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Dielectric properties of BZT ceramics for microwave applications

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High permittivity dielectric materials ($\varepsilon_r > 20$) are used in mobile communications due to low dielectric loss in microwaves and millimeter waves, specific temperature dependence of the dielectric properties and high dielectric permittivity, which allows device miniaturization. Preparation of $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramic materials (BZT) with optimal properties for applications requires special thermal treatments due to the difficult control of the cationic ordering. The samples were prepared by using solid-state reaction, doped with Eu_2O_3, ZrO_2, Nb_2O_5, or Al_2O_3-Y_2O_3 and sintered at the following temperatures: 1400, 1500, 1550 °C for 2 or 3 hours. In order to improve the microwave properties, annealing treatments at 1410 °C for 10 h or 30 h were performed on ceramic samples. XRD was used for compositional and structural characterization. The XRD data allowed the study of the transition from the pseudo-cubic cell to the hexagonal cell. The dielectric properties were measured in the microwave range and were correlated with additives and structural properties. Sintering temperatures greater than 1500 °C are required for doped BZT compositions, in order to obtain high dielectric constant ($\varepsilon_r \sim 28$) and high quality factor (Q = 10000 at 10 GHz).

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Keywords: Tantalates, Sintering parameters, Additives, Dielectric properties, High quality factor

1. Introduction

During the current worldwide revolution in the microwave-based communication technologies, the production of dielectric ceramics and resonators has emerged as one of the most rapid growth areas in electronic ceramic manufacturing. Complex perovskite ceramics have been extensively studied for their applications to dielectric resonators at microwave frequencies.

In particular, the $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) ceramics are known to exhibit a high dielectric constant (ε_r) , a small temperature coefficient of resonance frequency (τ_f) and a high quality factor (Q), all of which are important properties for the application of dielectric ceramics to microwave devices [2], in satellite broadcasting [3] and as a super-high Q dielectric resonator (DR) in mobile phone base stations or combiner filter for Personal Communication System (PCS) applications [3,4].

Zinc oxide evaporation, long range ordering (LRO) of cations, stabilization of micro domain boundaries and point defects have been considered to be the main factors influencing the Q values of Ba $(M_{1/3}^{2+}\ Ta_{2/3}^{5+})O_3$ perovskites, (M=Mg, Zn). The ordering of complex perovskite BZT is a subject of strong interest, as the 1:2 cationic ordering is related to the high-Q property of BZT [5]. Tamura explained the high Q value from the standpoint of the lattice vibrations of its superstructure [6]. The dielectric tangent at microwave frequencies was calculated by Sagala from the equation of ion motions, which was a function of B-site ordering [7]. Galasso concluded that the B-site ordering increased as the difference in charge and size between B and B" atoms increased [8]. There is a strong correlation between cationic ordering, zinc loss, domain growth and sintering parameters.

In this paper, the synthesis of compounds and the preparation of BZT sintered pellets are reported. The sinterability, crystalline structure, phase composition, and microwave dielectric properties were analysed. ZrO_2, Eu_2O_3, Nd_2O_3 and Al_2O_3-Y_2O_2 were added in small quantities (≤2% mol) and the effect of the additives on the structural and microwave dielectric properties of BZT ceramics was investigated. Different sintering temperatures (T_s) in the temperature range (1400 ÷ 1550) °C, and annealing treatments for 10 to 40h were applied in order to improve the $Q \times f$ value of BZT compositions.

2. Experimental

Ceramics with molar formula $Ba(Zn_{1/3}\ Ta_{2/3})O_3$ undoped and doped with Al^{3+}, Y^{3+}, Eu^{3+}, Nb^{5+} or Zr^{4+} ions, were prepared by using solid state reaction from oxides of 99,95% purity. Starting materials $BaCO_3$, ZnO, Ta_2O_5 – were weighted, ground and milled in absolute ethanol for 30 minutes, then dried at 60°C for 3 hours. The stoichiometric precursor mixtures were calcined at 1000 °C, 1310 °C and 1400 °C for 2 hours in air, then

cooled at a slow cooling rate. Oxide additives Al_2O_3, Y_2O_3, Eu_2O_3, Nb_2O_5 and ZrO_2 were added to the calcined BZT compound in quantities corresponding to the following molar compositions:

