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Ferroelectric ceramics based on the BaO–SrO–TiO_2 ternary system for microwave applications

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Abstract

$Ba_{1-x}Sr_xTiO_3$ solid solutions with $x = 0.25$, 0.5, 0.75 and 0.9 were prepared by solid-state reaction from powder oxides with high purity. In order to improve the granular growth 1 wt.% MgO and 1 wt.% MnO_2 was added to the calcined powders. Samples were sintered for 2 h at 1230 and 1260 °C. Structural parameters, grain sizes, bulk densities and microwave dielectric parameters were determined. A monotonic decrease of the Curie temperature with the increase of strontium content was determined by low-frequency dielectric measurements. Microwave measurements around 1 GHz showed substantial decrease of the permittivity with the x increase from about 1080 to 200. Also, the variation of losses from 1% to less than 0.2% was observed. The results indicate the BST ceramic as dielectric material, which can be utilized in paraelectric state for microwave devices.

Keywords: $BaTiO_3$ and titanates; Sintering; Ferroelectric properties; Microwaves

1. Introduction

Ferroelectric materials are very promising materials for a wide range of applications. In information technology, they are used in DRAM memories.[1,2] Moreover, the ferroelectric materials in paraelectric state present a high potential for microwave applications due to their moderate loss in microwave domain and high dielectric constant.[3,4] The dielectric constant of these materials can be modified by a bias electric field. Hence, the ferroelectric materials are employed for electrically controlled microwave devices. Such usual applications as phase shifters, tunable filters, ferroelectric varactors, etc., are using this property.[5–8]

$Ba_{1-x}Sr_xTiO_3$ (BST) ceramics prepared by solid-state reaction, with 1 wt.% addition of MgO and MnO_2 in order to improve the sintering process are presented in this paper. Furthermore, the effect of sintering temperature on the microwave dielectric parameters is discussed.

Structural parameters, grain sizes, bulk densities as well as dielectric parameters were determined. Crystalline structure of perovskite type was confirmed by X-ray diffraction (XRD) analysis. Low frequency (1 kHz) dielectric characterization of the ceramics was performed on a large temperature interval range (−175 to +175 °C). In addition, measurements on microwave dielectric parameters were carried out around 1 GHz at the room temperature.

2. Experimental

BST ceramics of molar formula $Ba_{1-x}Sr_xTiO_3$ were prepared by solid-state reaction as BST 25, 50, 75 and 90 samples with $x = 0.25$, 0.50, 0.75 and 0.90, respectively. Furthermore, 1 wt.% MgO and MnO_2 was added in order to improve the sintering process. The starting materials were carbonate ($BaCO_3$, $SrCO_3$, $MgCO_3$) and oxide (TiO_2, MnO_2) powders of purity higher than 99.9%. The raw materials were mixed in stoichiometric proportions, ball-milled in water for 2 h, dried and then calcined at $T = 1150$ °C for 2 h. A secondary milling in water for 2 h of the calcinated powder was performed. Mixing of the dopants

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Table 1
Bulk density and porosity of BST ceramics sintered at $T_s = 1230\,^{\circ}C/2\,h$ and $1260\,^{\circ}C/2\,h$

Sample	Sr content, x	Sintering temperature, T_s (°C)	Bulk density, $\rho \times 10^3$ (kg/m^3)	Relative X-ray density, ρ_r (%)	Porosity, P (%)
BST 25	0.25	1230	5.30	98.2	1.8
BST 50	0.50	1230	5.14	95.4	4.6
BST 75	0.75	1230	4.52	83.8	16.2
BST 90	0.90	1230	4.74	87.9	12.1
BST 25	0.25	1260	5.07	94.1	5.9
BST 50	0.50	1260	4.92	91.3	8.7
BST 75	0.75	1260	4.25	78.8	21.2
BST 90	0.90	1260	4.72	87.6	12.4

with the basic calcinated powders was carried out for 2 h in an agate bottle. BST samples were doped with 1 wt.% MgO and 1 wt.% MnO_2 in order to improve the granular growth and to control the porosity of the structure. Pellets of 9 mm diameter and 7.5 mm thickness were pressed at 50 MPa and sintered at 1230 and 1260 °C for 2 h.

The relative bulk densities of the sintered samples were measured by using the water immersion technique. Morphological and structural analyses were performed on the samples by X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM).

The values of the dielectric constant ε_r and losses at microwave frequencies were measured by using the Hakki–Coleman dielectric resonator method.[9] 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 −175/+175 °C.

