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The effects of thermal treatments on microwave dielectric properties of $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics

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$Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) dielectric materials were prepared by solid state reaction. The samples were sintered at temperatures in the range 1550 ÷ 1650 ^oC for 2 h. XRD, SEM and EDX were employed for compositional, structural and morphological characterization. An additional annealing at 410 ^oC for 10 hours was performed in order to improve the dielectric parameters. The dielectric constant and quality factor of BZT dielectric resonators measured by using Hakki-Coleman method around 6 GHz was between 25 and 29. The temperature coefficient of the resonance frequency exhibits positive values less than 6 ppm/ ^oC. The best parameters of BZT dielectric resonators were achieved for the samples sintered at 1650 ^oC with additional thermal treatment ($_r$ = 29, Q x f = 100 THz).

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1. Introduction

Dielectric materials continue to have a decisive influence on the evolution of the electrical and electronic engineering, communications and information technology. Among these, materials which exhibit high dielectric constant, low dielectric losses, and good temperature stability are required to reduce the size and weight of equipment, enhance its reliability, and lower the manufacturing and operational costs. Ceramic materials are from far the most utilized as they offer cost-effective solutions for applications [1-4].

The high dielectric constant materials are of particular interest for microwave domain, as they are used for microwave resonators and filters. These materials are presently employed as bulk ceramics in microwave communication devices, as discrete components in hybrid circuits. The ceramic pieces are designed to be dielectric resonators, resonating at the frequency of the carrier signal to allow that signal to be efficiently separated from other signals in the microwave band.

The $Ba(Zn_{1/3}Ta_{2/3})O_3$ dielectric materials (BZT) are very attractive for microwave devices due to their high dielectric constant and low losses in the microwave and millimeter wave range [5-7]. These materials exhibit a dielectric constant of $\varepsilon_r \sim 29$ and a high value of the Q x f product, around 100,000 GHz. Moreover, the temperature coefficient of the resonance frequency τ_f takes positive values lower than 6 ppm/ ^oC.

The aim of this work was to investigate the influence of the sintering temperature and the annealing treatment on microwave dielectric properties of BZT ceramics.

2. Experimental

$Ba(Zn_{1/3}Ta_{2/3})O_3$ samples were prepared by solid-state reaction. The starting materials were $BaCO_3$, ZnO and Ta_2O_5. Stoichiometric quantities were weighted, ground, homogenized and milled in an agate mill in water for 5 hours. The powders were calcined at $T = 1200\ ^oC$ for two hours. Then the powders were milled for 3 h and calcined at 1250 ^oC/ 2h. The double calcined powders were mixed with 2.5 % polyvinyl alcohol (PVA) and dried at $T = 80\ ^oC$, then were pressed into cylindrical samples of 12 mm diameter and 12 mm height. The pellets were slowly dried at 80 ^oC in order to eliminate the PVA.

The density of green ceramics was $\rho = 4.5$ g /cm^3. The sintering treatment for the BZT samples was performed in air for 2 h at three different temperatures: $T_s = 1550\ ^oC$, 1600 ^oC, and 1650 ^oC. In order to improve the dielectric properties, especially the quality factor Q, the samples were treated supplementary for 10 h at 1410 ^oC. The pellets were polished in order to remove the superficial zone and to obtain correct values of the microwave dielectric parameters.

The bulk densities of the sintered pellets were measured by using a water immersion technique. Structural and morphological analyses were performed on BZT samples by X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM). The structure of BZT samples was investigated by X-ray diffraction using a TUR-M62 diffractometer (Cu K_α = 0.1541 nm). The patterns were recorded at room temperature in a range of θ from 8^o to 30^o. The porous structure and grains shape were studied by using a HITACHI S 2600 N electronic microscope.

In microwaves, the BZT cylindrical samples exhibit very low dielectric loss, high dielectric constant, and a very good stability with temperature. Therefore, the dielectric parameters of BZT samples were investigated by using the Hakki-Coleman method [8]. A computer-aided measurement system, which combines an HP 8757C network analyzer and an HP 8350B sweep oscillator, was employed for the microwave measurements. The temperature coefficient of the resonant frequency τ_f in the microwave range was measured by heating the samples from +20 °C to +80 °C.

