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MICROWAVE DIELECTRIC PROPERTIES OF DOPED $Ba_{0.5}Sr_{0.5}TiO_3$ CERAMICS CORRELATED WITH SINTERING TEMPERATURE

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$Ba_{0.5}Sr_{0.5}TiO_3$ ferroelectric ceramics (BST) were prepared by solid-state reaction. The effect of sintering temperature T_s on microwave dielectric properties was studied. Also, the influence of 1 wt % MgO and 1 wt % MnO_2 doping on the dielectric parameters was investigated. The morphological aspects of samples were studied by scanning electron microscopy (SEM). The microwave measurements at room temperature revealed dielectric constant around 1.000 and loss smaller than 1% at 1.1 GHz. Also, the dielectric parameters at low frequency were determined. The results indicate that the BST dielectric ceramics are suitable for manufacturing electric field controlled components such as tunable resonators, phase shifters, steerable antennas etc.

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1. Introduction

Ferroelectrics are very attractive materials for a wide range of applications. In informatics, they are used in DRAM memories [1,2]. In the high frequency range, they have high applications potential, due to the nonlinear variation of their electric permittivity with the applied electric field. This property offers the opportunity to achieve the electrical control of microwave devices [3,4]. This type of applications requires ceramics in the paraelectric state in order to avoid thermal hysteresis and high loss in the microwave domain.

$Ba_{1-x}Sr_xTiO_3$ ferroelectric materials have been widely studied for use in tunable microwave devices, such as phase shifters, ferroelectric varactors, steerable antennas etc. [5-8]. The $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) material considered for such applications exhibits the transition from the ferroelectric state to the paraelectric state below room temperature [9]. The effect of sintering temperature on the microwave dielectric parameters is presented in this paper. Moreover, the influence of MgO and MnO_2 addition on sintering conditions and electrical properties was investigated.

2. Experimental

$Ba_{0.5}Sr_{0.5}TiO_3$ ceramics were prepared by solid-state reaction, from raw materials. The starting materials were carbonate ($BaCO_3$, $SrCO_3$) and oxide (TiO_2, MgO, MnO_2) powders of purity higher than 99%. The raw materials were mixed in stoichiometric proportions, ball-milled in water for 2 h, dried at 120 ^oC for 4 h and then calcined at 1.150 ^oC for 2 h. The obtained powder was crushed into a fine powder, followed by a secondary milling in water for 2 h. The compounds were pressed into pellets of 11 mm diameter and 12 mm hight and sintered at temperatures between

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1.220 C and 1.320 °C for 2 h. Some samples were doped with 1 wt.% MgO and 1 wt.% MnO_2 in order to improve the granular growth and to control the porous structure of the ceramics [10]. Mixing of these dopants with the basic compositions was carried out for 2 h in an agate bottle containing agate balls.

The bulk densities (ρ_r) of the sintered pellets were measured by the Archimede's method. Morphological analysis was performed on doped BST samples by using Scanning Electron Microscopy (SEM). The values of the dielectric constant ε_r and of losses at microwave frequencies were measured by using the Hakki-Coleman dielectric resonator method [11]. A computer aided measurement system combining a HP 8757C network analyzer and a HP 8350B sweep oscillator was employed for microwave measurements. Measurements of the temperature dependence of the dielectric constant at 1 kHz were performed on a test setup, which includes a Hioki 3511-50 LCR HiTester in the temperature range of –200 ÷ +150 °C.

3. Results and discussion

Two sets of samples were prepared from BST materials. The first set of undoped materials was sintered at 1.220; 1.270; 1.285; 1.300 and 1.320 °C for 2 h. The second set was prepared by doping the basic compositions with 1 wt.% MgO and 1 wt.% MnO_2. The sintering temperatures for the second set of samples were the same as for undoped materials. The other parameters of the sintering process were maintained unchanged.

