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Ceramics Materials Based on (Ba,Sr)TiO_3 Solid Solutions for Tunable Microwave Devices

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Abstract. Structure and electrical properties at radio frequencies as well as within the 3.5–35 GHz frequency range have been investigated for ceramic samples of the $(1-y)(Ba_xSr_{1-x})TiO_3 \cdot y$MgO (BSM) system where $x = 0.4$–0.6; $y = 0.15$–0.30. For the compositions studied the bulk ferroelectrics were synthesized with the dielectric constant of 400–600 and high tunability coefficient. We indicated that the quality factor of the samples was in the range of 100–1000 within the frequency band of 3.5–35 GHz. The phase correlations and unit cell constants of the perovskite phase of the BSM samples were studied. The low loss factor and high tunability of the bulk material allowed us using the BSM ferroelectric ceramic layer for tunable accelerating structures of the Argonne Dielectric Wakefield Accelerator and for high power switches design and development for the future linear colliders.

Keywords: ferroelectric, BSTO, magnesium oxide additives, tunability, dielectric loss factor

1. Introduction

Ferroelectric ceramics of (Ba,Sr)TiO_3 (BSTO) solid solutions with various additives are the basic ceramic materials to design microwave devices operated by the electric field, namely modulators, filters, phase shifters, and other [1–3]. Moreover, an interest appeared recently towards the use of bulk ferroelectrics as control elements of high-power phase-shifters and switches for linear colliders. Ferroelectric layers can be also used as control elements for accelerating structures with dielectric loading [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 in the range from 300 to 600 at the electric field tunability not worse than 10–20% (electric field magnitude $\sim$(2–5) V/μm) and low dielectric losses at the microwave range ($\tan\delta \leq 0.005$).

The required level of the dielectric constant in the system of (Ba,Sr)TiO_3 solid solutions with perovskite structure can be achieved by increasing the content of strontium titanate [6], which is accompanied by the shift of Curie temperature of the ferroelectrics towards lower temperatures and the decrease of dielectric loss tangent down to $(1–3)\cdot10^{-3}$ in a wide frequency range including microwave. Though for such materials electric field tunability of ε almost disappears.

Recently BSTO are being widely studied having compositions with the additives of rare earth and alkali earth oxides and compounds. These compositions are to provide with the combination of high tunability of ε and low dielectric losses [7]. The study of phase relations and structural characteristics of the phase mixture in connection with dielectric properties and tunability of BSTO:MgO system has not been completed in details in published study results, though these factors are crucial for the BSTO bulk applications.

In this work we studied the structure and dielectric properties of ceramics in the BSTO system with the additives of magnesia to select the optimal composition providing for the necessary combination of electrical parameters and promising to be used in accelerating

technique. We intended synthesizing the hetero-phase system consisted of main perovskite phase and MgO inclusions in order to decrease BSTO dielectric losses at the essential high level of tunability factor. In doing this, electrical properties were studied in a wide frequency range up to 35 GHz for $(Ba_xSr_{1-x})TiO_3$ ceramics with magnesia additives depending on the solid solution composition with x varying from 0.4 to 0.6 and the amount of magnesia being from 15 to 30% of the total amount of the solid solution.

2. Sample Preparation

The barium strontium titanate solid solutions $(Ba_xSr_{1-x})TiO_3$ ($x = 0.4$–0.6) were synthesized by ceramic processing from titanium dioxide (TiO_2) and strontium and barium carbonates ($SrCO_3$, $BaCO_3$) or prefabricated barium and or strontium titanates ($BaTiO_3$, $SrTiO_3$). Initial powder of the solid solutions and magnesium oxide of the required proportions have been developed by mixing them in a vibration mill for three hours to particle size 1 μm.

Samples of required geometrical shape and size were prepared by hydraulic pressing. 10% solution of polyvinyl alcohol was taken as a binder. The prepared samples were sintered in air atmosphere within the temperature range of 1380–1540°C (3 h) in a chamber electric furnace until zero water absorbance. Sintered samples were studied on a DRON-3 diffractometer with a Cu-K_α, Ni filter. To measure electrical properties at radio frequencies disc samples were covered with a silver-containing dope burnt-in at a temperature of 840 ± 20°C. The voltage dependencies of the dielectric characteristics were measured on disk samples ($h = 0.5$ mm) with evaporated copper electrodes. The thickness of Cu-electrodes was about 3–5 μm. We used the discs of 6 mm diameter and 0.5–1.3 mm thick as well as 20 $\times$ 30 $\times$ 1 mm plates at 3.5–11 GHz. Measurements at 35 GHz was done using 3.3 $\times$ 10 $\times$ 0.5 mm plate samples polished on both sides.

