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Thermal Treatments Effects on Microwave Dielectric Properties of $Ba(Zn_{1/3}Ta_{2/3})O_3$ Ceramics

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Abstract. $Ba(Zn_{1/3}Ta_{2/3})O_3$ dielectric materials were prepared by solid state reaction. The samples were sintered at temperatures in the range 1 400 ÷ 1 600°C for 4 h. Morphostructural characterization was performed by using SEM and XRD. The dielectric properties were measured in the microwave range (6 ÷ 7 GHz). An additional annealing at 1 400°C for 10 hours was performed in order to improve the dielectric parameters. The best parameters were achieved for the samples sintered at 1 600°C with additional thermal treatment.

1. Introduction

$Ba(B'_{1/3}\ B''_{2/3})O_3$ complex perovskites are very attractive materials for very high frequency applications due to owing to their attractive properties, especially the ultra high values of the quality factor Q. $Ba(Zn_{1/3}Ta_{2/3})O_3$ compound (BZT) has potential for applications in satellite broadcasting at frequencies higher than 10 GHz and as a very high Q dielectric resonators (DR) in mobile phone base stations or combiner filter for PCS applications [1]. The BZT ceramics exhibit a dielectric constant of 29, a $Q \times f$ product of 100 000 ÷ 160 000 GHz and a low temperature coefficient of resonant frequency τ_f close to zero in the presence of such additives as strontium-gallium [2].

There are several factors, which influence the Q values of perovskites $Ba(M^{2+}_{1/3}\ Ta^{5+}_{2/3})O_3$ with M = Mg, Zn such as: the long range ordering (LRO) of cations, the zinc oxide evaporation, the point defects and the stabilization of the microdomain boundaries [2]. The high Q values were explained from the point of view of the lattice vibrations of its trigonal superstructure. Sagala *et* Nambu calculated the dielectric loss tangent in microwaves from the equation of ion motions, which was a function of B-site ordering [3]. Galasso and co-workers concluded that the B-site ordering increased as the difference in charge and size between B′ and B″ atoms increased [4]. The ordering of complex perovskite BZT is important because the 1:2 ordering of the B′ and B″ cations along the $< 111 >$ axis is believed to be closely related to the high-Q property of BZT. There is a strong correlation between the cation ordering degree, domain growth, zinc loss and sintering parameters. The synthesis of a BZT material, its structural and morphologic characteristics as well as its microwave dielectric properties correlated to the thermal treatments parameters are reported.

2. Methods

$Ba(Zn_{1/3}Ta_{2/3})O_3$ 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 two hours. The powders were calcined at $T = 925°\mathrm{C}$ for two hours. Then the powders were milled for 2 h and calcined at 1 000°C/ 2 h. The third calcination was carried out at $T = 1\ 150°\mathrm{C}/2.5$ h, in air. The triple calcined powders were mixed with 1% polyvinyl alcohol (PVA) and dried at $T = 80°\mathrm{C}$, then were pressed into cylindrical samples of 12 mm diameter and 10 mm height. The pellets were slowly dried at 80°C in order to eliminate the PVA.

The density of green ceramics was $\rho = 4\ 400\ \mathrm{kg/m^3}$. The sintering treatment for the BZT samples was performed in air for 4 h at five different temperatures: 1 400°C, 1 450°C, 1 500°C, 1 525°C and 1 600°C. In order to improve the dielectric properties, especially the quality factor Q, the samples were treated supplementary for 10 h at 1 400°C. The pellets were polished in order to remove the superficial zone and to obtain correct values of the microwave dielectric parameters.

The relative bulk density of sintered disks was measured by the Archimedes method. Morphological, structural and compositional analyses were performed on 5 sets of samples by X-ray diffraction (XRD) analysis, and electron microscopy (SEM, EDX). The patterns were recorded in a 2θ range from 20° and 90° on a Seifert Debye Flex 2002 diffractometer into the $2\theta - \theta$ mode. Measurements were performed at room temperature using Cu K_α radiation, Ni filter and a detector scan speed of 7°/min.

