

Creating a composite material ZnO-Bi₂O₃ with a core-shell structure for varistor ceramics

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Abstract. This paper discusses use of the plasma dynamic synthesis to obtain ZnO-Bi₂O₃ composite powder. This method allows to get the main ZnO material with the formation of core-shell particles. Sintering of ceramics from this material was carried out using spark plasma sintering facility. Use of this sintering method provides obtaining a fine-grained structure of ZnO (average grain size of 1.3 μm). Comparison of the current-voltage characteristics of ceramics from commercial and plasma dynamic materials showed promise of using a ZnO- Bi₂O₃ composite with a core-shell structure.

1. Introduction

The increased reliability demands for power lines, need to increase the nominal voltage and to reduce the insulation level require to limit of lightning and switching overvoltages. High characteristics of surge protection are achieved by special resistors with high non-linear current-voltage characteristics (CVC) - varistors. Non-linear surge arresters are protection devices based on such components. The main material for creating the varistor is zinc oxide ZnO, which has semiconductor properties, and the percentage of which varies from 65% to 98% [1]. In addition to the main component, ZnO-based varistors use impurities from various metal oxides, such as, bismuth (III), antimony, yttrium, zirconium, cobalt, manganese, lead, and aluminum oxides [1-3], the addition of which characterizes the change and improvement of varistor characteristics.

Currently, there are various technologies for producing nanostructured zinc oxide: thermal decomposition of acetate, sol-gel method, chemical and hydrothermal synthesis [4-6]. Typically, these methods are complex with several steps and resulting product has difficult to remove impurity compounds, which is a negative factor.

This paper shows the possibility of obtaining the material of the ZnO-Bi₂O₃ system with a core-shell structure in a single process of the plasma dynamic synthesis. Using this method allows you to evenly distribute bismuth oxide in the synthesized material, where the main phase is zinc oxide. Volumetric ceramic samples with a microstructure typical of classical varistors based on materials of the Zn-Bi-O system were prepared from the obtained material, and their electrical characteristics were studied.

2. Methodology and experiments

The synthesis of ZnO-Bi₂O₃ composite material with a core-shell structure is performed in a system based on the use of a high-current pulsed coaxial magnetoplasma accelerator with zinc electrodes (Figure 1) [7]. The accelerator receives pulsed power from a capacitive energy storage device with a charging voltage of up to $U_{\text{charge}}=5$ kV and a total capacity of $C=28.8$ mF. At the beginning the central electrode (1) and the surface of the accelerating channel (2) are connected by a conducting jumper. A



carbon spray was applied to the surface of the channel (where plasma structure is formed) to use as a jumper. To obtain the composite material of the Zn-Bi-O system in one short cycle of the accelerator work, bismuth (99%) is additionally injected into the channel. When the keys K are closed (Figure 1), a breakdown of the interelectrode gap occurs in the plasma structure formation channel with the appearing of an arc discharge. A high-current arc discharge ensures the electroerosive production of zinc material from the surface of the accelerated channel. A supersonic plasma jet (9) containing zinc and bismuth is carried out from the accelerating channel into the space of the working reactor chamber. For the metal oxides synthesis, the reactor chamber is preliminarily filled with oxygen, and when the material is sprayed from the boundary of the plasma jet, a plasma-chemical reaction occurs between zinc, bismuth and oxygen with the formation of metal oxide phases [7-8]. The whole process takes about 1 ms. At the end of the plasma-chemical reaction material in the suspended state settles onto the walls of the reactor chamber and a finely divided product fraction can be collected.