- BZT - AlY → 99% BZT + 0,5% Al_2O_3 +0,5% Y_2O_3
- BZT - Eu → 99% BZT + 1% Eu_2O_3
- BZT – Nb → 99% BZT + 1% Nb_2O_5
- BZT - Zr → 98% BZT + 2% ZrO_2

The powder compositions were homogenised and milled in agate bottle with agate balls for half an hour in absolute ethanol, then dried at 60°C for 3 hours. The powders were uniaxial pressed in discs at 5 daN/mm^2 and thermal treated at three sintering temperatures: T_{s1} = 1400 °C/ 3h, T_{s2} = 1500 °C/ 2h and T_{s3} = 1550°C/ 2h, in air. The cooling of the furnace was performed at a low rate. In order to improve the dielectric properties, especially the quality factor Q, the samples were annealed at T_a = 1410°C, for 10 and 30 hours.

The pellets were polished to remove the superficial zone, which is porous and poor in Zn, and used for structural and morphological investigations and for high frequency measurements.

Differential scanning calorimetry (DSC) was used in order to study the changes, which occur during thermal treatments. The thermal analysis of the precursor mixture was performed up to 1500 °C, in static air atmosphere with α - Al_2O_3 as reference, at a heating rate of 10 °C/minute, using a DSC – Shimadzu DTA-TA-51H analyzer.

Structural analyses and investigations on the evolution of phase composition in isothermal conditions were performed by X-ray diffraction. A Shimadzu XRD 600 diffractometer with Ni filtered Cu K_α radiation, scan step increment of 0.02 degrees and a counting time of 1 s/ step for 2θ ranged between 20 ° and 80 ° was used. The sinterability of BZT ceramics, as function of the additive type and sintering temperatures, was investigated by absorption capacity and open porosity measurements using a Pascal 240/140 porosimeter at a pressure between 0.1 and 200 MPa, a 0.1 mm^3 resolution, at room temperature. The bulk density of the sintered pellets was measured by Archimede's method.

The Hakki-Coleman method was used for dielectric constant (ε_r) and loss tangent (tan δ) measurements in microwave domain at room temperature. A computer aided measurement system containing an HP 8757C scalar network analyser and an HP 8350 B sweep oscillator was used.

3. Results and discussion

3.1. Precursor powder characterization

Differential thermal analysis and X-ray diffraction were utilized to characterize the standard $Ba(Zn_{1/3}\ Ta_{2/3})O_3$ composition. The thermal behaviour of the mixture of BZT precursors versus temperature, in the temperature range 20 ÷ 1400°C, is shown in Fig.1.

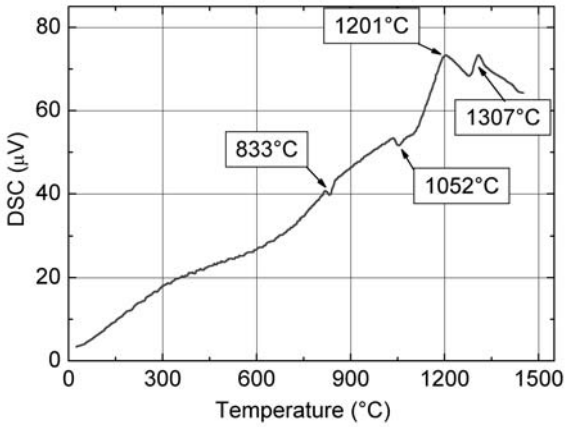

Fig. 1. Differential scanning calorimetry (DSC) data for the mixture of BZT precursors vs. temperature.

The BZT phase formation starts at 800 °C and the precursors disappear at around 1000 °C. A secondary phase identified as $Ba_5\ Ta_4\ O_{15}$ disappears at temperatures higher than 1100 °C [9]. The differential scanning calorimetry (DSC) curve indicates more effects:

- - the endopeak at T = 833 °C corresponds to the $BaCO_3$ decomposition with CO_2 loss;
- - the endopeak at T = 1052 °C can be attributed to the solid state reaction and the formation of BZT solid solution composition
- - the endopeaks at T = 1200°C and T = 1307 °C can be attributed to the structural ordering evolution and phase composition modification.

