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Preparation and properties of $BaTi_{1-x}Sn_xO_3$ multilayered ceramics

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Abstract

$BaTi_{1-x}Sn_xO_3$ (BTS) powders, with x ranging from 0 to 0.15, were synthesized by solid-state reaction technique. The powders were pressed and sintered at 1370 °C. Obtained BTS ceramics were investigated by X-ray diffraction and dielectric properties measurements. It is found that Curie temperature decreases while dielectric constant increases with increasing of tin content. A monolithic multilayered ceramics with up to five layers of BTS with different amounts of Sn were prepared. Their dielectric properties were examined. Relatively high dielectric constants in a wide temperature range were obtained. It is noticed that BTS mono- and multilayered ceramics have better dielectric properties if they are additionally treated in microwave oven for 10 min, after sintering at 1370 °C.

Keywords: Sintering; X-ray methods; Dielectric properties; $BaTiO_3$ and titanates

1. Introduction

Due to their dielectric and ferroelectric properties, functional ceramics based on barium titanate have found application in various electronic devices, like capacitors, thermistors, transducers and non volatile memories in semiconductor industries. Unique electric/dielectric properties of these materials can be achieved by varying the sintering conditions and by doping with various isovalent cations on both A (Ba) and B (Ti) sites.[1–7] By different sintering conditions microstructure and particle size can be controlled, while the introduction of isovalent cations can have a significant increasing effect on dielectric constant and shift the Curie temperature, too. Most of the isovalent A site dopants are effective in displacing or shifting Curie temperature but they do not have a dramatic effect on the value of ε_{max}.[1,7] The introduction of isovalent cations on the B site, however, can have a significant effect on ε_{max}.[5]

It was shown that the partial replacement of titanium by tin improve the dielectric behavior. Besides, the tin concentration increase systematically decreases the Curie point.[3,8,9] It is noticed that increasing of Sn content in $BaTi_{1-x}Sn_xO_3$ (BTS) powders decrease temperature of phase transformation, and, for example BTS sample with ∼12 mol% of Sn has cubic structure at room temperature.[8,10]

$BaTiO_3$ doped with Sn is important for practical application in ceramic capacitors as well as in functionally graded materials.[11–13] Functionally graded materials are very useful because they have a broad transition temperature and high dielectric constant in a wide temperature range.[2]

In the present work, we have synthesized barium–tin titanate powders by solid-state reaction. We prepared mono- and multilayered BTS ceramics and investigated their structural and dielectric characteristics as a function of tin contents and sintering conditions by using X-ray diffractometry, energy dispersive X-ray spectrometry, as well as dielectric measurements.

2. Experimental part

The starting materials were commercially available $BaCO_3$ (>99%), TiO_2 (>99.8%) and SnO_2 (>99%). Mixture of $BaCO_3$, TiO_2 and SnO_2 powders was homogenized for 24 h by steering in a polyethylene vessel with ethyl alcohol and zirconia ball. After that powder slurries were dried and calcined at 1100 °C for 2 h. After calcinations, obtained BTS powders were milled in isopropanol during several hours. The BTS powders were uni-axial pressed, under 300 MPa, into mono- and multilayered pellets. The dimension of monolayered samples were Ø 8 mm and $h = 2$ mm. In the case of multilayered samples, the prepared

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powders were stacked sequentially with changes in mixing ratio, besides; every layer was 300 μm in thickness. The pellets were sintered at 1370 °C, in air for 5 h (heating rate 5 °C/min). The sintered BTS ceramics were additionally microwave (MW) treated for 10 min, in a domestic oven (2.45 GHz, 800 W) equipped with a Pt–Rh thermocouple for temperature measurements. The dual quartz tube system was used with NiO as external MW susceptor in the outer tube. The use of NiO as external susceptor leads to an accelerated microwave heating of the ceramics.

The crystal structure of the BTS samples sintered at 1370 °C was investigated at room temperature using X-ray diffraction measurements. Samples for XRD were crushed and powdered in agate mortar in chlorophorm in order to ensure that the effects of preferred orientation were minimized. The XRD patterns were obtained on Philips PW-1050 diffractometer using Cu $K_{\alpha 1,2}$ radiation, at 40 kV and 20 mA. The diffraction measurements were done over scattering angle 2θ from 20° to 120° with a step of 0.02° and a counting time of 15 s. The FullProf program was used for structural refinement. JCPDS database[14] was used for phase identification.

