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Low permittivity ferroelectric composite ceramics for tunable applications

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ABSTRACT

Bulk ferroelectric composite ceramics based on mixtures of $BaTiO_3$/$SrTiO_3$ powders with Mg-containing additives such as Mg_2TiO_4, MgO in a wide range of compositions were fabricated and characterized. Phase relations, crystal structures, microstructures and dielectric properties of ferroelectrics were investigated. The best composition with respect to the overall combination of dielectric permittivity, tunability and loss factor was found to have $\varepsilon = 103$, $\tan\delta \leq 0.002$ at $f = 3.5$ GHz and tunability 5–6% at a 15 kV/cm biasing field. This combination of electrical parameters makes these materials among the most promising candidates for the development of high power tunable components.

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1. Introduction

Ferroelectric composite ceramics based on (Ba,Sr)TiO_3 (BSTO) solid solutions have become a superior candidate for development of a class of high power microwave control devices which employ their nonlinear properties, such as tunable filters, phase shifters, delay lines and other devices [1–3]. Moreover, there has been recent interest in the use of bulk ferroelectrics as control elements of high-power phase-shifters and switches for linear colliders as well as tuning layers for dielectric based accelerating structures [4, 5]. The main requirement for the electrical properties of ceramic materials to be used in such devices is a combination of relatively low dielectric constant ($\varepsilon \sim 100 - 500$) and low dielectric losses ($\tan\delta \leq 0.005$) in the microwave frequency range, and the electric field tunability $n > 1.02 - 1.20$ at bias fields $E = 10 - 50$ kV/cm (here $n = \varepsilon(0) / \varepsilon(E_0)$ where E_0 is the biasing field magnitude) [6, 7].

The first method used to decrease the value of the dielectric constant of ceramics to the required value is to increase the content of strontium titanate in BSTO solid solutions [8]. The barium/strontium correlation in the BSTO compound determines the Curie temperature of the ferroelectric. The value of the Curie temperature shifts towards lower temperatures with the increase of strontium concentration in the solid solution. Meanwhile, the

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increase in strontium titanate content leads to the sharp decrease of both the dielectric constant of the BSTO solid solution (from ~ several thousand close to the ferroelectric phase transition) and the dc electric field tunability. It is well known that the BSTO based compositions with high electric field tunability display very high dielectric losses, which seriously limit their practical applications.

The second way to decrease the value of the dielectric constant of BSTO ceramics is the use of additives of non-ferroelectric dielectrics with low dielectric constant and dielectric losses such as Al_2O_3, ZrO_2, MgO, $MgTiO_3$, $MgAl_2O_4$ etc. [9, 10]. It is found that a BSTO-MgO composite shows the better dielectric properties [3, 11, 12].

In our work [13–16] the composite BSTO-MgO-Mg_2TiO_4 ferroelectric ceramic was studied. It was determined that our ceramic materials display a combination of anomalous parameters, namely comparatively increased tunability of dielectric permittivity at relatively low values of ε, small dielectric losses over a wide microwave frequency range, and high electric breakdown strength. This combination of such electrical parameters makes these materials among the most promising candidates for the development of high power tunable components for accelerator applications.

As seen from ref [17], magnesium orthotitanate, Mg_2TiO_4, is a linear dielectric with ε of about 14 and the smallest dielectric losses ($\tan\delta = 0.6 \times 10^{-4}$ at a frequency of 10 GHz) among all known magnesium-titanium compounds. We have studied the influence of this substance on the dielectric properties of ferroelectric compositions of the BSTO type with the initial $BaTiO_3/SrTiO_3$ (BTO/STO) in the ratio of 55/45. The influence of this additive on the dielectric properties of a composite based on BTO/STO differs essentially from the influence of known earlier additives [3, 11]. On the one hand, the increase of the concentration of the Mg_2TiO_4-based additive in the BSTO composition leads to the decrease of the dielectric constant of the ferroelectric composite, analogous to the influence of traditional magnesium-containing additives on the value of ε [10]. However, an increase in the content of this linear dielectric in the volume of the composite results in the quite unusual increase of the tunability by a DC field (n_{dc}). It is especially important that these compositions demonstrate high tunability when applying short pulses (dynamic tunability n_{dyn}) at relatively low DC field magnitudes ~15 kV/cm. Our measurements showed that in this case n_{dyn} may even exceed n_{dc} [16]. These differences, as the measurements showed, are especially significant for samples of BSTO compositions with increased concentration of the additive (more than 40 wt.%) operating in a high biasing field range exceeding 30 kV/cm. As these studies showed, Mg_2TiO_4 based compositions are most promising for use in microwave devices operating in air, since the material demonstrated a significant increase in tunability with an increase of the biasing voltage as well. This is especially important for the use of ferroelectrics in the region of low bias fields (below 20 kV/cm), where the increase in the tunability strongly lags behind the increase in the voltage [18].

