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Investigation of approaches to the $BaTiO_3$ piezoceramics production: the influence of the shaping method and the powder particles size

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For the first time, the possibility of obtaining samples of $BaTiO_3$ piezoceramics with d_{33} values between 240−270 pC/N from commercially available powder by vibrational pressing (vibropressing) and semi-dry pressing without the use of expensive methods of doping and/or alloying the initial powder and texturing piezoceramics is shown. The method of vibropressing with a pressure of 10 MPa allows to get similar structure and properties of samples, as well as the method of semi-dry pressing with a pressure of 100 MPa.

Keywords: lead-free piezoceramics, barium titanate, piezoelectric properties, vibration pressing, pressing.

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Piezoelectric ceramic materials (PCM) are widely used in various applications [1]. The materials of the lead zirconate-titanate series have the best piezoelectric properties [2]. Lead-free alternatives are PCM based on barium titanate and solid solutions of potassium and sodium niobates, sodium-bismuth titanate [3]. Barium titanate ($BaTiO_3$) is the most common lead-free PCM due to its availability, manufacturability and environmental friendliness. However, $BaTiO_3$ ceramics has relatively low piezoelectric modulus $d_{33} = 180-190$ pC/N [4], which limits the range of its application. The approaches to the piezoelectric modulus d_{33} increasing over 200 pC/N (up to 450 pC/N) are known, they include doping, alloying, texturing, using nanosized powders and complex sintering methods [5]. Therefore, the search for technological approaches to improve the piezoelectric properties of $BaTiO_3$ ceramics is an urgent task.

In the present paper the influence of the formation method — traditional semi-dry pressing and vibration compression (vibrocompression) — and the particle size of the $BaTiO_3$ powder on the piezoelectric properties of PCM is studied. Semi-dry pressing is one of the most common formation methods. The disadvantage of the method is the formation of areas of increased stresses in the body of the pressed workpiece, which can lead to the defects appearance [6]. The pressing pressure of PCM is from 50 to 200 MPa. Vibration action allows to reduce the necessary efforts for compacting the powder during formation [7]. Vibrocompression has a number of advantages: the cost of pressing accessories is reduced, there is no need for expensive equipment, and the elastic deformation of workpieces is reduced. Compaction of the press powder occurs due to the increased fluidity of the mixture caused by vibration, i.e. reduction of dissipative resistances to shear deformations under the action of forces having a constant direction. Therefore, a relatively small pressing force (in the range of 5 to 20 MPa) is sufficient for dense packing of powder particles [8].

$BaTiO_3$ powder (Aril, Russia) was used as the initial powder material in this paper. Granulometric analysis of the initial powder, performed by laser diffraction on ANALYSETTE 22 NanoTec plus (Fritsch GmbH, Germany), showed that the powder consists of large particles $D50 = 19.96\,\mu$m. Fig. 1, *a* shows the diffraction pattern of the initial $BaTiO_3$ obtained on Rigaku D/Max-2500 diffractometer (Rigaku Corp., Japan). The main one is the tetragonal phase $BaTiO_3$ (COD #96-150-7757), along with which $Ba_4Ti_{12}O_{27}$ (COD #96-201-9331) phase was found. Fig. 1, *b* shows a micrograph of the initial $BaTiO_3$ powder obtained with JSM-6390LA scanning electron microscope (SEM) (JEOL Ltd., Japan). The particles are dense agglomerates consisting of $BaTiO_3$ crystallites ranging in size from 160 to 750 nm.

To assess the effect of powder particle size, the initial powder was ground in Pulverisette 6 ball mill (Fritsch GmbH, Germany) with the addition of isopropyl alcohol and zirconium balls with a diameter of 3 mm. Next, the powder was kept in a drying oven at 70°C for 3 h. Six powder samples were prepared (Table 1).

Samples were made in the form of a disk with a diameter of 10−11 mm and a height of 2−3 mm. Three samples were made for each type of powder. The composition of the temporary technological binder was identical for all samples: a solution of 5 mass% of paraffin in white spirit. Next, the mixture was dried in the drying oven at temperature of 70°C until the mass was constant and pushed through a mesh with a mesh size of 300 μm. The press powder was formed in a mold with an inner diameter of 12 mm by two methods: semi-dry pressing at pressure of 100 MPa, vibrocompression at pressure of 10 MPa with vibration frequency of 50 Hz and amplitude of 20 μm (vibrocompression time is 10 s).

