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Modification of the technique and main characteristics of piezoelectric ceramics $BiScO_3-PbTiO_3$

© E.G. Guk[1], E.P. Smirnova[1], V.N. Klimov[2], P.A. Pankratiev[1], N.V. Zaitseva[1], A.V. Sotnikov[1], E.E. Mukhin[1]

[1] Ioffe Institute,
St. Petersburg, Russia
[2] Central Research Institute of Structural Materials Prometey, National Research Centre Kurchatov Institute,
St. Petersburg, Russia

E-mail: elgrguk@gmail.com

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A modified technique for ceramics manufacturing without forced cooling from high-temperature first stage to the low-temperature second stage is proposed. The effect of the cooling regime between two sintering stages on the piezoelectric constants was investigated.This method was used to synthesize high-temperature piezoelectric ceramics $0.36BiScO_3-0.64PbTiO_3$. Structural and piezoelectric parameters of ceramics were studied. It is shown that the obtained ceramics have a tetragonal structure ($P4mm$) and a composition close to the morphotropic phase boundary, just like the solid solution synthesized by traditional one-step technique. Ceramics synthesized by modified technique are characterized by high density, up to 97% of theoretical value. The average grain sizes of ceramics are in the range of $0.8-1.0\,\mu$m. The obtained value of the piezoelectric constant d_{33} of samples synthesized by the modified technique reaches 525 pC/N.

Keywords: piezoelectric ceramics, two step sintering method, optimization.

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1. Introduction

Processes of manufacturing of ferroelectric ceramics have significant effect on its properties and are discussed in many publications [1–5]. Due to same reason the technique of these materials manufacturing is continuously developed and modified. So, piezoelectric ceramics with structure of perovskite type at the beginning of 2000s was mainly manufactured by a method of solid-phase synthesis method, which means use of baked high pure oxides of appropriate elements, first firing (calcination), disks pressing and their single stage high temperature sintering [6–8].

But in 2000 an article [9] was published which suggested new method of final sintering of the ceramics, namely, two stage sintering, which involves heating the initial samples at the first stage of firing to high temperature T_1 for short period of sintering t_1, further quick cooling to more lower temperature T_2 and long-time holding at temperature T_2 at second stage of sintering for time period $t_2 \gg t_1$. The method of two-stage firing ensures control of grain growth of ceramics, i. e. formation of high quality ceramics with high density and improved electrical and physical parameters.

We studied and identified the mechanism responsible for properties improvement of the ceramics formed by new method. In case of traditional single stage firing at high temperature the ceramics compaction is always accompanied by grain quick growth due to both migration of grain borders, and diffusion of grain borders [9–11]. During two-stage sintering at first stage the grain growth occurs, and rather high density of ceramic material is achieved, generally it is 75% of theoretical value [9,10]. At second stage at low temperature T_2 the grain borders are fixed, thus their growth stops [10–12]. The two-stage method is widely used in technique of piezoelectric ceramics manufacturing, one its application is active elements of piezoelectric drives (actuators) and piezoelectric motors [13–15].

The typical example of the transition from single stage technique to the two-stage process can be synthesis of ceramics $0.36BiScO_3-0.64PbTiO_3$ (BSPT). For the first time BSPT synthesis and properties of prepared samples are given in paper [6]. It is shown that BSPT solid solution is located near the morphotropic phase boundary (MPB), it is identified that composition has high Curie temperature ($T_C \approx 450^\circ$C) and significant value of piezoelectric constant $d_{33} = 450$ pC/N. Such combination of parameters provides possibility for BSPT use to manufacture actuators and piezoelectric motors intended for work, including at high temperatures, as tools for drilling of oil and geothermal wells [16,17], and in systems of diagnostic of nuclear and fission reactors [18].