3. Results and discussion

Before starting the sintering process, the double calcined powders were investigated by using XRD in order to establish the formation of BZT compounds. The X-ray diffraction pattern of synthesised BZT powders is shown in Fig. 1. There are neither peaks of unreacted raw materials nor secondary phases.

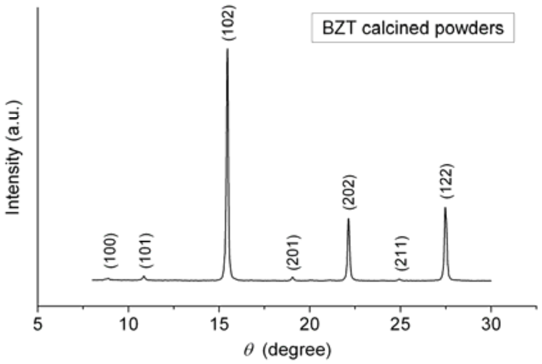

Fig. 1. X-ray diffraction patterns of BZT powders calcined at 1250 °C/ 2h.

Following the sintering process, ceramic materials with a good compactness were obtained for all sintering temperatures. The bulk density and porosity of the sintered samples is shown in Fig. 2. The bulk density increases monotonically with the increase of the sintering temperature (T_s), as well as the porosity decreases with T_s. The X-ray density of the $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramic is $\rho_t = 7.92$ g /cm^3 [5]. All samples exhibit porosity less than 10 %, which is sufficient for an optimum dielectric loss. The most dense ceramics exhibit a porosity value of 6.3 %. The dielectric loss due to the pores does not vary with the sample compactness for such small values of the porosity.

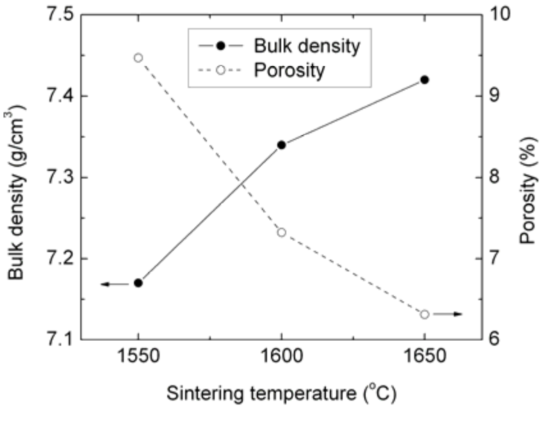

Fig. 2. Bulk density and porosity of BZT samples versus sintering temperature.

The X-ray diffraction patterns for BZT ceramic samples sintered at three different temperatures are given in Fig. 3. The patterns confirm the formation of the trigonal structure [9], which is the majority phase. For the BZT compounds sintered at $T_s \geq 1600$ °C, the patterns reveal the presence of $Ba_8ZnTa_6O_{24}$ secondary phase with low Zn content [10].

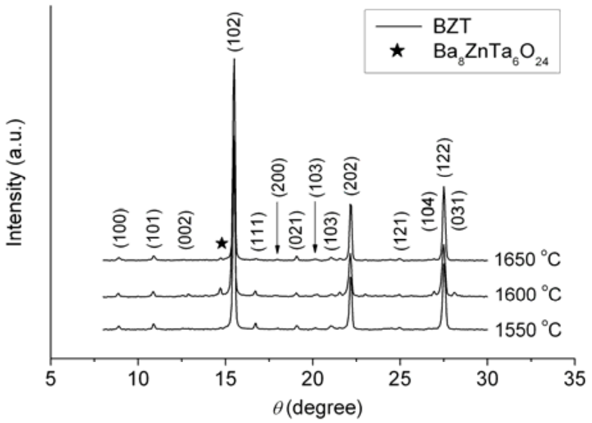

Fig. 3. X-ray diffraction patterns of BZT samples versus sintering temperature.

