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PRODUCTION OF FUNCTIONAL FILM COATINGS BASED ON BISMUTH FERRITE AND ITS SOLID SOLUTIONS

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The relevance of the work is due to the development of new ceramic ferroelectric materials based on modified bismuth ferrite and its solid solutions for nanocomposites, as well as functional coatings on microporous substrates using various dispersion media that are of interest for the manufacture of integrated executive elements of instruments and automation devices [1, 2].

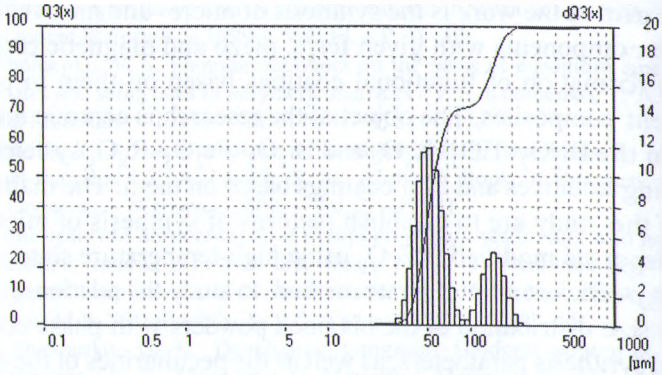
The aim of the work is the synthesis of micro- and nanocrystalline ceramic components with given ferro, piezo and magnetic properties and the formation of functional coatings based on them to produce intelligent composites. The object of the research is ceramic materials based on the Bi_2O_3–TiO_2–R_xO_y and Bi_2O_3–Fe_2O_3–R_xO_y systems using modifying additives and film coatings based on them. The main objectives of the study are to establish patterns of synthesis of micro- and nano-dispersed modified $BiFeO_3$ using high-temperature sintering and an energy-efficient nitrate-citrate method, to study the relationship of the particle size distribution of the obtained powders with phase composition and synthesis parameters, as well as the peculiarities of the process of filling nanostructures with a ceramic substance in various ways.

As mentioned earlier [3–5], the modified $BiFeO_3$, obtained by chemical nitrate – citrate synthesis, has a particle size of the micro and nano-dispersed range (10^{-7}–10^{-8}m). However, due to the high adsorption forces, the particles are grouped into more or less strong aggregates (up to 50–100 μm), which may complicate the preparation of thin films from synthesized materials and the filling of microporous structures.

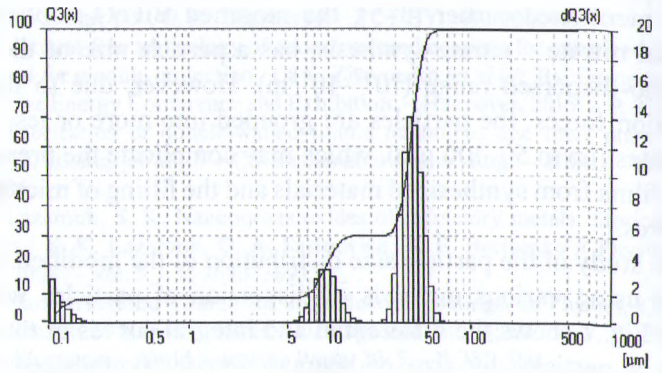
The study of the particle size distribution of the modified $BiFeO_3$ powder using various methods of dispersion of particles was presented. Fig. 1 shows the differential and integral curves of the distribution of particles by size of bismuth ferrite, synthesized by the nitrate-citrate method. Primary dispersion of the obtained cake was carried out by rolling with a roller with alternate mixing of the rolled mass and repeating the procedure of rolling to obtain a powder of uniform color.

As can be seen from Fig. 1, the synthesized aggregates have sizes from 30 to 250 μm. Calcination results in the disintegration of aggregates and the release of particles in the nanodispersed range (less than 0.15 μm): the maximum particle size is significantly reduced (less than 150 μm), and the aggregates are represented mainly by three fractions.