Paper [10] describes use of two-stage firing to form BSPT ceramics. While in single-stage firing [6] ceramic samples were obtained with grain size from 6 to 15 μm (T sintering $= 1000-1200^\circ$C respectively), transition to two-stage firing ensured abrupt decrease in average grain size of synthesized ceramics to 600–800 nm. The grain size decreasing resulted in a significant improvement in the properties of the studied ceramics. So, during two-stage synthesis value $d_{33} = 520$ pC/N [10] was achieved,

which by $\sim 15\%$ exceeded value $d_{33} = 450$ pC/N obtained in paper [6].

Optimization of sintering mode of ceramics remains actual problem till now, this is testified by new papers [11,18,19] related to this issue, they search suitable temperatures T_1 and T_2 and, respectively, time t_1 and t_2. This choice is primarily determined by how and for what purpose the ceramics is used, i.e. which of the many piezoelectric parameters shall have the maximum value. Minimum value T_1 is determined by the requirement to achieve required density of ceramics at the first stage, and maximum value T_1 is limited by the necessity to prevent significant losses of lead, and generally does not exceed 1200°C. Holding time (t_1) at maximum temperature at first stage is usually minimized (i.e. cooling starts immediately when T_1 is achieved), but in some studies it is from 1 to 5 min. The firing temperature from T_1 to T_2 during transition from first stage to second stage is generally decreased as result of forced cooling with rate 20−30°C/min. This process requires rather complex equipment, and this complicates its use. Thus, in paper [10] for abrupt temperature decreasing in the work zone the furnace was simply opened, and samples were cooled in air, this is not permitted when handling lead containing ceramics due to possibility of poisoning with lead vapors. This paper task is study of the effect on properties of BSPT ceramics of mode of cooling from T_1 to T_2 during two-stage firing.

2. Experiment

Solid solution $0.36BiScO_3-0.64PbTiO_3$ was synthesized from oxides Bi_2O_3, Sc_2O_3, TiO_2 and PbO of grade ACS, mixed in stoichiometry ratio. Preliminary these oxides were baked for 4 h — Sc_2O_3 and TiO_2 at 1000°C, and Bi_2O_3 and PbO — at 700°C. Then alcohol suspension of the initial mixture was crushed by grinding for 24 h. After drying at 85°C it was pressed under uniaxial pressure $P = 12$ MPa in die with diameter 25 mm, and preliminary firing (calcination) was performed for the formed sample of cylindrical shape with diameter of 2.5 mm and 3−4 cm high in open platinum crucible at 850°C for 4 h. Then calcined sample was crushed by grinding in alcohol suspension for 12 h. The obtained charge was dried, and discs with diameter 10 mm and 1 mm thick were pressed from it under uniaxial pressure $P = 8$ MPa, the discs were dried for 2 h at 150°C. The manufactured discs were divided into 2 batches. The first batch of discs was sintered in standard single-stage mode at 1150°C for 2 h, and the second batch was fired using modified two-stage technology.

The optimal range of temperatures for the modified two-stage synthesis of BSPT ceramics was determined in device of combined thermogravimetric analysis TGA/DSC/1600HF. Chemical and physico-chemical processes were studied in discs made after calcination, mixing and pressing under reproduced temperature and time modes of the modified

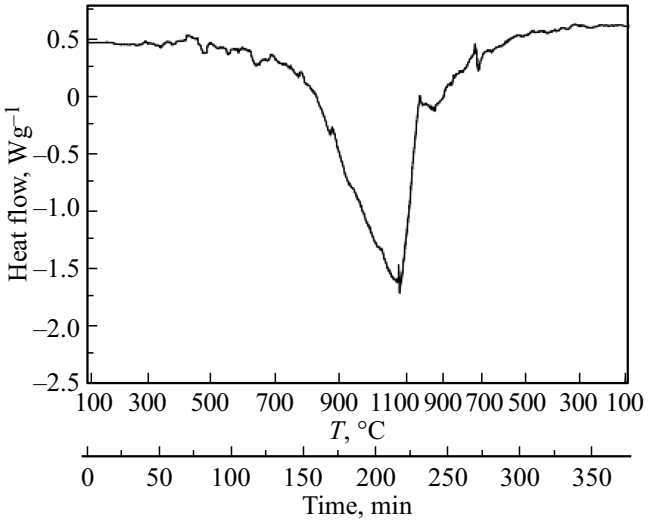

Figure 1. Results of differential thermal analysis obtained during reproduction of the temperature and time modes of modified sintering of BSPT.