The dielectric parameters, i.e. the dielectric constant ε_r, the quality factor Q and the loss tangent $\tan\delta$ were measured in the microwave range by Hakki-Coleman method. A computer aided measurement system containing a HP 8757 C scalar network analyzer and a HP 8350 B sweep oscillator was employed.

3. Results

The bulk density of the fired BZT ceramics was measured after grinding and polishing. The temperature dependence of densification after 4 h sintering in air is shown in Fig. 1. BZT ceramics sintered between 1 500°C and 1 600°C were well sintered.

The X-ray density of $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramic is $\rho_t = 7\ 920$ Kg/m^3. The most dense ceramics exhibit a porosity value of 10%. An abnormal grain growth together with an accentuated ZnO evaporation occurred above the sintering temperature $T_s = 1\ 525°C$, so the bulk density slightly decreased. Above $T_s = 1\ 525°C$, the bulk density continued to increase.

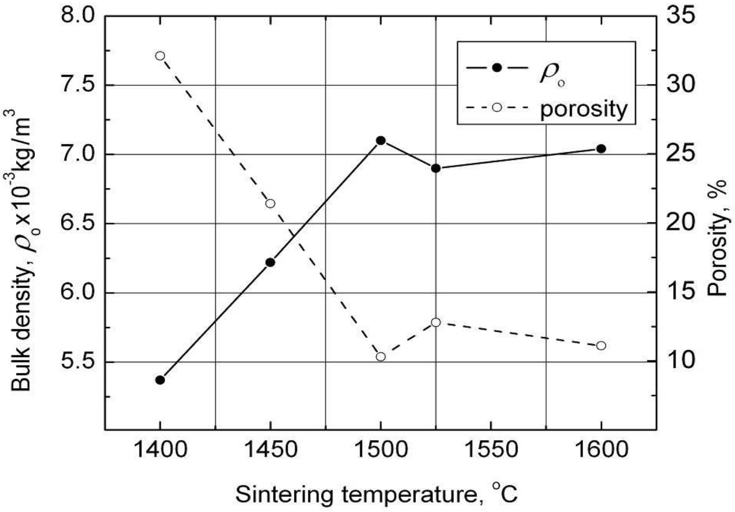

Fig. 1. Bulk density versus sintering temperature for BZT samples.

The X-ray diffraction patterns for BZT ceramic samples sintered at five sintering temperatures are given in Fig. 2. The patterns confirm the formation of the hexagonal structure, which is the majority phase. For the BZT compounds sintered at $T_s = 1\ 525°C$ the patterns reveal the presence of secondary phases $Ba_7Ta_6O_{22}$, Ba_8ZnTa_{24} and BaO, which disappear at higher sintering temperatures. The superlattice peaks at $2\theta = 17.6$ and 26.4 degrees increase in intensity with the increase of T_s up to 1 525°C. At $T_s = 1\ 600°C$ they practically disappear. For temperatures up to 1 525°C, the LRO gradually increases with the temperature increase.

The microstructure of BZT ceramics sintered in air at 1 500°C/4h and 1 600°C/4h was investigated by using SEM. The images are presented in Figs. 3–4. The micrograph presents a bimodal distribution of the grains size for BZT sample sintered at 1 500°C. Micron grains are located on the grain boundaries or on the grain surfaces; some grains with size in the range $3 \div 6$ μm are polyhedral with rounded corners and not well faceted and others are spherical with sizes up to 1.5 μm. Well faceted, polyhedral grains with smooth surfaces and edges and dimensions in the range $(10 \div 30)$ μm are observed for BZT sample sintered at 1 600°C. The abnormal granular growth together with the ZnO evaporation can explain the non-monotonic variation of the BZT bulk density with T_s, for $T_s > 1\ 500°C$. The relatively small difference between

1 500°C and 1 600°C sintering temperatures has as effect a strong granular growth, as can be noticed in Fig. 3 and Fig. 4.