Grinding in an agate mortar leads to a change in the differential distribution curve and an increase in the number of particles ranging in size from 10 to 50 μm. The dispersion of aggregates in a planetary


Q3(x)
dQ3(x)
100
90
80
70
60
50
40
30
20
10
0
20
18
16
14
12
10
8
6
4
2
0
0.1
0.5
1
5
10
50
100
500
1000
[µm]

a


Q3(x)
dQ3(x)
100
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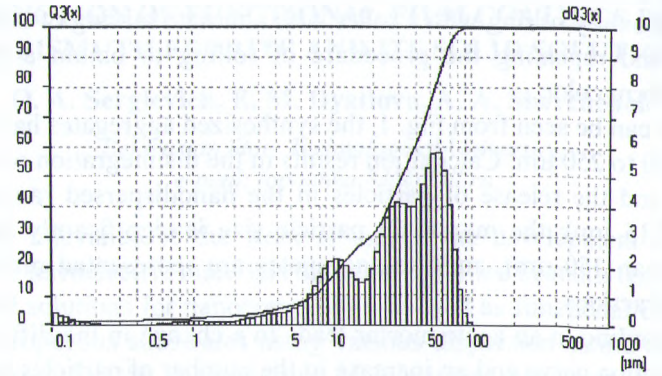
b


Q3(x)
dQ3(x)
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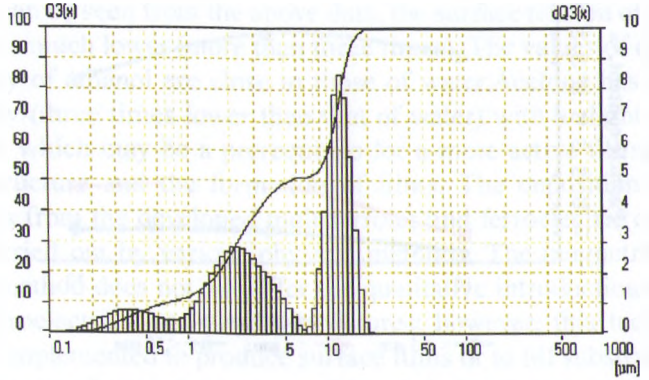
[µm]

c



d

Fig. 1. Differential and integral curves of particle size distribution of synthesized $BiFeO_3$ (*a*), calcined (*b*), with primary dispersion and trituration in an agate mortar (*c*), calcined and ground in a planetary mill (*d*)

mill is more efficient: the maximum size does not exceed about 10 microns with a content of over 50 % and particles of the nano-dispersed range with a size of less than 5.5 microns in an amount of 7.5 %.

Fig. 2 shows the dependences of particles less than the nominal size (<0.5 μm; <1μm; <10 μm) in the $BiFeO_3$ powder as a function of the grinding time.

As can be seen from the data presented in Fig. 2, the number of fine fractions increases with increasing grinding time, especially from 10 to 20 minutes, then the changes are less significant. The study showed that an increase in the grinding time causes the aggregation of $BiFeO_3$ particles, regardless of the method of its synthesis. However, using the nitrate-citrate method produces finer fractions of $BiFeO_3$ up to nanoscale particles, so it can be used to fill porous structures with pores exceeding the particle size.

A study was conducted on the possibility of filling nanoporous substrates using various dispersion and dispersion media, as well as deposition methods. In order to fill the porous structures in order to form functional coatings, the following methods of applying a coating on anodized Al_2O_3 substrates were proposed and investigated: suspension application with and without a magnetic field; applying a solution of $Fe(NO_3)_3$, followed by heat treatment; applying a solution

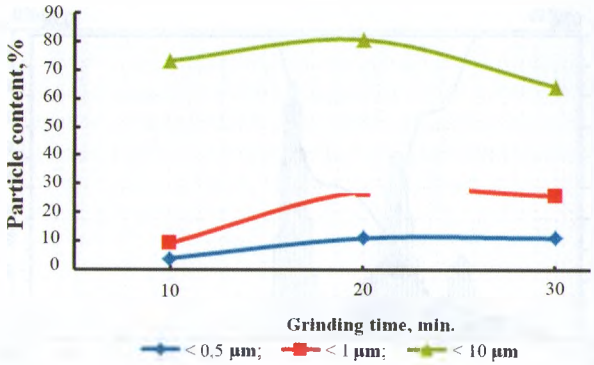


Fig. 2. The number of particles less than the nominal size in the powder $BiFeO_3$ depending on the time of grinding

