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Synthesis and properties of doped ZnO ceramics

Abstract. *In our work, we studied zinc oxide ceramic samples doped with aluminum and gallium. Structure peculiarities of ceramics depending on their synthesis regime were investigated by the SEM, EDX, XRD, and Raman spectroscopy methods. It was demonstrated that at some technological conditions the formation of indesirable phases of zinc aluminate or gallate may occur preventing an uniform material doping and reducing quality of samples. Single-phase ZnO ceramics were produced when the nanostructured alumina powders were used as a dopant source. The correlations between the synthesis regimes of ZnO ceramics and their electrophysical parameters essential for thermoelectric figure-of-merit (electrical conductivity and Seebeck coefficient) have been established. The best electrophysical characteristics were obtained when the nanostructured alumina produced by combustion in isopropyl alcohol was used as a dopant. Conductivity and Seebeck coefficient of such ceramics are equal to* $3\cdot10^3$ *S/m and -0.27 mV/K, respectively, corresponding to the power factor of* $2.2\cdot10^{-4}$ *W/(m·*K^2*).*

Streszczenie. *W naszej pracy zbadaliśmy próbki ceramiki tlenku cynku domieszkowanej aluminium oraz galem. Specyfikę struktury ceramiki zależącą od warunków syntezy zbadano metodami SEM, EDX, XRD oraz spektroskopią Ramana. Zaprezentowano, że dla niektórych warunków technologicznych tworzą się niepożądane fazy glinianu cynku lub galusanu zapobiegając jednolitemu domieszkowaniu materiału oraz zmniejszając jakość próbek. Jednofazowa ceramika ZnO została uzyskana w czasie, gdy nanostrukturalny proszek tlenku aluminium był używany jako źródło domieszki. Określono powiązania pomiędzy warunkami otrzymywania ceramiki ZnO oraz jej elektro-fizycznymi parametrami niezbędnymi do termoelektrycznego współczynnika jakości (przewodnictwo elektryczne oraz współczynnik Seebeck`a). Najlepsze elektrofizyczne charakterystyki otrzymano, gdy używano jako domieszkę nanostrukturalny tlenek aluminium produkowany poprzez spalanie w alkoholu izopropylowym. Przewodność oraz współczynnik Seebeck`a tego typu ceramik wynosi odpowiednio* $3\cdot10^3$ *S/m oraz -0.27 mV/K, co odpowiada współczynnikowi mocy równemu* $2.2\cdot10^{-4}$ *W/(m·*K^2*). (**Synteza i właściwości domieszkowanej ceramiki ZnO**).*

Keywords: ZnO, ceramics, doping, structure, electrical properties.
Słowa kluczowe: ZnO, ceramika, domieszkowanie, struktura, właściwości elektryczne.

1. Introduction

Great attention is paid today to the study of materials suitable for thermoelectric energy conversion. As is known, for efficient thermoelectric conversion it is necessary to use materials with high values of conductivity and Seebeck coefficient as well as low thermal conductivity [1]. Zinc oxide is one of the most promising materials for thermoelectric converters. Its advantages are relative availability of zinc, nontoxicity, resistance to oxidation and, consequently, possibility of use at high temperatures.

Zinc oxide is a wide-gap semiconductor with the bandgap equal to approximately 3.2 eV. For a long period of time it was used mainly for the fabrication of varistors. However, in recent years, the greatest interest in zinc oxide is related to optoelectronics [2 – 4]. Zinc oxide is characterized by relatively high Seebeck coefficient (up to 350 μV/K at high level of doping). However, its use in thermoelectric applications is limited today because of relatively high thermal conductivity as well as technological difficulty of doping. Despite the efforts made by researchers over the last decades, it is still not possible to obtain high-quality heavily doped p-type zinc oxide. Therefore, n-type zinc oxide is used to create the thermoelectric transducers. The most common dopants are such elements as Al, In, Sb, Ga [5 – 8]. In so doing, keeping of acceptable values of thermal conductivity and Seebeck coefficient is also a challenge. The aim of this study is to determine the influence of type of dopant sources on the thermoelectric characteristics of zinc oxide.

