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Microelectronics Materials Based on BST-Ceramics.

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ABSTRACT

The presented paper describes the production of specimens made from solid solutions of the system $Ba_{1-x}Sr_xTiO_3$ ($0 \leq x \leq 1.0$); the production technology included solid-phase synthesis with the following sintering using regular ceramic technology. On the basis of the study of their structure, granular structure and dielectric properties it was concluded that it is possible to apply compositions with x = 0.2 for production of materials with high dielectric permeabilities, which are promising in the field of microelectronics.
Keywords: Grain, Bimodal Structure, Dielectric Permeability, Curie Temperature

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INTRODUCTION

The range of the known applications of BST-materials (on the basis of solid solutions (SS) of the system $Ba_{1-x}Sr_xTiO_3$) in microelectronics (phase changers, delayers, resonators and filters) significantly expanded due to the development of amplifier devices. Advantages of these materials included high performance of design elements and the possibility of application of both fronts of control impulse in switching BST-based device, as compared with known powerful semiconductor plasma switches and phase changers. At that the mentioned compounds are in demand both in form of thin ferroelectric (FE) films and in the form volumetric ceramics, however, development of the latter is related with the need to use high temperature, and it requires complex study of process of formation of their crystalline structure, grain structure and electrophysical properties.

OBJECTS AND METHODS OF STUDY

The objects of the study were ceramics of solid solution (SS) system $Ba_{1-x}Sr_xTiO_3$ ($0 \leq x \leq 1.0$), which were produced using regular ceramic technology with two-stage solid-phase synthesis at T_1 = 1130 ºC, T_2 = 1150 ºC, $\tau_1 = \tau_2$ = 4 hours with intermediate milling and granulation of powders and the following sintering at (1375÷1500) ^oC в depending on composition. Selection of optimum procedures of production of specimens was carried out using the series of specimens (workpieces of Ø 12 mm and height h = 8 mm). As the initial products we used carbonates of Sr and Ba and Ti oxide with "chda" qualification. Microstructure of ceramics was analyzed using "Hitachi TM-1000" electronic microscope. Dielectric characteristics were identified on the basis of temperature-frequency measurements in the range of temperatures (25 ÷ 700) ºC (including in the mode of heating-cooling of the specimens) and in the frequency range of $0.25\text{-}1 \cdot 10^3$ kHz (with the following frequencies: 25; 60; 100; 500; $1 \cdot 10^3$, $1 \cdot 10^4$, $5 \cdot 10^4$, $1 \cdot 10^5$, $5 \cdot 10^5$ and $1 \cdot 10^6$ Hz).

EXPERIMENTAL RESULTS AND DISCUSSION

X-Ray diffraction analysis demonstrated that all SS has perovskite-type structure, there were irrelevant phases. Fig. 1. shows diagram of states of system with consequently appearing tetragonal (T), pseudocubic (PsC) and cubic (C) phases and zones, where they coexist (morphotropic phase transitions, MPT). Fig. 2 shows fragments of microstructures of the study specimens. Their analysis show that they are very nonuniform: in some case there are traces of submelting. Grain structure of some specimens is of clearly bimodal nature. It is worth mentioning that MPT T→ PsC, PsC → C in the vicinity of x = 0.3 and x = 0.7, which is accompanied by the growth of grain, especially in the second case (Fig. 2*a*), and "approaching" in $SrTiO_3$ leads to serious refinement of structure. The observed phenomenon is explained by the increase of mobility of structural elements in MPT, development of various kinds of defects (vacancies), which take part in mass transfer, which facilitates diffusion processes and recrystallization of ceramics. Electric probe analysis (Fig. 3.) allowed to identify liquid-like states (in Fig. 3 – double intercrystalline boundaries; amorphous inclusions; large euhedral grains), formation of which is related to melting during sintering of thermally stable hydroxide $Ba(OH_2)$.

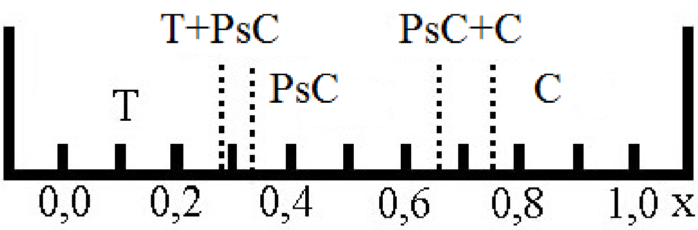

Fig. 1. Phase state diagram of the $Ba_{1-x}Sr_xTiO_3$ system.