The measurement of dielectric characteristics were carried out at frequencies 1 kHz and at 1 MHz and voltage amplitude 0.1 V [8]. The temperature dependence of the samples capacitances as well as voltage effect $C(U)$ have been studied. Tunability coefficient were estimated as $K = C(0)/C(U_{\max})$ where $U_{\max}$ is a peak voltage applied to the electrodes. The maximal field magnitude value did not exceed 2.4 V/μm.

Three techniques of electrode-less measurements have been used for a study of microwave (MW) dielectric characteristics of the ferroelectric ceramics: (A)—waveguide round resonator for 3.5–11 GHz; (B)—rectangular cavity resonator for (9–12) GHz with tunable dimensions; and (C)—the same resonator type for (27–35) GHz [9]. Three methods mentioned above were used to verify the obtained results and to expand the frequency measurement range from 3.5 to 35 GHz.

3. Results and Discussion

The unit cell parameters of the perovskite solid solutions of $(Ba,Sr)TiO_3$ synthesized of barium and strontium titanate of proportion variety and dielectric constant and loss factor values measured at 1 MHz are presented in Table 1. One can see that the barium content of the BSTO solid solution extension causes the unit cell parameter rising along with the dielectric constant increasing, especially after $x = 0.45$. Magnesium oxide adding into the furnace charge in the range of 15–30% of the total amount of the solid solution results in heterogeneity composition forming that contents the main phase of the solid solution with the perovskite structure of BSTO and MgO. It should be mentioned that the magnesium oxide phase increases for high value of y at $(1 - y)(Ba_xSr_{1-x})TiO_3 \cdot yMgO$ composition. Some admixture phase presence was found, and the content of these phases depended on the charge makeup and sintering temperature. The total number of the additives did not exceed 5% if the barium and strontium titanate were synthesized before sintering and reached of 10% for the furnace charge consisted of the barium and strontium carbonates. We observed mostly barium polytitanium, spinel as admixtures and rarely magnesium titanium $MgTi_2O_5$ and strontium polytitanium. The samples with the minimum admixture phase

Table 1. X-ray data of the dielectric properties of the solid solution samples of $(Ba_xSr_{1-x})TiO_3$ ($T_{\sin} = 1540$°C).

Composition (x)	Unit cell parameter (a, Å)	ε (20°C)	tan δ (1 MHz)
0.40	3.9366 (8)	490	0.0028
0.45	3.9456 (10)	540	0.0042
0.50	3.9475 (7)	1350	0.0065
0.55	3.9498 (11)	1480	0.0136
0.60	3.9568 (5)	1620	0.0174

Table 2. X-ray analysis data of the $(1-y)(Ba_xSr_{1-x})TiO_3 \cdot y$MgO samples.

Composition		Unit cell parameter (a,Å) perovskite structure phase	
X	y	Sintering temperature, 1400°, (3 h)	Sintering temperature, 1540°, (3 h)
0.40	0.15[b]	3.9497	—
0.45	0.20	3.9563	—
0.50	0.15	3.9477	—
0.50	0.20[a]	3.9461	3.9499
0.50	0.25	3.9482	3.9488
0.50	0.30	3.9530	3.9542
0.55	0.20	3.9563	—

[a]BSM-1 composition.
[b]BSM-2 composition.

content and magnesium oxide adding showed (Table 2) increased unit cell parameter with the perovskite structure in comparison with solid solution BSTO cell parameters (see Table 1).

One can see, for instance, that for the $(Ba_{0.5}Sr_{0.5})TiO_3$ compositions consisted of 20, 25 and 30% magnesium oxides the unit cell parameter enlarged significantly with the sintering temperature increasing from 1400 to 1540°C. It can be the consequence of the inter-phase interactions followed by the composition redistribution and crystal phases forming in the samples that causes dielectric properties changes of the ceramic samples.

Electrical properties measured data for the BSM-1 and BSM-2 are shown in the Tables 2 and 3. Data of

Table 3. The characteristics of ferroelectric BSM ceramics.