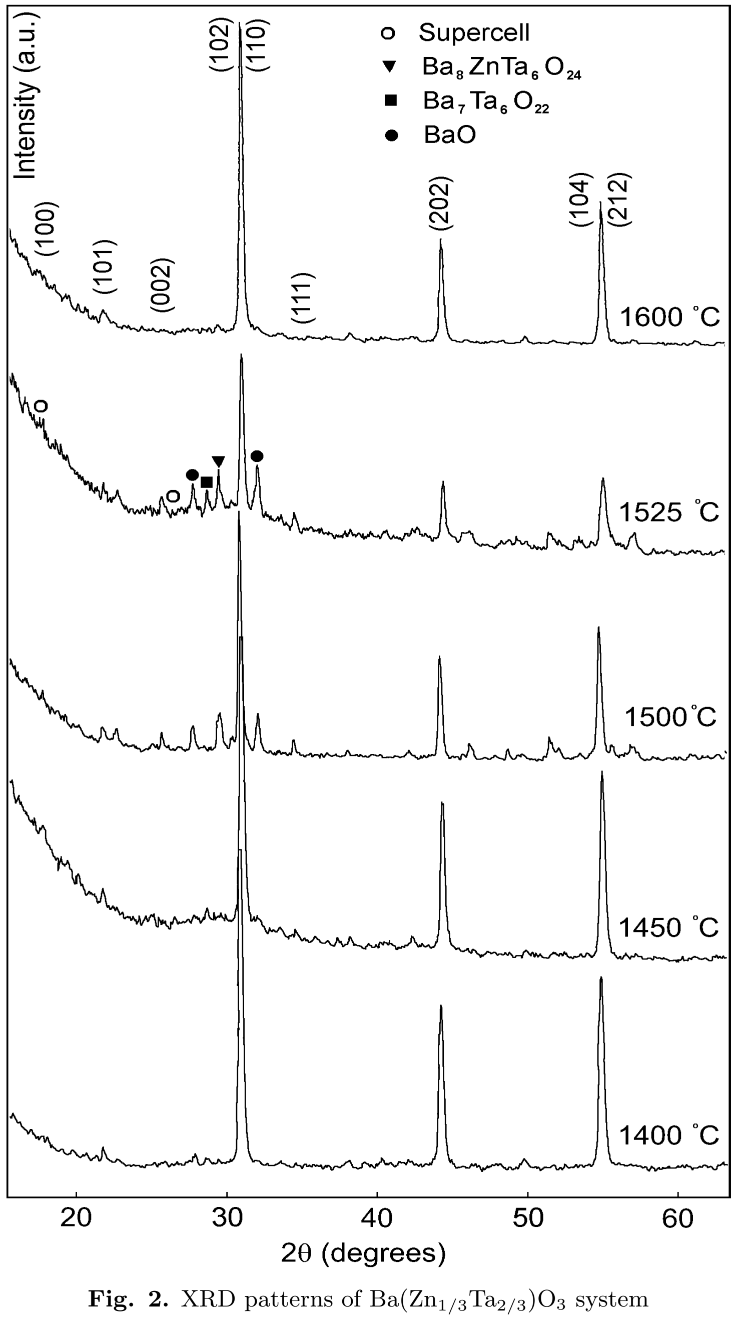

Fig. 2. XRD patterns of $Ba(Zn_{1/3}Ta_{2/3})O_3$ system versus sintering temperature.

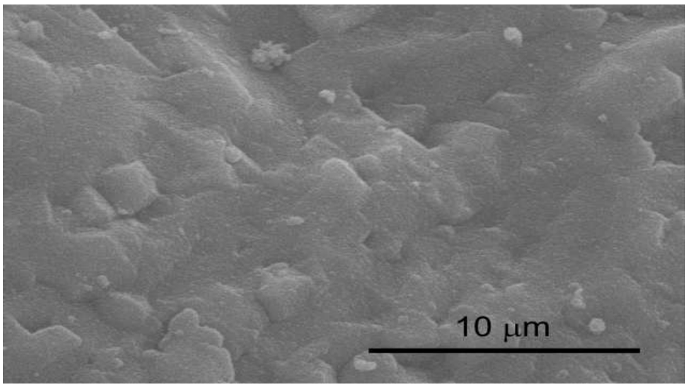

Fig. 3. Micrographs of the BZT sample sintered 1 500°C/4 h.