In refs [19–21], the anomalous increase of tunability of the dielectric permittivity at relatively low values of ε has been confirmed on $(Ba_{0.5}Sr_{0.5})TiO_3$-MgO-Mg_2SiO_4 and (Ba,Sr)TiO_3-Mg_2TiO_4 samples.

It was shown in ref [22] that the result of increasing the content of Mg-contained additives in the BSTO composition to >50% and the corresponding decrease in the dielectric constant (from 450 or less) was also a decreased tunability, accompanied by a significant reduction in the dielectric losses of the samples.

In this study we have investigated the structure and the electric properties (mainly ε, tanδ and n) of ferroelectric BSTO ceramics as a function of the composition of a mixture of magnesium orthotitanate Mg_2TiO_4 and MgO. The Mg_2TiO_4-MgO mixture was introduced into the initial BSTO powder in a wide range of concentrations from 40% to 160% relative to the BSTO. The purpose of the study was to reveal basic factors that influence the dielectric parameters, and to obtain materials with given values of ε and maximum tunability together with minimum losses at microwave frequencies.

2. Materials and methods

High purity MgO and TiO_2 (99.95%) were used as the starting materials for the preparation of the Mg_2TiO_4 additive. After milling in a vibration mill for 3 h the MgO-TiO_2 mixture was calcined in air at 1200°C for 4 h, then the calcined powder was re-milled by ball milling for 3 h to a grain size ≤ 1 μm. Pre-synthesized $BaTiO_3$ (HPBT-1) and $SrTiO_3$ (HST-1) with Ba/Ti and Sr/Ti 0.996 mol. ratio and the Mg-containing compositions were mixed in the desired ratios in a vibration mill for 3 h.

Samples of the required geometrical shape and size were prepared by hydraulic pressing with a 10% solution of polyvinyl alcohol taken as a binder. The prepared samples were sintered in an air within the temperature range of 1360–1420°C (3 h) in a chamber electric furnace until zero water absorbance and porosity less than 4% was obtained. The measurements of the relative dielectric constant, tanδ and Q factor (1/tanδ) were performed at 1 MHz and at 0.7–11 GHz with disc samples 6 to 30 mm in diameter and 0.8 – 20 mm thick. Microwave properties were measured by the waveguide dielectric resonator method [23]. Measurements of the dielectric properties and tunability were performed using a 1 MHz rf voltage and a constant bias DC voltage applied to the metalized disk samples.

Sintered samples were studied on a DRON-3 diffractometer with a Cu-K_α, Ni filter. Further measurements were made using scanning electron microscopes (SEM) JSM-6460LV and JSM-7001F (JEOL, Japan) and an EDS-spectrometer for X-ray microanalysis.

3. Results and discussion

X-ray studies of the influence of the complex Mg-containing MgO-Mg_2TiO_4 additive to the (Ba,Sr)TiO_3 composition on the structure of the ferroelectric ceramic showed that at least three major crystalline phases in its phase composition: BSTO solid solution and two phases of magnesia and magnesium orthotitanate. A sample of the spectrum is shown in Fig. 1. X-Ray data for samples of the BTO/STO = 55/45 system, containing 40 – 160 wt.% total additions of MgO and Mg_2TiO_4 over 100% of the initial mixture (T_{sin} = 1400°C) are presented in Table 1. Analysis of these data showed that the unit cell parameter for the main perovskite-type phase of BSTO does not change significantly depending on the total amount of additives and their percentage correlation within the concentration range investigated. In addition, two accompanying phases with the perovskite structure were always present in the phase composition of the samples, with their total amount not exceeding 5%.