Material	Sample	ε	Tan $\delta \times 10^4$ 1 MHz	Tan $\delta \times 10^4$ 1 kHz	T_m (K)	K_u (E, V/μ)
BSM-1	1	520	2.0	1.5	190	
	2	510	2.4	1.7	190	1.004 (0.39)
	3	502	3.2	2.5	195	1.090 (0.80)
	4	515	2.0	1.5	190	1.110 (2.40)
	5	517	2.2	1.6	195	
BSM-2	1	500	1.2	0.9	170	
	2	495	1.2	1.1	175	1.003 (0.35)
	3	490	1.0	0.8	170	1.030 (0.87)
	4	480	1.5	1.2	175	1.060 (2.00)
	5	484	1.4	1.2	170	
BST0 $x = 0.5$	1	1350	84	65	245	1.110 (2.0)

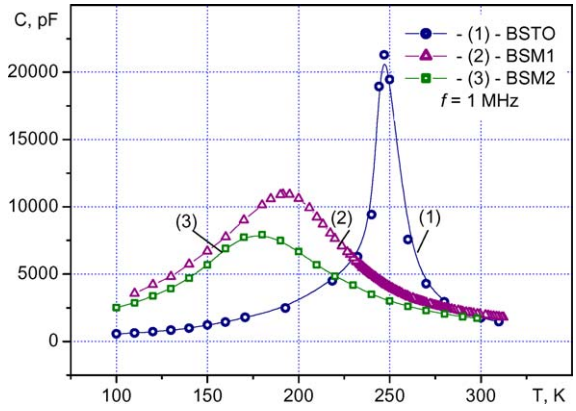

Fig. 1. Temperature dependence of the capacitance of the ceramic sample measured at frequency of 1 MHz: (1) $(Ba_{0.5}Sr_{0.5})TiO_3$ – BSTO; (2) BSM-1; and (3) BSM-2 ceramic samples.

the Table 3 and Fig. 1 showed that Sr titanium content increasing in the solid solution composition as well as magnesium oxide proportion growing result in temperature (corresponding to the maximal capacitance) shift into the low value area down to T_m of 170 K. Based on the Table 3 data we can conclude that magnesium oxide content of 20% (BSM-1 composition) for the BSTO solid solution $x = 0.5$ causes dielectric constant decreasing from 1350 to 500 for the same value of the tunability coefficient.

Figure 2 shows the frequency dependence of quality factor ($Q \sim 1/\tan\delta$) of BSM ceramics in range 3.5–35 GHz where the results of three techniques

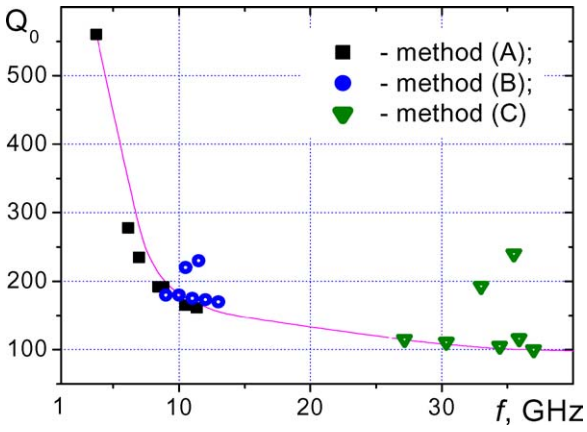

Fig. 2. Frequency dependence of the quality factor Q of the BSM ceramic samples.

have been used. The nonlinear dependence of $Q(f)$ was found that indicates the different physical mechanisms of MW dielectric losses in BSM ceramics to be discussed.

An estimation of MW dielectric losses of BSM ceramics showed rather low values of $\tan\delta = (0.005–0.01)$ for wide frequency region of (10–35) GHz. The low loss factor and high tunability coefficient allow utilizing the BSM ferroelectric ceramics for tunable accelerating structures of the Argonne Wakefield Accelerator [4]. The same BSM ceramics could be used in high power 11.42 GHz switches of the linear colliders applications [4, 5].

4. Conclusions

The electrical properties at the RF and MW frequency range and microstructure of the ceramic samples of $(1-y)(Ba_xSr_{1-x})TiO_3 - y$MgO (BSM) for $x = 0.4–0.6$; $y = 0.15–0.30$ have been studied. It was shown that the magnesium oxide content increasing causes lowing dielectric constant value of the heterogeneous composition and decreasing of the tunability for the low loss factor samples at the wide frequency range up to (1–10) GHz. The heterogeneity of the phase composition, defined by the charge makeup as well as sintering technology and temperature, was found to influence the microwave electrical properties of the tested samples.

The ceramic ferroelectric of the studied concentrations range have been developed with the dielectric constant of $\varepsilon = 400–600$, high tunability rate and quality factor of $Q = 100–1000$ at 3.5–35 GHz frequency range.

The materials and their properties presented in this paper satisfy the requirements of bulk ceramic ferroelectric demand for high power tunable devices for future linear colliders applications.

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