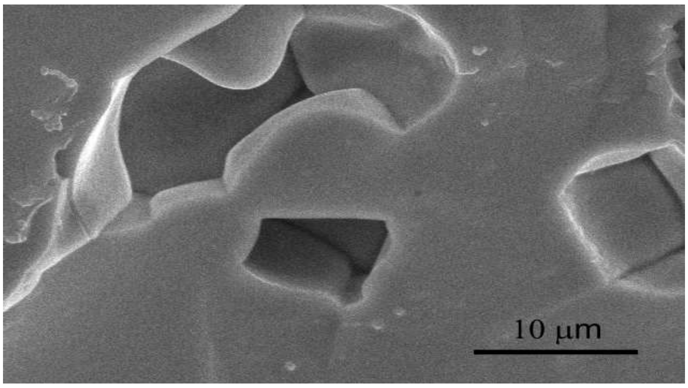

Fig. 4. Micrographs of the BZT sample sintered 1 600°C/4 h.

Microwave measurements on dielectric constant and loss tangent were carried out on the BZT samples. The obtained data revealed a determinant influence of the sintering temperature on the complex dielectric constant. The variation of the dielectric constant and dielectric loss with the sintering temperature can be observed in Fig. 5. 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. 1.

The loss tangent exhibits values around 2×10^{-4} for samples sintered at 1 400°C and 1 450°C. With the sintering temperature increase, the dielectric loss tangent increases up to 7×10^{-4} for $T_s = 1\ 500°\mathrm{C}$, then decreases down to 2×10^{-4} for $T_s = 1\ 600°\mathrm{C}$, as can be noticed in Fig. 5. This variation could be related to the Zn and Ta cation ordering process and with the secondary phases, which appear for sintering temperatures between 1 450°C and 1 525°C as shown in Fig. 2. For temperatures higher than 1 525°C, these phases disappear and, consequently, the dielectric loss decreases.

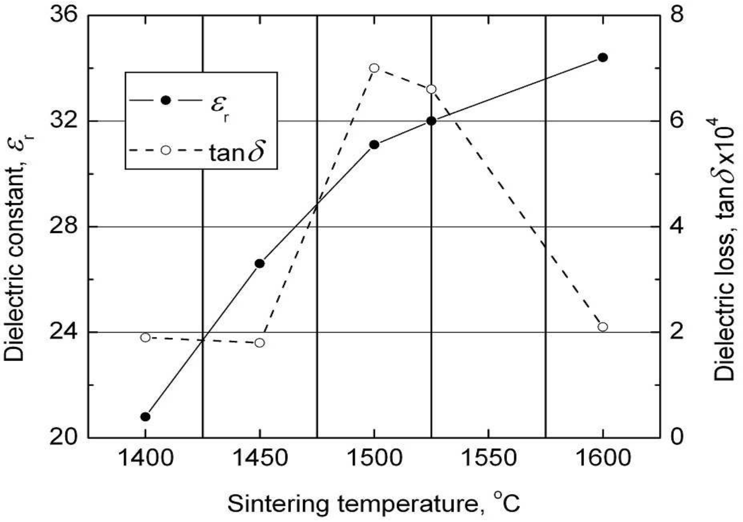

Fig. 5. Dielectric properties versus sintering temperature for BZT samples without annealing.

