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Processing of $Bi_{1.5}ZnNb_{1.5}O_7$ ceramics for LTCC applications: Comparison of synthesis and sintering methods

S.A. da Silva [a], S.M. Zanetti [b,*]

[a] *Departamento de Química, Instituto Tecnológico de Aeronáutica, Praça Marechal Eduardo Gomes, 50, Vila das Acácias, 12228-900 São José dos Campos - SP, Brazil*

[b] *Laboratório Associado de Sensores e Materiais, Instituto Nacional de Pesquisas Espaciais, Av. dos Astronautas, 1758, Jardim da Granja, 12227-010 São José dos Campos - SP, Brazil*

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Abstract

Bismuth zinc niobate posses a cubic pyrochlore structure and normally is obtained by the conventional solid-state reaction. The great disadvantage of this method is the lack of chemical homogeneity, requiring high synthesis and sintering temperatures (higher than 1000 °C), which is an impeditive for BZN application in LTCC with silver as the internal electrode. The aim of this paper is to compare, from synthesis to sintering, BZN ceramics, derived either from chemically or conventionally synthesized powders, sintered either in both conventional oven for 2 h or microwave oven for 15 min. The results showed that chemically synthesized BZN ceramics sintered in microwave oven at 900 °C for 15 min presented a relative density of 97%, while those obtained by conventional method required 1000 °C to reach the same density. Despite the short period for thermal treatment in microwave oven, the electrical properties of BZN ceramics are compatible with those sintered in conventional oven for 2 h.

Keywords: A. Powders: chemical preparation; C. Dielectric properties; D. Niobates

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1. Introduction

Recent literature presents several publications on Bi–Zn–Nb ternary system, which show the great interest attracted by Bi_2O_3–ZnO–Nb_2O_5 (BZN) compounds, mainly for applications in electronic devices. The driven force for part of those publications is the understanding of their electrical properties depending on the occupancy of metallic cations in sites A and B [1–4]. The other matter of concern is reducing the sintering temperature of those compounds aiming to make them suitable for LTCC using silver as internal electrode [5–8].

Normally some additives are incorporated to the material to reach lower sintering temperatures. Among them, vanadium oxide, copper oxide, boron and silver have been extensively used. These additives promote the formation of a liquid phase which leads to BZN ceramics be sintered at temperatures around 900 °C. Nonetheless, these compounds may react with silver altering the BZN electrical properties, which is deleterious to the devices [7–10].

Alternatively, chemically [11,12] or high energy milling [13,14] synthesized compounds can lead to a more homogeneous powder with small particle sizes, which contributes to diminish the temperature of phase crystallization and that required to sinter their ceramics. Another approach is to use non-conventional techniques for sintering, such as by laser beam [15,16] or microwave energy [17,18].

The aim of this work is to investigate comparatively, from synthesis to sintering, the process conditions for obtaining $Bi_{1.5}ZnNb_{1.5}O_7$ (α-BZN) ceramics. Therefore, α-BZN powders were synthesized by both solid-state reaction and polymeric precursor methods, and their ceramics were sintered either in conventional oven or in microwave oven. The results derived from synthesis and sintering methods were compared with respect to the structural, microstructural and electrical properties.

2. Experimental procedure

Nanoparticulate α-BZN powder was obtained by the polymeric precursor method using urea as pH stabilizing agent, as well as an inductor for organics elimination at low temperatures, whose detailed procedure was published

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* Corresponding author. Tel./fax: +55 16 3361 9233.
E-mail address: zanettism@gmail.com (S.M. Zanetti).

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elsewhere [19]. The sample obtained by this method was dubbed U2. For comparison sake, α-BZN powder was also prepared by the conventional oxide mixture, followed by milling in isopropyl alcohol medium for 6 h, drying and sieving. The obtained powder was heat-treated at 900 °C for 2 h. The sample obtained by oxide mixture was dubbed OM.

To diminish the quantity of agglomerates and aggregates, both powders were milled in isopropyl alcohol for 3 h. The powder's crystalline phases were determined by X-ray diffraction (XRD; PHILIPS PW1380) with Cu Kα radiation. The surface area was measured based on the N_2 adsorption/desorption curves, using the BET method (BET; MICROMETRICS 2000). The particle size was calculated from the values of surface area, by the equation:

$$D_{BET} = \frac{6}{\rho S_{BET}},$$

where D_{BET} is the mean particle size, S_{BET} the surface area and ρ the theoretical α-BZN density (7.12 g cm^{-3}).

