complexes formed on their basis, and the mechanisms of electrical conductivity of ceramics.

The aim of this work is to study the structure and electrical properties of ZnO-based ceramics doped with iron using various types of Fe_xO_y doping agents.

Experimental

The conventional ceramic technology was used to obtain the ZnO-based samples .The initial compounds for the preparation of the charge were high-purity powders of ZnO, and Fe_xO_y (FeO, Fe_2O_3, Fe_3O_4) oxides. For preparation of the investigated samples we used the compound $(ZnO)_{90}(Fe_xO_y)_{10}$, where the mass of the Fe_xO_y powders corresponded to 10 wt. %.The initial powders were milled for one hour in agate mortar with the addition of distilled water and then dried at room temperature. After this 3% (by weight) of PVA glue was added to the powder as a binder, then mixture were mixed and compacted into tablets with press. These tablets were subjected to two different heat treatment procedures. In the first case (one-stage synthesis), after the compacting the tablets were annealed in air at 1200°C for 2 hours. In the second case (two-stage synthesis), the tablets were annealed first at 900 °C, than re-milled, mixed with a binder and compacted with press again. Finally, these samples were annealed in air at 1200°C for 2 hours. For both one- and two-stage synthesis procedures the environment pressure was 200 MPa.

Structure and phase compound was analysis of compacted tablets was carried out on the basis of X-ray difraction (XRD) patterns measured with DRON-9 (Russia) and confocal micro-Raman spectrometer Nanofinder Hi-End (LOTIS-TII, Japan-Belarus). Grain structure of samples was studied using scanning electron microscope (SEM) LEO 1488VP Oxford Instruments in secondary electrons regime. Concentrations of chemical elements in sampels were measured using electron-probe X-ray spectral microanalyzer addon for SEM. Mössbauer spectra on the ^{57}Fe isotope were measured in transmission geometry on Janis spectrometer at room temperature using a $^{57}Co/Rh$ source (20 mCi). The electrical resistivity was measured using a 4-contact potentiometric method on rectangular ceramic samples, cut from ZnO tablets, with indium probes in the temperature range 6-300 K using High Field Measurement System (Cryogenic Ltd, London).

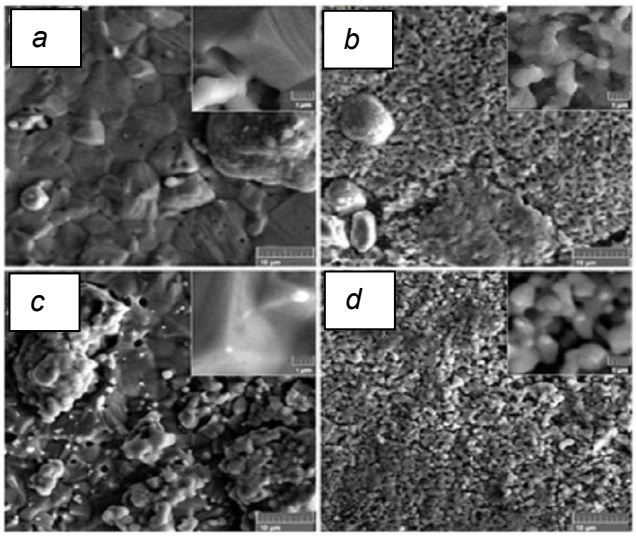

Fig.1. Microstructure of ceramics $(ZnO)_{90}(Fe_xO_y)_{10}$, obtained with one- (a, c) and two-stage (b, d) synthesis using FeO (a, b) and Fe_2O_3 (c, d) oxides as doping agents. The insets in a-d pictures show SEM images with a larger magnification.

Results and Discussion

It is seen in Fig. 1 that in case of 2-stage procedure with preliminary synthesis of ceramics the typical size of grains reduces from micron to the submicron range (while, as can be seen from Fig. 1b, some large particles still occur.), as well as homogenizes the distribution of grain size and composition.

XRD, Raman (see, Fig. 2) and Mössbauer spectroscopy detected at least 3 phases in ceramics: Majority of grains of $Zn_{1-\delta}Fe_{\delta}O$, as the iron enriched (up to 25-30 at.%) microparticles of the $ZnFe_2O_4$ spinel and/or the residual iron oxides used for doping. This is similar to the observed in single crystals and thin films [1-4].

X-ray spectral microanalyzer addon for SEM have shown that the Fe concentration in the crystal lattice of wurtzite phase is $0.66 < \delta < 0.90$ at.%, while an average iron concentration in the samples approached to 1-3 at.%. The XRD showed, the substitution of Zn by Fe atoms which results in compression of the ZnO lattice. This is confirmed by the shift of XRD lines positions 2θ to the lower values of Bragg angles (Fig. 3).