X-ray data are in a good agreement with the electron microscopy microstructure data (Fig. 2–4).

Each sample studied includes three main phases: light/clear BSTO type, gray Mg_2TiO_4 and dark MgO. This has been verified by SEM data, for example for a composition BTO/

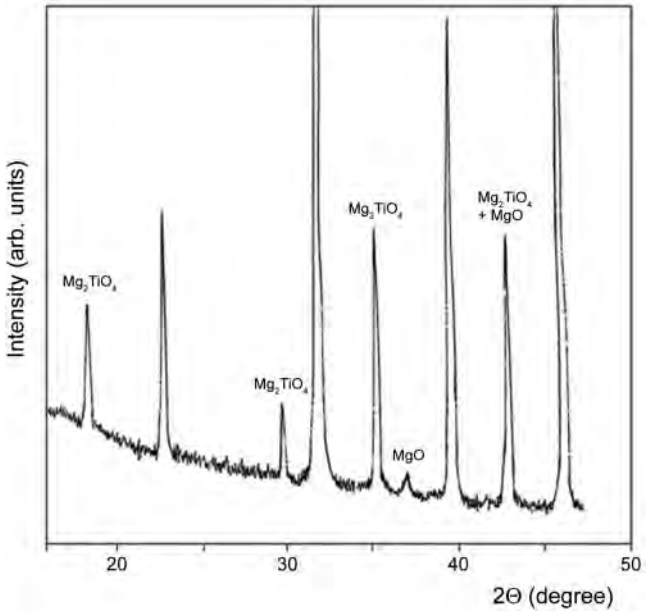


Figure 1. X-ray spectrum of ceramic sample BTO/STO = 55/45 + wt.% MgO/Mg_2TiO_4 = 20/20 additives.

Table 1. X-Ray analysis data for the samples of the system BTO/STO = 55/45, containing 40 – 160 wt.% total additions of MgO and Mg_2TiO_4.

Composition №	M_2TiO_4 additive	MgO additive	Unit cell of main perovskite phase	Unit cell of additive perovskite phases
1	30	30	$a_1 = 3.9527(10)$	$a_2 = 3.961(3)$ $a_3 = 3.940(3)$
2	30	35	$a_1 = 3.9529(10)$	$a_2 = 3.962(2)$ $a_3 = 3.937(2)$
3	35	25	$a_1 = 3.9542(10)$	$a_2 = 3.964(2)$ $a_3 = 3.937(2)$
4	35	30	$a_1 = 3.9538(10)$	$a_2 = 3.964(2)$ $a_3 = 3.937(2)$
5	40	0	$a_1 = 3.9534(10)$	$a_2 = 3.969(3)$ $a_3 = 3.946(2)$
6	40	45	$a_1 = 3.9544(10)$	$a_2 = 3.965(3)$ $a_3 = 3.946(2)$
7	40	60	$a_1 = 3.9501(11)$	$a_2 = 3.965(3)$ $a_3 = 3.946(2)$
8	80	0	$a_1 = 3.9506(10)$	$a_2 = 3.954(2)$ $a_3 = 3.927(3)$
9	80	20	$a_1 = 3.9503(11)$	$a_2 = 3.962(3)$ $a_3 = 3.943(2)$
10	80	80	$a_1 = 3.9503(12)$	$a_2 = 3.962(3)$ $a_3 = 3.943(2)$
11	100	0	$a_1 = 3.9518(10)$	$a_2 = 3.952(2)$ $a_3 = 3.940(3)$
12	100	20	$a_1 = 3.9525(11)$	$a_2 = 3.960(3)$ $a_3 = 3.944(2)$
13	100	35	$a_1 = 3.9505(11)$	$a_2 = 3.960(3)$ $a_3 = 3.943(2)$