The powders were compacted into discs (8 mm diameter and 3 mm thick) followed by sintering at specific conditions which are displayed in Table 1.

For the microwave sintering, the samples were heat-treated at 900 and 1000 °C for 15 min using a simple domestic microwave oven (2.45 GHz, 900 W) by means of a pair of SiC susceptors (positioned bellow and above the pellet) in order to absorb the microwave energy and rapidly transfer the heat to the sample. A 50 °C/min heating rate was applied, using an automatic temperature controller. The temperature was measure by a grounded K-type thermocouple which is in contact with the bottom SiC susceptor. Fig. 1 depicts a schematic representation of the sample holder system.

After sintering, the samples apparent relative density was measured by the Archimedes method. The pellets microstructure was examined by scanning electron microscopy (SEM; JEOL 6400) and their electrical properties were evaluated by impedance spectroscopy (HP 4192).

3. Results

XRD results for powders U2 and OM are displayed in Fig. 2. It can be observed that the α-BZN is the only crystalline phase detected for both samples. The crystallization occurs at 700 °C for sample U2 and at 900 °C for sample OM. The lower crystallization temperature observed for sample U2 can be attributed mainly to the atomic scale homogeneity reached when the polymeric precursor method is employed [20–23].

Table 1
Parameters used for thermal treatment of U2 and OM samples.

Sample	Oven	Temperature (°C)	Rate (°C min^{-1})	Soaking time (min)
U2	CF	900	10	120
U2	MW	900	50	15
OM	CF	1000	10	120
OM	MW	1000	50	15

CF, conventional furnace; MW, microwave oven.

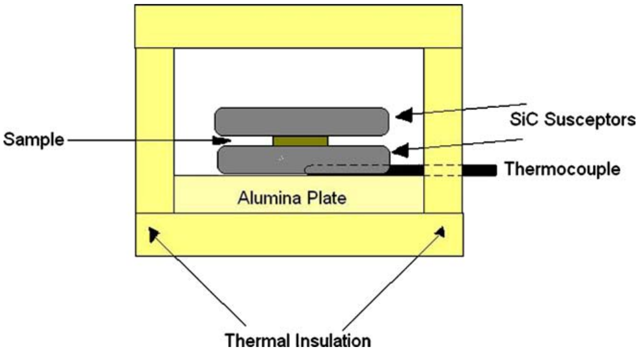

Fig. 1. Schematic arrangement for the sample sintering inside the microwave oven.

The progressions of relative apparent density as a function of the temperature for the sample U2, sintered in conventional furnace (CF) or in microwave oven (MW), are displayed in Fig. 3. One can observe that the samples sintered in microwave oven present higher apparent density values than those sintered in conventional furnace at temperatures between 850 and 950 °C. Probably the mass transport mechanisms involved in the solid-state sintering process are favored by the high heating rate reached in the microwave oven [17]. The samples sintered at 900 °C presented the highest relative density values, 97% for U2-MW and 95% for U2-CF. Between 950 and 1000 °C a decrease in the relative apparent density occurs due to the expansion of the trapped gas in isolated pores. These isolated pores are generated by the aggregates and agglomerates present in the precursor powder, which were not destroyed by the milling.

Fig. 4 displays the apparent relative density results as a function of temperature for ceramics prepared by the conventional oxide mixture (OM) sintered either in conventional furnace or in microwave oven. It can be observed that the samples sintered in conventional furnace presented higher relative density values at 900 and 950 °C. This result can be attributed to the bigger mean particle size of the powder, as well as to the mass transport mechanisms involved in the sintering process, which is not enhanced by the higher heating rate

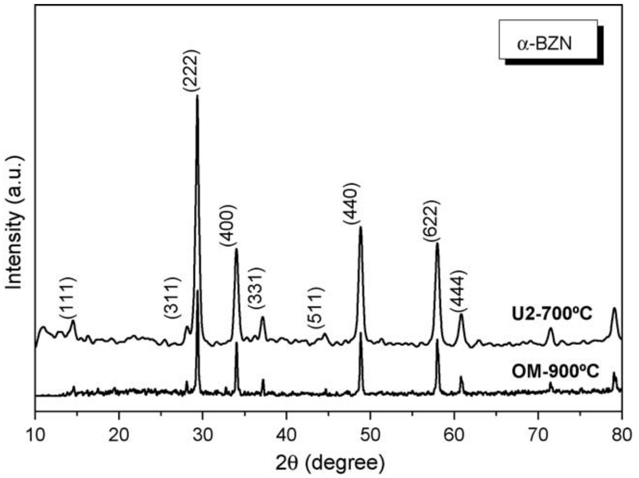

Fig. 2. X-ray patterns of U2 and OM powders heat-treated at 700 and 900 °C, respectively.