2. Experimental

Synthesis of ceramics. A commercial zinc oxide powder consisting of needle-shaped particles with an average length of 0.2-0.5 mm and diameter of 50 μm was used. Nanostructured Al_2O_3 obtained in P.O. Sukhoi State Technical University of Gomel by burning of aluminum nitrate in isopropyl alcohol or saccharose was used for doping of ceramics by aluminium. A commercial Ga_2O_3 powder was used for doping of ZnO ceramics by gallium.

A convenient muffler or a microwave oven with a maximum microwave power of 800 W were used for the synthesis of ceramics. Zinc oxide powder with alumina (gallium oxide) powder were carefully triturated in a porcelain mortar with ethanol. Then the half-dry mixture (moisture of 15-18%) was mixed with a 3% PVA solution and placed in a mold (diameter of 10 mm), where it was subjected to a semi-dry compaction under pressure of 100 MPa. After removal from the mold, the samples were dried in an oven at 60 °C for 0.5 h. The dried cylindrical blanks were heat treated in a muffler. The temp of the temperature growth was 800 °C/h, and the duration of soaking at the maximal temperature of 1200 °C was 3–6 h. The total time of process did not exceed 18 h. A part of the pressed samples were placed into 800 W microwave oven and sintered in a silicon carbide powder bitstone that absorbs microwaves.

Characterization of ceramics. X-ray analysis was carried out with a Rigaku ULTIMA IV diffractometer (Bragg-Brentano geometry, Cu Kα emission, 0.5 deg./min). Scanning electron microscopy (SEM) and Energy-dispersive X-ray (EDX) analysis were realized with a LEO 1455 VP microscope. Raman spectra were measured using a Nanofinder HE confocal spectrometer (Lotis TII, Belarus – Japan) with a 473 nm solid-state laser as an excitation source. Incident optical power was attenuated to a few hundreds of microwatts to minimize a thermal impact on the samples. Back-scattered light without analysis of its polarization was dispersed with a spectral resolution of 3 cm^{-1} and detected with a cooled CCD-matrix.

The resistivity of the samples was determined from their current-voltage characteristics measured using the standard 4-probe method. For measurement of Seebeck effect, the temperature gradient about 10–15 K was created along the sample. ThermoEMF was measured by nanovoltmeter as a function of temperature difference between the “hot” and “cold” sample edges. Seebeck coefficient was calculated by differentiation of the experimental dependence of thermoEMF on the temperature difference on the sample.

3. Results and Discussion

3.1 Structure of undoped ZnO ceramics

Typical heat treatment conditions, as well as results of primary characterization of the aluminum doped zinc oxide ceramics obtained using muffler or microwave oven are presented in Table 1.

Table 1. Characteristics of zinc oxide ceramics obtained at different sintering regimes

Dopant	Bitstone composition	Heat treatment	Density of ceramics, g/cm^3	Notes
Al_2O_3, burning in isopropanol	SiC	Microwave oven, 800 W, 25 min	3.38	Partial sintering
Al_2O_3, burning in isopropanol	No bitstone	Muffler, 1200 °C, 3 h	4.75	Dense
Al_2O_3, burning in isopropanol	No bitstone	Muffler, 1200 °C, 6 h	5.10	High-dense
Al_2O_3, burning in saccharose	No bitstone	Muffler, 1200 °C, 6 h	4.76	Dense

