# Synthesis and properties of Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$ for microwave and millimeter wave applications

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## Abstract

High dielectric materials have gained an important position in microwave electronics by reducing the size and cost of components for a wide range of applications from mobile telephony to spatial communications. Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$ (BZT) is an A(B'B'')O$_3$ type perovskite material, showing ultra high values of the quality factor $Q$. Ceramic-based BZT dielectric materials were prepared by solid state reaction. The samples were sintered at temperatures in the range 1400÷1600 °C for 4 h. Compositional, structural and morphological characterization were performed by using XRD, SEM and EDX analysis. The dielectric properties were measured in the microwave range (6÷7 GHz). An additional annealing at 1400 °C for 10 h has improved some dielectric parameters. For samples sintered at temperatures higher than 1500 °C, the permittivity values were obtained in the interval 30÷35 and almost do not change its value after the annealing. The $Q \times f$ product substantially increases up to about 135,000 GHz, exhibiting a low temperature coefficient of the resonant frequency ($\tau_f$) in microwaves. The best parameters were obtained for the samples sintered at 1600 °C with additional annealing. The achieved high values of the $Q \times f$ product recommend these materials for microwave and millimeter wave applications.
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## 1. Introduction

Complex perovskites A B'$_{1/3}$ B''$_{2/3}$ O$_3$ are very promising materials for electroceramic applications 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 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 $\tau_f$ close to zero in the presence of such additives as strontium–gallium [2].

The long range ordering (LRO) of cations, zinc oxide evaporation, point defects and stabilization of microdomain boundaries have been considered to be the factors which influence the $Q$ values of such perovskites as Ba(M$_{1/3}^{2+}$Ta$_{2/3}^{5+}$)O$_3$ with M=Mg, Zn [2,3]. The high $Q$ values were explained from the point of view of the lattice vibrations of its trigonal superstructure. Sagala and Namb [4] calculated the dielectric loss tangent at microwave frequencies from the equation of ion motions, which was a function of B-site ordering. Galasso and co-workers [5] concluded that the B-site ordering increased as the difference in charge and size between B' and B'' atoms increased. 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.

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## 2. Experimental

Ceramics with molar formula $Ba(Zn_{1/3}Ta_{2/3})O_3$ 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 2 h. The powders were calcined at $T = 925$ °C for 2 h. Then the powders were milled for 2 h and calcined at 1000 °C/ 2 h. The triple calcined powders were mixed with 1% polyvinyl alcohol (PVA) and dried at $T = 80$ °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 third calcination was carried out at $T = 1150$ °C/2.5 h, in air.

The density of green ceramics was $\rho = 4400$ kg/m$^3$. The sintering treatment for the BZT samples was performed in air for 4 h at five temperature values: 1400 °C, 1450 °C, 1500 °C, 1525 °C and 1600 °C. In order to increase the dielectric properties, especially the quality factor $Q$, the samples were treated supplementary for 10 h at 1400 °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 $2\theta$ 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$_\alpha$ radiation, Ni filter and a detector speed of 7/min.

The dielectric parameters, i.e. the dielectric constant $\varepsilon$, 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 an HP 857 C scalar network analyzer and an HP 8350 B sweep oscillator was employed.

## 3. Results and discussion

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.
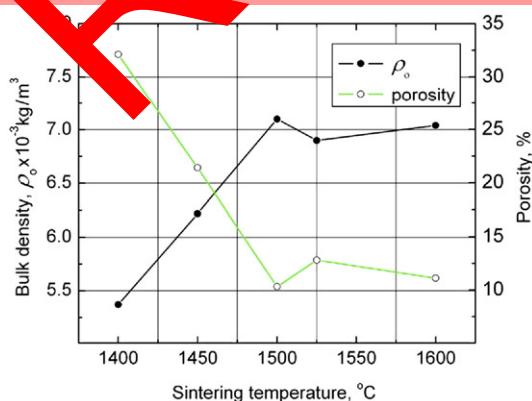