The samples were sintered in air at temperature of 1300°C for an hour. At the first stage the heating rate was 100°C/h. After reaching 300°C, the samples were hold at

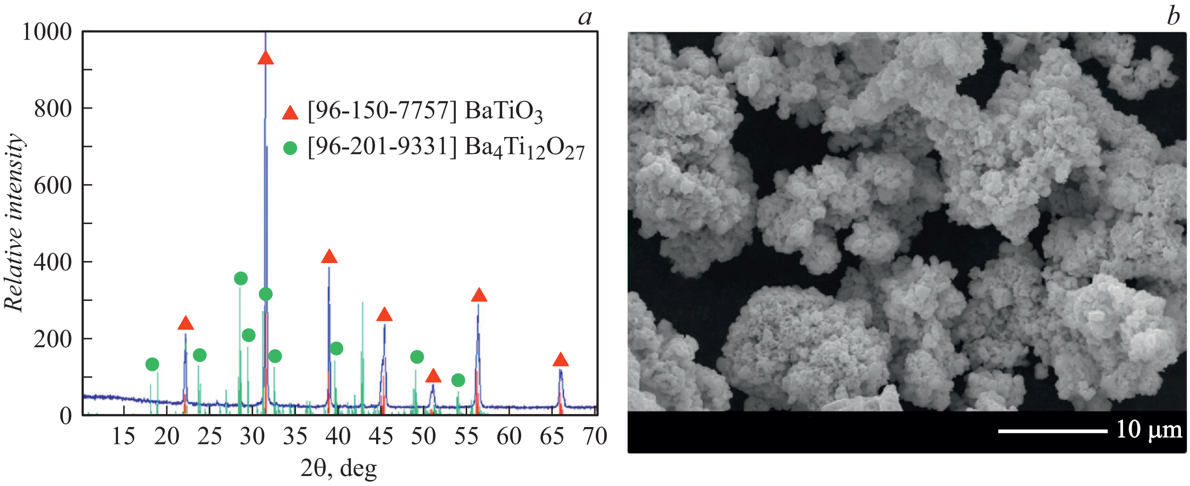

Figure 1. *a* — diffraction pattern of initial $BaTiO_3$; *b* — SEM image of the initial $BaTiO_3$ powder.

Table 1. Results of grinding of initial powder $BaTiO_3$

Number of sample	Grinding time, min	Modal diameter, μm	$D90$, μm	$D50$, μm	$D10$, μm	Specific surface, cm^2/cm^3
1	15	1.53	26.21	1.5	0.26	68591
2	30	1.49	1.89	1.2	0.23	97836
3	45	1.27	1.85	0.93	0.21	110538
4	60	0.67	1.48	0.68	0.23	118969
5	120	0.24	30.67	0.72	0.22	112420
6	0	20.82	26.94	19.96	9.42	3855

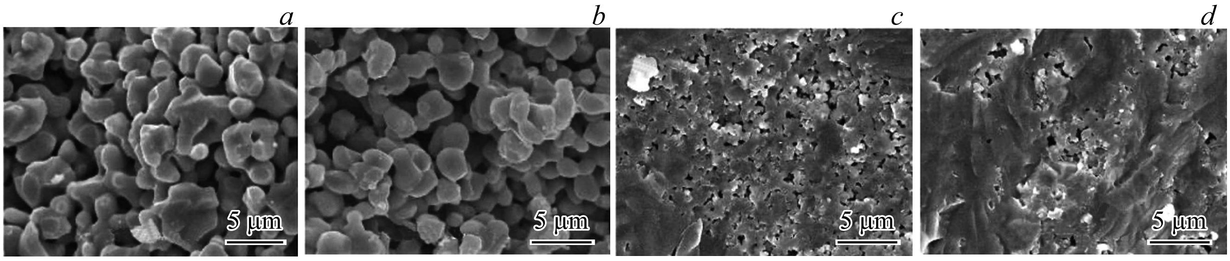

Figure 2. SEM images of $BaTiO_3$ piezoceramic microstructures. *a* — sample P6, *b* — sample V6, *c* — sample P5, *d* — sample V5.

this temperature for 0.5 h. Then heating continued at rate of 200°C/h until the sintering temperature was reached. The temperature-time mode was chosen in accordance with the results of the paper [9]. After firing, the relative density of the samples was measured by the Archimedes method (Table 2). Density varies significantly due to the difference in granulometry of powders with an identical technological chain.