The grain morphology and the porous structure of the doped BST ceramics sintered at 1270 °C and 1300 °C were investigated by using the electron microscopy. The SEM pictures are shown in Fig. 1 and Fig. 2, respectively. For the doped BST sample sintered at 1270 °C, the grain dimensions are in the range of 1 ÷ 5 μm. However, the micrographs reveal many submicronic grains at the grain boundaries. The grain shape is mostly spherical. The samples present a developed porous structure with most of the pore dimensions under 1 μm and only a few in the range of 5 ÷ 10 μm. At the contrary, the SEM picture of the doped BST sample sintered at 1300 °C shown in Fig. 2, exhibits polyhedral well-facetted grains, which indicates the benefic effect of the high T_s value. The majority of grains exhibit a cubic shape with dimensions in the range of 10 ÷ 40 μm. The grains with dimension between 5 and 10 μm have a cubic shape with rounded corners or a spherical shape. The submicronic grains have practically disappeared in this case. The sample presents a reduced porosity comparatively with the sample sintered at 1270 °C and pores size in the range 1 ÷ 15 μm. The micrographs of undoped samples sintered at the same T_s reveal a glassy aspect and grains only in incipient stade of formation.

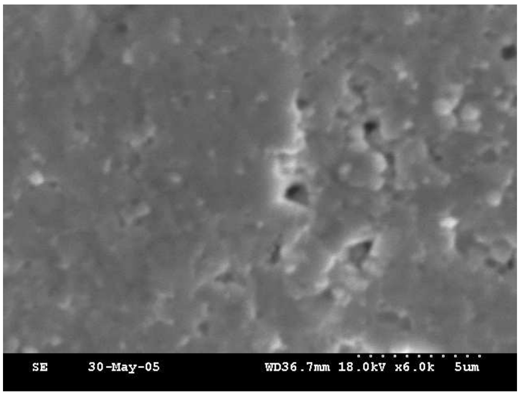

Fig. 1. SEM image of doped BST sample sintered at 1270 °C.

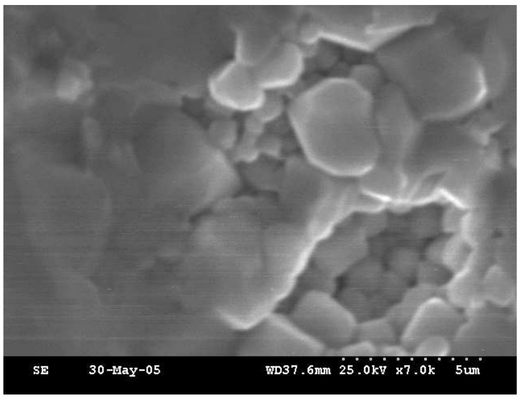

Fig. 2. SEM image of doped BST sample sintered at 1300 °C.

The dopants improve the sintering process, resulting in an increase of the bulk density, for the entire temperature range considered, as shown in Fig. 3.

For both undoped and doped BST samples, the temperature of 1285 °C seems to be very close to the optimum sintering temperature. Moreover, the data shown in Fig. 3 and Fig. 4 indicate a strong correlation between the bulk density and the dielectric constant in microwave range.

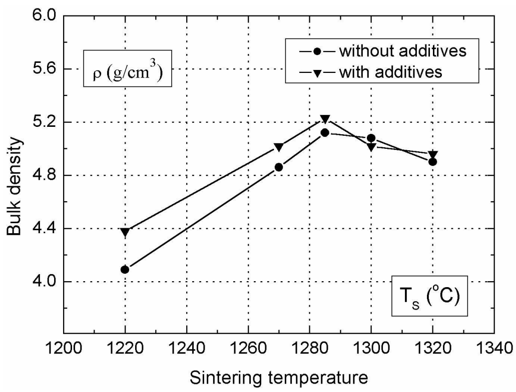

Fig. 3. The bulk density versus sintering temperature for BST samples.

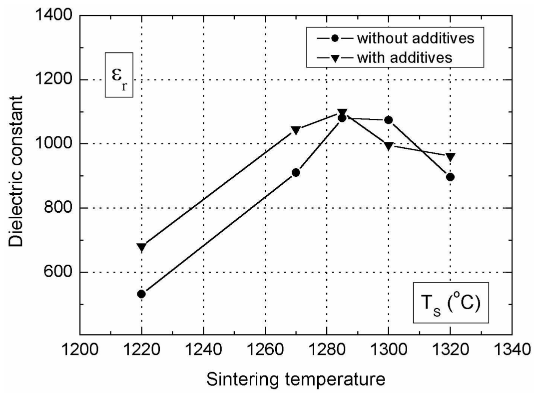

Fig. 4. The dielectric constant in microwaves range versus sintering temperature for BST samples.