Fig. 1. Bulk density versus sintering temperature for BZT samples.
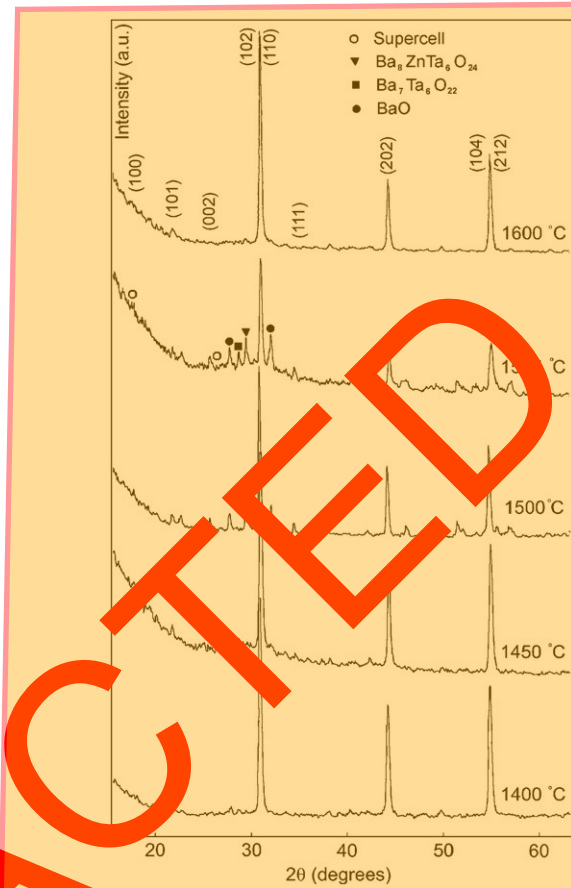


Fig. 2. XRD patterns of Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$ system versus sintering temperature.

BZT ceramics sintered between 1500 °C and 1600 °C were well sintered.

The X-ray density of $Ba(Zn_{1/3}Ta_{2/3})O_3$ compound was considered as $\rho_t = 7920$ kg/m$^3$ [6]. 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 $T_s = 1525$ °C, so the bulk density slightly decreased. Above $T_s = 1525$ °C, the bulk density continued to increase.

The crystal structure of $Ba(Zn_{1/3}Ta_{2/3})O_3$ is the structure of a classic ordered perovskite with two transition metals (B′ and B″) on the octahedral site. The B′ and B″ ions occur on alternating (111) planes in a 1:2 ratio. Each (111) plane contains only one type of small oxygen octahedron, and the planes are ordered in the 1:2 stoichiometric ratio, in the sequence Zn-Ta-Ta-Zn-Ta-Ta-.... The resulting symmetry, due to the (111) type plane stacking and accompanying small oxygen displacement strongly, depends on processing parameters. Consequently, the ordering of Zn and Ta depends of firing temperature and of the sintering time. The BZT samples sintered at low temperatures ($T_s < 1300$ °C) exhibit a pseudo-cubic perovskite type structure where Zn and Ta cations are in disorder. At higher sintering temperatures ($T_s > 1300$ °C), BZT presents a hexagonal structure, with Zn and Ta ions showing 1:2 order in the B site. The order of Zn and Ta cations expands the original perovskite unit cell along the <111> axis and contracts the unit cell in the (111) plane. Consequently, $c/a$

ratio has a value greater than $\sqrt{3/2} \approx 1.2247$ and the unit cell is distorted.

The increase of cation ordering on B site in BZT compounds creates a superlattice with a trigonal supercell. The degree of long range-structural order (LRO) can be evaluated by X-ray methods and it can be expressed as the ratio between the intensity of the super structure reflection peak and that of a basic unit cell reflection peak. The X-ray diffraction patterns for BZT compound, sintered at five sintering temperatures, using Cu $K_\alpha$ radiation 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 $T_s = 1525$ °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 super-lattice peaks at $2\theta = 17.6°$ and $26.4°$ increase in intensity with the increase of $T_s$ up to 1525 °C. At $T_s = 1600$ °C they practically disappear. For temperatures up to 1525 °C, the LRO gradually increases with the temperature increase.

The perfectly ordered structure is produced by the following process: (a) the perovskite-type structure is formed, but Zn and Ta cations are in disorder; (b) Zn and Ta cations are partially in order; and (c) Zn and Ta cations are completely in order and the lattice is distorted.

At high sintering temperatures, ZnO evaporates, thus a supplementary distortion can be produced by the ZnO loss. The $Zn^{2+}$ ions on B'-site are partially replaced by $Ba^{2+}$, which ha... much larger ionic radius of 0.161 nm comparatively to 0.074 n...
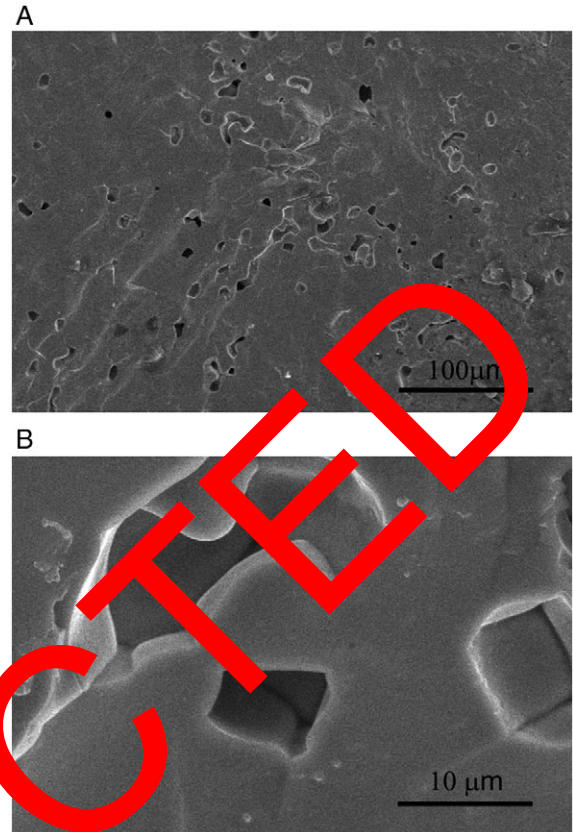


