Effect of bismuth oxide dispersivity on the dielectric properties of zinc oxide ceramics

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The dielectrics properties and microstructure of fractured surfaces of ZnO electroceramics samples with different Bi2O3 dispersivity was studied. It is shown that the change of dispersion leads to an insignificant change in the grain structure, but has no effect on character of the dispersion of the permittivity ZnO ceramic.

1. Introduction
Ceramics on the base of zinc oxide (ZnO) is of great practical use in protective facilities for power engineering [1, 2]. There exist a number of theories explaining the mechanism of conductivity in ZnO varistors [1]. At the present time it is recognized that nonlinearity in ZnO varistors is conditioned by intergrain boundaries characterized by a barrier in the depleted layers of adjacent grains for maul charge carriers (electrons). It is believed that the most feasible model of the intergrain boundary is that of double Schottky barrier. As this takes place the negative surface charge at the grain boundary (electron trap) compensates the positive charge in the depleted layer at both sides of the boundary surface. Thereby the properties of zinc-oxide ceramics are substantially affected by the quality of raw materials, composition and component ratio as well as preparation technology. According to literature [3, 4], the concentration of additives are introduced into the ZnO ceramics could effect on the grain growth of zinc oxide.

We have studied ceramics produced by JSC "Plant energoaschitnyh devices". In addition to ZnO in the burden included the following oxides: Bi2O3, Sb2O3, Cr2O3, MnO2, Co3O4, SiO2. Bismuth oxide (Bi2O3) is an important additive necessary for the production of ZnO varistors. Another is the Sb2O3, which affects the structural features and the grain size of ZnO ceramics [5, 6]. Hereupon it is of interest to compare the properties of zinc-oxide ceramics prepared using bismuth oxide of different dispersivity in the charge.

In the present work we researched the effect of Bi2O3 dispersivity on the structure and dielectric properties of zinc oxide ceramics. A study was made of the samples prepared with the aid of Bi2O3 of usual dispersivity (particle size 3…10) and highly disperse one (particle size < 1 μm). The structure and element composition were studied by the methods of scanning electron microscopy (SEM) (JEOL 6510LV) by inspection of the topography and energy-dispersive analysis (EDA) of the sample cross sections.

2. Results and discussion
The distinctions due to different Bi2O3 dispersivity are clearly revealed by the images of lateral cleavages of ZnO ceramics obtained in the regime of back scattered electrons (BEC) (Fig. 1), thus indicative of the variations in the element composition. In samples with high-disperse Bi2O3 the interlayer enters the ceramics by large portions (Fig. 1b), while in samples with usual additive the...
interlayer distributes in the material in a more uniform way and contains inclusions of main zinc oxide (Fig. 1a).

Table 1 and 2 presents the element composition of both types of ceramics. The results are given in weight percent. The spectra were measured for the regions marked in Fig. 1. It is seen that the main grains contain only zinc oxide, while all other oxides of the charge are concentrated in the interlayer between grains.

![Figure 1. Lateral cleavage images ZnO ceramics for ordinary (a) and finely dispersed Bi$_2$O$_3$ (b). Scale mark length 30 µm](image)

Table 1. The element composition (in weight %) of ordinary dispersed Bi$_2$O$_3$.

| Spectrum | O  | Si | Cr | Mn | Co | Zn  | Sb | Bi | Total  |
|----------|----|----|----|----|----|-----|----|----|--------|
| 2        | 21.66 | 78.34 | 100.00 |
| 3        | 21.95 | 78.05 | 100.00 |
| 4        | 11.10 | 0.71 | 13.68 | 4.22 | 70.30 | 100.00 |
| 5        | 21.14 | 0.77 | 0.68 | 20.84 | 5.68 | 50.89 | 100.00 |
| 6        | 21.21 | 1.20 | 20.24 | 9.47 | 47.87 | 100.00 |
| 7        | 21.35 | 78.65 | 100.00 |
| 9        | 24.62 | 71.67 | 3.71 | 100.00 |
| 10       | 25.53 | 0.27 | 1.47 | 0.65 | 2.94 | 55.82 | 13.33 | 100.00 |
| 11       | 13.83 | 5.17 | 5.71 | 1.12 | 28.98 | 19.57 | 25.61 | 100.00 |

Spectra: 2, 3, 7 – grains, 4, 5, 6, 9, 10, 11 – layer between the grains.

