Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 27 (2007) 2845–2848
www.elsevier.com/locate/jeurceramsoc

Tunability and microwave dielectric properties of $BaO–SrO–Nd_2O_3–TiO_2$ ceramics

E.A. Nenasheva [a,c,*], N.F. Kartenko [b], O.N. Trubitsina [c], V.F. Matveichuk [d], S.N. Sibirtsev [d], I.M. Gaidamaka [e]

[a] *GIRICOND Research Institute, 10 Kurchatov Street, St. Petersburg 194223, Russia*
[b] *A.F. Ioffe Physicotechnical Institute Russian Academy of Sciences, 26 Politechnicheskaya Street, St. Petersburg 194021, Russia*
[c] *Ceramics Co. Ltd., 10 Kurchatova Street, St. Petersburg 194223, Russia*
[d] *Siberian State Research Institute of Metrology, 4 Dimitrova Street, Novosibirsk 630004, Russia*
[e] *St. Petersburg State Mining Institute, 2, 21st Line, St. Petersburg 199106, Russia*

Available online 15 December 2006

Abstract

Ferroelectrics such as barium–strontium titanates (BSTO) and Mg-doped BSTO are well known as promising candidates for the application in microwave tunable devices including phase shifters, filters, and others operating at microwave frequencies. In this study new bulk ceramics based on $BaTiO_3$ (BTO)–$SrTiO_3$ (STO) with addition of $BaNd_2Ti_4O_{12}$ (BNT) solid solution was investigated. The phase correlations, size, and nature of boundaries between phases were studied using scanning electron microscopy (SEM). The effect of compositional change on the unit cell parameters of the perovskite phase, microwave dielectric properties, and tunability under DC field had been studied. The materials with dielectric constant ~320–700, Qf = 1950–3000 GHz at 3.5 GHz and tunability ~8.0–31.7% at E = 1 V/μm were achieved.

Keywords: Sintering; Microstructure; Electron microscopy; Electrical properties; $BaTiO_3$ and titanates

1. Introduction

Ferroelectrics such as barium–strontium titanate (BSTO) are well known as promising candidates for the application in microwave tunable devices including phase shifters, filters, and others operating at microwaves.[1–3] 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 the optimal value of the dielectric constant (ε), high level of electric field tunability, and low dielectric losses ($\tan\delta \leq 0.005$) in the microwave range. To prepare a series of compositions with a wide range of the dielectric constant values linear dielectrics with low dielectric constant values, like magnesium oxide, are added in a wide concentration range.[6] The additives do not interact chemically with the basic phase of the BSTO solid solution. The value of the ε tunability at a constant electric field in such materials is almost identical to this parameter of the equivalent BSTO compositions without additives,[7] but the increase of tunability is accompanied with the decrease of the Q-factor of the samples.

The main goal of this work was to search for new compositions of ferroelectrics with high ε tunability at a constant electric field and small dielectric losses in the microwave range.

In this study bulk ferroelectrics ceramics based on $BaTiO_3$ (BTO)–$SrTiO_3$ (STO) with addition of $BaNd_2Ti_4O_{12}$ (BNT) solid solutions was investigated. $BaNd_2Ti_4O_{12}$ (BNT) is the linear dielectric with the increased value of $\varepsilon \approx 85$.[8,9] Compositions of BTO/STO–BNT system were studied into two sections: with 65 mass% $BaTiO_3$ in BTO/STO mixture with the additives of 10–70 mass% BNT solid solution and with 50–80 mass% $BaTiO_3$ in BTO/STO mixture with the additives of 50 mass% BNT over 100 mass% of the mixture.

2. Experimental procedure

High purity $BaCO_3$, TiO_2 (99.95%) and Nd_2O_3 (99.99%) were used as the starting materials for BNT preparation. After the milling in a vibration mill for 3 h the BNT-mixture was calcined

* Corresponding author at: Ceramics Co. Ltd., 10 Kurchatova Street, St. Petersburg 194223, Russia. Tel.: +7 812 552 9434; fax: +7 812 552 6057.
E-mail address: info@ceramics.sp.ru (E.A. Nenasheva).