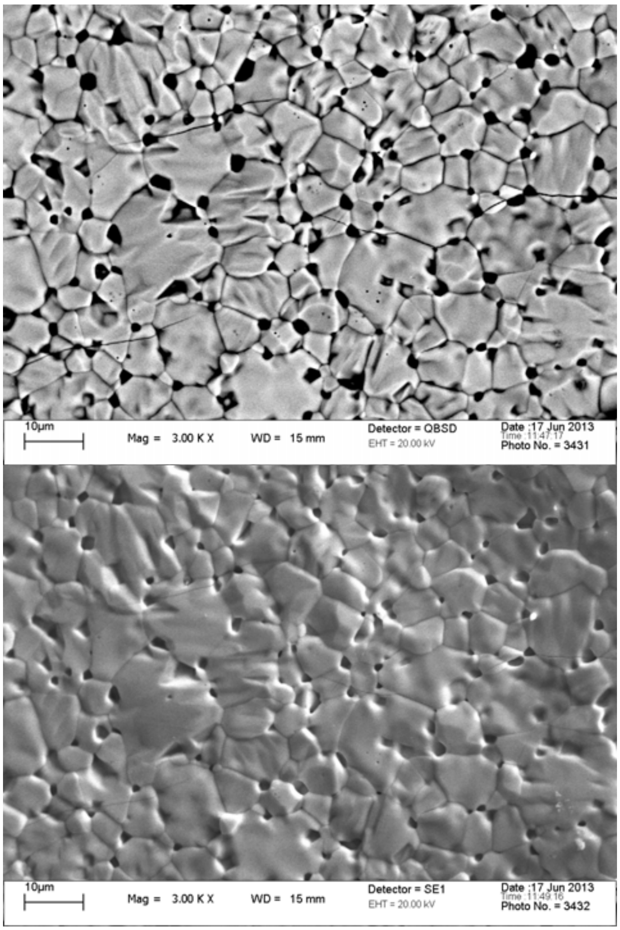

Fig.1. Typical SEM images of undoped ZnO ceramics (on the left – back-scattering electron detection mode; on the right – secondary electron detection mode)

Figure 1 shows typical SEM images for the undoped ZnOceramic. As is seen, the ceramics are formed by grains with the size of a few micrometers. There is practically no contrast within individual grains that indicates a uniform distribution of components therein.The performed EDX analysis showed the absence of any elements other than Zn and O in the undoped ceramics. The concentration of zinc atoms within the framework of experimental error equals to the concentration of oxygen atoms.

Figure 2 demonstrates typical X-ray diffraction pattern and Raman spectrum for undoped ZnO ceramics.

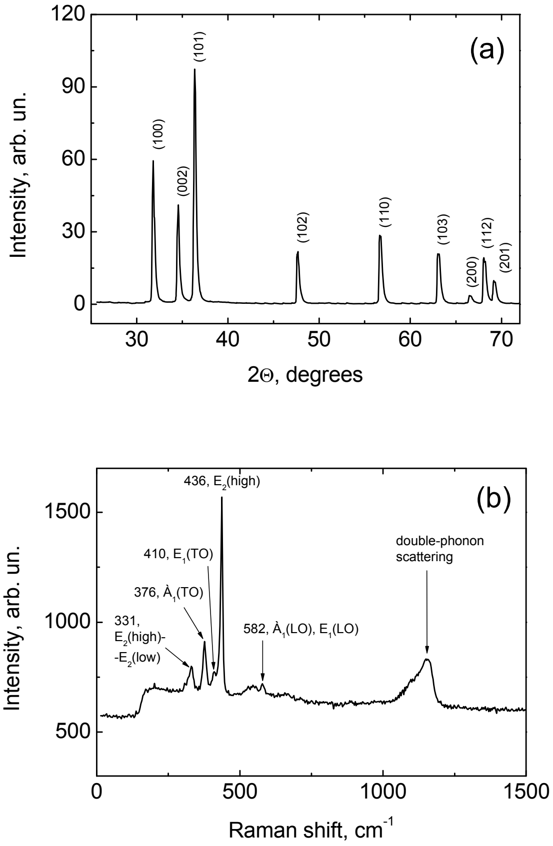

Fig.2.Typical X-ray diffraction pattern (a) and Raman spectrum (b) of undoped ZnO ceramics

Analysis of diffraction patterns has demonstrated that the observed reflexes correspond to (100), (002), (101), (102), (110), (103), (200), (112), and (201) plain families of the hexagonal zinc oxide indicating a phase purity of the synthesized material. The peak intensity ratio points to absence of the dominant texture.