BTS ceramics have been electrically studied as a function of temperature and Sn contents. The electrical measurements were done on BTS pellets electroded with Ag pastes. The measurements were performed on air, at 1 kHz (internal frequency) using a Wayne Kerr Universal Bridge B224. All dielectric measurements were done in cooling, from 160 to −20 °C. The dielectric constants (ε_r) were calculated.

Samples for EDS examination were prepared in cross-sectional view. The microstructure was analyzed using a JEOL–JSM 5300 scanning electron microscope equipped with EDS QX 2000S system.

3. Results and discussion

Fig. 1 shows the room temperature XRD patterns of seven different BTS powders (0, 2.5, 5, 7, 10, 12 and 15 mol% Sn) obtained after sintering at the same conditions as the multilayer ceramics later (1370 °C, 5 h). It is evident that all of the samples were crystallized into single-phase solid solutions of perovskite structure. From Fig. 1, it can be observed that increasing of Sn content causes systematic shift of peaks towards lower 2θ angles, because the substitution of Ti^{4+} [$R(Ti^{4+}) = 74.5$ pm] by Sn^{4+} [$R(Sn^{4+}) = 83.0$ pm][15] increases the d spacing. This is a clear indication that Sn^{4+} is systematically dissolved in $BaTiO_3$ lattice in the studied composition range. Besides, the (0 0 2) and (2 0 0) peaks ($2\theta = 45°$) were merged into (0 0 2) peak as consequence of phase transition from tetragonal to cubic structure. For pure barium titanate, phase transformation from tetragonal to cubic structure is near to 120 °C.[16,17] However, in the case of the BTS samples investigated in this work, increasing of Sn content decreases the temperature of phase transformation. Also, XRD patterns confirmed that BTS sample with ∼12 mol% of Sn has cubic structure at room temperature, as we expected.

The increasing of the lattice parameter with increasing of Sn content in BTS solid solution was confirmed after Rietveld refinement. Lattice parameters calculated from the diffraction data are presented in Table 1. Fig. 2 shows the lattice parameters

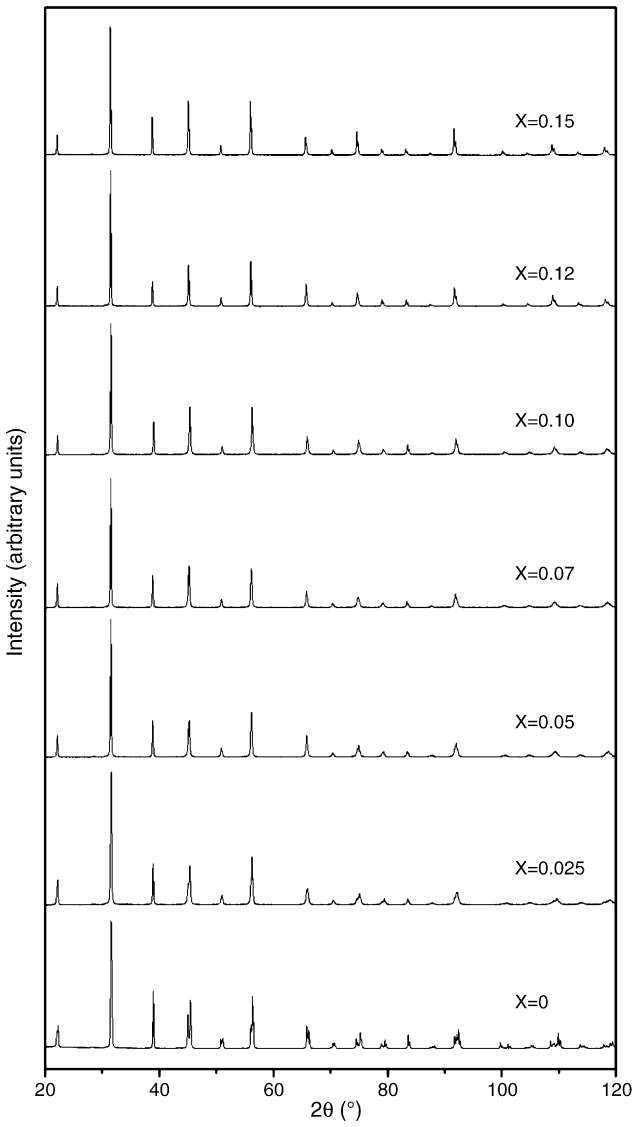

Fig. 1. Powder XRD patterns of $BaTi_{1-x}Sn_xO_3$ ($x = 0$–0.15) sintered at 1370 °C for 5 h.

