# Correlation of Structural and MW-MMW Dielectric Properties with Vibrational Modes in $BaX_{1/3}Ta_{2/3}O_3$ Complex Perovskites

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***Abstract*—Ceramic based $Ba(Zn_{1/3}Ta_{2/3})O_3$ materials were prepared by solid-state reaction. Studies on microwave dielectric parameters in correlation with structural and Raman investigations were performed. Sintering temperatures higher than 1600 °C are required in order to obtain dielectric properties suitable for millimeter wave applications.**

## I. Introduction And Background

Since 1980's dielectric materials have been developed and put in practical use as resonators for filters in microwave communications, antennas, and oscillators, in satellite broadcasting at frequencies higher than 30 GHz, miniaturizing these components and saving costs. High quality factor ($Q$) dielectric resonators are required in applications.

Perovskite $Ba(X_{1/3}\,Ta_{2/3})O_3$ (X=Mg, Zn) ceramics[1] exhibit a super-high value of $Q$, (12,000 ÷ 35,000 at 10 GHz) among microwave dielectric materials with low temperature coefficient of resonant frequency ($\tau_f \sim 5$ppm/°C) and a large dielectric constant ($\varepsilon_r$ =24 - 29).

The factors influencing $Q$ values of complex perovskites $Ba(X_{1/3}\,Ta_{2/3})O_3$ (X= Mg, Zn) have been considered to be long range ordering (LRO) of cations, ZnO/MgO evaporation, point defects and stabilization of microdomain boundaries[2]. This explained the high $Q$ values from the point of view of the lattice vibrations of its hexagonal superstructure. Sagala et Nambu[3] calculated the dielectric loss tangent at microwave frequencies from the equation of ion motions which was a function of B-site ordering in the $A(B'_{1/3}B''_{2/3})O_3$ perovskite structure. Galasso and coworkers[4] 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 is important because the 1/3 <111> (1:2) ordering is believed to be closely related to the high-$Q$ property of $Ba(X_{1/3}\,Ta_{2/3})O_3$. There is a strong correlation between the cation ordering, domain growth, zinc or magnesium loss and sintering parameters. In this paper we report the synthesis of a $Ba(Zn_{1/3}\,Ta_{2/3})O_3$ materials and the correlation of their structural, microwave and millimeter wave properties with Raman vibrational modes.

## II. Results

The $Ba(Zn_{1/3}\,Ta_{2/3})O_3$ samples prepared by solid-state reaction were sintered in air at temperatures in the range 1550-1650 °C, for 2 hours. In order to improve the microwave and millimeter wave properties, annealing treatments at 1400 °C for 10 hours were made[5]. A Shimadzu XRD6000 diffractometer was employed for structural characterization.

The X-ray diffraction patterns for BZT samples, sintered at three temperature values are given in Fig. 1. The patterns confirm the formation of the hexagonal structure, which is the major phase.

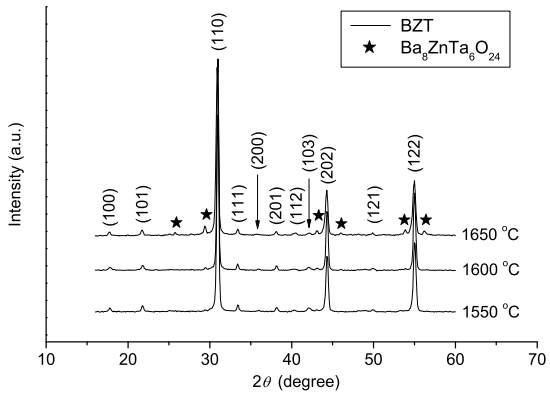


Fig. 1 X-ray diffraction patterns of BZT samples versus sintering temperature.

The long-range order with a 2:1 ratio of Ta and Zn ions on the octahedral positions of the perovskite structure was evidenced as well as the unit cell distortion $c_o / a_o$ higher than 1.224, depending on the sintering temperature. Table 1 presents the main structural parameters as a function of the sintering temperature.

Table 1. Structural parameters and LRO parameter $S$ of BZT samples versus sintering temperature $T_s$.

| Sample | $T_s$ (°C) | Unit cell parameters | | | $S$ |
|---|---|---|---|---|---|
| | | $a_o$ (Å) | $c_o$ (Å) | $c_o / a_o$ | |
| 1 | 1550 | 5.774 | 7.093 | 1.2252 | 0.79 |
| 2 | 1600 | 5.785 | 7.091 | 1.2257 | 0.81 |
| 3 | 1650 | 5.773 | 7.089 | 1.2279 | 0.86 |

The Raman studies were performed at room temperature under 1064 nm excitation wavelength using a FT Raman Bruker RFS 100 spectrophotometer. The 10mW output of a YAG-Nd laser was used as the excitation source. The obtained Raman spectra exhibited a resolution approximately 0.5 $cm^{-1}$. The vibrational modes as function on sintering temperature were investigated by using Raman spectroscopy from 50 to 1200 $cm^{-1}$. Four $A_1g$ and five Eg Raman modes were unambiguously assigned. The obtained Raman spectra for BZT calcined at 1250 °C/2h and for the sample sintered at 1550 °C and 1650 °C are depicted in Fig. 2. It was expected that the calcined powder would have a cubic perovskite

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structure and thus show no Raman lines. However, are no considerable differences in shape intensities and position between calcined and sintered sample for Raman lines corresponding to 1:1 ordering. The 1:2 ordering is not well evidenced for calcined samples. The three weak extralines in the range of 150-300 $cm^{-1}$ are the characteristic feature of the 1:2 ordered perovskite and these can be observed only for the sintered sample.