3. Results and discussion

Both sets of samples sintered at $T_s = 1230$ and 1260 °C exhibit a good compactness. The porosity and bulk density of BST ceramics are shown in Table 1.

The $Ba_{1-x}Sr_xTiO_3$ ceramics were structurally characterized by X-ray diffraction (XRD). The patterns were recorded in a 2θ range from 20° to 60° on a Seifert Debye Flex 2002 diffractometer in the 2θ–θ mode at room temperature using Cu Kα radiation, Ni-filter and a detector scan speed of $2^{\circ}(2\theta)$/min. A Si sample was used for calibration.

Fig. 1 presents the X-ray diffraction patterns of BST samples sintered at 1260 °C with different Sr content. In all samples, $Ba_{1-x}Sr_xTiO_3$ is the majority phase. The peaks at $2\theta = 23.1^{\circ}$ and 27.2° can be attributed to the presence of very small amounts of $Sr_3Ti_2O_7$ and TiO_2. On the other hand, the peaks at $2\theta = 28.9^{\circ}$ and 29° show the presence of BaO and $BaTi_4O_9$ compounds. The X-ray diffraction peaks, which are specific to the secondary phases, decrease in intensity with the increase of Sr content and the XRD pattern indicates a single-phase solid solution for $x = 0.9$. The samples with large Sr concentration show a small shift in the XRD peaks towards larger 2θ. The shift increases with the increase in Sr content and corresponds to a decrease of the distances between the crystalline planes. When the Sr

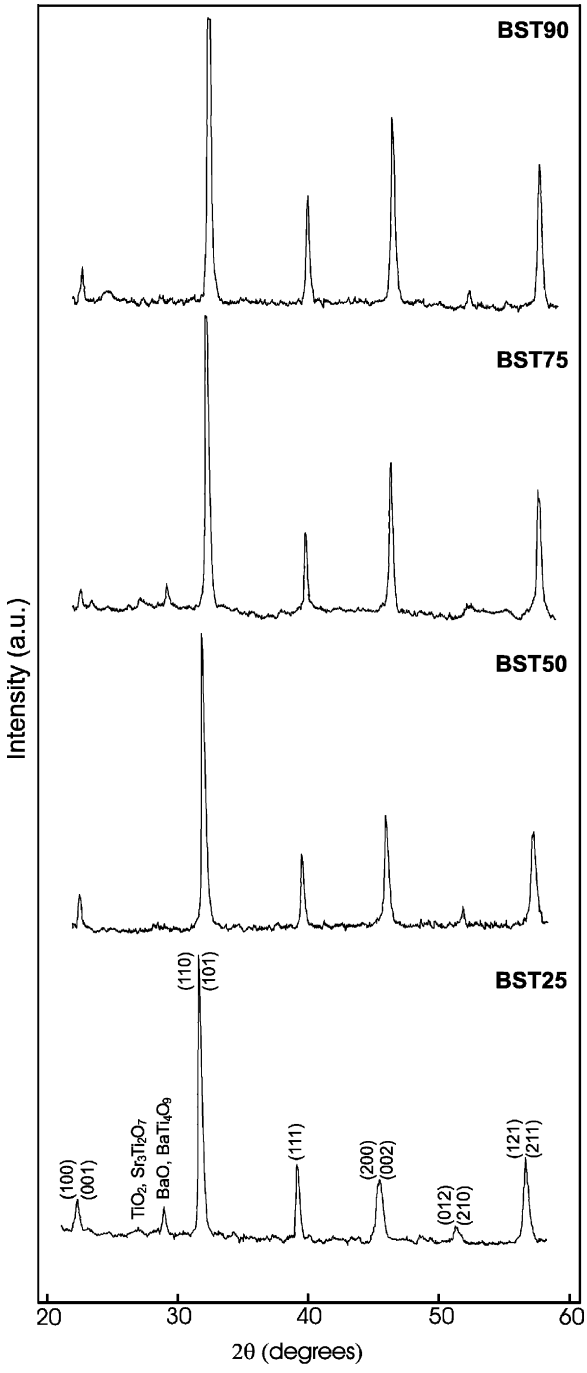

Fig. 1. X-ray diffraction patterns of BST samples sintered at $T_s = 1260\,^{\circ}C/2\,h$.