of the tetragonal and cubic phases in the $BaTi_{1-x}Sn_xO_3$ system at room temperature. Tetragonality (axial ratio c/a) decreases with the increasing of Sn content, and approaches 1.0 of the cubic phase for composition $x = 0.12$ (Fig. 3). Similar results have been reported by Chang et al.[18]

Table 1
Lattice parameters obtained from the structural refinement using X-ray powder diffraction data at room temperature

$BaTi_{1-x}Sn_xO_3$	Lattice parameter (Å)		Tetragonality
x	a	c	c/a ratio
0	3.99914 (8)	4.03014 (10)	1.0775
0.025	4.00116 (21)	4.02450 (29)	1.0583
0.05	4.00447 (21)	4.01923 (33)	1.0369
0.07	4.00708 (22)	4.01764 (37)	1.0264
0.10	4.01189 (39)	4.01381 (64)	1.0048
0.12	4.01580 (21)	4.01580 (41)	1.0000
0.15	4.02025 (24)	4.02025 (44)	1.0000

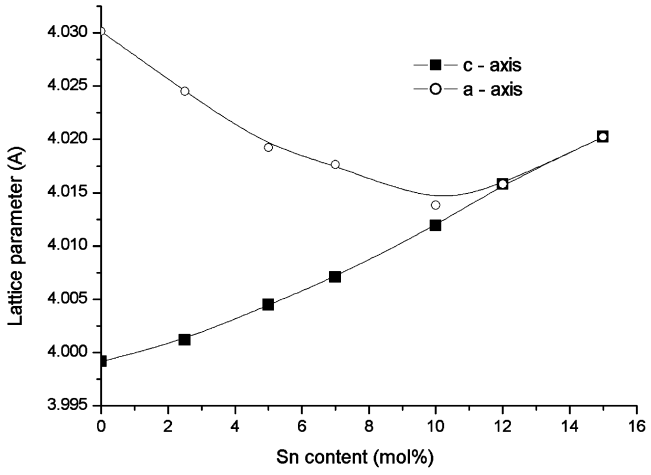

Fig. 2. Relationship between the lattice parameters and the Sn content.

The heat up behavior of the $BaTiO_3$ sample (previously sintered at 1370 °C for 5 h) in the MW oven during 10 min is shown in Fig. 4.

The temperature dependence of dielectric constant (ε_r) for BTS samples sintered at 1370 °C for 5 h in air and those additionally treated in MW oven, is shown in Figs. 5 and 6, respectively. From Fig. 5, it can be seen that doping with Sn causes an increase in ε_{max} followed by broadening. It is already known from the literature that the broadening of ε_{max} can be attributed to the coalescence of the low temperature phase transformations, such as rhombohedral to orthorhombic and orthorhombic to tetragonal.[4] However, the substitution of Sn into Ti sites leads to a crossover from sharp to a diffuse phase transformation when the Sn content was in the range between 0.025 and 0.15 (Fig. 5).

Dielectric properties of BTS materials sintered at 1370 °C and those additionally treated in MW oven are presented in Table 2. For pure materials sintered at 1370 °C, the values of dielectric constant range from 6000 to 8000, besides; dielectric constant has values from 6700 to 8900 for samples sintered at 1370 °C and additionally treated in MW oven for 10 min. Sn substitution on

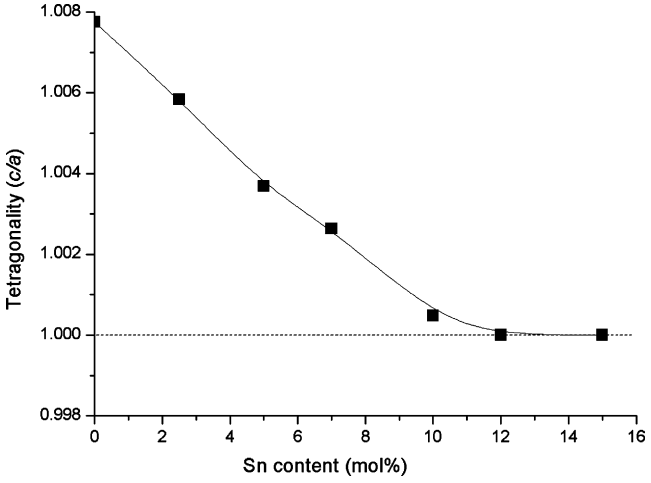

Fig. 3. Relationship between the Sn content and tetragonality (axial ratio *c*/*a*).