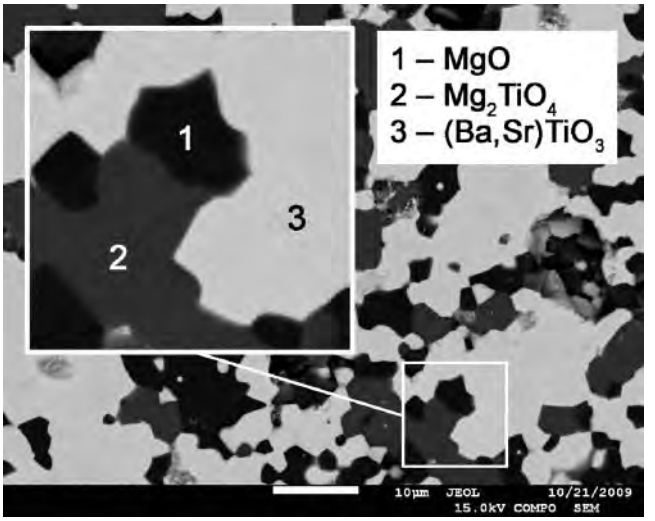


Figure 2. SEM image of ceramic sample BTO/STO = 55/45 + wt.% MgO/Mg_2TiO_4 = 30/30 additives.

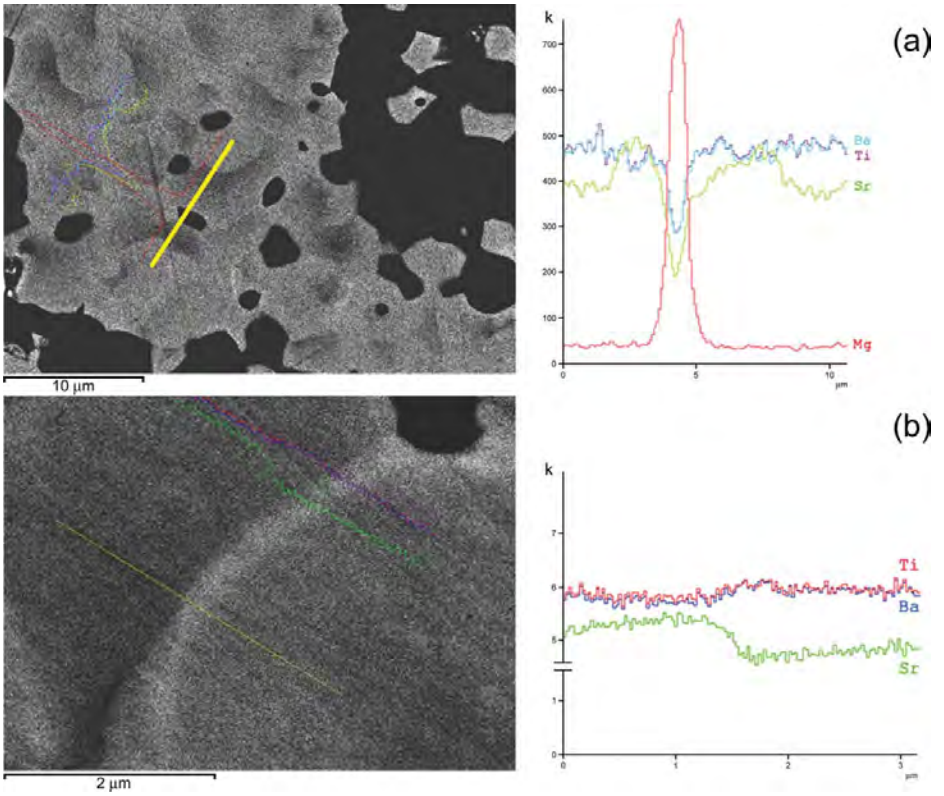
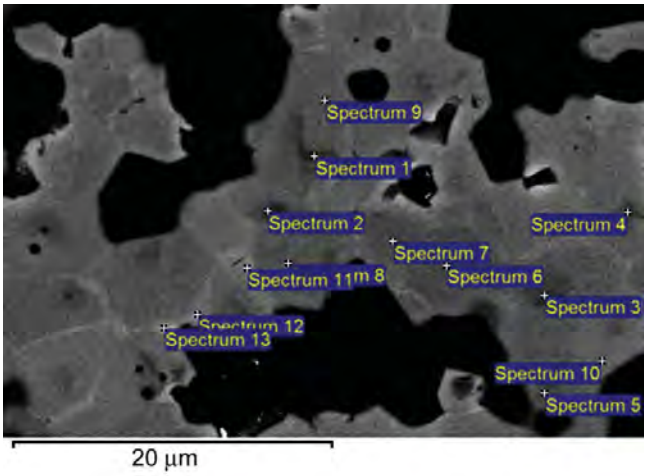


Figure 3. SEM image of ceramic sample BTO/STO = 55/45 + wt.% MgO/Mg_2TiO_4 = 25/35 additives.