0955-2219/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2006.11.009

in air at 1240 °C/4 h, then calcined powder was re-milled by ball milling for grain size ∼1 μm. Pre-synthesized $BaTiO_3$ (HPBT-1) and $SrTiO_3$ (HST-1) (Fuji Titanium Industry Co., Japan) with Ba/Ti and Sr/Ti 0.996 molar ratio and the BNT solid solution have been mixed in various ratios in a vibration mill for 3 h. The prepared samples were sintered in air within the temperature range of 1360–1450 °C (3 h) in a chamber electric furnace until zero water absorbance and porosity less than 5%. Sintered samples were studied on a DRON-3 diffractometer with a Cu Kα, Ni filter and scanning electron microscope (SEM) JSM-6460LV JEOL with backscattering electrons (signal COMPO and TOPO) and EDS-spectrometer for X-ray microanalysis. The X-ray quantitative analysis of samples is executed by a standard technique with use of artificial mixes of phases BSTO and BNT.

The measurements of a relative dielectric constant and Q-factor ($1/\tan\delta$) were performed on the disc samples 6 mm in diameter and 0.8–1.5 mm thick at 3.5–10 GHz by the method of waveguide dielectric resonator.[10] The measurements of the dielectric properties at 3.5 GHz under the temperature change from −60 to +80 °C and constant electric voltage applied to the samples were performed on the metallized disk samples 6.0 mm in diameter and 3.0 mm thick using the measurement cell specially developed according to the international standard.[11]

3. Results and discussion

Table 1 presents the results of the investigations for the samples of the BTO/STO (65 mass% $BaTiO_3$) composition with the additive of 10–70 mass% BNT. Analysis of the data shows that up to 25–30% of the BNT solid solution dissolves in the perovskite phase. The increase of the BNT content in the solubility range is accompanied with the decrease of the unit cell parameter of the basic perovskite phase. Further increase of the BNT content does not result in a significant change of these parameters. It is accompanied with a corresponding increase of the volume content of the second phase, the BNT type, in the composition of the ceramics. Additional two phases of perovskite with unit cell parameters in the ranges of 3.956–3.962 and 3.931–3.941 Å and barium polytitanates phases in some samples are detected; their total content does not exceed 5%.

The value of ε decreases from 1100 to 415 with the increase of the BNT content, while the Q-factor of the samples is relatively high, Qf being within the 900–2800 GHz range depending on the composition. Meanwhile, the relative tunability $K_t = \varepsilon(0) - \varepsilon(E)/\varepsilon(0)$ at $E = 1$ V/μm, being 31.7% for the composition with 20% BNT, sharply decreases with the BNT content in the heterogeneous mixture.

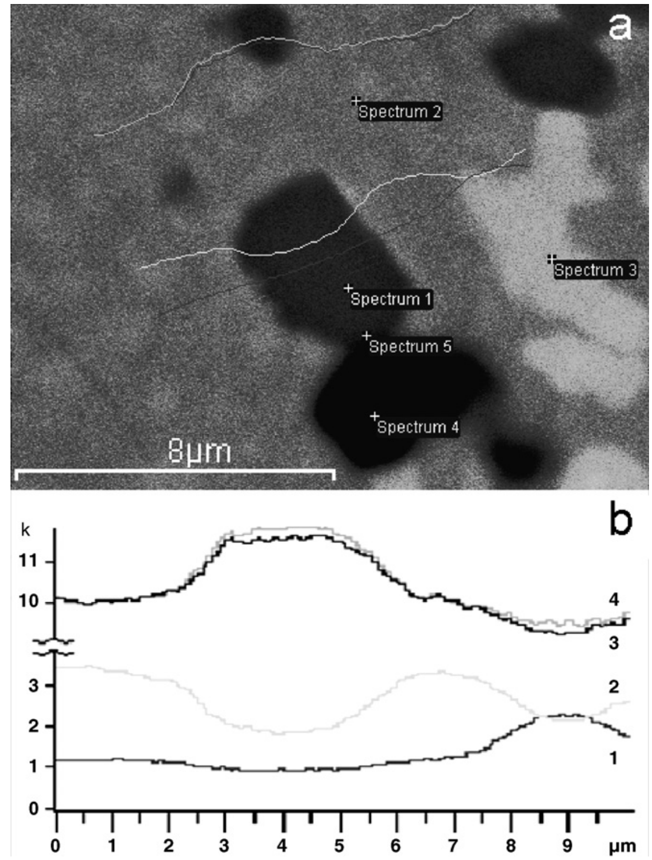

Fig. 1. Micrograph of the polished surface of the 65 mass% $BaTiO_3$–35 mass% $SrTiO_3$ sample with addition of 30 mass% BNT solid solution ($T_{sin} = 1380$ °C) obtained in the COMPO regime together with the images of linear scanning profiles of X-ray elements (a) and changes in the intensity of characteristic radiation of the elements Ti (1), Sr (2), Ba (3), and Nd (4) along the selected scanning line (b).