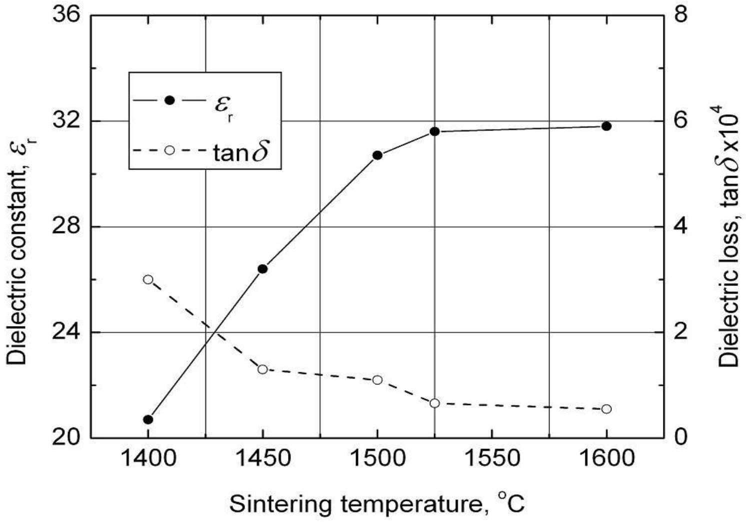

Fig. 6. Dielectric properties versus sintering temperature for annealed BZT samples.

The additional thermal treatment at 1 400°C for 10 h for all the samples resulted in the reduction of the BZT dielectric loss as can be seen in Fig. 6. For annealed samples, the dielectric loss continuously decreases with the increase of the sintering temperature. The dielectric constant values were not substantially modified by the annealing treatment, with only one exception of the BZT samples sintered at 1 600°C.

The quality factor Q values normalized at 10 GHz for the BZT samples are presented in Fig. 7. The Q is higher for annealed samples than for the samples without thermal treatment; this difference is more significant especially for BZT samples sintered beyond 1 525°C, which indicate the necessity of post sintering thermal treatment. The BZT samples sintered at 1 600°C exhibit a dielectric constant of about 31 and a quality factor normalized to 10 GHz up to 13 500.

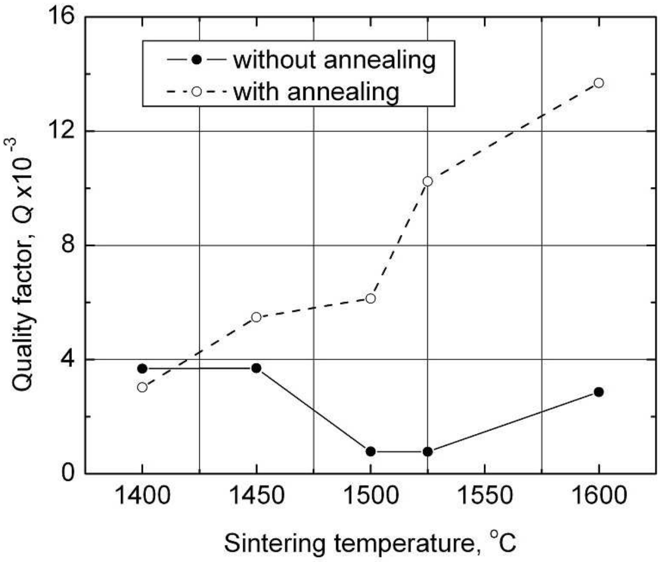

Fig. 7. Quality factor normalized at 10 GHz versus sintering temperature for BZT samples with and without annealing.

4. Conclusions

$Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics with low loss in microwave domain were obtained by solid state reaction in the temperature range 1 400 ÷ 1 600°C.

For sintering temperatures higher then 1 500°C, the XRD patterns reveal the BZT multiphase compositions with the presence of trigonal supercell peaks and low Zn content secondary phases. The last two disappear for samples sintered at 1 600°C.

The quality factor Q strongly depends on the BZT crystalline structure: the unit cell distortion and cationic order. Dielectric loss decreases with the increase of ordering degree in the structure and with the disappearance of secondary phases. Lowest loss is obtained for a Zn and Ta completely ordered BZT ceramic with a strongly distorted unit cell. Porosity has small effect on dielectric loss of BZT material.

Well-sintered and annealed BZT samples exhibit a dielectric constant around 31 and a $Q \times f$ product up to 135 000 GHz. The achieved very-high values of the quality factor Q recommend the BZT materials for microwave applications.

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