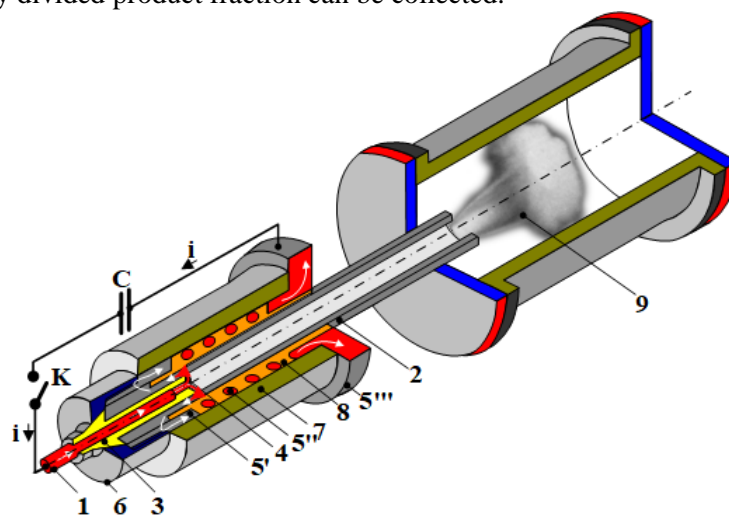


Figure 1. The scheme of the coaxial magnetoplasma accelerator: 1 – central electrode, 2 – electrode-barrel, 3 – central electrode insulator, 4 – Z-pinch, 5 – inductor (5' – contact cylinder, 5'' – solenoid, 5''' – contact flange), 6 – cap, 7 – case, 8 – insulation, 9 – plasma structure.

Experimental studies to get ultradispersed bulk samples of a powdery product were performed using the spark plasma sintering method at the GT Advanced Technologies installation (model 10-4 SPS). For comparative analysis, bulk materials were obtained for two types of products: 1 - the obtained product by the plasma dynamic method of the Zn-Bi-O system, 2 - a mixture of commercial powders of zinc oxide ZnO and bismuth oxide Bi₂O₃ in a ratio of 95%: 5%, respectively. The sintering process of the samples was carried out in vacuum in a graphite mold with a diameter of 12.7 mm with graphite punches under a pressure of 60 MPa and at a sintering temperature of T=1200 °C.

The obtained powdery material and ceramic samples were studied by X-ray diffractometry (Shimadzu XRD 7000S) with a copper cathode (CuK α_1 radiation, $\lambda_1=1.540598$ Å), without additional thermal or other treatments. X-ray structural phase analysis was performed using PowderCell 2.4 software and the PDF4 + structural database. The size and morphology of the materials were studied using scanning electron microscopy (Hitachi TM3000). High resolution transmission electron microscopy was performed on a JEOL JEM 2100F microscope.

3. Results and conclusions

Figure 2 presents X-ray diffraction patterns of the synthesized material (a), structural models of the allegedly formed materials of zinc oxide ZnO and bismuth oxide Bi₂O₃ (c, d), X-ray diffraction patterns of commercial zinc and bismuth oxides (b). It was found that the main crystalline phase of the material obtained by the plasma dynamic synthesis is zinc oxide ZnO, which is closest to the structural model PDF:00-036-1451 of hexagonal syngony with space group SG: P63mc. Also, the bismuth oxide phase

Bi_2O_3 , which is closest to the tetragonal structural model PDF 73-6885 with the space group SG: P-42/c, is present in the XRD patterns. The XRD picture of commercial products (b) confirms that they fully correspond to the declared phase composition - zinc oxide (blue, open circle) and bismuth oxide (red, open circle).

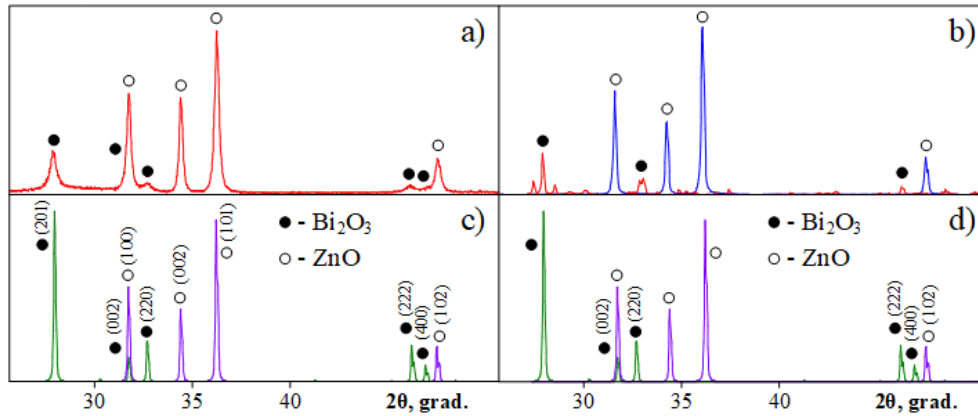


Figure 2. a) Diffractogram of the obtained powdery product of the plasma dynamic synthesis; b, d) Material cards from the PDF4+ database; c) Diffractogram of commercial sample.