The microwave dielectric parameters of the BST samples are presented in Table 1 and Table 2, respectively. As the sintering temperature T_s increases, there is an increase in the dielectric constant, followed by a slight decrease, for both sets of samples. The microwave dielectric constant reaches its maximum at $T_s = 1.285$ °C for BST materials with and without additives. In the temperature range $1.220 \div 1320$ °C, the dielectric loss tangent varies non-monotonically between 2.2×10^{-3} and 9.3×10^{-3}. The lowest value of the loss tangent was achieved for doped BST samples sintered at 1.285 °C for 2 h. Therefore, the sintering temperature $T_s = 1.285$ °C is the most appropriate for simultaneously achieving the highest dielectric constant and the lowest dielectric loss in the microwave range.

The dielectric constant of the doped samples is higher than of the undoped samples except the samples sintered at 1.300 °C. Therefore, the effect of MgO and MnO_2 addition is to enhance the sintering process. The doped samples show higher values of the bulk density and of the microwave dielectric constant, and generally lower dielectric loss in the microwave range than the undoped samples.

Table 1. Microwave dielectric parameters of undoped BST ceramicsas a function of the sintering temperature.

Sample	Sintering temperature T_s (°C)	Measurement frequency f (GHz)	Dielectric constant ε_r	Loss tangent $tan\ \delta$ ($\times 10^{-3}$)
1	1.220	1.336	532	6.9
2	1.270	1.084	910	8.2
3	1.285	1.002	1,080	2.8
4	1.300	1.008	1,074	4.6
5	1.320	1.091	896	2.4

Table 2. Microwave dielectric parameters of doped BST ceramics as a function of the sintering temperature.

Sample	Sintering temperature T_s (°C)	Measurement frequency f (GHz)	Dielectric constant ε_r	Loss tangent $tan\ \delta$ ($\times 10^{-3}$)
6	1.220	1.218	681	9.3
7	1.270	1.035	1.045	7.6
8	1.285	0.984	1.100	2.2
9	1.300	1.025	996	3
10	1.320	1.076	962	2.3

The dependence of the dielectric constant versus temperature at 1 kHz is shown in Fig. 5 and Fig. 6 for the samples sintered at 1.270 °C and 1.300 °C, respectively. The doped samples exhibit a narrower transition from the ferroelectric to paraelectric state and a higher maximum dielectric constant than the undoped samples. However, the dopants do not influence significantly the Curie temperature.

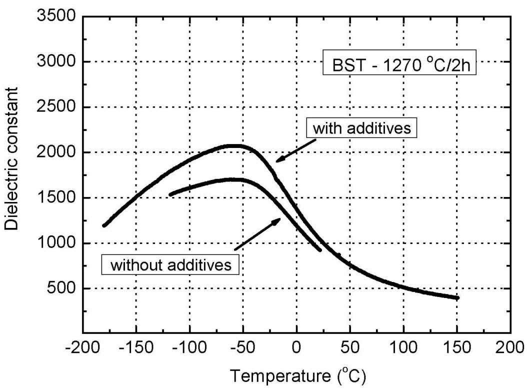

Fig. 5. Temperature dependence of dielectric constant measured at 1 kHz for BST samples sintered at 1270 °C.

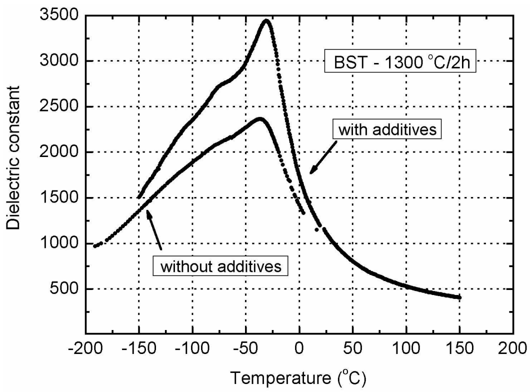

Fig. 6. Temperature dependence of dielectric constant measured at 1 kHz for BST samples sintered at 1300 °C.

