

Dielectric properties of $\text{Bi}_2\text{O}_3\text{-ZnO-Ta}_2\text{O}_5$ ceramics sintered by microwave

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Abstract Here we report dielectric studies carried out on a $\text{Bi}_2\text{Zn}_{2/3}\text{Ta}_{4/3}\text{O}_7$ (abbreviated as β -BZT) composition. The material was synthesized by conventional ceramic method and microwave sintering processing. The dielectric properties were studied as a function of frequency and temperature. Dielectric constant of $\text{Bi}_2\text{Zn}_{2/3}\text{Ta}_{4/3}\text{O}_7$ ceramics prepared from microwave is slightly smaller than that of the conventional sintered ones. The dissipation factor and temperature coefficient of dielectric constant are low for microwave-sintered samples. Microwave sintering of $\text{Bi}_2\text{Zn}_{2/3}\text{Ta}_{4/3}\text{O}_7$ ceramics led to higher densification and the fine microstructure in much shorter time duration compared to conventional procedures, improved microstructure and dielectric properties. To achieve the same densification, it requires 4 h of soaking at the same temperature in conventional sintering process. Microwave sintering method may lead to energy savings because of rapid kinetics of synthesis.

Keywords Microwave sintering · $\text{Bi}_2\text{O}_3\text{-ZnO-Ta}_2\text{O}_5$ · Electronic ceramics · Microwave dielectric properties

1 Introduction

$\text{Bi}_2\text{O}_3\text{-ZnO-Ta}_2\text{O}_5$ systems were studied as candidate materials for microwave dielectric ceramics [1–5]. However, no literature is available on the microwave sintering of $\text{Bi}_2\text{O}_3\text{-ZnO-Ta}_2\text{O}_5$ ceramics. On the basis of cooperative thermic and electrodynamic effects (microwave effect), the

application of microwave energy opens new and effective technological possibilities for materials science. This technique requires less time and temperature to achieve the same quality of materials as sintered by conventional route [6, 7]. In this work the microwave sintering of $\text{Bi}_2\text{Zn}_{2/3}\text{Ta}_{4/3}\text{O}_7$ (abbreviated as β -BZT) ceramics is examined. The main interest was directed to comparative studies of microwave and conventional sintered bodies with respect to their microstructure development and microwave dielectric properties. In this paper, we report dielectric studies of $\text{Bi}_2\text{Zn}_{2/3}\text{Ta}_{4/3}\text{O}_7$ composition sintered by conventional and microwave methods. The structure of microwave sintered (MS β -BZT), its sinter ability and microstructure, have been compared with those of β -BZT prepared by conventional method (CS β -BZT).

2 Experimental procedure

The material powder with compositional formula $\text{Bi}_2\text{Zn}_{2/3}\text{Ta}_{4/3}\text{O}_7$ was synthesized by conventional ceramic method using high purity (99% above) Bi_2O_3 , ZnO and Ta_2O_5 . Initially, ZnTa_2O_6 was prepared through mixing, drying and calcinations at 1000 °C. Then, appropriate amounts of Bi_2O_3 were added and mixed with ZnTa_2O_6 . The powder mixture was ball milled using zirconia balls and distilled water as wetting agent. The dried powders were compacted and calcined at 800 °C for 4 h. The reacted compacts were granulated and milled for 24 h. The milled powders were then pressed into disks and cylinders under a uniaxial pressure of 8 MPa. The diameter of both is 12 mm, thickness is about 1.2 and 6.2 mm respectively. All samples were experienced cold isostatic pressing process at a pressure of 230 MPa. Cold isostatic process gives homogeneous and better compaction of green cylinders. One set of cylinders and disks was sintered at 1050 °C for 4 h in a conventional

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muffle furnace. The heating rate of conventional sintering method was maintained at 2.5 °C/min. Another set of compacted cylinders and disks was sintered using a custom-made 2.45 GHz furnace (multimode microwave applicator, model MFM-863I, Institute of Metal Research Chinese Academy of Sciences). The performed microwave sinters were based on the heat developed by its interaction with 2.45 GHz electromagnetic waves. For all microwave synthesis procedures present, the heating rate was kept in the range of 15 °C/min by controlling the input power to microwave oven. Microwave synthesis of β -BZT composition is achieved in 3 h. By contrast, it takes 35 h to synthesis β -BZT of the same composition in conventional sintering method. Presence of large microwave fields at interparticle junctions and in cavities leads to ponderomotive forces which bring about rapid sintering in microwaves.