In Raman spectra of undoped ceramics all peaks correspond to scattering on ZnO phonons. The observed small (a few cm^{-1}) difference between Raman peak positions in our experiments and by other researchers [9] can be naturally explained by difference in elastic stresses and local sample temperature during Raman spectra measurement. One-phonon bands in the Raman spectra have a rather small spectral width (about 10 cm^{-1}) indicating a high degree of material quality.

3.2 Structure and electrical properties of doped ZnO ceramics

Figure 3 shows SEM images of aluminum and gallium doped ZnO ceramics. As can be seen, in the case of Al doping (Fig. 3a), along with bright grains of dominant phase with the size of several micrometers, there are dark inclusions of about 10 micrometers. Their darker color in the back-scattered electron detection mode indicates enrichment by lighter elements (Al) being in agreement with EDX results.

As is seen from Fig. 3b, in the gallium doped ceramics there are two types of grains. Along with dominant grains (globules) of approximately spherical shape also the lamellar grains present. The lack of contrast in the back-scattered electron detection mode does not mean composition uniformity since zinc and gallium have close atomic numbers.

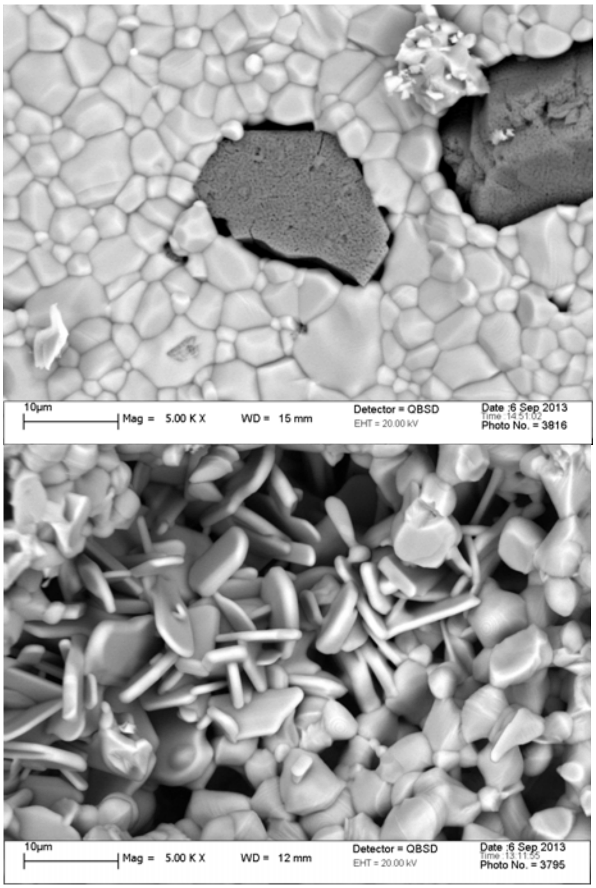

Fig.3. SEM images of Al- (on the left) and Ga-doped (on the right) ZnO ceramics

The possibility of formation of additional phases in the case of aluminum and gallium doping is confirmed by the Raman spectra measured under excitation of dopant-enriched regions (Fig. 4).

Thus, the lack of thorough mixing of the particles of the main phase (ZnO)and dopant source prior to synthesis, as well as not enough temperature and (or) duration of ceramics heat treatment may be reasons for their micro-heterogeneity and ineffective penetration of the impurity atoms into the ZnO lattice.