At temperatures higher than 1307 °C, the single phase BZT is well formed as is shown in Fig.2. The factors, which can influence the calcinations, are the temperature level and treatment duration. The standard mixture of BZT precursors were triple-calcined at temperatures T_c 1100 °C, 1310 °C and 1400 °C for 2 hours in air with a slope of 300 °C h^{-1}. The structural XRD investigation of BZT precursors mixture calcined for 2h at different temperatures was performed and the X-ray patterns are presented in Fig. 2.

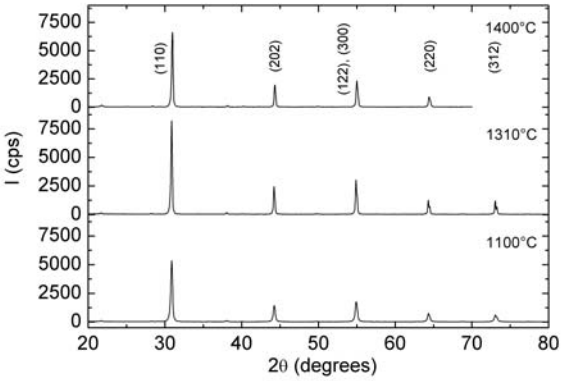

Fig. 2. X-ray diffraction pattern of synthesized BZT powder for different calcination temperatures.

Both BZT samples, which were calcined at 1100 °C and 1310 °C, reveal a well-formed BZT cubic single-phase structure. The diffraction peaks intensity increases with T_c. Nevertheless, we can observe that the crystallinity degree decreases at $T_c = 1400$ °C, where there is a large probability to form the $Ba_5Ta_4O_{15}$ compound without zinc. The results are in good correlation with thermal analysis data. The lattice parameter "a_o" calculated from the indexed powder patterns was ~ 4.08 Å.

3.2. Structural characterization and phase composition of sintered BZT ceramics

The five BZT compositions were homogenised, pressed and sintered at temperatures (T_s): 1400 °C, 1500 °C and 1550 °C. The slope was established as 600 °C h^{-1}. The sintering time was 3 h for $T_s = 1400$ °C and 2 h for $T_s = 1500$ °C and 1550 °C. The cooling was realized at low cooling rate.

The X-ray spectra of 1-5 specimens sintered at different T_s are presented in Figs. 3-7.

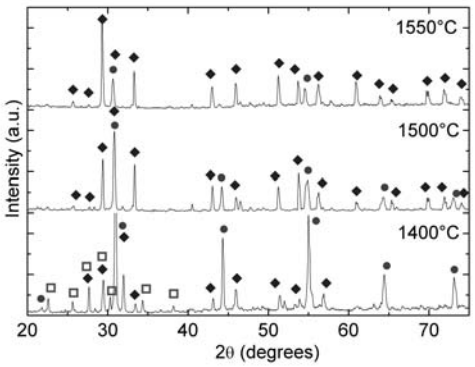

Fig. 3. XRD patterns of undoped BZT ceramics for different sintering temperatures: filled circles indicate the $Ba(Zn_{1/3}Ta_{2/3})O_3$ compound, diamonds - $Ba_8ZnTa_6O_{24}$ and squares indicate a secondary phase without Zn.

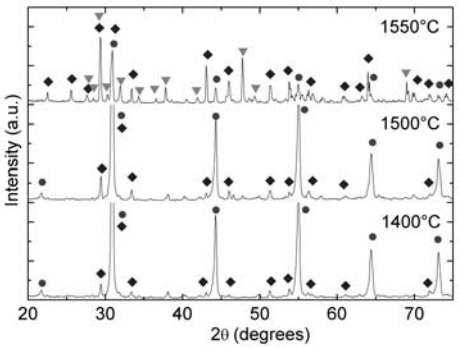

Fig. 4. XRD patterns of BZT-AlY ceramics for different sintering temperatures: filled circles indicate $Ba(Zn_{1/3}Ta_{2/3})O_3$ compound, diamonds - $Ba_8ZnTa_6O_{24}$ and down-pointing triangles indicate a secondary phase without Zn.