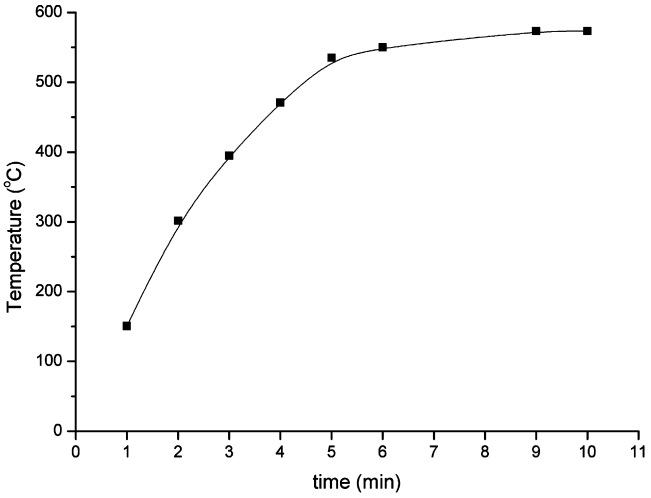

Fig. 4. Heat up behavior of $BaTiO_3$ sample in the MW oven (sample was presintered in a classical furnace at 1370 °C for 5 h).

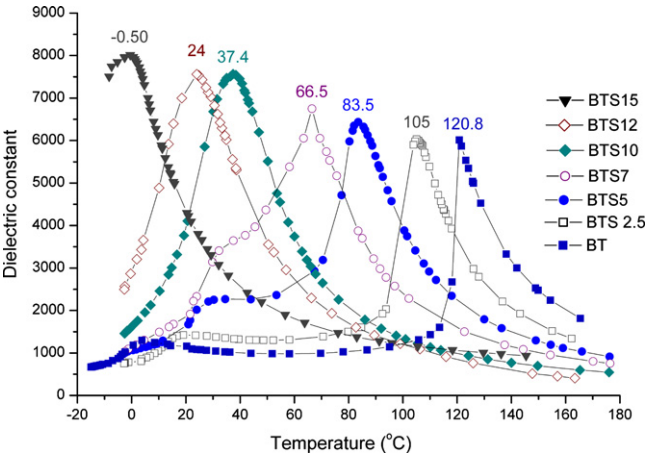

Fig. 5. The temperature dependence of dielectric constant as a function of Sn content in BTS ceramics sintered at 1370 °C for 5 h.

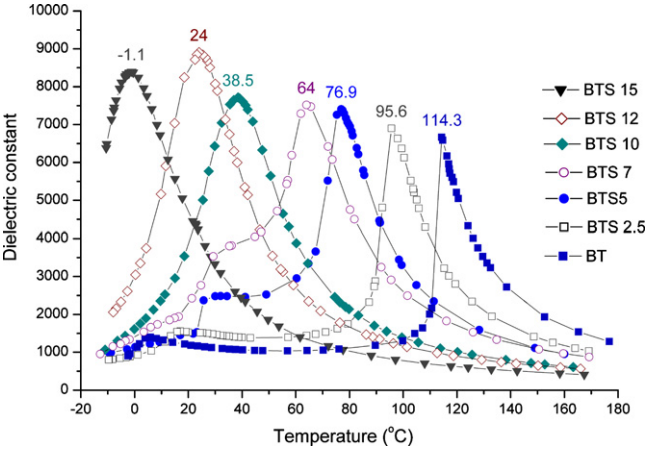

Fig. 6. The temperature dependence of dielectric constant as a function of Sn content in BTS ceramics sintered at 1370 °C for 5 h and MW treated for 10 min.