Spectrum	Mg	Ti	Sr	Ba	O	Total
Spectrum 1	0.23	23.00	24.79	28.61	23.37	100.00
Spectrum 2	0.21	23.88	23.04	29.16	23.70	100.00
Spectrum 3	0.29	22.95	26.32	26.97	23.47	100.00
Spectrum 4	0.28	23.15	24.84	28.25	23.48	100.00
Spectrum 5	2.91	21.35	22.90	29.08	23.75	100.00
Spectrum 6	0.33	22.35	21.09	33.34	22.88	100.00
Spectrum 7	0.33	22.86	21.90	31.73	23.18	100.00
Spectrum 8	0.31	22.54	21.24	32.93	22.98	100.00
Spectrum 9	0.33	22.10	21.35	33.44	22.78	100.00
Spectrum 10	0.78	22.24	20.84	33.12	23.03	100.00
Spectrum 11	0.28	22.15	18.81	36.13	22.63	100.00
Spectrum 12	1.04	22.54	18.53	34.73	23.17	100.00
Spectrum 13	0.22	22.28	18.31	36.56	22.63	100.00

Figure 4. SEM image of ceramic sample BTO/STO = 55/45 + wt.% MgO/Mg_2TiO_4 = 20/40 additives.

STO = 55/45 + wt.% MgO/Mg_2TiO_4 = 30/30 (over 100%) at Fig. 2. However, as seen from the photos, the MgO phase links the Mg_2TiO_4 phase crystal grains making the crystalline aggregates longer. These consist of Mg-containing non-ferroelectric crystalline phases and therefore promote the formation of a so called frame or grid, the cells of which are filled with BSTO type ferroelectric. A similar structure was observed in ref [15]. This effect is considerable, especially for compositions with high concentrations of Mg-containing additives.

Fig. 3a displays micrographs for the BTO/STO = 55/45 + wt.% MgO/Mg_2TiO_4 = 25/35 additives (over 100% of the initial mixture). Red corresponds to Mg content in the MgO phase. One can see that the Mg content increases in the dark phase with decreasing content of Ba and Sr (darker regions).

Sintering of the BTO/STO mixture with the composite MgO and Mg_2TiO_4 additives is accompanied (similar to the samples described above) by the formation of perovskite impurity phases with increased and decreased lattice parameters compared to the perovskite main phase (see Table 1). The volume content of the perovskite impurity phases does not exceed 3–5%. Distribution of these phases in the heterogeneous ferroelectric structure is clearly seen in Fig. 3b. The light phase with the increased Ba content is concentrated on the

Table 2. Dielectric properties: relative dielectric constant, tanδ, Q × f factor and n of the new compositions based on BSTO-MgO-Mg_2TiO_4 system.

№	∑ wt.% additives	ε	tanδ × 10^4	ε	Q × f, GHz	n_{dc}	n_{dc}	n_{dyn}	n_{dc}
		at 1 MHz		at 3.5 GHz		E = 15 kV/cm	E = 50 kV/cm		E = 80 kV/cm
1	60	279	2.4	263	1025	1.089	1.302	1.302	1.434
2	65	237	2.2	235	1090	1.092	1.306	1.318	1.433
3	60	302	2.0	246	965	1.102	1.332	1.332	1.478
4	65	257	2.6	246	1008	1.088	1.309	1.327	1.440
5	40	600	2.9	527	650	1.102	1.337	—	1.621
6	85	147	2.4	138	1270	1.065	1.220	1.253	1.357
7	100	108	1.8	103	1540	1.057	1.174	1.230	1.278
8	80	284	3.6	253	550	1.127	1.363	–	1.650
9	100	146	1.8	139	990	1.087	1.285	1.337	1.438
10	160	57	3.2	55	2370	1.024	1.091	1.109	1.128
11	100	195	3.3	170	485	1.111	1.332	–	1.571
12	120	109	2.1	101	960	1.072	1.230	1.273	1.340
13	135	81	2.4	77	1570	1.045	1.148	1.179	1.215

main phase crystal boundaries, while the phase with decreased Ba content (the darker one) can be seen inside the crystals of the main solid solution BSTO phase. EDS data confirm these results (Fig. 4).