Table 2
Calculated unit cell parameters for BST sintered at $T_s = 1260\,^{\circ}C/2\,h$

Sample	XRD peak position, 2θ (°)	Inter-planar spacing, d (nm)	Unit cell parameters		Unit cell volume, $V_0 \times 10^3$ (nm^3)	Tetragonal ratio c_0/a_0
			a_0 (nm)	c_0 (nm)		
BST 25	45.67 45.48	0.1984 0.1992	0.3974	0.3985	63.01	1.004
BST 50	45.92	0.1974	0.3949	0.3949	61.58	1
BST 75	46.20	0.1963	0.3926	0.3926	60.53	1
BST 90	46.22	0.1962	0.3924	0.3924	60.45	1

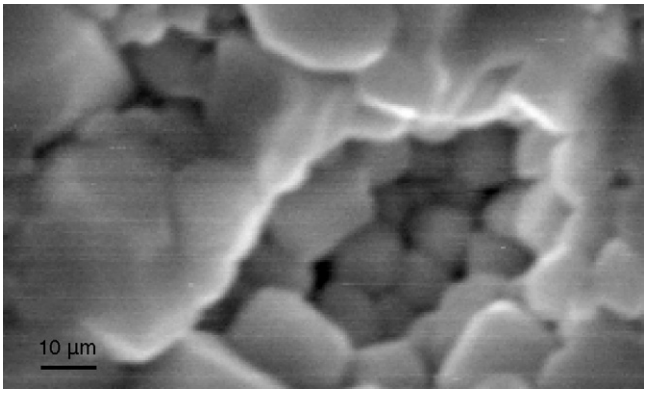

Fig. 2. SEM images for BST 50 samples sintered at $T_s = 1260\,^{\circ}C/2\,h$.

content increases from $x = 0.25$–0.9, the XRD data processing exhibits the decrease in the unit cell volume V_0 from (63.01 to 60.45) $\times 10^{-3}$ nm^3, as shown in Table 2. This effect can be explained by the fact that the ionic radius of Sr^{2+} is smaller than the ionic radius of Ba^{2+}.

The XRD peak at $2\theta \approx 46^{\circ}$ shows a small splitting for BST 25, which indicates a tetragonal structure with a tetragonality $c_0/a_0 \approx 1.004$. The strontium ion Sr^{2+} enters substitutionally for Ba^{2+} ion in the lattice, and decreases considerably the tetragonal distortion of the unit cell. On the other side, the BST 50, BST 75 and BST 90 samples exhibit a cubic structure.

The morphology of grains and the porous structure of polycrystalline BST ceramics were investigated by electron microscopy. The SEM pictures of the BST 50 and BST 75 sintered at 1260 °C/2 h are shown in Figs. 2 and 3, respectively. For the BST 50 samples the grain dimensions are in the range

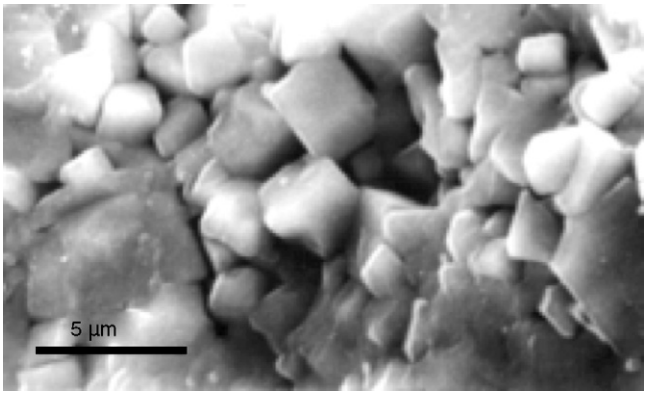

Fig. 3. SEM images for BST 75 samples sintered at $T_s = 1260\,^{\circ}C/2\,h$.

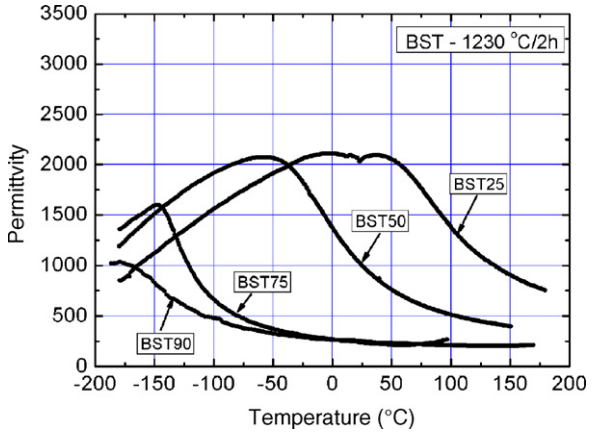

Fig. 4. The dielectric constant measured at 1 kHz vs. temperature for the BST samples sintered at $T_s = 1230\,^{\circ}C$.