The measured values of dielectric parameters at low frequency are presented in Table 3. The increase of the sintering temperature T_s leads to a shift in the Curie point toward higher values. The peak value of dielectric constant ε_r^{peak} increases with the increasing of T_s. This increase is more emphasized for doped samples. Also, the dielectric constant measured at room temperature ε_r presents an increase with T_s.

Table 3. Dielectric parameters measured at 1 kHz of BST ceramics sintered at 1270 °C and 1300 °C.

Samples	Sintering temperatures T_s (°C)	Additives	Curie temperature T_c (°C)	Peak value of dielectric constant ε_r^{peak}	Dielectric constant measured at room temperature ε_r
2	1270	No	-61	1700	941
4	1300	No	-37	2363	1151
7	1270	Yes	-57	2072	1060
9	1300	Yes	-31	3441	1190

4. Conclusions

The sintering temperature is a determinant factor for preparation of BST samples with appropriate structural, morphologic and dielectric characteristics. The variation of the bulk density versus the sintering temperature shows a maximum at 1285 ^{o}C. Near this temperature, the morphological investigations reveal well faceted grains and reduced porosity. Moreover, the dielectric constant, which is strongly correlated with the bulk density, reaches its maximum at the same sintering temperature of 1285 ^{o}C for BST samples with or without additives.

The addition of 1 wt% MgO and 1 wt% MnO_2 improves the sintering process results in the improvement of dielectric properties: the doped samples exhibit higher dielectric constant values and generally lower loss in the microwave range than the undoped samples.

The low frequency (1 kHz) dielectric measurements revealed the increase of the Curie temperature and of the peak permittivity with the increase of the sintering temperature. The doped samples exhibit a narrower transition from the ferroelectric to paraelectric state and a higher maximum dielectric constant than the undoped samples.

Doped BST materials sintered 1285 ^{o}C with dielectric constant ε_r = 1100 and losses $tan\ \delta = 2.2\times10^{-3}$, offer an attractive solution for tunable microwave devices.

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References

[1] J. F. Scott, Ann. Rev. Mat. Sci. **28**, 79 (1998).
[2] H. Takasu, J. Electroceram. **4**, 327 (2000).
[3] S. J. Fiedziuszko, I. C. Hunter, T. Itoh, Y. Kobayashi, T. Nishikawa, S. N. Stizer, K. Wakino, IEEE Trans. Microw. Theory Tech. **MTT 50**, 706 (2002)
[4] A. Kozyrev, A. Ivanov, T. Samoilova, O. Soldatenkov, K. Astafiev, L. C. Sengupta, J. Appl. Phys. **88**, 5334 (2000).
[5] Wontae Chang, Steven W. Kirchoefer, Jeffrey M. Pond, James S. Horwitz, Louise Sengupta, J. Appl. Phys. **92**, 1528 (2002)
[6] K. A. Jose, V. K. Varadan, V. V. Varadan., Microw. Opt. Tech. Lett. **20**, 166 (1998).
[7] D. Kim, Y. Choi, M. G. Allen, J. S. Kenney, D. Kiesling, IEEE Trans. Microwave Theory Tech. **MTT 50**, 2903 (2002).
[8] S. W. Kirchoefer, J. M. Pond, A. C. Carter, W. Chang, K. K. Agarwal, J. S. Horwitz, D. B. Chrisey, Microw. Opt. Tech. Lett. **18**, 168 (1998).
[9] A. Ioachim, M. I. Toacsan, M. G. Banciu, L. Nedelcu, C. Plapcianu, H. V. Alexandru, C. Berbecaru, D. Ghetu, G. Stoica, R. Ramer, J. Optoelectron. Adv. Mater. **5**, 1389 (2003).
[10] H. V. Alexandru, C. Berbecaru, F. Stanculescu, A. Ioachim, M. I. Toacsan, M. G. Banciu, L. Nedelcu, D. Ghetu, G. Stoica, Mat. Sci. Eng. B **118**, 92 (2005).
[11] B. W. Hakki, P. D. Coleman, IRE Trans. Microwave Theory Tech. **MTT 8**, 402 (1960).