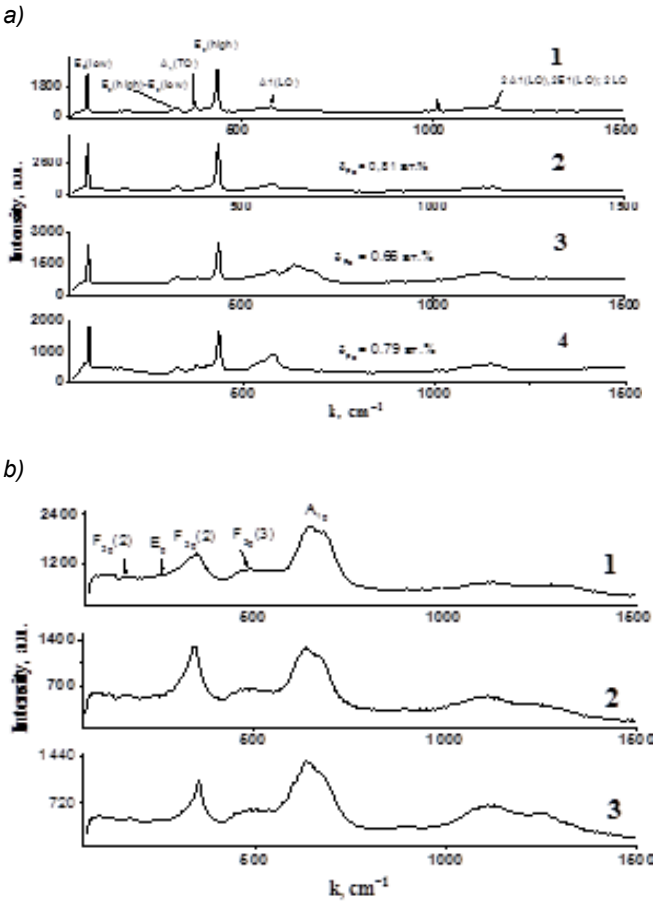

Fig.2. An examples of the Raman spectra of the wurtzite phase in undoped ZnO (1a) and precipitates of the $ZnFe_2O_4$ spinel and the rest oxides (1b-3b) in composite ceramics $(ZnO)_{90}(Fe_xO_y)_{10}$, obtained by the two-stage synthesis method for ZnO (1a), $(ZnO)_{90}(FeO)_{10}$ (2a and 1b), $(ZnO)_{90}(Fe_2O_3)_{10}$, (3a and 2b) and $(ZnO)_{90}(Fe_3O_4)_{10}$ (4a and 3b)

The observed decrease of the lattice parameters is not directly related to Fe doping, since according to [2, 4], the replacement of Zn^{2+} by Fe^{2+} ions should on the contrary expand the wurtzite lattice. We assume that because pf enrichment of ZnO with oxygen (remind that they were synthesized in air), Fe cations and some oxygen anions will replace Zn vacancies, forming Fe-O-based complexes. Probably the compression of the lattice with the loss of electrons during the interaction of Fe ions with oxygen anions, as well as increase of number of oxygen vacancies just lead to the observed compression of the lattice.

The observed temperature dependences of DC resistivity $\rho(T)$ shown in Fig. 4 can be separated into 2 groups. In ceramics obtained by the two-stage synthesis, as well as ceramics with one-stage synthesis, in which the α-Fe_2O_3 and Fe_3O_4 oxides were used for doping, $\rho(T)$ are linearized in Arrhenius scale in the range of 150-300 K. The slopes of the curves $\lg\rho(T)$-$(1/T)$ correspond to the activation energies of the conductivity $\Delta E \approx$ (0.34-0.38) eV, which are much higher than the values (0.25 ± 0.02 eV) mentioned in [2] for polycrystalline $Zn_{1-\delta}Fe_{\delta}O$ films with δ = 0.2 Fe wt.%.

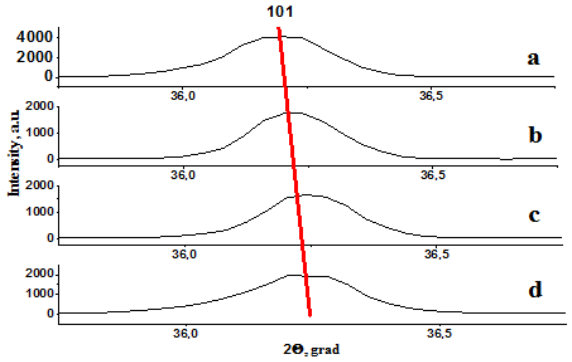

Fig.3. Displacement of the most intense line (101) on the XRD spectra in undoped ZnO and composite ceramics $(ZnO)_{90}(Fe_xO_y)_{10}$, obtained by the two-stage synthesis method: a) ZnO, b) $(ZnO)_{90}(FeO)_{10}$, c) $(ZnO)_{90}(Fe_2O_3)_{10}$, d) $(ZnO)_{90}(Fe_3O_4)_{10}$