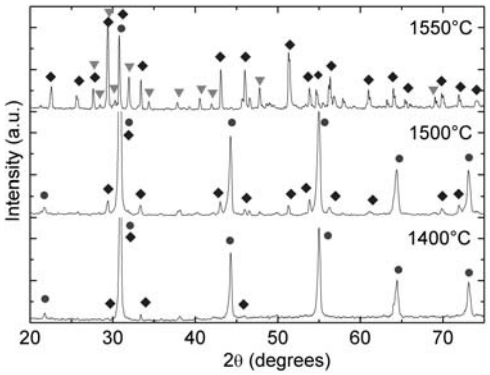

Fig. 5. XRD patterns of BZT-Eu ceramics for different sintering temperatures: filled circles indicate $Ba(Zn_{1/3}Ta_{2/3})O_3$ compound, diamonds - $Ba_8ZnTa_6O_{24}$ and down-pointing triangles indicate a secondary phase without Zn.

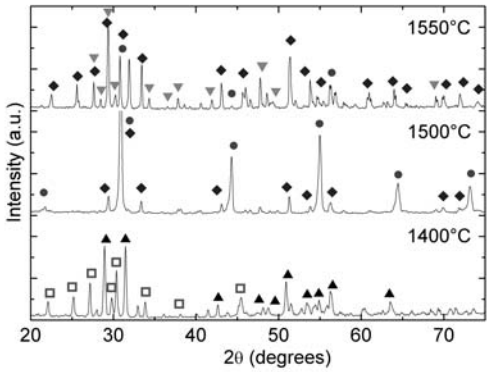

Fig. 6. XRD patterns of BZT-Nb ceramics for different sintering temperatures: filled circles indicate the $Ba(Zn_{1/3}Ta_{2/3})O_3$ compound, diamonds - $Ba_8ZnTa_6O_{24}$ and square , down-pointing triangles and up-pointing triangles indicate secondary phases without Zn.

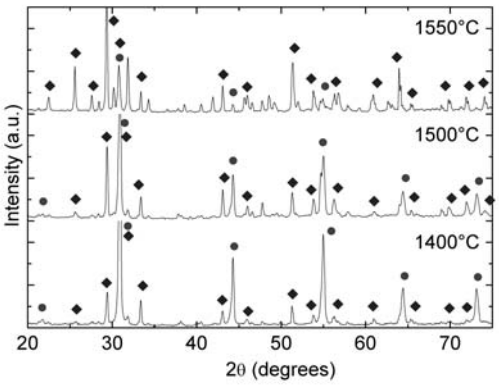

Fig. 7. XRD patterns of BZT-Zr ceramics for different sintering temperatures: filled circles indicate the $Ba(Zn_{1/3}Ta_{2/3})O_3$ compound and diamonds – $Ba_8ZnTa_6O_{24}$.

The XRD patterns analysis indicates well-structured BZT ceramics and also secondary phases. The sintering treatment parameters influence the formation and the stability of the samples. The pure $Ba(Zn_{1/3}Ta_{2/3})O_3$ exhibits hexagonally order beyond 1400 °C. The drawback effect of the T_s increase consists in the Zn loss due to its volatilisation. Consequently, secondary phases with low Zn content ($Ba_8ZnTa_6O_{24}$) or even without zinc ($Ba_{0.5}TaO_3$, $Ba_5Ta_4O_{15}$, $BaTa_4O_9$) are present. These secondary phases depend on the sintering temperature and on the type of the dopant. For undoped BZT, the $Ba_{0.5}TaO_3$ disappears at $T_s > 1400$ °C. The additives improve the sintering process of BZT and increase the solid solutions stability.

The $Al_2O_3 + Y_2O_3$ mixture reduces the appearance probability of the secondary phases without zinc at low sintering temperatures. The XRD pattern revealed only $Ba_8ZnTa_6O_{24}$ presence up to 1500 °C.

The Eu^{3+} presence leads to a multiphase system. The number of compounds with barium and tantalum without Zn increases with T_s. The same observation occurs in the case of Zr as additive.

The niobium reduces the formation kinetic of BZT and the specific BZT diffraction peaks appears with high intensities only at sintering temperatures ~ 1500°C. At lower and upper sintering temperatures the $Ba_8ZnTa_6O_{24}$ compound becomes dominant, associated with the other compounds without zinc.