Density and microstructure information were obtained on microwave and convention processed samples by Archimedes principle and SEM (scanning electron microscope, JSM-5510 LV), respectively. X-ray diffraction patterns of the compounds were obtained using a Bruker D8 X-ray diffractometer. To measure low frequency electrical characterization, both faces of the sintered disks were well polished, then coated with silver paste and followed by annealing at 520 °C. For microwave dielectric properties measuring, polished cylinders of 6 mm in thickness were obtained carefully. Measurements of dielectric properties were performed on the measurement system composed of a HP4284A LCR meter, a temperature chamber and a computer, as a function of frequency (1,000 Hz~1 MHz) and temperature (−50–160 °C). Heating rate was maintained at 2.5 °C/min and data were recorded automatically. Microwave dielectric characteristics of the samples were measured by the post resonant method [8]. A HP8753E network analyzer was used for the microwave measurement. The dielectric properties were calculated from the frequency of the TE₀₁₁ resonant mode.

3 Results and discussion

Samples prepared by conventional sintering (CS) and microwave sintering (MS) were subjected to XRD analysis in order to determine phase structure. XRD patterns of β -BZT prepared by conventional and microwave methods are presented together in Fig. 1 for 2θ values between 20 and 70°. The XRD of CS and MS samples are also in excellent agreement between themselves. All the samples reveal a single-phase formation with a monoclinic zirconolite-like structure [2].

In Fig. 2 SEM micrographs of both CS and MS samples are presented. The grain size is significantly smaller in cases of MS processed samples and when the sample is

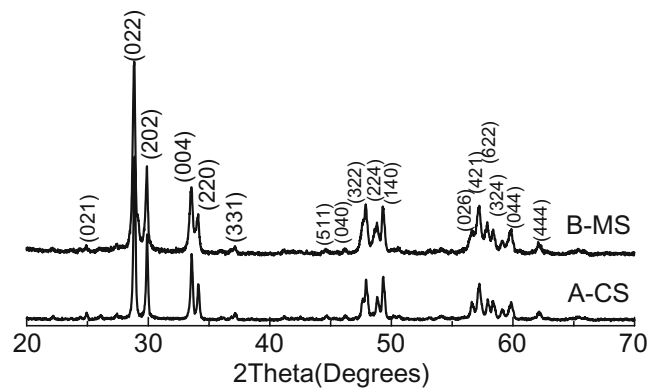


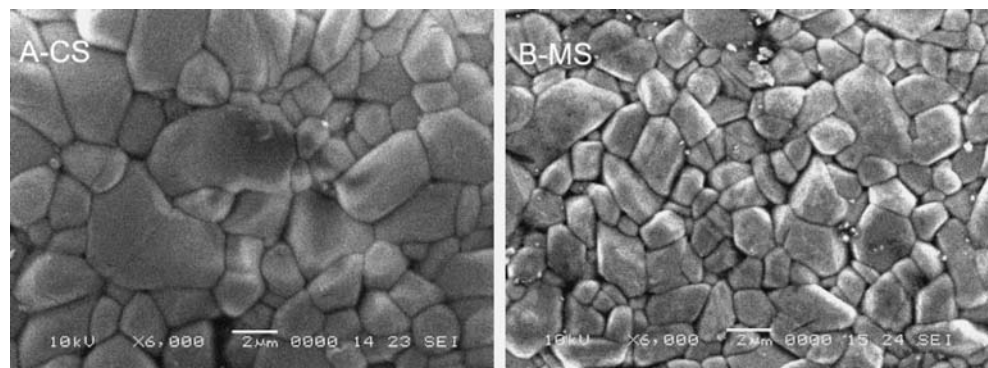
Fig. 1 XRD patterns of samples prepared by (A) conventional sintering and (B) microwave sintering