Measurements of current-voltage characteristics of the synthesized ceramics enabled one to calculate their conductivity. Experiments have shown that for undoped ceramics conductivity is about 10 S/m (Table 2). The efficiency of electrical conductivity elevation by aluminum and gallium doping depends essentially on the method of introducing of impurities. It has been experimentally established that in the case of impurity introduction followed by formation of the aluminum- or gallium-enriched precipitates discussed above, the electrical conductivity is almost unchanged. The best results have been obtained using nanostructured dopant sources. In the case of introduction of aluminum from nanostructured alumina obtained by burning in isopropyl alcohol, the conductivity was about $3{\cdot}10^3$ S/m.

ThermoEMF measurements showed that the Seebeck coefficient independing of the used synthesis regimes is negative and its absolute value is equal to 0.54–0.75 mV/K for the undoped ceramic. Introduction of aluminum and gallium leads to decrease in absolute value of the Seebeck coefficient. For the samples with the highest electrical conductivity the Seebeck coefficient was of 0.26–0.27 mV/K corresponding to the power factor $2.2{\cdot}10^{-4}$ W/(m·K^2).

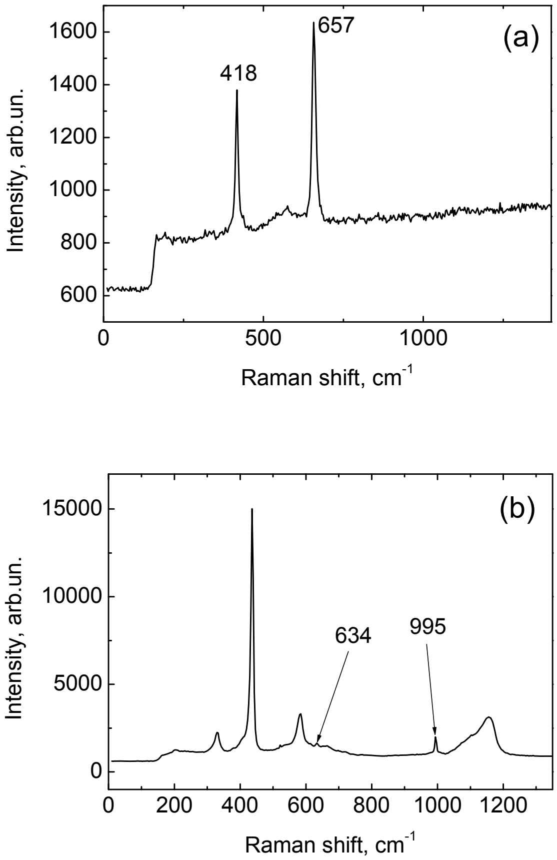

Fig.4. Raman spectra measured under excitation of dopant-enriched regions of Al- (a)and Ga-doped (b) ZnO ceramics

Table 2. Electrical characteristics ofz inc oxide ceramics

Sample	Conductivity [S/m]	Seebeck coefficient [mV/K]	Power factor [W/(m·K^2)]
Undoped	10	-0.54	$2.9{\cdot}10^{-6}$
Al-doped (combustion in isopropyl alcohol)	$3{\cdot}10^3$	-0.27	$2.2{\cdot}10^{-4}$

Conclusions

Structure peculiarities of the aluminium and gallium doped ZnO ceramics were established depending on the synthesis conditions by the Scanning Electron Microscopy, X-ray diffraction, and Raman spectroscopy methods. It is shown that certain technological regimes lead to formation of unwanted phases of zinc aluminate and gallate, which impede an effective doping of ceramics. ZnO single phase ceramics have been prepared using a nanostructured alumina powders as a dopant source. Regularities in influence of the synthesis conditions of ZnO ceramics on their electrical properties determining thermoelectric figure-of-merit (conductivity and Seebeck coefficient) were established. The best electrical characteristics were achieved by using a nanostructured alumina obtained by burning in isopropyl alcohol as a dopant source. The resistivity and Seebeck coefficient of such ceramics are respectively equal to $3.3{\cdot}10^{-4}$ Ohm·m and -0.27 mV/K corresponding to the power factor of $2.2{\cdot}10^{-4}$ W/(m·K^2).

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