Partial solubility of the phases is confirmed by microanalysis (Fig. 1a and Table 2). In particular, neodymium is detected in the basic phase perovskite solid solutions (up to 6.86%), which might result in the decrease of the unit cell constant. Scanning the surface of the samples reveals the non-uniformity of the distribution of both neodymium (Fig. 1b) and strontium close to the phase boundaries.

Table 1
X-ray data and electric properties at f ≈3.5 GHz of the 65 mass% $BaTiO_3$–35 mass% $SrTiO_3$ samples depending on the BNT solid solution additive content ($T_{sin} = 1380$ °C)

BNT content (mass%)	Unit cell parameter of perovskite phase (Å)	BNT-type phase content (%)	ε	Qf (GHz)	K_t (% at $E = 1$ V/μm)
10	3.9552 (7)	–	1100	900	–
15	3.9531 (8)	–	746	1180	22.6
20	3.9510 (8)	<2	678	1950	31.7
30	3.9506 (8)	5	575	2400	16.5
40	3.9520 (6)	17	500	2600	9.6
50	3.9512 (7)	20	467	2800	1.7
70	3.9506 (6)	40	415	2600	1.2

Table 2
Results of the microregion analysis of the 65 mass% $BaTiO_3$–35 mass% $SrTiO_3$ sample with addition of 30 mass% BNT solid solution (T_{sin} = 1380 °C) obtained with EDS

Spectrum	Ti	Sr	Ba	Nd	O	Total
Spectrum 1	30.73	6.94	32.48	3.67	26.19	100.00
Spectrum 2	23.12	14.51	33.85	5.55	22.96	100.00
Spectrum 3	24.08	8.70	24.23	19.29	23.70	100.00
Spectrum 4	24.56	12.33	32.65	6.86	23.60	100.00
Spectrum 5	29.54	8.16	32.11	4.47	25.71	100.00

Fig. 2 presents unit cell parameters of the perovskite phase for the sintered ceramic samples depending on the barium titanate content in the initial mixtures with the addition of 50 mass% of the BNT solid solution. The increase of the barium titanate content the unit cell parameter increases, though for all studied samples it remains lower than the ones for the corresponding BSTO solid solutions without additives. The unit cell parameter of the perovskite phase somehow decreases with the increase of the sintering temperature from 1360 to 1400 °C for all samples with the addition of BNT solid solution, which is accompanied with the decrease of the volume content of the second BNT type phase in the compositions. Investigation of the microstructure of the sample sintered at 1450 °C (Fig. 3) revealed the existence of well-formed phase shells 0.1–0.3 μm thick besides the stretched crystals of BNT-type phase.

X-ray phase analysis shows that all studied samples of this system contained about 20–25% of the BNT-type phase, which indicates the 25–30% solubility of the added BNT phase into BSTO.

Fig. 4a shows the values of ε and Qf for the samples of the studied system depending on the composition. It is seen that together with the increase of the barium titanate content the dielectric constant of the samples increases from 320 to 700 and Qf at 3.5 GHz for the samples with y = 50–65 mass% $BaTiO_3$ is sufficiently high being 2600–3400 GHz and falls to 400 GHz when content of $BaTiO_3$ increases to 80 mass%. The increase of the $BaTiO_3$ content in the studied samples is accompanied by

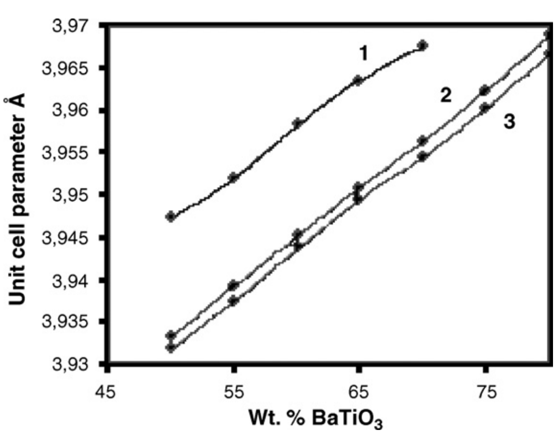

Fig. 2. Dependence of the unit cell parameter of the perovskite solid solution phase on the $BaTiO_3$ content for the samples in the BSTO system (1) and BSTO with the addition of 50 mass% of the BNT solid solution sintered at T_{sin} = 1360 °C (2) and T_{sin} = 1400 °C (3).