Results of the study of dielectric properties are demonstrated in Fig. 4, which shows relationships of temperature and relative dielectric permeability $\varepsilon/\varepsilon_0$, dielectric dissipation factor, tgδ, at one frequency (f = $5 \cdot 10^5$ Hz) (*a*–*d*), (direct and opposite movement) and at various frequencies (f = $2\text{-}2 \cdot 10^6$ Hz) (*f*-*i*), as well as relationships of concentration $SrTiO_3$(x) and Curie temperature, T_C, (continuous lines) and temperature hysteresis, ΔT_C, peak values of $\varepsilon/\varepsilon_0$ (dotted line) (*e*) of SS system $(BaSr)TiO_3$.

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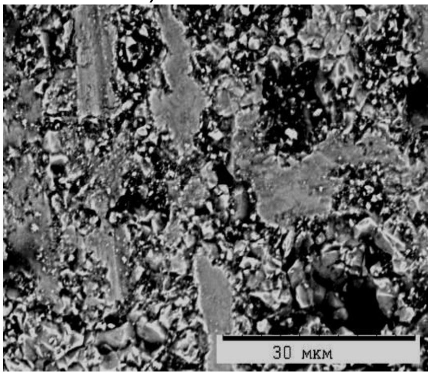
a) x=0.0



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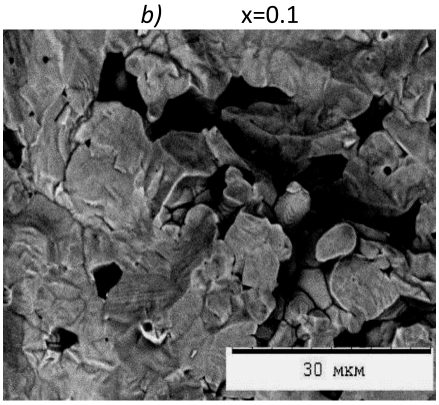

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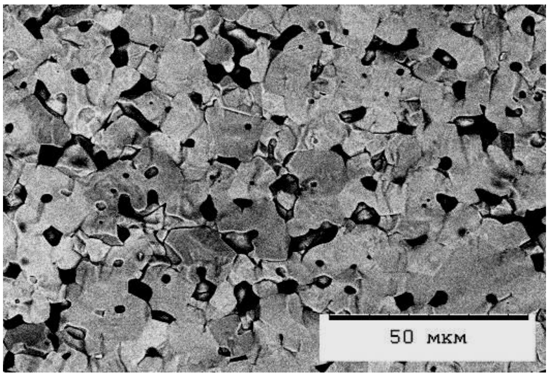
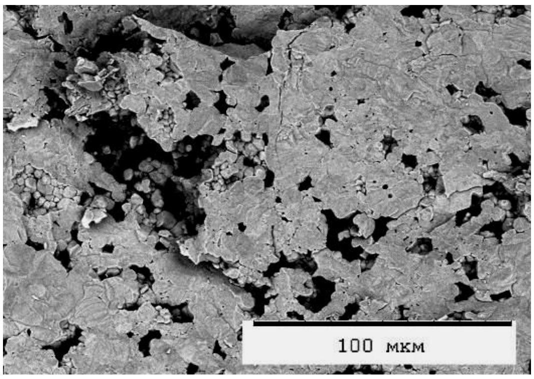
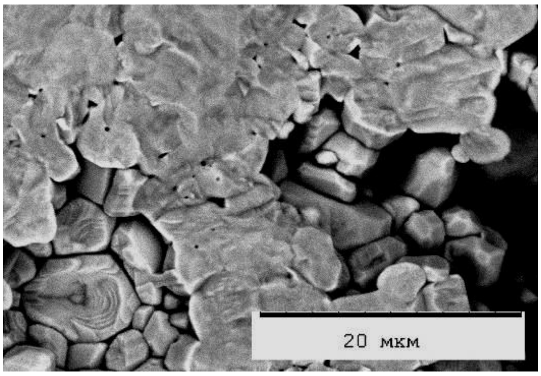