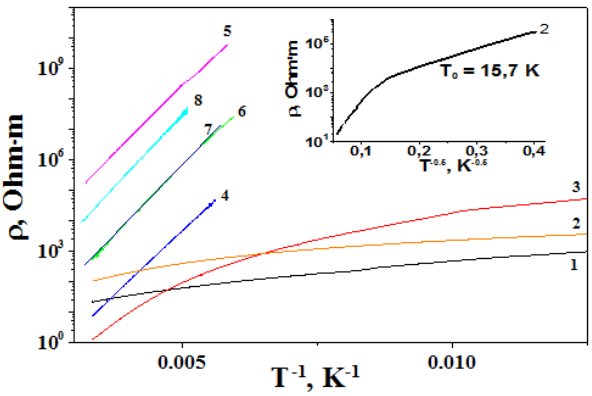

Fig.4. Temperature dependencies of DC resistivity $\rho(T)$ of composite ceramics ZnO (1,2) and $(ZnO)_{90}(Fe_xO_y)_{10}$ (3-8) samples obtained by one- (3-5) and two-stage (6-8) synthesis for FeO (3,6), Fe_2O_3 (4,7) and Fe3O (5.8) doping agents. Insert presents $\rho(T)$ of non-doped ZnO (2) in Arhenius scale.

This indicates the formation of additional deep centers in wurzite structure $Zn_{1-\delta}Fe_{\delta}O$. It is also seen that the values of ρ(300 K) for ceramics obtained by the one-stage synthesis method are always lower than for the case of two-stage procedure. Moreover, lattice parameters a (Fig. 5a) and c (Fig. 5b) of the samples studied at 300 K decrease with the increasing of oxygen concentration in the doping agent while the electrical resistivity ρ(300 K) increase on average for the same samples on the contrary (Fig. 5c).

At the same time, as our experiments have shown, for the same samples obtained by the one-stage synthesis method such a trend does not appear.

The second group of samples related to undoped ZnO and ceramic sample $(ZnO)_{90}(FeO)_{10}$ produced by one-stage regime is characterized by the activation energy dropping with cooling in the range 0.05-0.1 eV. Lower 15 K, we associate such behavior with the Shklovski-Efros mechanism of electron hopping by localized states [5] (presumably interstitial zinc and/or oxygen vacancies with ionization energy of about 0.05 eV [4] and Fe-O-based deep centers). This is confirmed by the linearization of the curves $\rho(T)$ shown in the inset to the Fig. 2 in the Mott

coordinates Lnρ- [(1/T)$^{0.5}$] with the slope T_o = 15.7 K lower 15 K. Such behavior was observed earlier in ZnO single crystals and attributed to hopping by shallow intrinsic defects [5, 6].