Dielectric properties: the relative dielectric constant, loss tangent (tanδ), Q factor (Q × f) and tunability (n) of the composition developed in this work are listed in Table 2. It is shown that increasing the total amount of linear additives from 40 to 160 wt.% in the ferroelectric composite (based on the solid solution with the ratio $BaTiO_3/SrTiO_3$ = 55/45) led to correspondingly reduced levels of the relative permittivity from 600 to 57. Values of tunability and quality factor of the materials are determined by both the composition of the additives and their ratio in the heterogeneous mixture. Concerning the level of tunability, the samples in Table 2 were found to be qualified as ferroelectric ceramics for use in accelerator physics devices in the L-band frequency range. The figure of merit values (Q × f in the table) essentially depend on the ratio of linear components in the additive. The investigations showed that the quality factor of ferroelectric samples increases with increasing magnesia concentrations. The best composition with respect to the combination of parameters is sample № 7 with permittivity on the order of 100 and

Table 3. Frequency dependence of the ferroelectric response parameters (ε, tanδ, Q × f) of the ceramic composition BTO/STO = 55/45 + wt.% MgO/Mg_2TiO_4 = 25/35 for different sample geometries and frequencies.

D, mm	L, mm	f, GHz	ε	tanδ	Q	Q × f, GHz
30	20.18	0.756	312	0.0007	1300	1000
24	20.18	0.911	320	0.0012	850	770
	11.20	0.981	323	0.0014	730	720
	6.97	1.081	327	0.0015	660	710
20	11.20	1.138	326	0.0016	640	730
	6.97	1.252	322	0.0017	590	740
	6.97	1.256	320	0.0016	640	805
14	11.20	1.530	336	0.0021	470	720
	6.97	1.711	306	0.0024	420	710
10	11.20	2.131	321	0.0025	400	850
	6.97	2.150	344	0.0031	320	700
	5.00	2.401	304	0.0029	350	840
	5.01	2.431	296	0.0028	350	860

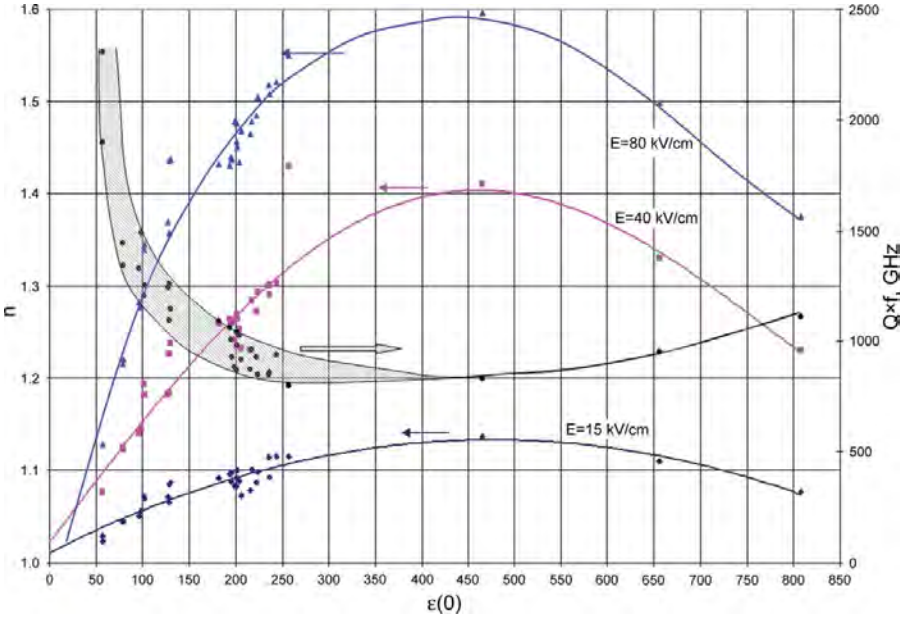


Figure 5. Electrical parameters of samples of composite ferroelectrics BSTO-MgO-Mg_2TiO_4 system.