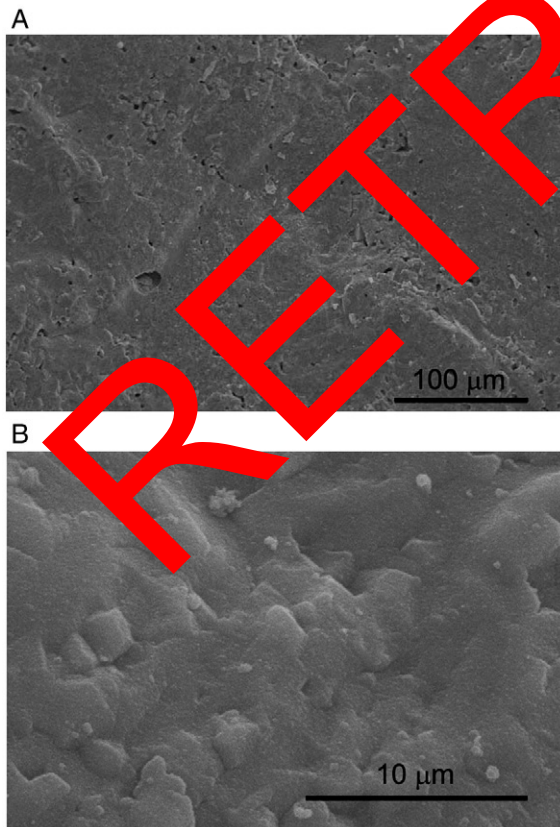Fig. 4. SEM micrographs of BZT sample sintered in air for 4h at 1600 °C: (A) general view; (B) detail.

for Zn cations. This substitution creates a supplementary unit cell distortion, even when the LRO is saturated and leads to an increase of $Q$.

The microstructure of BZT ceramics sintered in air at 1500 °C/ 4h and 1600 °C/ 4 h was investigated by using SEM. The images are presented in Figs. 3 and 4. The BZT samples sintered at $T_s > 1500$ °C present grains with concentric ordered shells. BZT samples have a large porous structure due to ZnO evaporation during the sintering process. In Fig. 3, micrographs of the sample sintered in air at 1500 °C/4 h are presented. The SEM image in Fig. 3A reveals an extended inter-aggregates porosity, with pore size in the range $(10 \div 30)$ µm. In addition, few small pores with sizes between 3 and 5 µm are located between grains. Submicron pores appear only on the grain surfaces. The large grains of a polyhedral shape, well faceted and with sizes in the range $(50–100)$ µm, are present in all the samples. 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 poly-hedral with rounded corners and not well faceted and others are spherical with sizes up to 1.5 µm.

The SEM image of the central zone of BZT sample sintered at 1600 °C for 4 h is shown in Fig. 4. In this case, the porous structure is reduced comparatively with the samples sintered at 1500 °C. The large pores disappear. There are inter-aggregates pores with sizes between 5 and 10 µm and smaller ones with sizes $(1 \div 3)$ µm located between three or four grains.