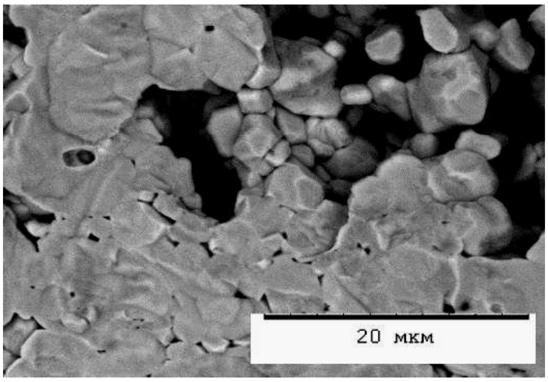
d) x=0.3



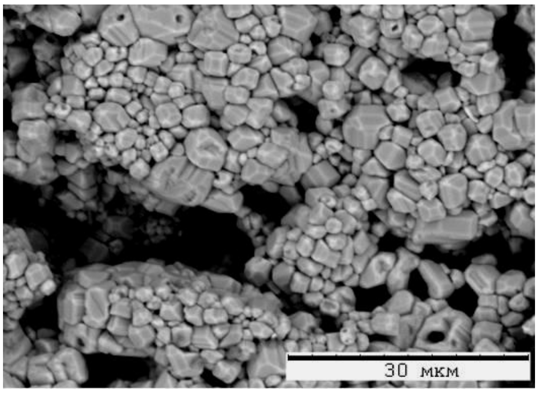
e) x=0.3



f) x=0.4



g) x=0.5



h) x=0.6

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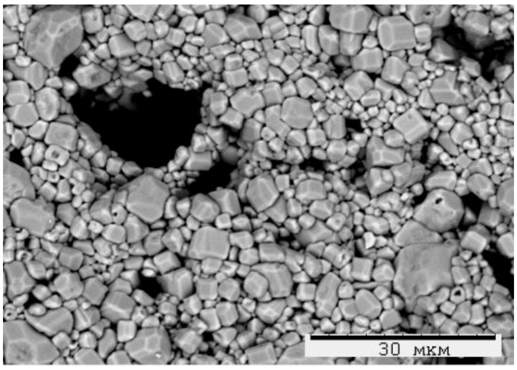
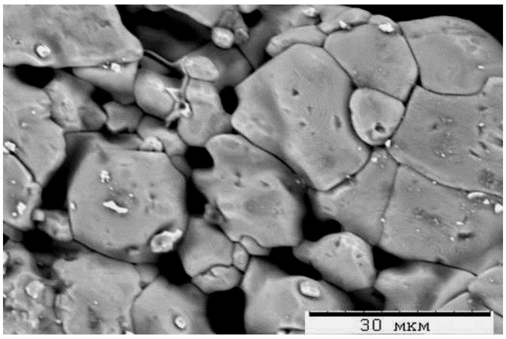
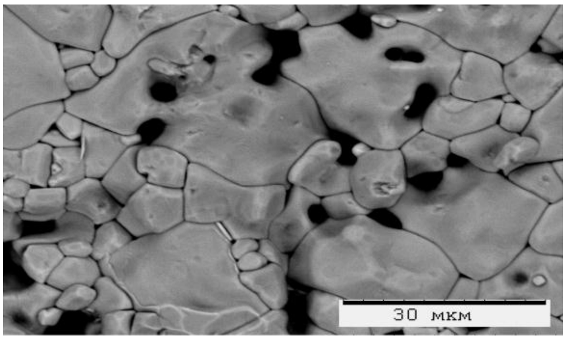