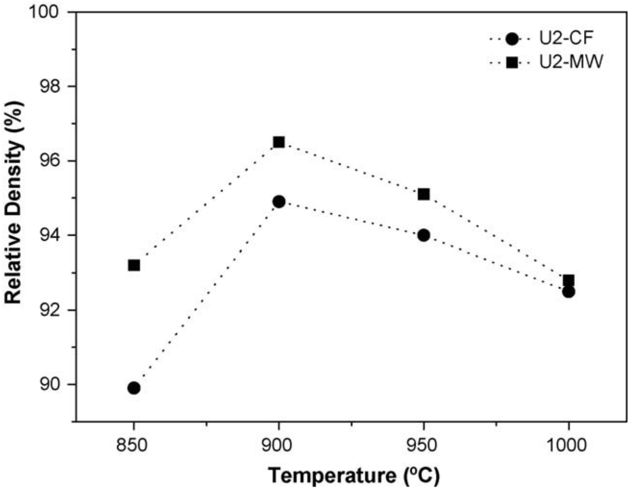

Fig. 3. Relative apparent density as a function of temperature for samples U2 heat-treated: (a) in conventional furnace (CF) for 120 min at a heating rate of 10 °C min^{-1}; (b) in microwave oven (MW) for 15 min at a heating rate of 50 °C min^{-1}.

reached in microwave oven. In this case, the sintering process is more effective in isotherms, which are longer (2 h soaking) in conventional furnace treatments.

At 1000 °C, both sintering treatment, 15 min in microwave oven or 2 h in conventional furnace, lead to the same relative density value (99%). Probably, at this temperature only 15 min at microwave oven was enough to develop the liquid phase responsible for the ceramics densification. Moreover, the treatment at 1050 °C promotes a volumetric expansion of sample, consequently decreasing the relative density, as already observed for sample U2.

From these results, one can infer that sintering treatment in microwave oven is advantageous in terms of energy savings, since 15 min at the sintering temperature is enough to reach the same apparent relative density as that reached in conventional oven after 2 h treatment. Moreover, the high heating rates reached in microwave oven are very interesting for sintering nanoparticles, which in the involved mass transport mechanisms are more effective.

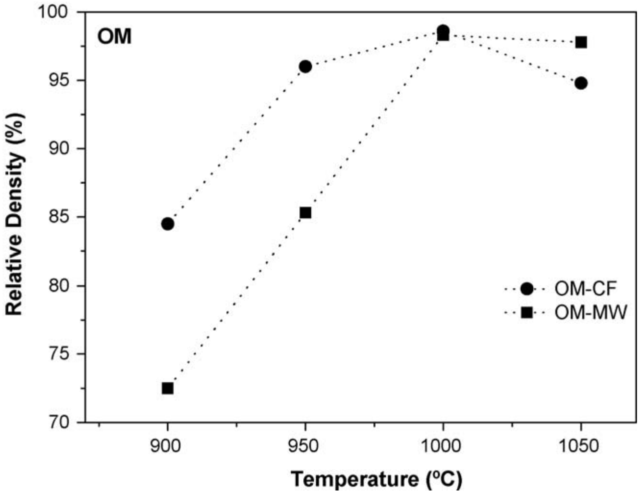

Fig. 4. Apparent relative density as a function of temperature for samples OM heat-treated: (a) in conventional furnace (CF) for 120 min at a heating rate of 10 °C min^{-1}; (b) in microwave oven (MW) for 15 min at a heating rate of 50 °C min^{-1}.

Samples U2 sintered at 900 °C in conventional furnace or microwave oven were examined by SEM, and the images are displayed in Fig. 5. The SEM images show that both samples presented a similar grain structure with isolated spherical micrometric pores located mainly at the grain contact points. The pressure generated by the trapped gas in these pores promotes the volumetric expansion of the samples, as verified before in the apparent density results (Fig. 3).