3.3. Additions effect on BZT sinterability

The sintered BZT samples were analysed by immersion method and the Brunauer-Emmet-Teller (BET) adsorption in order to obtain informations about the bulk density, open porosity and adsorption capacity as function on sintering temperature and additives. The results are presented in Figs. 8-9. The undoped BZT samples exhibit the highest values of open porosity and adsorption capacity. In the same time the bulk density presents the lower values for all the sintering temperatures. The beneficial effect of ZrO_2 , Nb_2O_5, Al_2O_3+Y_2O_3 or Eu_2O_3 additives upon the BZT ceramics sinterability consists in higher values of the bulk density for this type of compounds. For the 1500 °C sintering temperature, Zr Nb and Eu doped BZT pellets exhibit the highest density values, as well as the lowest absorption capacitance and open porosity.

The increase of T_s up to 1500 °C induces the BZT sample densification. On the other hand, the open porosity and the adsorption capacity decrease. At $T_s = 1550$ °C, Figs. 8-9 reveal a decrease of the bulk density, which can be attributed to the zinc loss during the thermal treatment. The Al and Y presence induces a decrease of ceramics densities due to the small mass of dopants, comparatively with undoped BZT samples or doped with Zr, Nb, Eu. All dopants have a beneficial role in the formation of BZT materials.

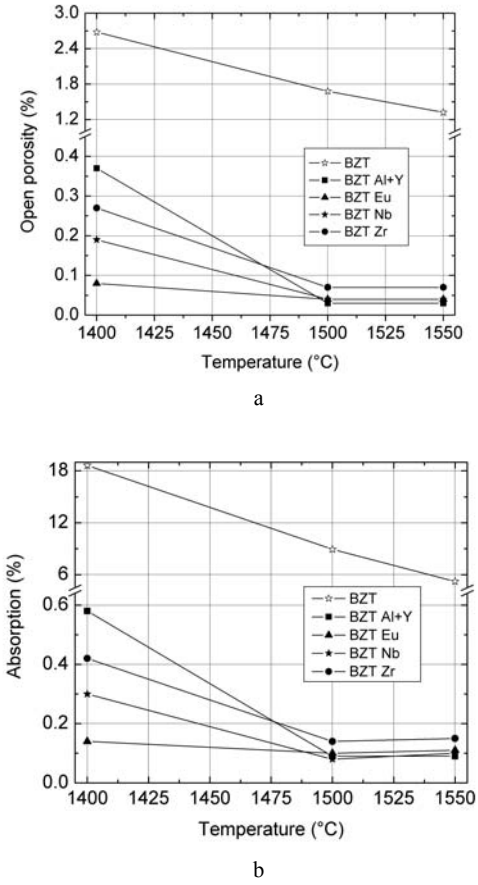

Fig. 8. The dependence of open porosity (a) and absorption capacity (b) of BZT samples on the sintering temperature.

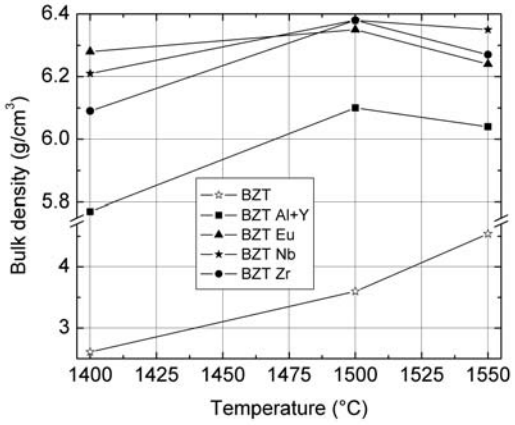

Fig. 9. The bulk density of sintered BZT ceramics versus sintering temperature.

3.4. Microwave dielectric properties

Microwave measurements were performed in the $5 \div 12$ GHz frequency range. Figs. 10-15 present the variations of the dielectric constant (ε_r) and of the product ($Q \times f$) between the quality factor Q and the frequency f for the BZT samples versus sintering temperature for different annealing temperatures.