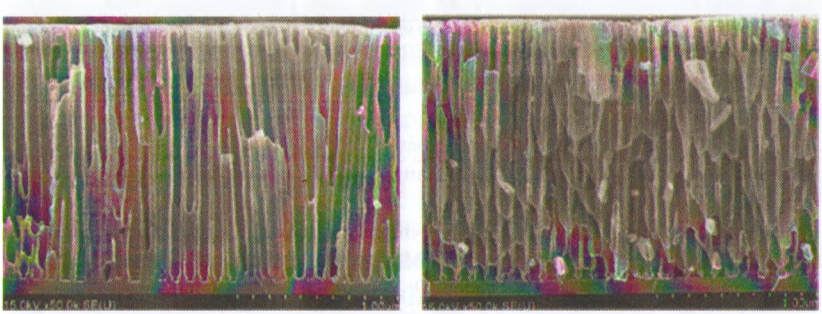
of $Bi(NO_3)_3$, followed by heat treatment; the application of the precursor solution (salt mixture) followed by heat treatment; deposition of dispersed phases $BiFeO_3$ and $BaTiO_3$ by pulsed laser spraying. Synthesized ferroelectric materials based on modified $BaTiO_3$, $Bi_4Ti_3O_{12}$ and $BiFeO_3$, obtained by high-temperature sintering and energy-efficient nitrate-citrate exothermic synthesis, were chosen as the dispersed phases for the preparation of film coatings.Samples of materials obtained by high-temperature sintering were milled in a micro-ball mill and sieved through a 0056 sieve, i.e. they had a continuous grain composition, the particle size ranges from microns to 56 microns.

The pores and the substrate of anodized Al_2O_3 have a diameter of less than 300 nm and are located with a step of 350 microns. Liquids with different rheological characteristics were used as dispersion media during coating. The properties of the used dispersion media in comparison with water are presented in Table.

Properties of dispersion media for the preparation of suspensions

Property	Water	Ethanol	Acetone
Chemical formula	H_2O	C_2H_5OH	$CH_3–C(O)–CH_3$
Molarmass, g/mol	18.0	46.07	58.08
Density, $\rho \cdot 10^{-3}$, kg/m^3	1.0	0.7899	0.7905
Viscosity at 20 °C, $\eta \cdot 10^3$, Pa·s	1.002	1.19	0.322
Surface tension at 20 °C, $\sigma \cdot 10^3$, n/m	72.0	22.3	23.7

As can be seen from the above data, the surface tension of organic liquids is much lower (more than three times). The values of dynamic viscosity of ethanol are close to those of water.Acetone has a lower viscosity (three times lower than that of water) with a slight surface tension, which may be a prerequisite for a more active filling of the pore structure and the formation of films. The deposition of film coatings from the developed multiferroics and ferroelectric ceramics was carried out by various physical methods. The magnetron sputtering method does not allow for the qualitative introduction of ceramic ferroelectrics into porous structures; however, this technology can be implemented to produce surface films or to fill substrates with larger pores. Laser deposition of bismuth ferrite on an anodized aluminum substrate provides for the formation of a surface layer with a thickness of about 2 microns, and in some areas there is a slight filling of the volume of the porous structure. It should be noted that the resulting film of bismuth ferrite has a wave-like structure, the wave step is 150–200 nm. A more uniform and high-quality coating on the surface of the substrate was observed when using ethanol, as compared with acetone, it has a higher viscosity. Filling the pore structure is also more effective from suspensions with ethanol. When acetone is used as the dispersion medium, ceramic suspensions are aggregately unstable, poorly applied to the surface, so no further studies have been carried out with them.



a *b*

Fig. 3. The microstructure of the cleaved substrate coating of the aqueous suspension: *a* – without the application of a magnetic field; *b* – with the application of a magnetic field

The microstructure of nanocomposite samples was studied using a scanning electron microscope. Images are captured at 50,000 times magnification (Fig. 3).

The pore channels have a relatively uniform diameter in length. Fig. 3 shows that particles of the ceramic substance penetrate into the channels, but in the case of application of a weak magnetic field, particles penetrate more intensively, which allows to conclude that the application of a magnetic field is promising when filling pores with magnetosensitive materials.

Thus, it was established that the developed materials with a micro- and nano-dispersed structure based on modified $BaTiO_3$ and $Bi_4Ti_3O_{12}$, $BiFeO_3$ are of interest for the production of composite materials in combination with other metal oxide compounds, as well as materials of other chemical nature (polymers). Stable formation of coatings is achieved using nanodispersed $BiFeO_3$ and ethanol dispersion phase. Ferrite bismuth high-temperature sintering after grinding for an optimum time of 20 minutes It has an average particle size of about 5–6 μm and can be recommended for the preparation of film surface coatings, which are also in demand by electronic equipment.

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