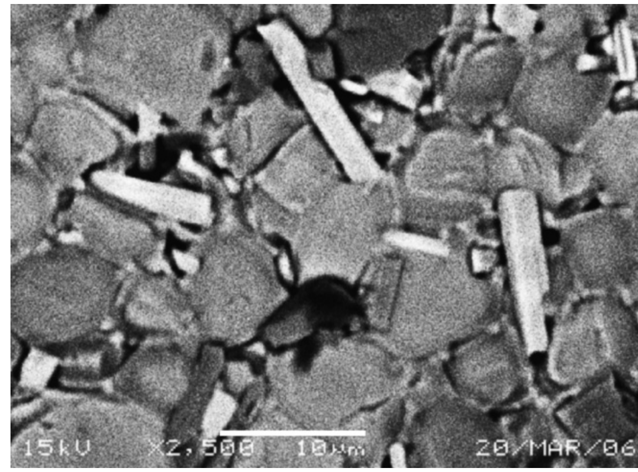

Fig. 3. Micrograph of the polished surface of the sample with 65 mass% $BaTiO_3$–35 mass% $SrTiO_3$ and with the addition of 50 mass% BNT solid solution (T_{sin} = 1450 °C) obtained in the COMPO regime.

the shift of the Curie temperature to the high temperature range (Fig. 4b) but ε tunability measurements at ~3.5 GHz (Fig. 4b) show that within the range from 50 to 65 mass% $BaTiO_3$ K_t is maximum achieving the value of 16%. Meanwhile the investigation of the temperature dependence of K_t revealed the anomalous behavior of this parameter with temperature (Fig. 5). Opposite to known ferroelectrics based on BSTO with low Curie temperature, the samples studied in this work demonstrated the increase of K_t with temperature up to 80 °C. Fig. 6 shows the dependences of the electrical parameters in the 3.5–10 GHz frequency range. It is seen that ε remains constant while Qf somewhat decreases to 2200–3000 GHz within a wide frequency range.

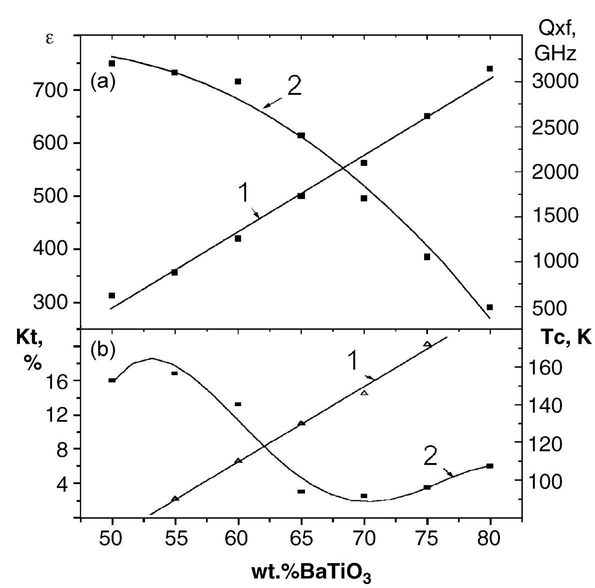

Fig. 4. Dependence of the ε (1) and Qf (2) (a), Curie temperature T_c (1) and K_t (2) (b) on $BaTiO_3$ content for the BSTO system samples with addition of 50 mass% BNT solid solution (T_{sin} = 1380 °C).

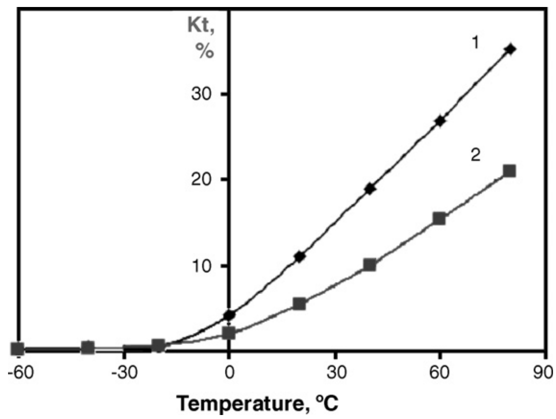

Fig. 5. Dependence of K_t at $f \approx 3.5$ GHz on temperature for the 60 mass% $BaTiO_3$–40 mass% $SrTiO_3$ (1) and 55 mass% $BaTiO_3$–45 mass% $SrTiO_3$ samples (2) with the addition of 50 mass% BNT solid solution (T_{sin} = 1400 °C).