$Q \times f = 1540$ GHz. The frequency dependence of the electrical parameters of ferroelectric samples is shown in Table 3. In the frequency range from 0.76 to 2.43 GHz the dielectric constant does not change significantly and tanδ increases from 0.0007 to 0.0031. $Q \times f$ values of the sample do not vary much over the frequency range studied.

Our study of the microstructure and dielectric properties of synthesized ferroelectric composite materials based on BSTO solid solutions with a >40 wt.% Mg-containing linear additive increase revealed a group of features that critically impact the dielectric response properties of the ceramics. First of all, these features are defined by the formation of the main phase crystal boundaries on the borders of BSTO solid solution crystallites. The research revealed that these boundary phases are of a diffusive nature. Their composition is characterized by the increased barium content compared to the composition of the main solid solution.

The thickness of these interface regions depend on the sintering temperature of the samples and is strongly connected with the dielectric response parameters of the ferroelectric samples. The volume ratio of the phases and surface phenomena on their borders are important for engineering a ferroelectric material with desired electrical properties in a given range of frequencies from rf to microwave.

In Fig. 5 the main parameters of all samples of composite ferroelectrics studied are listed. Samples of ceramic with permittivity of ~50 to ~500 distinguished by a low level of dielectric losses and increased tunability of the dielectric constant, especially in range of increased electric field intensity were obtained.

4. Conclusions

In this study the phase relation, crystal structure, microstructures and dielectric properties of composite ferroelectrics based on BSTO were investigated as a function of the composition of a mixture of magnesium orthotitanate Mg_2TiO_4 and MgO.

The volume ratio of the phases and surface phenomena on their borders are important for the formation of a ferroelectric material with desired electrical properties ranging from radio frequency to microwave.

It was shown that increasing the overall content of linear additives of the ferroelectric composite (based on the solid solution with $BaTiO_3/SrTiO_3 = 55/45$) from 40 to 160 wt.% led to a reduction of the dielectric permittivity from 600 to 55. Tunability and tanδ of the materials are determined by both the composition of the additives and their ratio in the heterogeneous mixture. The investigations showed that the quality factor of ferroelectric samples increases with increasing magnesia concentration. The best composition with respect to the overall combination of dielectric permittivity, tunability and loss factor was found to have $\varepsilon \sim 100$, figure of merit $Q \times f =$ 1540 GHz and tunability 5–6% at a 15 kV/cm biasing field. This combination of electrical parameters makes these materials among the most promising candidates for the development of high power tunable components for accelerator physics applications.