Fig. 3. Micrographs of the BZT sample sintered 1500 °C/4 h: (A) general view; (B) detail.
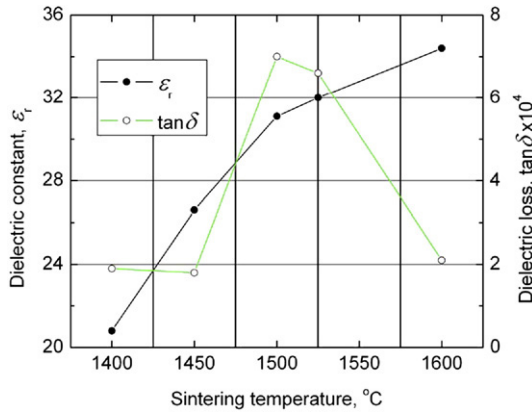
Fig. 5. Dielectric properties versus sintering temperature for BZT samples without annealing.
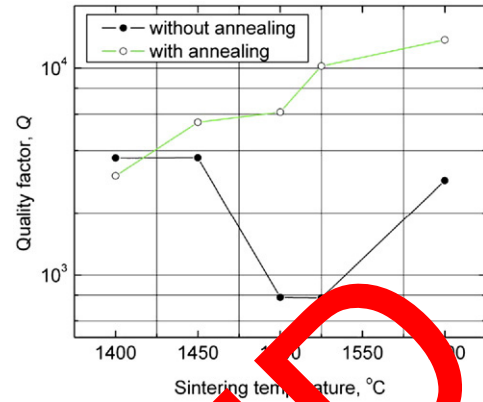


Fig. 7. Quality factor normalized at 10 GHz versus sintering temperature for BZT samples with and without annealing.

The micrograph presents a bimodal distribution of the grains size. Well-faceted polyhedral grains with smooth surfaces and edges and dimensions in the range $(30 \div 80)$ µm are present. The abnormal granular growth together with the ZnO evaporation can explain the non-monotonic variation of the BZT bulk density with $T_s$, for $T_s > 1500$ °C. The relatively small difference between 1500 °C and 1600 °C sintering temperatures has as effect a strong granular growth, as can be noticed in Figs. 3B and 4B.

We used microanalysis (EDX) in an attempt to examine whether a composition trend such as a "paucity" of the $B'$ element could explain the correlation between the structural long range ordering and dielectric properties. The BZT cylinders sintered at 1600 °C exhibit two different zones: a central axial light-colored zone and a peripheral dark-colored zone. In the outer zone, where the ZnO evaporation is more possible, the Zn atomic concentration indicates a non-stoichiometric composition. On the other hand, the experimental data indicate a variation of $Ba^{2+}$ content with higher concentration at the sample boundary. In this case, $Ba^{2+}$ can enter on the free Zn-octahedron sites, producing a supplementary deformation of the unit cell.

Microwave measurements on dielectric constant and loss tangent were carried out on the BZT samples. The obtained data revealed a dominant 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 $2 \times 10^{-4}$ for samples sintered at 1400 °C and 1450 °C. With the sintering temperature increase, the dielectric loss tangent increases up to $7 \times 10^{-4}$ for $T_s = 1500$ °C, then decreases down to $2 \times 10^{-4}$ for $T_s = 1600$ °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 1450 °C and 1525 °C as shown in Fig. 2. For temperatures higher than 1525 °C, these phases disappear and, consequently, the dielectric loss became lower. The additional thermal treatment at 1400 °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 1600 °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 1525 °C, which indicate the necessity of post sintering thermal treatment. The BZT samples sintered at 1600 °C exhibit a dielectric constant of about 31, a temperature coefficient of resonance frequency $\tau_f$ between 3 and 7 ppm/°C and a quality factor normalized to 10 GHz up to 13,500.

## 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 $1400 \div 1600$ °C. The increase of the sintering temperature leads to a normal granular growth, with a polyhedral grains size development.
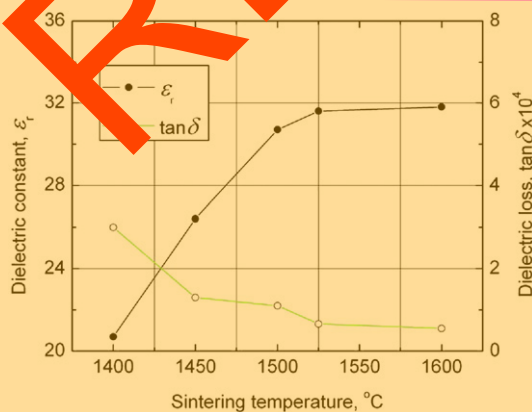


Fig. 6. Dielectric properties versus sintering temperature for annealed BZT samples.

For sintering temperatures higher then 1500 °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 at temperatures higher than 1600 °C.

The investigations on dielectric properties revealed that the increase of the sintering temperature decreases the dielectric loss especially when an annealing of 10 h at 1400 °C is performed.

The quality factor $Q$ strongly depends on the BZT crystalline structure, that is on 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, a $Q \times f$ product up to 135,000 GHz and a temperature coefficient of resonance frequency $\tau_f$ between 3 and 7 ppm/°C, similar to literature data. The achieved very high quality factor $Q$ and small $\tau_f$ recommend the BZT materials for such microwave and millimeter wave applications as resonators and filters for wireless communication systems.

## Acknowledgments

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