The values of the calculated lattice constants a_o, c_o, the unit cell distortion c_o / a_o and the unit cell volume V_o are given in Table 1. Even though, these parameters present only a small variation in the sintering temperature interval, the cell volume V_o exhibits a minimum value for samples sintered at 1650 °C/2h. BZT has an ABO_3 perovskite type structure, with Zn and Ta showing 1:2 order in the B site. The order of Zn and Ta expands the original perovskite unit cell along the <111> direction and contracts the unit cell in the plane normal to <111>. Consequently, c_o/a_o exhibits a value greater than $\sqrt{3/2} \approx 1.224$ and the unit cell is distorted. The unit cell distortion increases c_o / a_o with the increase of the sintering temperature.

Table 1. Unit cell parameters of BZT samples versus sintering temperature.

Sample	Sintering temperature T_s (°C)	Unit cell parameters			Unit cell volume V_o (Å^3)
		a_o (Å)	c_o (Å)	c_o/a_o	
1	1550	5.802	7.106	1.224	207.16
2	1600	5.792	7.094	1.225	206.09
3	1650	5.766	7.089	1.229	204.11

The microstructure of BZT ceramics sintered in air at 1550 °C/ 2h and 1650 °C/ 2h was investigated by using SEM. The images are presented in Figs. 4-5. The micrograph presents a sharp distribution of the grains size for BZT sample sintered at 1550 °C. The grains with size in the range 2 ÷ 7 μm are spherical and not well faceted (Fig. 4). Well faceted, polyhedral grains with smooth surfaces and edges showing dimensions in the range

(5 ÷ 20) μm are observed for BZT sample sintered at 1650 °C (Fig. 5). The difference between the 1550 °C and 1650 °C sintering temperatures has as effect a strong granular growth, as can be noticed in Fig. 4 and Fig. 5. For both samples, the porous structure is represented by submicron intergranular pores and few inter-aggregates large pores with dimension up to 10 μm.

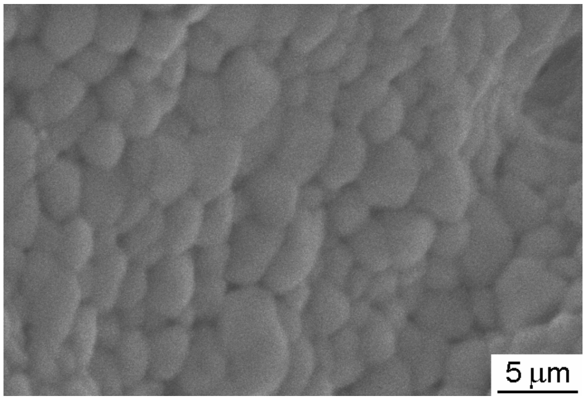

Fig. 4. SEM micrograph of BZT sample sintered 1550 °C/ 2h.

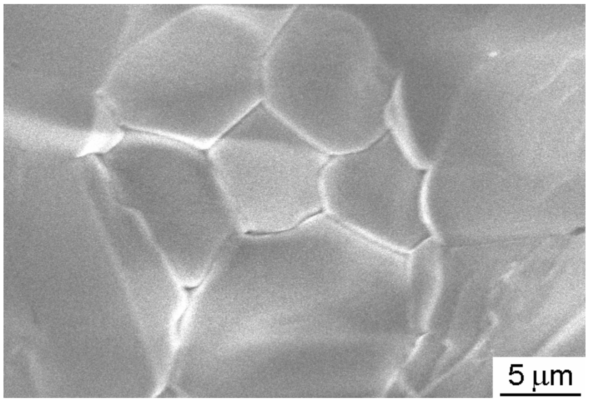

Fig. 5. SEM micrograph of BZT sample sintered 1650 °C/ 2h.

Microwave measurements on dielectric constant and loss tangent were carried out on the BZT dielectric resonators. The obtained data revealed a determinant influence of the sintering temperature on the complex dielectric constant. The variation of the dielectric constant and quality factor with the sintering temperature can be observed in Table 2. This can be considered as an effect of the reduced porosity resulting in a better densification at high sintering temperatures, as can be seen in Fig. 2.

Table 2. Microwave dielectric parameters of BZT sintered resonators versus sintering temperature.