The content of crystalline ZnO in the plasma dynamic synthesis product is about 95.0 % with an average size of coherent distance regions (CDR) of 184 nm and a degree of internal microdistortion of the structure $\Delta d/d \approx 3,5 \cdot 10^{-4}$, while Bi_2O_3 is about 5.0 % with an average size of $\text{CDR} \approx 43$ nm and $\Delta d/d \approx 2,5 \cdot 10^{-3}$. It should be noted that the main advantage of the plasma dynamic method is the absence of residual phases of pure bismuth and zinc metals in the synthesized product, also the synthesis of phases of ternary systems of Zn, O, Bi elements.

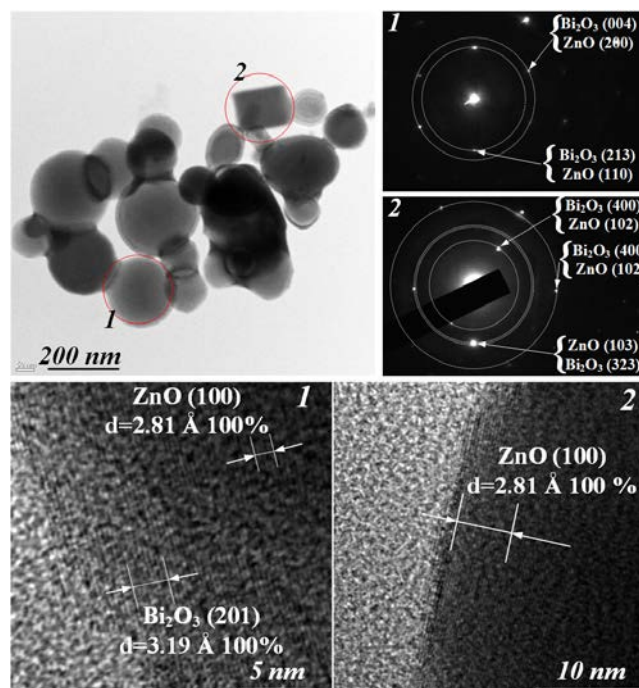


Figure 3. HRTEM images of synthesized material.

HRTEM images of the synthesized product in a coaxial magnetoplasma accelerator were obtained using a high-resolution transmission microscope (Figure 3). The rounded particle 1 of a characteristic shape for most particles of the obtained material and about 200 nm in size is close to spherical. In the

diffraction pattern (nanoSAED nanodiffraction) obtained from this particle, reflections related to reflections of phase planes of both zinc oxide ZnO and bismuth oxide Bi₂O₃ are identified. A similar result was obtained by the indexation of reflections on nanoSAED-2 on a geometrically regular crystal 2, which, as noted earlier in [7–8], corresponds to a single crystal of pure hexagonal zinc oxide.

The average interplanar spacing of object 1 is distinguished by two specific values $d=2.81 \text{ \AA}$ and $d=3.19 \text{ \AA}$, which most closely belong to the phases of zinc oxide ZnO (100) and bismuth oxide Bi₂O₃ (201). Moreover, it is worth noting that Bi₂O₃ is identified only in the shell of particle 1. Thus, the result of indexing reflections showed that reflections can correspond to two phases, which indicates the core-shell structure of the synthesized by the plasma dynamic method ZnO-Bi₂O₃ material. On a more regular geometric particle 2 (rectangular), two phases (ZnO and Bi₂O₃) are also determined by nanoSAED, however, a certain interplanar spacing on this particle defines it only as zinc oxide ZnO. Based on the above, it is worth noting that the most correct geometric particles refer only to the phase of zinc oxide, while rounded ones have a ZnO core with a Bi₂O₃ shell.

Figure 4 shows SEM images of chips and thin sections of circular surfaces of samples of composite zinc oxide ceramics made of the ZnO-Bi₂O₃ material with core-shell structure synthesized obtained by the plasma dynamic synthesis, in comparison with ceramics obtained from commercial ZnO and Bi₂O₃ powders. A comparison of the sample's microstructure undoubtedly shows that the use of ultradisperse composite plasma dynamic ZnO-Bi₂O₃ powders makes it possible to get a more uniform desired microstructure in the form of ZnO grains in a matrix of a denser Bi₂O₃-based material without additional mixing (Figure 4 b). This structure is due to the implementation of the direct plasma dynamic synthesis process, where the obtained powders have a specific distinguishing feature, namely, that the powder particles consist of zinc oxide grains in a bismuth oxide shell. This structure of the particles of the composite powder eliminates the need for mixing the powder to uniformly distribute the small-mass additives. During sintering under pressure, the shells of fusible bismuth oxide in a liquid state are combined to form a matrix that consolidates ZnO grains with the subsequent formation of zinc oxide ceramics. Composite ceramics made from commercial powders have larger grain sizes compared to a sample sintered from a synthesized product, although the sintering regime for the two samples was the same. It was noted in [7] that this fact worsens the characteristics of bulk samples.