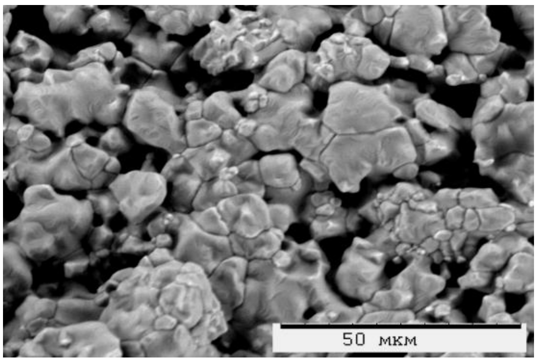
i) x=0.7



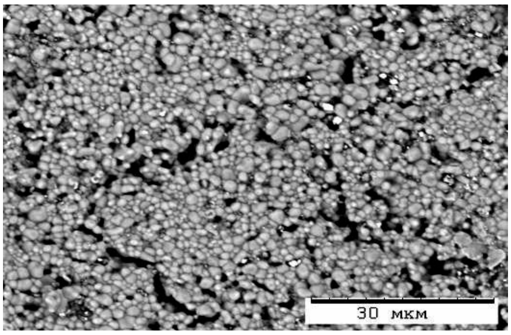
j) x=0.8



k) x=0.9



l) x=1.0

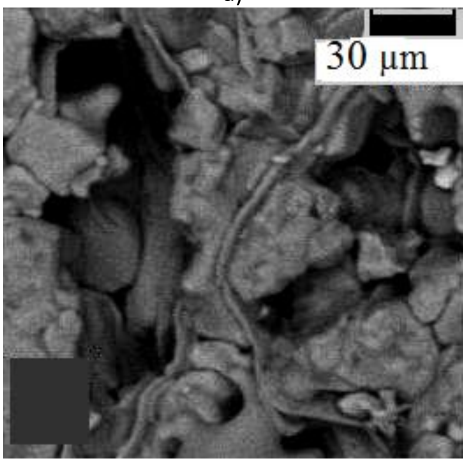


Мкм	µm

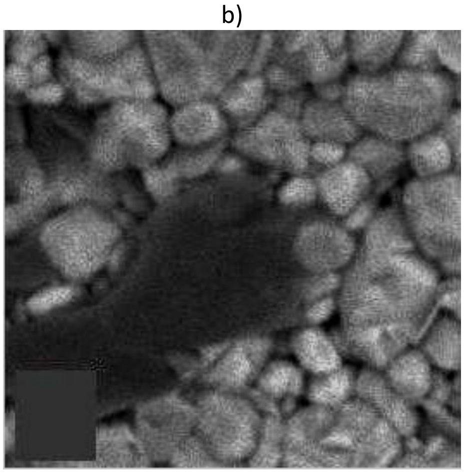
Fig. 2. Fragments of microstructure of ceramics of SS of the system (1-x) $BaTiO_3$– $xSrTiO_3$ in the interval $0.0 \leq x \leq 1.0$ (Figure shows values of x).

The analysis of Figures demonstrated that descending relationships of T_C and Δ T_C and x, which conforms with the data from literature and shows correspondence of results of measurements of dielectric characteristics at phase diagram of the system (Fig. 1): at x > 0.3 structures become practically cubic, which causes rapid decrease of T_C, when approaching to that concentration. Decrease of ΔT_C with increase of x also in good agreement with the data of X-Ray diffraction analysis: change of types of phase transitions (PT) from primary in the vicinity of $BaTiO_3$ to secondary in the case of increase of content of $SrTiO_3$ and explains presence (in the first case) and practical absence (in the second case) of temperature hysteresis, ΔT_C of peak values of $\varepsilon/\varepsilon_0$.

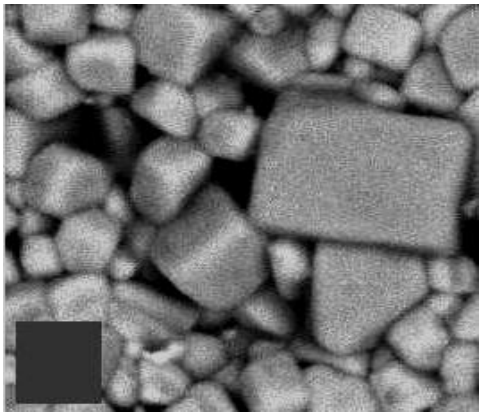
a)



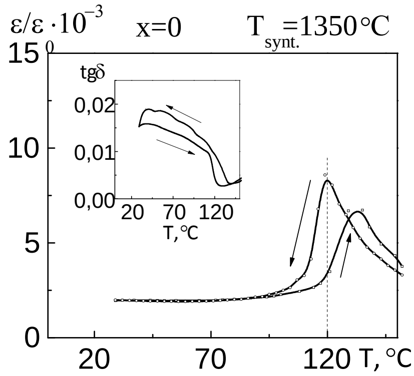
b)



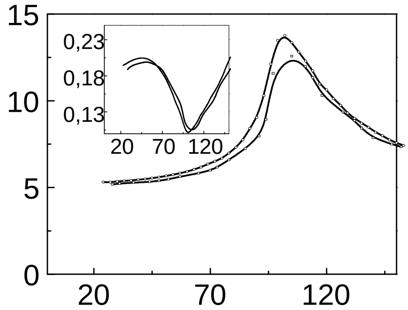
c)



a)


ε/ε0 ·10−3
x=0
Tsynt.=1350°C
15
10
5
0
20
70
120
T, °C
tgδ
0,02
0,01
0,00
20
70
120
T,°C

b)