5/25 μm. On the other hand, the grain dimensions are in the range 1/5 μm for the BST 75 sample. However, many submicronic grains at the large grain boundaries can be observed. The SEM images presented in Figs. 2 and 3 show polyhedral grains, better-facetted for BST 75 than for BST 50.

Dielectric measurements at low frequency (1 kHz) in the −175/+175 °C indicate that the Curie temperature decreases with the increase of the Sr concentration as shown in Figs. 4 and 5. The samples sintered at 1260 °C exhibit a narrower transition from the ferroelectric to paraelectric state and a higher maximum dielectric constant than the samples sintered at 1230 °C. It can be noticed that, with the exception of BST 25,

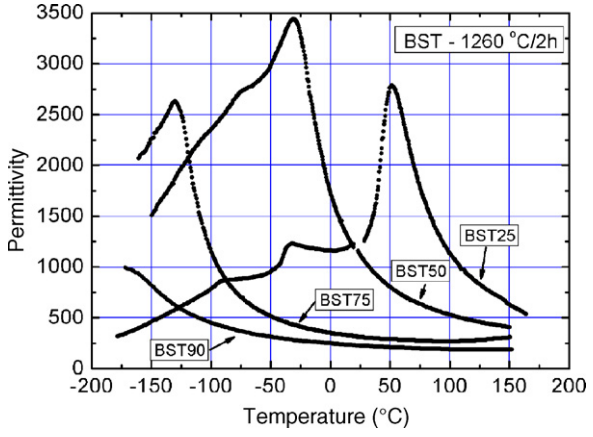

Fig. 5. The dielectric constant measured at 1 kHz vs. temperature for the BST samples sintered at $T_s = 1260\,^{\circ}C$.

Table 3
Low and high frequencies dielectric constant ε_r and loss tangent $\tan\delta$ at room temperature of BST samples sintered at $T_s = 1230\,^\circ$C/2 h and 1260 °C/2 h

Sample	Sr content, x	Sintering temperature, T_s (°C)	Dielectric constant, ε_r (1 GHz)	Dielectric loss, $\tan\delta$ (%) (1 GHz)	Dielectric constant, ε_r (1 kHz)	Dielectric loss, $\tan\delta$ (%) (1 kHz)
BST 25	0.25	1230	–	–	2300	1
BST 50	0.50	1230	976	0.80	998	0.2
BST 75	0.75	1230	212	0.21	237	2.4
BST 90	0.90	1230	218	0.17	249	1
BST 25	0.25	1260	–	–	1200	0.3
BST 50	0.50	1260	1089	0.29	1115	0.2
BST 75	0.75	1260	202	0.21	310	2.6
BST 90	0.90	1260	235	0.16	225	1.9

the samples are in the paraelectric state at room temperature for both sintering temperatures.

The dielectric parameters measured at low (1 kHz) and high (1 GHz) frequencies at room temperature are listed in Table 3. It can be noticed that the microwave dielectric constant and loss tangent decrease with the increase of strontium content for BST 50, BST 75 and BST 90 samples sintered at both 1230 and 1260 °C.

The BST 25 materials exhibit high dielectric loss, which indicates a ferroelectric state. This is in agreement with the tetragonal structure (Table 2). For this reason, the BST 25 samples could not be measured in microwaves by the usual Hakki–Coleman method and the values of their dielectric parameters are missing from Table 3.

Data obtained indicate that the BST 50 and BST 75, due to their low loss and high dielectric constant at room temperature, are suitable for microwave applications.

4. Conclusions

$Ba_{1-x}Sr_xTiO_3$ ceramics were prepared by solid-state reaction from raw materials, at molar concentrations $x = 0.25$, 0.50, 0.75 and 0.90. In order to improve the sintering process, 1 wt.% MgO and MnO_2 were added.

XRD diffraction analysis shows that the BST crystalline structure is well formed for all the samples. However, some residual products were detected.

Low frequency dielectric measurements versus temperature were performed on a large temperature range (−175 to +175 °C). The microwave measurements have been performed at 1 GHz.

The increasing concentration of Sr has the following effects: (i) decreases the unit cell volume; (ii) decreases considerably the ferroelectric transition temperature; (iii) decreases substantially the permittivity and losses, for both high and low frequency ranges.

Due to their high dielectric constant and low loss, the MgO and MnO_2 doped BST 50 and BST 75 are very attractive for microwave devices.

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