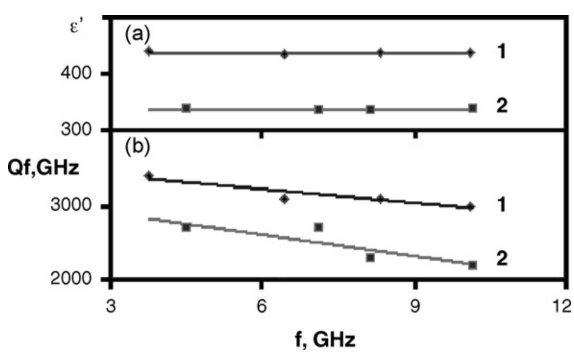

Fig. 6. Dependence of ε' (a) and Qf (b) on frequency for the 60 mass% $BaTiO_3$–40 mass% $SrTiO_3$ (1) and 55 mass% $BaTiO_3$–45 mass% $SrTiO_3$ samples (2) with the addition of 50 mass% BNT solid solution (T_{sin} = 1400 °C).

4. Conclusions

In this study new bulk ceramics based on $BaTiO_3$ (BTO)–$SrTiO_3$ (STO) with addition of $BaNd_2Ti_4O_{12}$ (BNT) solid solution was investigated. Compositions of BTO/STO–BNT system were studied into two sections: with 65 mass% $BaTiO_3$ in BTO/STO mixture with the additives of 10–70 mass% BNT solid solution and with 50–80 mass% $BaTiO_3$ in BTO/STO mixture with the additives of 50 mass% BNT and over 100 mass% of the mixture. The effect of compositional change on the unit cell parameters of the perovskite phase, microwave dielectric properties, and tunability under dc field had been studied. The existence of non-uniformity of the distribution of both neodymium and strontium close to the phase boundaries and well-formed phase shells 0.1–0.3 μm thick around the grains of the basic perovskite phase were detected. The materials with dielectric constant ∼320–700, Qf = 1950–3000 GHz at 3.5 GHz and tunability ∼8.0–31.7% at E = 1 V/μm were achieved.

References

1. Verbitskaja, T. N., Variconds. Gosenergoizdat, Moscow-Leningrad; 1958 [in Russian].
2. Vendik, O. G., ed., *Ferroelectrics in microwave engineering*. Sov. Radio, Moscow, 1979 [in Russian].
3. Chang, W. and Sengupta, L. C., MgO-mixed $Ba_{0.6}Sr_{0.4}TiO_3$ bulk ceramics and thin films for tunable microwave applications. *J Appl Phys*, 2002, **92**, 3941–3946.
4. Kanareykin, A. D, Nenasheva, E. A., Accelerator of charged beams. Russian Patent 2234204, March 5, 2003.
5. Kanareykin, A. D., Gai, W., Power, J. G., Nenasheva, E. A., Karmanenko, S. F. and Sheinman, I., A method for tuning dielectric loaded accelerating structures. In *Proceedings of the Particle Accelerator Conference, PAC-2003*, 2003, pp. 1888–1890.
6. Sengupta, L., Ngo, E., Stowell, S., O-Day, M., Lancta, R., Ceramic ferroelectric composite material BSTO-MgO. US Patent 5,427,988, June 27, 1995.
7. Nenasheva, E. A., Kanareykin, A. D., Kartenko, N. F., Dedyk, A. I. and Karmanenko, S. F., Ceramic materials based on (Ba, Sr)TiO_3 solid solutions for tunable microwave devices. *J Electroceram*, 2004, **13**, 235–238.
8. Nenasheva, E. A. and Kartenko, N. F., High dielectric constant microwave ceramics. *J Eur Ceram Soc*, 2001, **21**, 2647–2701.
9. Nenasheva, E. A., Kartenko, N. F., A way to form the composition of solid solutions with predefined parameters for the wares of high frequency and microwave technique. Russian Patent 2209191, July 27, 2003.
10. Matveichuk, V. F., Sibirtsev, C. N., Karikh, N. M. and Serov, A. V., Resonance methods and measurement means for the materials at super high frequencies. In *Proceedings of the VII International Conference Urgent problems of electron instrument-making, APEP-2004*, 2004, pp. 175–182 [in Russian].
11. IEC 61338-1-3, Waveguide type dielectric resonators, Part 1–3. General information and test conditions. Measurement method of complex relative permittivity for dielectric resonator materials at microwave frequency, 1999.