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References

1. T. N. Verbitskaja, Variconds. Gosenergoizdut, Moscow-Leningrad, 1958.
2. O. G. Vendik et al., Ferroelectrics in microwave engineering. Sov. Radio, Moscow, 1979.
3. W. Chang, L. Sengupta, MgO-Mixed $(Ba_{0.6}Sr_{0.4})TiO_3$ bulk ceramics and thin films for tunable microwave applications. *J Appl Phys.* **92**(7), 3941–3946 (2002).
4. C. Jing, A. Kanareykin, J.G. Power, M. Conde, W. Lie, S. Antipov, P. Schoessow, W. Gai, Experimental demonstration of wakefield acceleration in a tunable dielectric-Loaded accelerating structure. *Phys Rev Lett.* **106**(16), 164802 (2011).
5. A. Kanareykin, S. Kazakov, E. Nenasheva, A. Tagantsev, V. P. Yakovlev, Ferroelectric based high power components for L-band accelerator applications. Proceedings Particle Accelerator Conference PAC'09, Canada, Vancouver. 2009; 824–826.
6. S. Kazakov, S. Shchelkunov, V. Yakovlev, A. Kanareykin, E. Nenasheva, J. L. Hirshfield, Fast ferroelectric phase shifter design for ERLs. Proceedings of the 45th ICFA Beam Dynamics Workshop ERL09: Energy Recovery Linac, NY, Ithaca. 2009; 67–71.
7. A. Kanareykin, S. Kazakov, E. Nenasheva, A. Tagantsev, V. P. Yakovlev, Tunable ferroelectric based technologies for accelerator components. Proceedings EPAC 2008, Italy, Genova. 2008; 1646–1648.
8. G. A. Smolensky, Ferroelectrics and related materials. Academic Press, New York, 1981.
9. L. Sengupta et al., "Ceramic ferroelectric composite material-BSTO-ZrO_2". U.S. Patent 5 486 491, Juny 23, 1996.
10. L. H. Chiu, L. C. Sengupta et al., "Ceramic ferroelectric composite materials with enhanced electronic properties BSTO-Mg based compound-rare earth oxide". U.S. Patent 6 074 971, Juny 13, 2000.
11. L. Sengupta, S. Sengupta, Novel ferroelectric materials for fased array antennas, IEEE Trans. *Ultrason. Ferroelectr Freq Control.* **44**(4), 792–797 (1997).
12. U. C. Chung, C. Ellissalde, M. Maglione, C. Estournes, M. Pateand, J. P. Ganne, Low-loss, highly tunable $(Ba_{0.6}Sr_{0.4})TiO_3$/MgO composite. *Appl Phys Lett.* **92**(4), 042902 (2008).
13. E. A. Nenasheva, A. D. Kanareykin, "Ceramic ferroelectric composite material with low dielectric losses". RU Patent 2422404, November 26, 2007.
14. E. A. Nenasheva, A. D. Kanareykin, "Low dielectric loss ceramic ferroelectric composite material". U.S. Patent 8 067 324, November 29, 2011.

15. E. A. Nenasheva, N. F. Kartenko, I. M. Gaidamaka, O. N. Trubitsyna, S. S. Redozubov, A. I. Dedyk, A. D. Kanareykin, Low loss microwave ferroelectric ceramics for high power tunable devices. *J Eur Ceram Soc.* **30**(2), 395–400 (2010).
16. A. B. Kozyrev, A. D. Kanareykin, E. A. Nenasheva, V. N. Osadchy, D. M. Kosmin, Observation of an anomalous correlation between permittivity and tunability of a doped (Ba,Sr)TiO_3 ferroelectric ceramic developed for microwave applications. *Appl Phys Lett.* **95**(1), 012908–012910 (2009).
17. Y. L. Daniluk, I. V. Maslovskaya, E. A. Nenasheva, V. P. Pyshkov, O. N. Trubitsina, Electrical properties at microwave frequencies of ceramic materials based mechanical mixtures for capacitors. *Electronic Technique.* **3**, 13–14 (1988).
18. E. A. Nenasheva, A. D. Kanareykin, A. I. Dedyk, S. F. Karmanenko, A. A. Semenov, High frequency characteristics of (BaSr)TiO_3 ceramic with various additives intended for accelerator physics applications. *Integrated Ferroelectrics.* **70**, 107–113 (2005).
19. Y. He, J. Zhao, Y. Xu, C. Li, Anomalous correlation between dielectric constant and tunability in (BaSr)TiO_3-MgO-Mg_2SiO_4 composite ceramics. *J Am Ceram Soc.* **96**(4), 1203–1208 (2013).
20. M. Lei, Z. Feng, Z. He, B. Liu, Y. He, B. Li, Y. Xu, The tunability in (BaSr)TiO_3-Mg_2TiO_4 system. *Ceram. Intern.* **41**(7), 8791–8800 (2015).
21. M. Lei, The impact of composite effect on dielectric constant and tunability in ferroelectric-dielectric system. *J Am Ceram Soc.* **98**(10), 3250–3258 (2015).
22. E. A. Nenasheva, G. A. Kashutina, N. F. Kartenko, A. B. Kozyrev, A. D. Kanareykin, I. M. Gaidamaka, Low-permittivity microwave ferroelectric composite ceramics for tunable devices. 7th International Conference on Microwave Material and their Application MMA-2012, Taiwan, Taipei. 2012; 141–142.
23. V. F. Matveichuk, C. N. Sibirtsev, N. M. Karikh, A. V. Serov, Resonance methods and measurement means for the materialsat super high frequencies. In Proceedings of the VII International Conference APEP-2004, Russia, Novosibirsk. 2004; 3, 175–182.