Table 2
Dielectric constants of mono- and multilayered BTS ceramics at room and Curie temperatures

BTS ceramics	Sintered at 1370 °C			Sintered at 1370 °C and MW treated		
	ε_r at $T_{20\,°C}$	ε_r at T_c	T_c	ε_r at $T_{20\,°C}$	ε_r at T_c	T_c
BT	1160	6013	120.8	1225	6668	114.3
BTS 2.5	1423	6033	105.0	1516	6901	95.6
BTS 5	1673	6434	83.5	1516	7409	76.9
BTS 7	1835	6751	66.5	2352	7520	64.0
BTS 10	4093	7566	37.4	3988	7717	38.5
BTS 12	7364	7559	24.0	8496	8909	24.0
BTS 15	4093	7958	−0.5	4606	8399	−1.1
2.5-0-7	1792	4371	108.5	1956	4664	106.8
2.5-7-10-12	2356	3845	51.2	2829	4698	48.6
2.5-0-7-10-12	1956	2561	59.6	2356	3163	45.7

Ti sites increased the room temperature dielectric constant from about 1100 for pure $BaTiO_3$ up to 7300 for $x = 0.12$. Moreover, Curie temperature decreased with increasing of Sn content. It is evident that BTS ceramics sintered at 1370 °C and additionally treated in MW oven have better dielectric properties than those sintered at 1370 °C, only.

It can be inferred so far that the BTS monolayer ceramics have a high dielectric constant but in narrow temperature intervals. Curie temperature intervals can be broadened by producing of multilayer BTS ceramic devices with different BTS composition.

Multilayer ceramics investigated in this work were prepared by using different combination of BTS powders. Powders are stacked sequentially with changes in composition; they are pressed and sintered at 1370 °C. After sintering, these multilayer ceramics have thickness in the range from 900 to 1500 μm, depending on the number of layers (3–5 layers). Fig. 7 shows

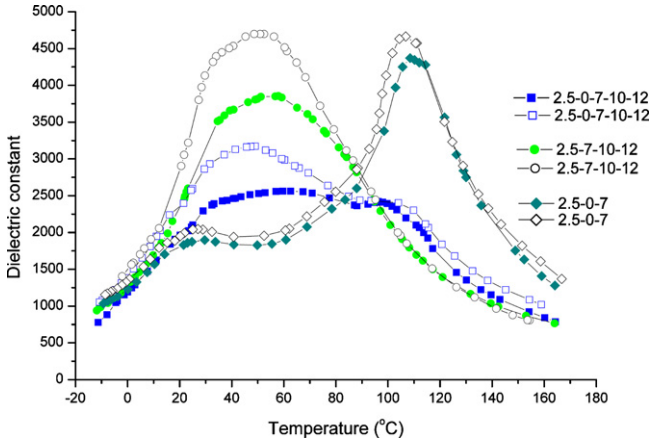

Fig. 7. The temperature dependence of dielectric constant in BTS multilayered ceramics sintered at 1370 °C for 5 h (full symbols) and those additionally MW treated for 10 min (empty symbols).