denser than the conventional one. The rapidity of microwave sintering method avoids undesirable grain growth and provides a relatively fine and uniform microstructure, which is an attractive feature for the processing of electroceramics [9]. That the microwave-sintered samples possess pronouncedly smaller grains than the conventionally sintered ones has also been observed in other materials system [9, 10]. The results imply that the microwave sintering process can preferentially improve the densification process without inducing the grain growth, resulting in a fine grain microstructure. The probable explanation for this phenomenon is that the densification results by the interdiffusion between the vacancies and the adjacent cations or anions. Such a process is markedly enhanced in the presence of the microwave, since the vacancy-cation (or vacancy-anion) pairs are polar in nature. The presence of microwave does not result in a change of polarity when the ions jump from one-site to another of the grain boundaries in the grain growth process [10].

Temperature dependence of dielectric constant (α_ϵ) and dissipation factor ($\tan\delta$) for CS and MS β -BZT samples is shown in Fig. 3 respectively. The densification level and the value of the dielectric properties of conventional sintering and microwave sintering samples are given in Table 1. The observed densities of 8.75 g/cm³ of the MS and 8.71 g/cm³ of the CS samples, it is evident that slightly better sintering is achieved in microwaves than in the conventional method. Dielectric properties obtainable are similar or superiority to those achieved in conventional sintering after much longer heating cycles.

The dielectric constant (ϵ) of the MS is slightly smaller than that of the CS samples both in low frequency regime (1 kHz to 1 MHz) and high frequency regime (a few thousands of more megahertz). Lower dielectric constant can arise from various factors such as weak ions polarization when field is applied, lower density and higher porosity. The previous one appears to be more suitable for here. The microwave magnetic field effect on volume of lattice in the case of microwave sintering process and

Fig. 2 The surface morphology of samples prepared by (A) conventional sintering and (B) microwave sintering



sublattice disordering has been well established in other materials [7, 11]. The results reported in this paper indicate that at least the charged cations interact to a limited extent to create a finite, nonzero distortion locally, which can significantly alter the dielectric properties [12]. Our preliminary dielectric measurements indicate that the high frequency at 5.5 GHz Q value ($1/\tan\delta$) of the microwave-sintered (1050 °C, 30 min) β -BZT ceramic is higher than the conventionally sintered (1050 °C, 240 min) β -BZT

sample. These results imply clearly that the ϵ is relatively sensitive to the microstructure of the samples, the proportion of grain boundaries contained in the materials. The Q value is quite microstructurally and densely dependent.

In addition, the conventional processing of bismuth-based ceramics also suffers from the problems of Bi_2O_3 loss at high reaction temperatures and long synthesis time [13, 14], which can often lead to products with degraded properties. Prolonged heating at high temperatures is partly disadvantageous as it involves volatilization of some constituents and results in a nonstoichiometric product. Two-phase mixture of α -BZT pyrochlore and β -BZT zirconolyte composites could be induced for nonstoichiometric Bi_2O_3 -ZnO-Ta₂O₅ product. Relaxation behavior was observed for the pyrochlore/zirconolyte composite, although β -BZT is a nominally pure single phase examined by X-ray diffraction, it may include a small amount of α -BZT phase, which leads to the appearance of a slight dielectric relaxation. The relaxation behavior of the pyrochlore structure is responsible for enhanced dielectric loss at microwave frequencies [2].

According to the classical dispersion theory, microwave dielectric loss is mainly caused by Lorentz damping factor [15]. Presence of microwave fields that densify the samples would probability decrease the Lorentz damping factor and then results in a higher $Q \times f$ value in β -BZT material is proposed. In the case of the microwave procedure, however, an