15
10
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70
120
0,23
0,18
0,13
20
70
120

c)

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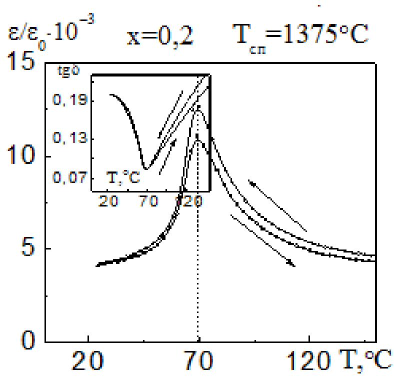
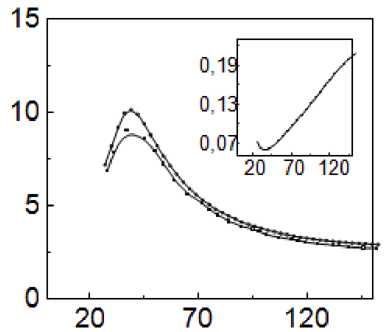
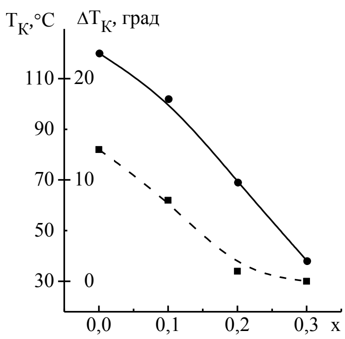


d)



e)



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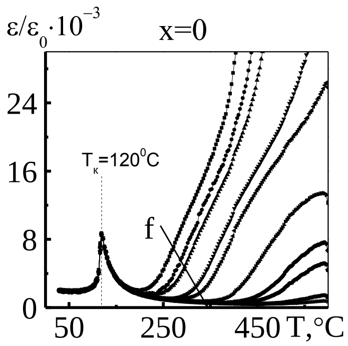

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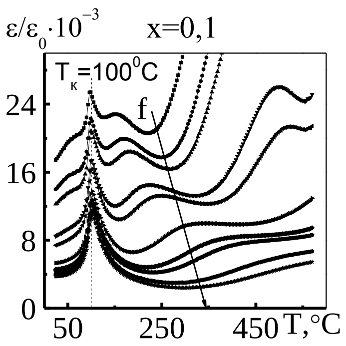
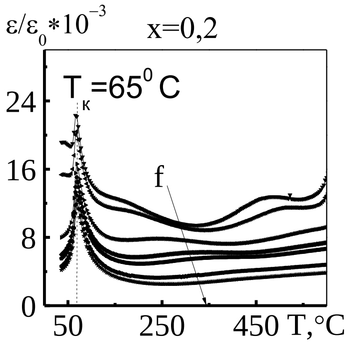


h)



i)

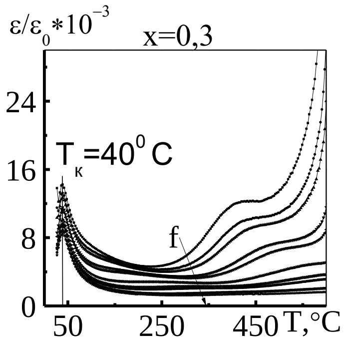


Fig. 4. Relationships of temperature and relative dielectric permeability $\varepsilon/\varepsilon_0$, dielectric dissipation factor, tgδ, at one frequency (f = 500·105 *Hz) (*a-d), (direct and opposite movement) and at various frequencies (f = 2-2·10^6 Hz) (f-i), as well as relationships of concentration $SrTiO_3$(x) and Curie temperature, T_C, (continuous lines) and temperature hysteresis, ΔT_C, peak values of $\varepsilon/\varepsilon_0$ (dotted line) (*e*) of SS system (BaSr)TiO_3.

Rapid increase of $\varepsilon/\varepsilon_0$ in paraelectric area of $BaTiO_3$ and other SS at temperatures, which are increasing with the increase of frequency of measuring electric fields, is, presumably, caused by irregularities of composition of stoichiometry, including change of oxidation level Ti ($Ti^{4+} \rightarrow Ti^{3+}$). Fluctuation of composition is, without a doubt, become the reason for development of Maxwell-Wagner (interphase, interlayer) relaxation, and, thus, dispersion phenomena, which were observed. For SS with $x \geq 0.1$ dispersion of $\varepsilon/\varepsilon_0$ is developing, also, in FE region, which is, clearly, caused by increased conductance of SS.