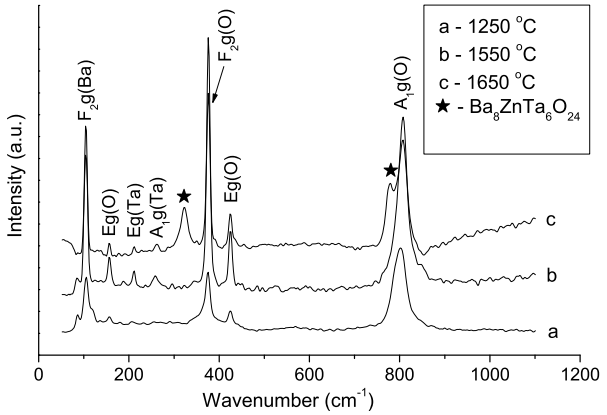


Fig. 2. Raman spectra for BZT sample calcined at 1250 °C (a), sintered at 1550 °C (b) and sintered at 1650 °C (c).

The $A_1g(O)$ phonon of the oxygen-octahedron stretch mode, which posses the largest energy and width of all the observed phonons, significantly influences the microwave dielectric properties of the material. A lower vibration intensity of $A_1g(O)$ oxygen mode results in a higher dielectric constant and a wider width of the mode corresponds to a lower $Q$ value.

The dielectric parameters of BZT samples were investigated by using the Hakki-Coleman method. The parameters of the BZT resonators in the microwave range (Fig. 3) were correlated with structural and Raman investigations. Sintering temperature higher than 1600 °C is required for BZT ceramics in order to obtain low dielectric loss.

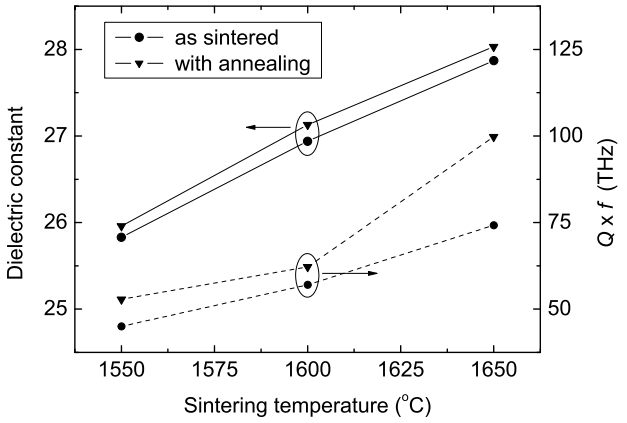


Fig. 3. Dielectric constant and $Q$ x $f$ product versus sintering temperature for BZT resonators.

In order to evaluate the relationship between the ordering, the normal vibration modes and $Q$ x $f$ product the LRO parameter $S$, the FWHM of the $A_1g(O)$ Raman line and microwave dielectric loss were investigated. The calculated data for annealed BZT samples are presented in Table 2.

Table 2. $Q$ x $f$ product, FWHM of the $A_1g(O)$ Raman line and LRO parameter for annealed BZT samples versus sintering temperature $T_s$

| Sample | $T_s$ (°C) | $Q$ x $f$ (THz) | FWHM $A_1g(O)$ ($cm^{-1}$) | S |
|---|---|---|---|---|
| 1 | 1550 | 53 | 25.47 | 0.79 |
| 2 | 1600 | 62 | 24.75 | 0.81 |
| 3 | 1650 | 100 | 24.43 | 0.86 |

There are not shift observed for $A_1g(O)$ Raman lines, only the intensity slowly decreases with the increasing of the sintering temperature. The same behavior presents the three Raman lines Eg(O), Eg(Ta) and $A_1g(Ta)$ corresponding to the 1:2 ordered structure. In the same time, the FWHM for $A_1g(O)$ Raman line decreases with the increase of the sintering temperature.

From XRD and Raman analysis it was concluded that the increase of sintering temperature and annealing treatments improves the cation ordering in BZT ceramics, which leads to higher values of $Q$ x $f$ product. Moreover, the XRD and Raman investigation evidenced the appearance of the Zn-poor secondary phase at the BZT sample surface. $Q$ x $f$ product values monotonically increases with the LRO parameter increase and with the decrease of the FWHM for $A_1g(O)$ Raman line.

Well-sintered and annealed BZT resonators exhibit a dielectric constant around 28, $\tau_f$ in the 3 ÷ 6 ppm/ °C range and a $Q$ x $f$ product up to 100 THz. The achieved high values of the quality factor $Q$ recommend the BZT materials for microwave and terahertz domain applications.

**Acknowledgments**

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