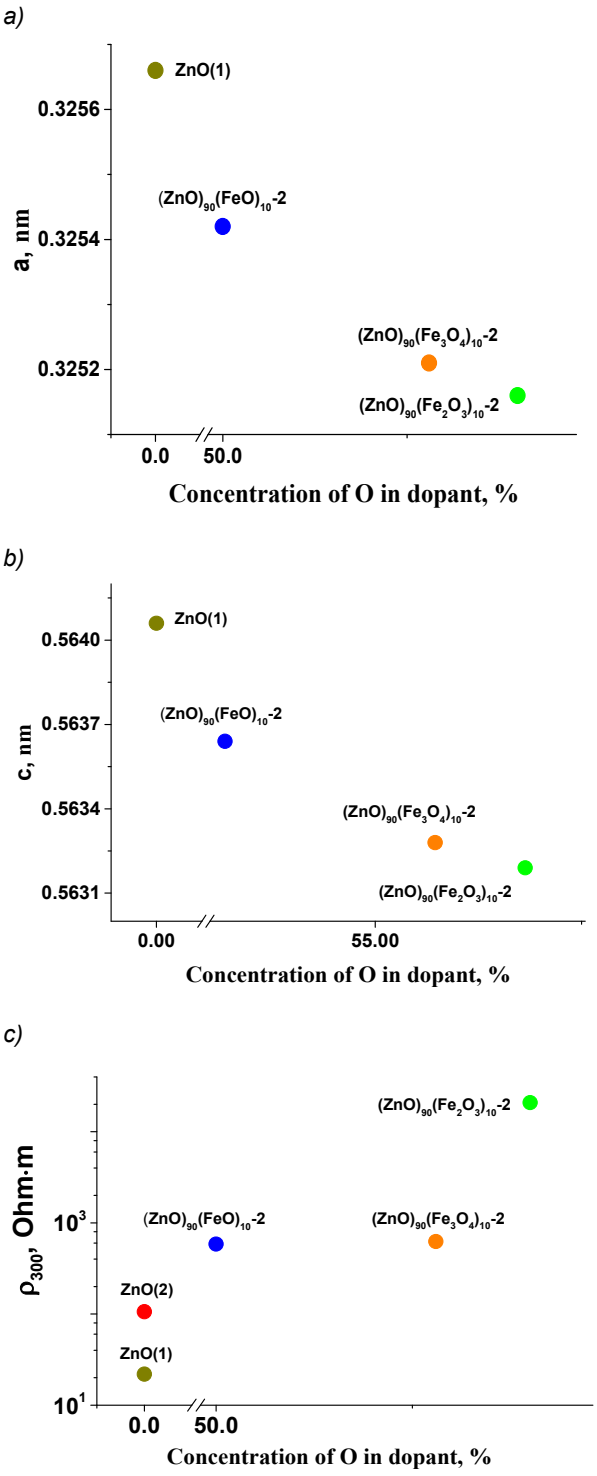

Fig.5. Dependences of lattice parameters *a* (a) and *c* (b) and also ρ(300 K) values (c) on oxygen concentration in the doping agent for samples obtained by the two-stage synthesis method

Above 20 K the course of $\rho(T)$ can be due to the percolation of electrons owing to potential fluctuations created by intrinsic defects of ZnO and impurities (for example, background impurities, like nitrogen from air during synthesis procedure).

Resume

The performed studies show certain connection between the conductivity mechanisms, the type of the used doping agents (iron oxides) and the conditions for the synthesis of ceramics:

1. In iron-doped zinc oxide ceramics obtained by the two-stage synthesis method, the electrical resistivity at 300 K on average increases with increasing oxygen concentration per one formula unit of the doping iron oxide.
2. In the crystal lattice of iron-doped wurzite phase $Zn_{1-\delta}Fe_{\delta}O$ in ceramic samples, deep donor centers are formed with an ionization energy of $\Delta E \approx (0.36 \pm 0.02)$ eV, which can be attributed to the formation of complexes based on iron and oxygen atoms, are formed.
3. In non-doped ZnO ceramics below 15 K, the temperature behavior of the electrical conductivity $\rho(T)$ obeys the Shklovskii-Efros law for hopping conductivity over localized states.

Autorzy: *Aleksander S. Fedotov, A.V. Pashkevich, prof. Aleksander K. Fedotov, Ivan A. Svito, Belarusian State University, 4, Nezavisimosti Av., 220030 Minsk, Belarus, E-mai:lfedotov@bsu.by; L.A. Bliznyuk, Scientific-Practical Materials Research Center of NAS of Belarus, 19,Brovka Str., 220072 Minsk. Belarus; Julia Kasiuk, N.A. Basov, Research Institute for Nuclear Problems of BSU, 11,Bobrujskaya Str., 220030, Minsk, Belarus;*

prof. M. Budzyński, M. Wierteł, Department of Mathematics, Physics and Informatics, Maria Curie-Skłodowska University, 1, Maria Curie-Skłodowska Sq., 20-031 Lublin, Poland; prof. Paweł Żukowski, Department of Electrical Devices and High Voltage Technology, Lublin University of Technology, 38a, Nadbystrzycka Str., 20-618 Lublin, Poland E-mail: p.zhukowski@pollub.pl

REFERENCES

[1] Janotti C.G., de Walle V., Reports on Prog. ff Phys. 72, (2009), 26501-26530

[2] Sawalha A., Abu-Abdeen M., Sedky A., Electrical conductivity study in pure and doped ZnO ceramic system, *Physica B: Condensed Matter*, 404 (2009), n. 8, 1316-1320.

[3] Kasiuk J.V, Bliznyuk L.A., Basov N.A., Fedotov A.S., Svito I.A., Fedotov A.K. Actual Problems of Solid State Physics. Proceedings of the International Scientific Conference, 22-25 November 2016, Minsk, Belarus. «Kovcheg», 2, (2016), 84-86.

[4] Winarski D., Synthesis and characterization of transparent conductive zinc oxide thin films by sol-gel spin coating method, Thesis of master of science, (2015).

[5] Lien C.C., Wu C.Y., Li Z.Q., Lin J.J., Electrical conduction processes in ZnO in a wide temperature range 20-500 K. *Journal of Applied Physics*, 110 (2011), n. 6, 063706-063713.

[6] Shklovskii B.I., Efros A.L., Electronic Properties of Doped Semiconductors, Berlin, Springer, (1984).