Fig. 6 shows the SEM images for samples OM sintered at 1000 °C in conventional furnace or microwave oven. Both samples presented less pores of different shapes than those observed for sample U2. Sample OM-CF presents either intergranular pores, in the grain contact points, or intragranular pores, inside the grains. The formation of intragranular pores occurs preferably in the grain growth step due to the coalescence of small grains. It is also possible to observe that the microstructure of OM-MW sample is more homogeneous concerning to the grain size distribution because the grain growth is considerably inhibited by the treatment in microwave oven. The mean size grain for sample OM-MW is significantly smaller than that observed for sample OM-CF.

The mean grain sizes determined by the intercept method [24] for samples U2-CF and U2-MW, sintered at 900 °C, and OM-CF and OM-MW, sintered at 1000 °C, are presented in Table 2. It is possible to verify no significant differences in the mean grain size for samples U2-MW and U2-CF, around 3.7 and 4.2 μm, respectively. This result can be attributed to high reactivity of U2 powder which maximizes the thermal effects promoted by the high heating rates reached in microwave oven, as it has been already verified in the relative density results.

For sample OM-CF the mean grain size is almost twice the observed for sample OM-MW, 10 and 4.8 μm, respectively. For this sample it has been observed that the grain growth is considerably inhibited in the microwave oven, which can be attributed to two main factors: (i) the high heating rate reached in the microwave oven, which maximizes the mass transport mechanisms involved in pore elimination; (ii) the shorter soaking time, which makes the grain growth more difficult [25].

Electrical measurements by impedance spectroscopy were performed at temperatures ranging from 25 to 300 °C. Table 2 also displays the electrical permittivity values (ε) and the temperature coefficient of capacitance (TCC) between 50 and 250 °C obtained by impedance spectroscopy at 1 MHz frequency. The results reveal that, for samples U2, the treatment in microwave oven do not alter their microstructure or their electrical properties. The ε value was about 150 independently of the sintering method. On the other hand, for samples OM, the thermal treatment highly alters the microstructure, which can considerably influence the electrical properties. For the sample sintered in conventional furnace, ε value was 164, and for the sample sintered in microwave oven ε was reduced to 155, which value is similar to those obtained by chemical method. One can also observe that permittivity and

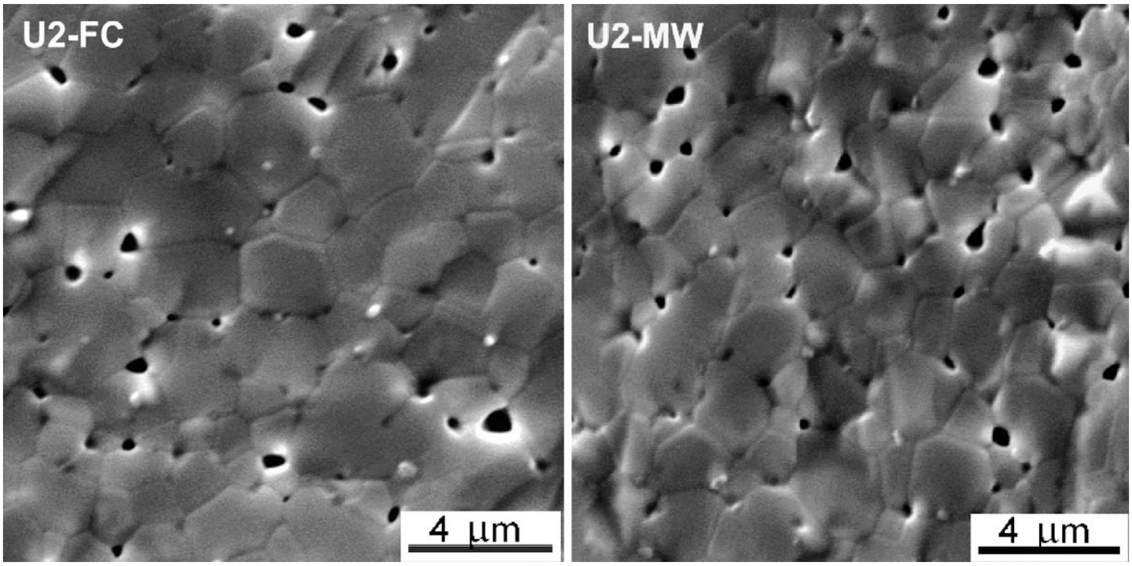

Fig. 5. SEM images for samples U2, sintered at 900 °C in conventional furnace (CF), and in microwave oven (MW).