The dielectric measurements carried out on sintered samples indicate the same trend for the dielectric permittivity as the bulk density with maximum values at $T_s = 1500\ ^oC$. The ε_r values (Fig.10) for Eu, Nb and Zr doped BZT samples are in the range $(27 \div 28.5)$.

For the BZT samples without annealing, the dependence of the dielectric constant on the sintering temperature (Fig. 10) is correlated with the dependence of the bulk density (Fig. 9). For all samples, the $Q \times f$ product (Fig.11) presents low values down to 24000 for $T_s = (1400 \div 1500)\ ^oC$ and increased values up to 35 000 GHz for $T_s = 1550\ ^oC$. The BZT: Zr samples make an exception: the $Q \times f$ continuously decreases with the increase of T_s.

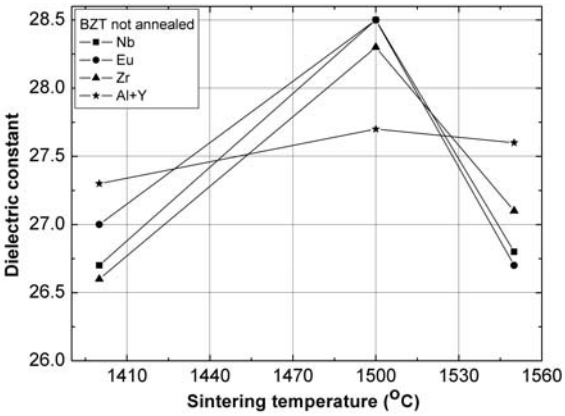

Fig. 10. The dielectric constant of sintered BZT samples as function of sintering temperature for different dopants.

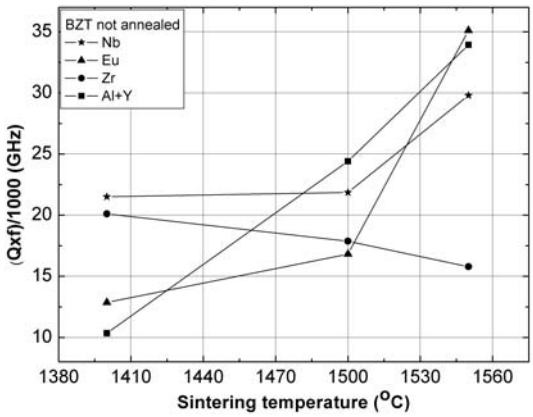

Fig. 11. The $Q \times f$ product values of sintered BZT samples versus sintering temperature for different dopants.

The BZT ceramics annealed at 1410 ^{o}C for 10 hours exhibit interesting modifications of microwave parameters as can be seen in Figs. 12 and 13. Due to the annealing, the relative dielectric permittivity ε_r decreases to values lower than 27.6, as shown in Fig. 12. This is presumably due to the Zn volatilisation.

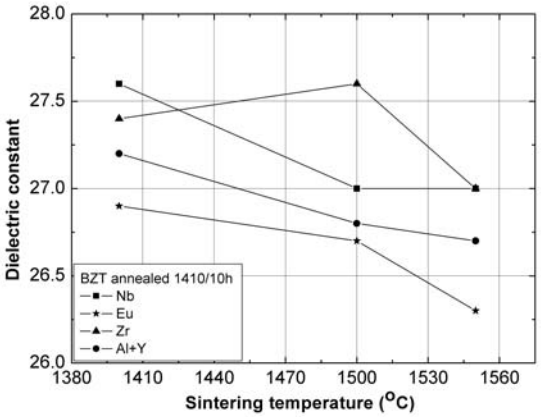

Fig.12. The dielectric constant of the BZT samples annealed at 1410 ^{o}C/ 10h function of the sintering temperature and dopants.

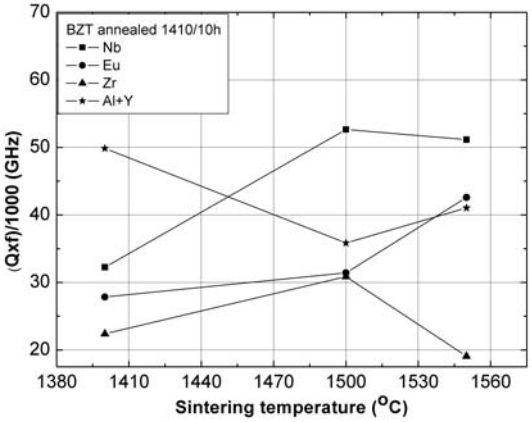

Fig. 13. The $Q \times f$ product of the BZT samples annealed at 1410 ^{o}C/ 10h versus the sintering temperature and dopants.