Sample	Sintering temperature T_s (°C)	Height h (mm)	Diameter D (mm)	Resonance frequency f (GHz)	Dielectric constant ε_r	Dielectric loss $\tan\delta$ (x 10^{-4})	Quality factor Q	τ_f (ppm/°C)
1	1550	10.13	10.27	5.84	25.7	1.28	7800	+3 ÷ +6
2	1600	10.22	10.15	5.74	26.9	1.01	9900	
3	1650	10.03	10.18	5.67	27.9	0.81	12400	

The additional thermal treatment at 1410 °C for 10 h for all BZT samples resulted in the increase of the dielectric constant and of the quality factor as can be seen in Table 3. The dielectric constant values were not substantially modified by the annealing treatment. On the other hand, for annealed samples, the quality factor substantially increases for samples sintered at 1650 °C/2h.

The BZT dielectric resonators exhibit a positive temperature coefficient of the resonance frequency τ_f in the 3 ÷ 6 ppm/ °C range.

Table 3. Microwave dielectric parameters of BZT resonators annealed at 1410 °C/ 10h versus sintering temperature.

Sample	Sintering temperature T_s (°C)	Height h (mm)	Diameter D (mm)	Resonance frequency f (GHz)	Dielectric constant ε_r	Dielectric loss $\tan\delta$ (x 10^{-4})	Quality factor Q	τ_f (ppm/°C)
1	1550	10.10	10.25	5.82	26	1.06	9400	+3 ÷ +6
2	1600	10.20	10.13	5.73	27.1	0.95	10500	
3	1650	10.02	10.17	5.67	28	0.56	17600	

For non-polar dielectric resonators, in the microwave domain, the product between the resonance frequency f and quality factor Q is constant [3]. Consequently, the product Q x f is more frequently encountered as resonator parameter rather than the quality factor. The influence of the annealing treatment on dielectric constant and the Q x f

product of BZT resonators is presented in Fig. 6. The $Q \times f$ value increases especially for samples sintered at 1650 °C/2h and takes values up to 100 THz. On the other hand, the annealing treatment slightly increases the dielectric constant.

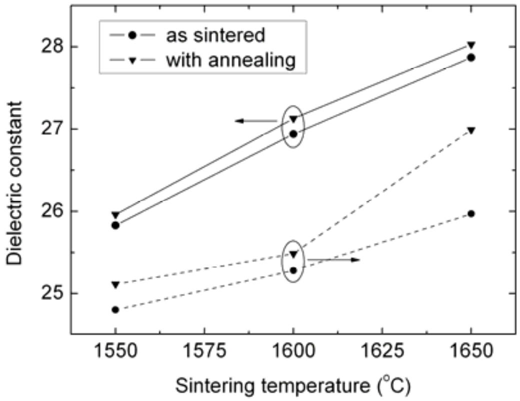

Fig. 6. Dielectric constant and Q x f product versus sintering temperature for BZT sintered and annealed resonators.

The high values of $Q \times f$ product obtained for BZT resonators sintered at 1650 °C/2h and annealed at 1410 °C/10h recommend this type of materials for application in communication systems and electrical and electronic engineering.

5. Conclusions

$Ba(Zn_{1/3}Ta_{2/3})O_3$ dielectric materials with high dielectric constant and low loss in microwave domain were achieved by solid-state reaction and sintered in the temperature range 1550 ÷ 1650 °C for 2h. It was shown that the additional annealing treatment at 1410 °C for 10 hours improves the microwave dielectric parameters.

The X-ray diffraction patterns confirm the formation of the BZT materials with trigonal structure. For sintering temperatures higher than 1600 °C, the XRD patterns reveal the BZT multiphase compositions with a secondary phase with low Zn content.

The dielectric constant and $Q \times f$ product increase with the increasing of the sintering temperature. The annealing has small effect on the dielectric constant value. On the other hand, the $Q \times f$ product substantially increases after annealing, especially for samples sintered at 1650 °C/2h. The temperature coefficient of the resonance frequency exhibits positive values less than 6 ppm/ °C.

Well-sintered and annealed BZT resonators exhibit a dielectric constant around 28 and a $Q \times f$ product up to 100 THz. The achieved high values of the quality factor Q recommend the BZT materials for microwave and millimeter wave applications.

Acknowledgements

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