Table 2. The element composition (in weight %) of finely dispersed Bi$_2$O$_3$.

| Spectrum | O  | Si | Cr | Co | Zn  | Sb | Bi | Total  |
|----------|----|----|----|----|-----|----|----|--------|
| 1        | 20.32 | 1.25 | 78.43 | 100.00 |
| 2        | 20.75 | 79.25 | 100.00 |
| 3        | 22.45 | 77.55 | 100.00 |
| 4        | 12.93 | 0.50 | 3.60 | 82.97 | 100.00 |
| 5        | 13.14 | 0.64 | 41.05 | 45.17 | 100.00 |
| 6        | 15.71 | 1.02 | 7.04 | 76.23 | 100.00 |
| 7        | 19.51 | 66.37 | 14.12 | 100.00 |
| 8        | 21.95 | 0.37 | 1.64 | 2.78 | 29.56 | 14.79 | 28.92 | 100.00 |
| 9        | 16.25 | 0.43 | 66.87 | 4.96 | 11.49 | 100.00 |

Spectra: 1, 2, 3 – grains, 4, 5, 6, 7, 8, 9 – layer between the grains.
In spite of the decrease of both dielectric permittivity and dielectric loss tangent values which are observed when finely dispersed Bi$_2$O$_3$ is used for the preparation of the samples instead of standard ingredient, the shape of the corresponding frequency dependences remains unchanged (Fig. 2). Two regions having different behaviour of the complex dielectric permittivity may be distinguished at the dispersion diagrams $\varepsilon''(\varepsilon')$ (Fig. 3). It means that there are two different relaxation processes: one dominate in low-frequency part of the spectra and one – in high frequency part of the spectra [7, 8]. The frequency of $\sim 8$ kHz corresponding to the change of the dispersion type is independent of the Bi$_2$O$_3$ dispersivity. In the low frequency region a linear dependence of the imaginary component on the real part of dielectric permittivity is observed, while in the high frequency region this dependence may be approximated by a circular arc. On the graph of the dielectric loss frequency dependence this region corresponds to the smeared maximum (Fig. 2). This type of dielectric response is described by the Cole-Cole theory [7]. It means that there is a strongly pronounced relaxation process with set of relaxation times. It is usually caused by dipole relaxation [8]. The most probable relaxation time is defined by the condition $\tau_0 = 1/\omega_{\text{max}}$, where $\omega_{\text{max}} = 2\pi f_{\text{max}}$. $f_{\text{max}}$ is shown on Fig. 3 (it equal to 100 kHz). It is independent of the Bi$_2$O$_3$ dispersivity. Therefore the most probable relaxation time is $1.6\cdot 10^{-6}$ s for ceramics of both dispersivity.

![Figure 2](image2.png)

**Figure 2.** Permittivity (a) and dielectric loss tangent (b) of ZnO ceramics. Ordinary (curve 1) and finely dispersed (curve 2) Bi$_2$O$_3$.

![Figure 3](image3.png)

**Figure 3.** Dielectric permittivity dispersion diagrams for ordinary (a) and finely dispersed Bi$_2$O$_3$ (b)

**Conclusion**

The results of the present study show that the grains of zinc-oxide ceramics are composed of zinc oxide while other oxides from the charge are concentrated in the grain interlayer. The existing structural differences have an influence on the dielectric permittivity magnitudes and do not change the character of the dispersivity. The observed behaviour of the dielectric response is indicative of two mechanisms of dispersion. With the increase of the measurement frequency one mechanism is replaced by another.

According to Jonscher [7, 8] the experimental dielectric responses can be distinguished into two
cases. The first one is characterized by a maximum on the $\varepsilon''(f)$ (or $\tan\delta(f)$) dependences, while it is absent in the second case. According to our experiments both types of dielectric response behaviour are realized in the studied ZnO ceramics. Former occurs for the high frequency region, which relates to dipole relaxation. Another takes place for the low frequency regions. The linear dependence $\varepsilon''(\varepsilon')$, occurring for ZnO ceramics at low frequencies, usually associated with pass-through conductivity [7]. We did not find the relation between dielectric response and Bi$_2$O$_3$ dispersivity.

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