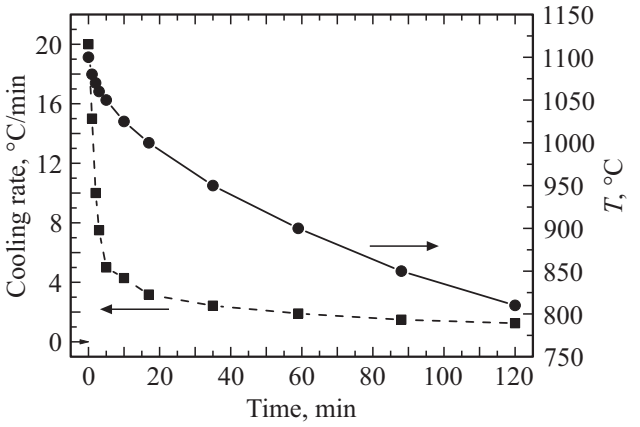

Figure 2. Temperature change from T_1 to T_2 without forced cooling.

sintering. Analysis of the obtained results showed that in curve of differential thermal analysis (DTA) at temperature 1050°C the significant endoeffect with sharp extremum is observed (Figure 1), which, obviously, is due polymorphous conversion of the disc material with formation of the final perovskite structure. Based on this result the temperature of the first stage of high-temperature firing T_1 was selected equal to 1050°C.

During modified two-stage sintering at the first stage the discs were heated to $T_1 = 1050$°C with rate 5°C/min, in 1 min after achievement of temperature T_1 the furnace was switched off, and samples were cooled together with furnace cooling to $T_2 = 800$°C, then at this temperature the second stage of sintering was performed for 4 h.

Cooling together with furnace cooling takes 2 h, at that the cooling rate decreased non-linearly with time (Figure 2). For these samples PbO losses were below 1%.

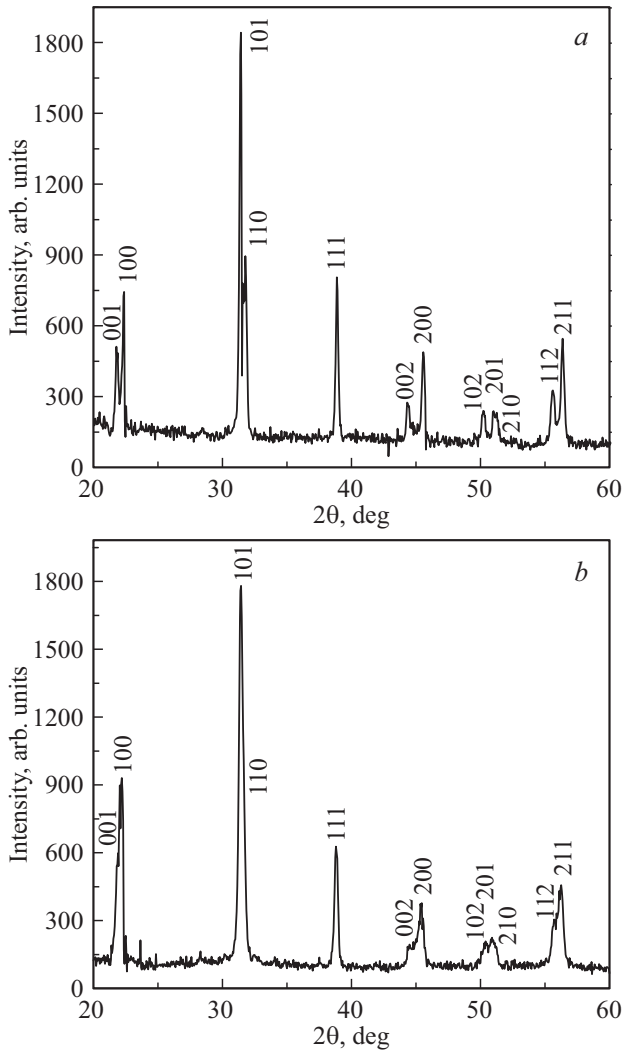

Figure 3. X-ray patterns of samples obtained using single-stage (a) and modified (b) two-stage sintering.