The $Q \times f$ product of the samples annealed for 10h (Fig. 13), exhibits increased values in the range $40000 \div 52000$ GHz for a sintering temperature $T_s = 1550\ ^oC$. Once again, the Zr doped samples exhibit $Q \times f$ values lower then 30000 GHz. A slightly decrease of the dielectric constant for all the samples, presumably due to the formation of the secondary phases, with low Zn content at the the sample surface can be observed in Fig. 14.

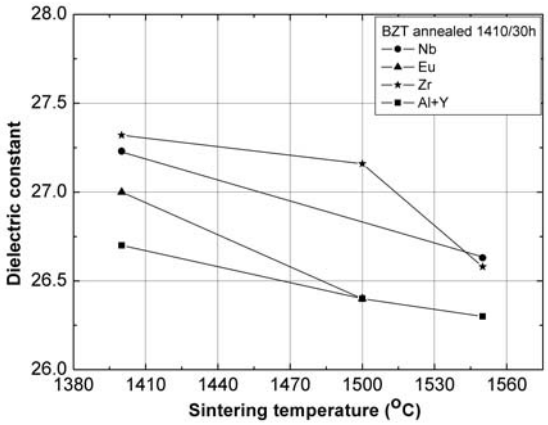

Fig. 14. The dielectric constant of the BZT samples annealed at 1410 °C/30h as function of sintering temperature and dopants

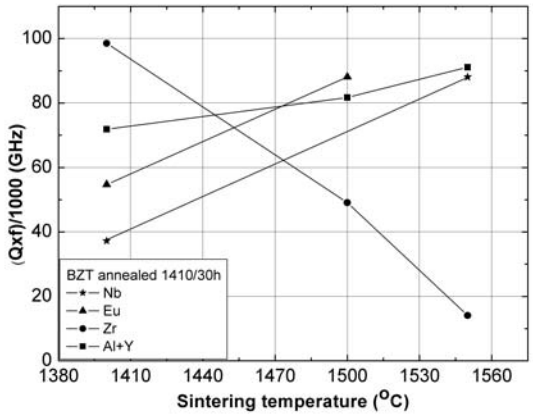

Fig. 15. The $Q \times f$ product values of the BZT samples annealed at 1410 °C/30h versus sintering temperature and dopants.

The 30 h annealing time at 1410 °C, leads to a spectacular increase of the $Q \times f$ product up to near 90000 GHz for samples doped with Al+Y, Eu and Nb and sintered at $T_s \geq 1500$ °C and for the BZT:Zr samples sintered at $T_s = 1400$ °C. On the other hand, the BZT: Zr ceramics sintered at $T_s = 1550$ °C exhibit $Q \times f$ values lower than 20000 GHz, which can be attributed to the high Zr concentration (Fig. 15).

4. Conclusions

Undoped and doped BZT ceramics were prepared obtained by solid-state reaction. The dopants used were Nb or Zr, Al+Y and Eu.

The calcination was carried out at a temperature of 1310 °C for two hours as optimal treatment in order to obtain well formed and structured single-phase BZT compound.

The Nb, Zr, Al+Y, Eu dopants improve sintering process. For $T_s = 1500$ °C, the doped BZT pellets exhibit the maximum bulk density values, the lowest absorption capacitance and open porosity, together with high values for dielectric constant.

The lower dielectric loss was obtained for the Nb, Al+Y and Eu doped BZT samples sintered at 1550 °C. The annealing treatment at 1410 °C for 30 h leads to the increase of the $Q \times f$ product values up to 90000 GHz.

Zr doped BZT ceramics sintered at 1400 °C/3h and annealed at 1410 °C for 30 hours with $Q \times f = 98000$ GHz represent a cost effective solution for microwave application.

Acknowledgements

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