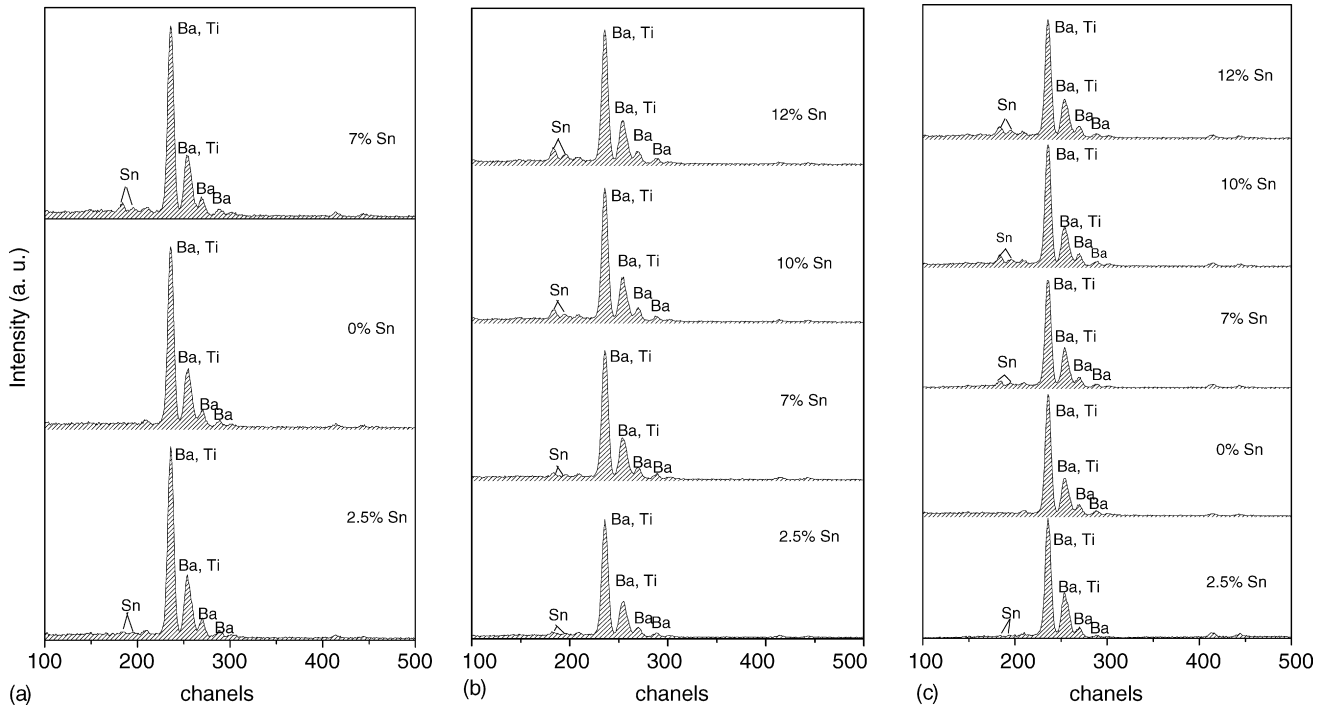

Fig. 8. The EDS analysis of ions distribution through the multilayer materials: (a) 2.5-0-7, (b) 2.5-7-10-12 and (c) 2.5-0-7-10-12.

the dielectric constant of a $BaTi_{1-x}Sn_xO_3$ multilayered materials consisted of three (2.5-0-7), four (2.5-7-10-12) and five (2.5-0-7-10-12) layers, where each layer has the same thickness (300 μm). The obtained multilayer BTS ceramics have a broadened ε_{max}, i.e., a relatively high dielectric constant in a wide temperature range. Besides, multilayered ceramics expresses relatively flat dielectric constant versus temperature features in a wide temperature range, even they were obtained from single layers with sharp dielectric constant versus temperature curves. This effect is more pronounced for ceramics with more layers. Moreover, it is shown that dielectric constants and Curie temperature intervals of these multilayer BTS ceramics may be modified by combination of different BTS powders as well as by layers number.

After additional treatment of multilayer samples in MW field dielectric constant got higher values. Dielectric constant is higher in the region of lower Curie temperatures which corresponds to larger Sn amount in layers. This is consistent with results for single BTS ceramics which (in average) have higher dielectric constant raise than pure BT after MW treatment (Figs. 5 and 6 and Table 2).

The EDS analysis of multilayer BTS ceramics was done after sintering at 1370 °C and additional MW treatment and shows Sn content altogether with other elements in cross-sectional view (Fig. 8). The Sn content is consistent with starting layer arrangement before sintering in all cases.

4. Conclusions

$BaTi_{1-x}Sn_xO_3$ ceramics, with $x = 0.00$, 0.025, 0.05, 0.07, 0.10, 0.12 and 0.15 compositions, were synthesized by solid-state reaction technique. The phase composition and lattice parameters were determined by XRD after Rietveld refinement. The BTS samples were found to be single-phase solid solutions. The XRD results show that when the amount of Sn increases in the BTS system, the crystal structure will be transformed from a tetragonal to cubic phase. Moreover, samples with $x \geq 0.12$ have cubic structure even at room temperature.

It is shown that mono- and multilayered (3–5 layers, 900–1500 μm) BTS ceramics can be produced by uni-axial pressing and sintering at 1370 °C. In monolayered ceramics, as the substitution of Ti^{4+} by Sn^{4+} ions increases, dielectric constant increases, while, the Curie point shifts to a lower temperature. These results are essentially influenced by the phase transformation from tetragonal to cubic structure.

Furthermore, it is shown that multilayer BTS ceramics have a relatively high dielectric constant in a wide temperature range. Besides, dielectric properties of these materials can be modified by combination of different BTS powders as well as layers number.

It is noticed that BTS ceramics additionally MW sintered during 10 min has better dielectric properties than those sintered at 1370 °C.

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