Samples obtained using single-stage, and modified two-stage sintering were single-phase and had perovskite structure. The measured density corresponds to 93 and 97% of theoretical X-ray density for samples after single-stage sintering and modified two-stage technique, respectively.

Analysis of elementary composition and size of grains of ceramics was performed in scanning election microscope Tescan Mira with system of elementary composition determination. The piezoelectric constant d_{33} was measured using displacement indicator M-048 and high voltage source PS350/5000V-25W during measurement of displacement occurred due to reverse piezoelectric effect upon external electric field application. Measurements were made on samples obtained both single-stage and two-stage firing. As material for electrodes the argentum was used, it was deposited on disc surfaces using magnetron sputtering, the electrode thickness was $1\,\mu$m.

3. Results and discussion

X-ray patterns of samples obtained using single-stage (a) and two-stage (b) are shown in Figure 3. Structure of samples and solid solution of BSPT, located on MPB is identified as tetragonal ($P4mm$). The decrease in the degree of tetragonality of the lattice from $c/a = 1.025$ (single-stage firing) to $c/a = 1.017$ (two-stage firing) attracts attention. The microstructure of BSPT samples obtained by two methods was compared, and the efficiency of the proposed firing mode was assessed.

The electronic images and graphs of ceramic grain size distribution, shown in Figures 4 and 5, demonstrate the grain size decreasing by order of magnitude. Average sizes of grains formed as the result of modified two-stage sintering are in range $0.8-1.0\,\mu$m, and sizes of grains synthesized during single-stage sintering — in range $8-10\,\mu$m. Note