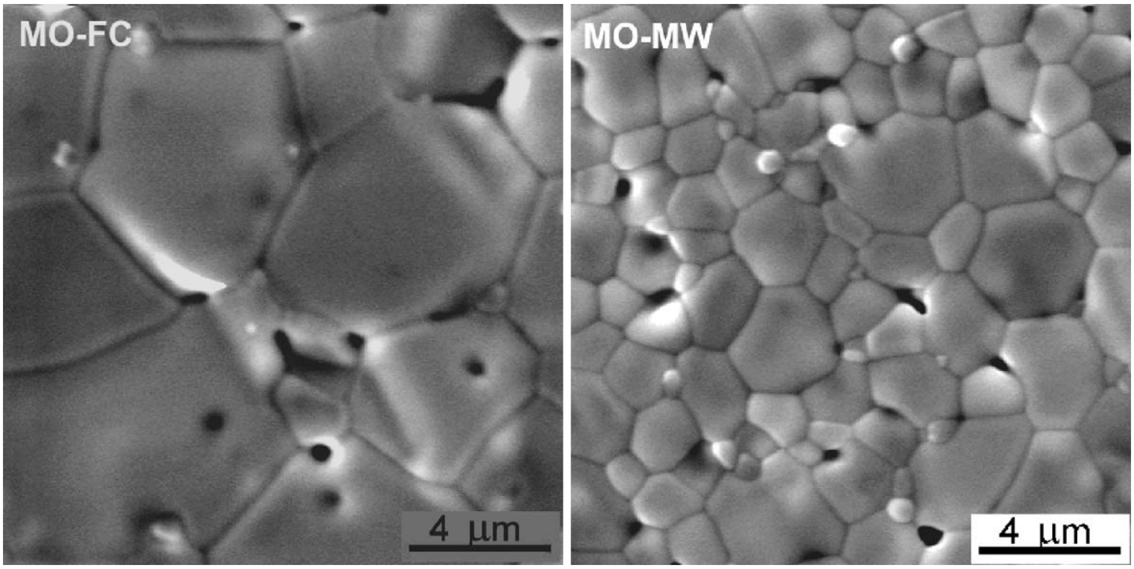

Fig. 6. SEM images for samples OM, sintered at 1000 °C in conventional furnace (CF) and microwave oven (MW).

mean grain size have good relation irrelevant to sample density. Samples with smaller mean grain size presented lower permittivity which is consistent to the fact that the grain boundaries act as defects and may contribute significantly into extrinsic dielectric loss. The total number of the grain boundaries decreases with increase of the average grain size. In other words, the thermal treatment in microwave oven greatly influences the microstructure of OM samples reducing their ε values. The temperature coefficient of capacitance (TCC) for the different samples showed in Table 2 is in agreement with the literature for α-BZN, approximately -400 ppm °C^{-1} [2].

Table 2
Apparent density, mean grain size, electrical permittivity, and temperature coefficient of capacitance (TCC) values for samples U2 and OM, sintered in conventional furnace and microwave oven.

Sample	Apparent density (%)	Mean grain size (µm)	ε (25 °C; 1 MHz)	TCC (ppm °C^{-1})
U2-CF-900	95	4.2 ± 0.2	153	-367
U2-MW-900	97	3.7 ± 0.4	147	-377
OM-CF-1000	99	10 ± 1	164	-427
OM-MW-1000	99	4.8 ± 0.5	155	-390

4. Conclusions

These results allow concluding that the synthesis by chemical method leads to BZN phase crystallization at 700 °C, while for the conventional oxide mixture method it occurs at 900 °C. Chemically synthesized ceramics sintered at 900 °C reached apparent density values of 97% regardless the sintering method used. Probably, this process allows employing BZN ceramics as LTCC using silver as internal electrode. The microwave thermal treatment greatly influences the microstructure of the conventional oxide mixture ceramics by diminishing their mean grain size; consequently, it influences their electrical properties. The microwave thermal treatment does not alter the electrical properties of the chemically synthesized ceramics. Additionally, it allows controlling the grain growth due to the high heating rates and short soaking times employed. For chemically synthesized α-BZN ceramics the microwave thermal treatment is also cost-effective in terms of energy savings, forasmuch a soaking time of 15 min at the sintering temperature is enough to reach the same relative density obtained for ceramics sintered during 120 min in conventional furnace.

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