Metallization was carried out by burning in silver paste at temperature of 800°C for 15 min. Polarization of the samples was carried out in compressed air at temperature of 120°C, voltage of 1500 V, holding time was 15 min, and then cooling to 60°C under voltage was carried out. Capacitance and dielectric loss tangent were measured by RLC-781 05G device (Good Will Instrument Co., Taiwan) at a frequency of 1 kHz. The piezoelectric modulus d_{33} was measured by a quasi-static method using a D33 Test Meter (Sinoceramics, Inc., China).

A common feature of the microstructures of samples obtained from unground powder by pressing (Fig. 2, *a*) and vibrocompression (Fig. 2, *b*) (samples P6 and V6, respectively), is a limited grain growth (on average up to a size of 1−2 μm) and a developed system of pores. The reason for this is the morphology of the initial commercial powder, which is rigid agglomerates of particles smaller than 1 μm. Such agglomerates destruction during formation is difficult, this exclude the dense packing of grains achievement. Grains of the specified size in $BaTiO_3$ ceramics provide the maximum values of the piezoelectric modulus d_{33}, exceeding 200 pC/N. Besides, the high porosity of materials (36−45%) contributes to bending and tensile deformations under mechanical action or under the influence of the

Table 2. Properties of $BaTiO_3$ piezoceramics (P — pressing, V — vibropressing)

Sample	Grinding time, min	Relative density	$\varepsilon/\varepsilon_0$	$\tan\delta$	d_{33}, pC/N
P1	15	0.84	2300	0.14	78
V1		0.88	2300	0.065	81
P2	30	0.89	2380	0.11	97
V2		0.94	2200	0.055	94
P3	45	0.80	2430	0.098	104
V3		0.92	2250	0.038	93
P4	60	0.90	2500	0.113	108
V4		0.77	2340	0.028	105
P5	120	0.90	2480	0.025	90
V5		0.91	2100	0.036	142
P6	0	0.64	1325	0.02	270
V6		0.55	1020	0.018	240

electric field larger than in the case of dense ceramics [10]. The destruction of the initial agglomerates in the powder after prolonged grinding provides a greater number of contacts between the particles during formation by the considered methods and makes it possible to increase the ceramics density up to 90–94% (Table 2). Squeezing is naturally accompanied by the values of d_{33} (to 90 and 142 pC/N in samples P5 and V5, respectively) decreasing and to the dielectric constant increasing to 2300–2400. The presence of a nonstoichiometric impurity in the initial $BaTiO_3$ powder limits the squeezing, since it leads to the growth of anomalous grains (Fig. 2, *c* and it d). As a result, the values of ε do not reach the values previously known for dense single-phase ceramics $BaTiO_3$ [9]. The dielectric losses of the manufactured ceramics do not show a pronounced sensitivity to the duration of grinding and the method of powder formation and are about 10^{-2}. An exception is some samples of the P series with $\tan\delta \sim 10^{-1}$, which may be due to the introduction of impurities through the ends of the workpieces during pressing.

Thus, the paper shows for the first time that vibrocompression is as efficient as pressing in the problem of manufacturing $BaTiO_3$ piezoelectric ceramics. The best indicators of the piezoelectric modulus d_{33}, exceeding 200 pC/N, were achieved in samples P6 and V6 obtained from the initial commercial powder. Ground powder samples showed average piezoelectric properties for $BaTiO_3$ ceramics. The values of the piezoelectric modulus d_{33} exceeding 200 pC/N are reported extremely rarely and mainly for doped and textured PCMs. The results obtained using the agglomerated commercial powder open up the prospect of achieving higher piezoelectric properties of ceramics based on barium titanate with careful selection of the initial material in terms of purity and morphology.

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Conflict of interest

The authors declare that they have no conflict of interest.

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