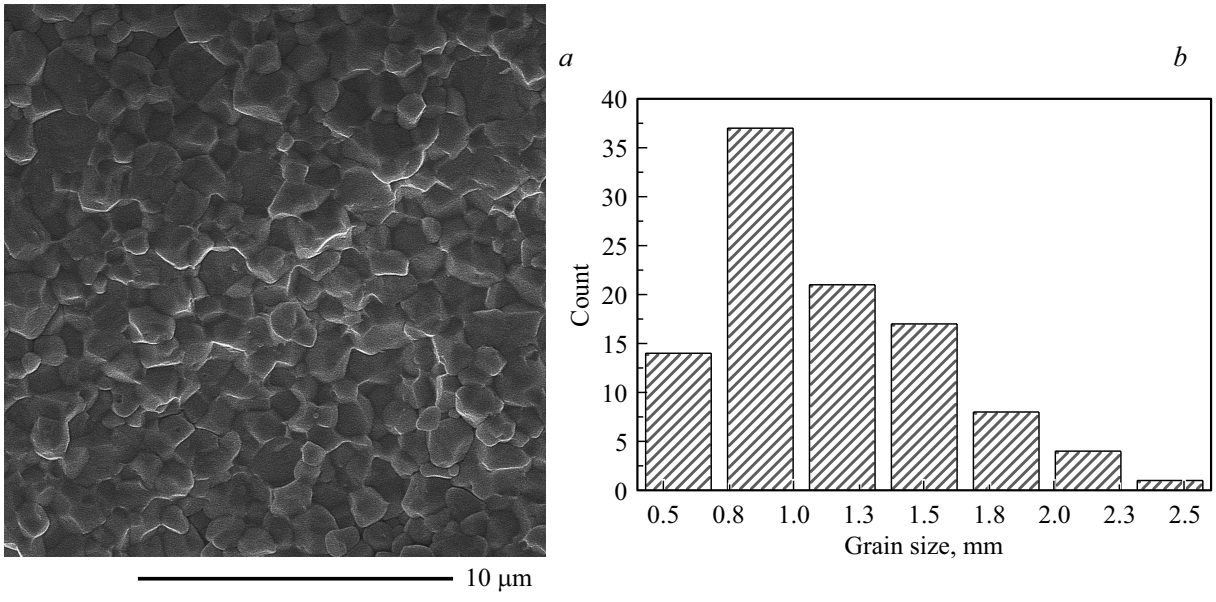

Figure 4. a — Electronic image of end face of ceramics, obtained as result of modified two-stage sintering, and b — grain size distribution histogram.

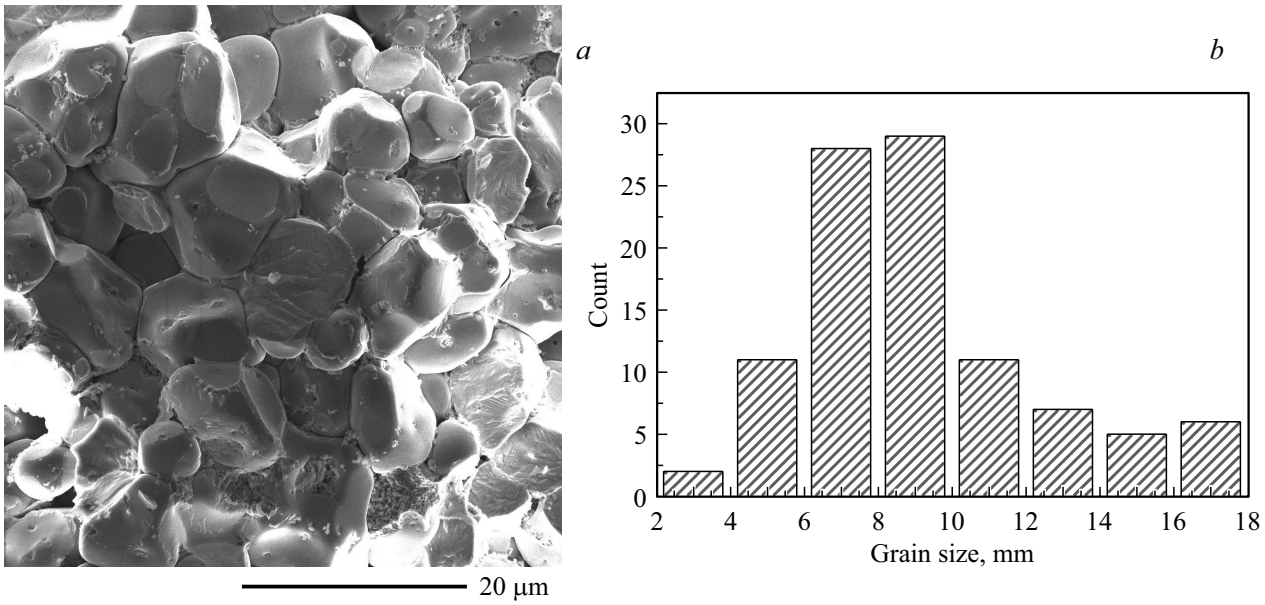

Figure 5. *a* — electronic image of end face of ceramics, obtained as result of single-stage firing, and *b* — grain size distribution histogram.

that model [20–23], supposing that at the second stage of sintering the triple points of grain boundaries contact are frozen, can be applied also to mode of modified sintering without forced cooling T_1 to T_2.

I. e., at nonlinear two hour decreasing of the furnace the mobility limitation and deceleration of grain boundaries movement occur. In electronic image of the ceramics obtained during two-stage cooling mode the triple points of grain boundaries contact are observed, they can serve also as channels increasing mobility for diffusion of grain boundaries (Figure 6).