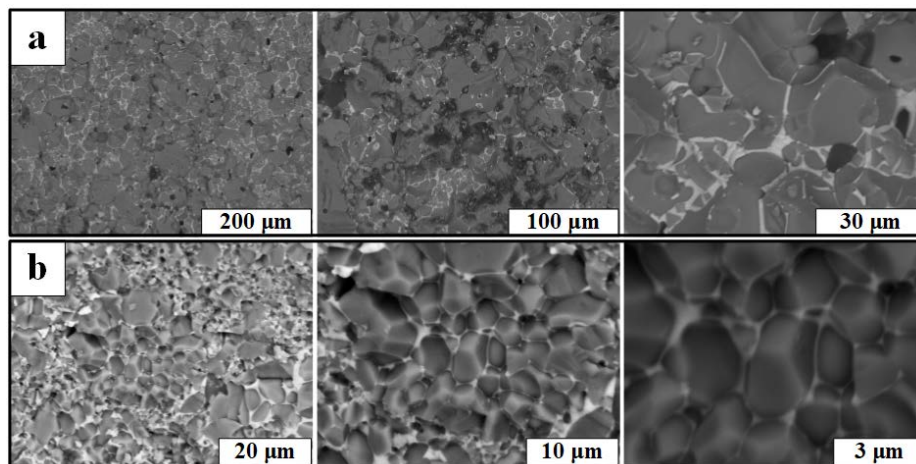


Figure 4. SEM images of commercial sample (a) and synthesized material (b).

Figure 5 shows the nonlinear current-voltage characteristics of the obtained samples from commercial powders (a) and a dispersed PDS product with a core-shell structure (b). Since spark plasma sintering allows one to limit grain growth during sintering, this, together with one of the advantages of PDS, namely, the small size of the obtained crystallites, affects the final size of the average grain size of zinc oxide in the resulting ceramic. This in turn determines the breakdown voltage value, which, when using products with a core-shell structure, is much higher compared to a sample obtained from commercial powders. There is also an increase in the coefficient of nonlinearity to 4.6.

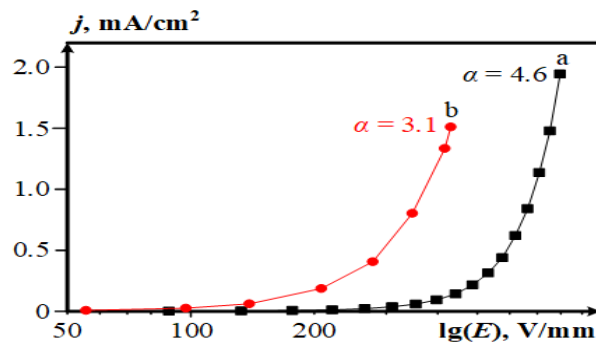


Figure 5. Current-voltage characteristics of the plasma dynamic synthesis sample (a) and commercial sample (b).

A comparison of the obtained values of the nonlinearity coefficients with the known data shows that they are small. Nevertheless, they can be significantly increased by introducing additional oxides into the discharge plasma of a coaxial magnetoplasma accelerator. And in a single short-term operation cycle (1 ms) to obtain the required phase composition for use as a material for varistors without any extra processing. The noted method of the plasma dynamic synthesis seems quite promising for the creation of composite products with a core-shell structure, since it allows uniform distribution of the components throughout the volume of the original powder mixture in much shorter time intervals. A positive effect from the implementation of such a method of product activation is observed on the corresponding current-voltage characteristics.

4. Conclusion

The paper shows the fundamental possibility of obtaining ultradispersed ZnO-Bi₂O₃ composite materials with a core-shell structure in a single short-term process of the plasma dynamic synthesis. The use of such a powder composite with a core-shell structure positively affects the structure of ceramics obtained by spark plasma sintering. It is characterized by a fine-grained structure of zinc oxide (average grain size of 1.3 μm) with bismuth oxide uniformly filling intergranular space. The study of the current-voltage characteristics in comparison with other ceramic samples (from a commercial product) showed the promise of using the plasma dynamic synthesis to obtain the raw composite materials as the basis for varistors. Improving the electrical properties of the obtained ceramics is possible due to the direct introduction of other oxide additives into the process of the plasma dynamic synthesis.

Acknowledgments

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