Table 1 and Fig.5 present electrophysical characteristics of $BaTiO_3$ and SS of the analyzed system (because of the high conductance attempt to polarize the latter failed). According to the logic of change of structure of SS, maximum of $\varepsilon/\varepsilon_0$ is realized inside MPT area (Fig 5.).

Table 1.Electrophysical characteristics of $BaTiO_3$ (at room temperature).
($\varnothing$ 10 mm, $T_{synt.}$ = 1350 °C)

ρ_{exp}, g/cm³	P_{rel}, %	$\varepsilon/\varepsilon_0$	$\varepsilon_{33}^T/\varepsilon_0$	tgδ dl	tgδ dl	Q_M	V^E_1, km/s	$Y^E_{11}\cdot10^{-11}$, N/m²	Z, mraul	Literature
		1400	1620							[1]
5.79	0.963				0.014	154				[2]
5.71	0.944	2137	1833	0.003	0.013	72	3.31	0.628	18.94	The obtained data

$\lvert d_{31}\rvert$, pC/T	d_{33}, pC/T	$\lvert g_{31}\rvert$, mV·m/N	g_{33}, mV·m/N	K_p	Literature
79	191	4.7	11.4	0.354	[1]
163	419			0.354	[2]
78	180	4.8	11.09	0.34	The obtained data

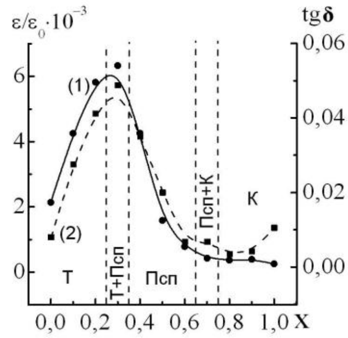
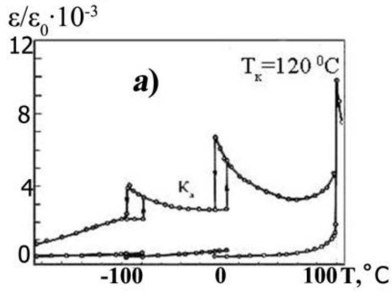
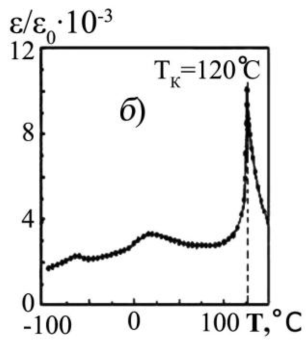


Fig. 5. Relationships of relative dielectric permeability, $\varepsilon/\varepsilon_0$(1), dielectric dissipation factor tgδ (2) TP (1-x) $BaTiO_3$–x$SrTiO_3$ and concentration of $SrTiO_3$.

a)



b)



c)

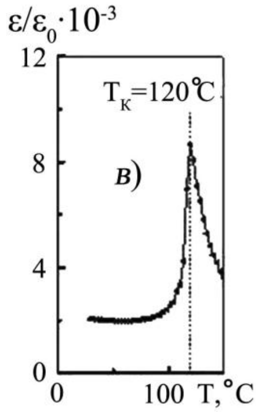


Fig. 6. Relationships of relative dielectric permeability, $\varepsilon/\varepsilon_0$, and temperature of $BaTiO_3$ *a*) – [3]; *b*) – [1]; *c*) – the obtained data.

High piezoactivity of the specimens of $BaTiO_3$, which were obtained in the studies [5–8], is related to the extremely small values of ceramics grains and, thus, another domain structure. In the studies [5-8] it is provided by hydrothermal synthesis of ultrafine powders of source components, and in [8] – by mechanical activation (ultrafine grinding of products synthesizes in solid-phase) prior to sintering. Those procedure also allowed to decrease temperature of sintering of $BaTiO_3$ by 100 ºC (from 1300 ºC, which is usual for production of dense sintering products), to ≈1200 ºC (Table 2).

The obtained data shows that materials with x ≈ 0.2 and high values of dielectric permeability are prospective from the point of view of application in microelectronic devices.

CONCLUSION

The study presents the results of investigation of structure, grain structure and dielectric properties of solid solutions of the system $Ba_{1-x}Sr_xTiO_3$ ($0 \leq x \leq 1.0$). The developed materials have high dielectric permeability, and they have prospects for application in microelectronic devices.

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