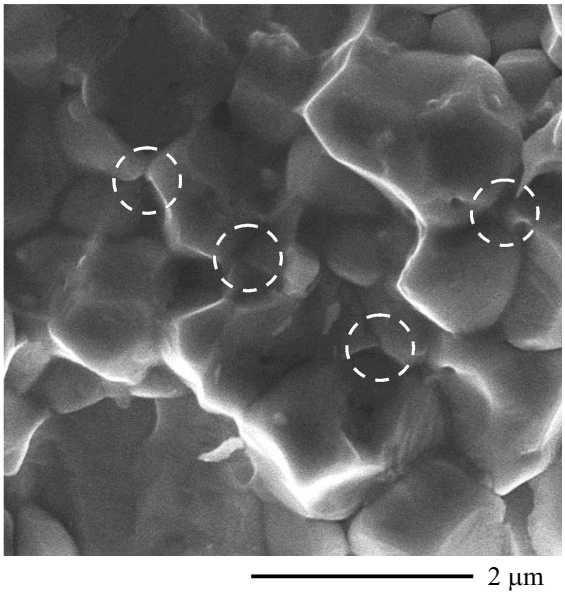

Figure 6. Electronic image of ceramics synthesized using modified two-stage technique. Typical triple points of grain boundaries contact are marked by dashed circles.

So, the modified two-stage cooling technique ensures „growing" of grain of required size by selection of temperatures T_1 and T_2 an holding time at these temperatures. Comparison of single-stage and modified two-stage modes shows that for the traditional and modified two-stage modes the stage of ceramics formation that determines the average size of graine is not stage of temperature decreasing from T_1 to T_2, but second stage of the two-stage process, i. e. long-time low-temperature firing.

Publications described the microstructure effect on the piezoelectric characteristics of the ceramics [10,11]. First of all the grain size decreasing increases the ceramics density. The present paper shows that use of the modified two-stage sintering results in density increasing from 95 to 97% of the theoretical value. In paper [8] it was obtained that BSPT has maximum value of the parameter $d_{33} = 520$ pC/N in ceramics with grain size within range $0.8-1.5\,\mu$m. The measured piezoelectric response of the polarized ceramics with average grain size about 800 nm (Figure 4, *b*), synthesized by the suggested modified two-stage demonstrated high value of the piezoelectric constant $d_{33} = 525$ pC/N. At the same time, due to two-stage sintering with sudden forced cooling from temperature T_1 to T_2 the obtained piezoelectric constant d_{33} is 520 pC/N [10]. Value of piezoelectric constant $d_{33} = 525$ pC/N is one of maximum achieved for BSPT piezoceramics, and indicates improved piezoelectric properties of this composition during manufacturing using modified two-stage technique.

4. Conclusion

Using the suggested modified technique of two-stage sintering without forced cooling between the first and

the second sintering stages the synthesis was performed of high-temperature ceramics of composition $0.36BiScO_3-0.64PbTiO_3$ (BSPT). The formed ceramics is characterized by average grain size ~ 800 nm, this ensures high density achieving 97% of theoretical value. So, the model, supposing freezing of grain contact points at the second firing stage, which prevents the boundaries migration during ongoing diffusion along the grain boundaries, describes also the results obtained under natural cooling (together with furnace cooling) from T_1 to T_2. The obtained samples of BSPT ceramics, synthesized using the modified technique, demonstrate maximum value of parameter $d_{33} = 525$ pC/N, this slightly exceeds $d_{33} = 520$ pC/N, obtained for samples synthesized by the method of two-stage sintering with abrupt forced cooling. The suggested method demonstrates the possibility and advantage of manufacturing of high quality BSPT piezoceramics under the simplified technology without stage of forced cooling due to natural nonlinear cooling from temperature T_1 to T_2. It appears that the proposed modified method of two-stage sintering can be successfully applied to the synthesis of piezoelectric ceramics of other compositions.

Conflict of interest

The authors declare that they have no conflict of interest.

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