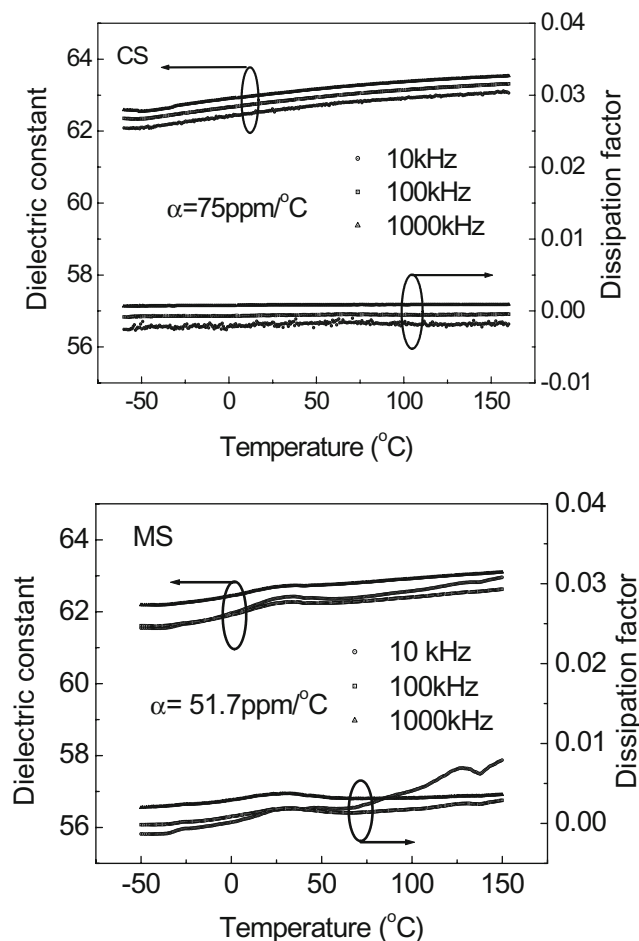


Fig. 3 Temperature dependence of dielectric constant and dissipation factor for CS and MS β -BZT

Table 1 Characteristics of CS and MS β -BZT samples.

Properties	Conventional sintering	Microwave sintering
Sintering temperature/time (°C/min)	1050/240	1050/30
Bulk density (g/cm ³)	8.71	8.75
ϵ (20 °C, 1 MHz)	63.1	62.0
$\tan\delta$ ($\times 10^{-4}$, 20 °C, 1 MHz)	2.72	2.2
α_ϵ (ppm/°C, 1 MHz)	75.0	51.7
ϵ (20 °C, 5.5 GHz)	61.5	60.0
$\tan\delta$ ($\times 10^{-4}$, 20 °C, 5.5 GHz)	8.3	6.81
Q value (20 °C, 5.5 GHz)	1205	1468

electromagnetic field effect exists in addition to the usual heat transfer effects. A good combination of dielectric constant, $Q \times f$ value and α_ε is observed for microwave sintering at 1050 °C: $\varepsilon \sim 60$, $Q \times f \sim 8,074$ GHz, $\alpha_\varepsilon \sim 51.7$ ppm/°C. Finally, bringing together all the different explanations mentioned above, it is concluded that the higher $Q \times f$ value is associated with higher density, lower Bi₂O₃ loss (stoichiometric) and decrease in the Lorentz damping factor.

Conventional sintering methods overcure the surface while undercuring the interior of samples. Moreover, the unique internal heating phenomenon associated with microwave energy can lead to samples and processes that cannot be achieved using conventional sintering methods. Smaller grain sizes and more uniform microstructure are developed due to volumetric heating and rapid sintering in microwave processing [16]. It is believed that the above features are germane to microwave reactions because of the coupling of ionic motions (through their charge) with the local electric fields of penetrating microwaves. Such interactions give rise to ponderomotive forces, which in turn are responsible for the observed features of microwave reactions [17]. Anyway, lower sintering temperatures; shorter process time and improved material properties may result from effects created by the electro-magnetic field of microwaves.

4 Conclusions

Fast sintering of β -BZT sample is feasible by direct microwave sintering, starting from room temperature, in multimode applicators at 2.45 GHz. The use of microwave energy resulted in the formation of single-phase β -BZT with monoclinic zirconolite-like structure in just 30 min. Microwave sintered samples show improvement in Q value. Microwave sintering of β -BZT leads to higher densification and fine microstructure in much shorter time duration

compared to conventional procedures. Fine microstructure and better densification are the main advantages of the microwave sintering in this study. The microwave method is found to be simple, fast and quite general for the preparation of technologically important electroceramics.

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