

SYNTHESIS AND PROPERTIES OF BISMUTH ZINC NIOBATE PYROCHLORE POWDERS PREPARED BY CHEMICAL METHOD

S. M. Zanetti*, G. P. Thim

Departamento de Química, Instituto Tecnológico de Aeronáutica, Centro Técnico Aeroespacial, Pça. Marechal Eduardo Gomes, 50, Vila das Acácias, 12228-900, São José dos Campos - SP, Brazil

Bismuth zinc niobate pyrochlores $\text{Bi}_{1.5}\text{Zn}_{0.5}(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$ - α -BZN, and $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$ - β -BZN were synthesized by chemical method based on the polymeric precursors. The pyrochlore phase was investigated by DSC, FT-IR and X-ray diffraction (XRD). The morphology of the powders and sintered pellets was examined by scanning electron microscopy (SEM). The phase formation study for α -BZN reveals that at 500 °C the pyrochlore phase is already present and a single-phased nanopowder is obtained after calcination at 700 °C, and no intermediary phase (reported for solid state reaction) was observed. For β -BZN it was found some secondary phases due to the lack of stoichiometry in the obtained powder. The pellets, sintered at 950 °C for 2 h presented a relative density of almost 90 % for both compositions.

Key Words: Synthesis, Bi_2O_3 -ZnO- Nb_2O_5 , pyrochlore, nanopowders, polymeric precursor.

I- INTRODUCTION

The general formula of stoichiometric pyrochlores is $\text{A}_2\text{B}_2\text{O}_7$. The structure is composed by two different types of cation coordination polyhedra where the A-site positions, eight coordinate, are typically occupied by larger cations, while the B-site positions, six coordinate, are occupied by smaller sized cations.¹ The structural formula is often written as $\text{B}_2\text{O}_6 \cdot \text{A}_2\text{O}'$, which emphasizes that the arrangement consists of a three dimensional network of octahedra (B_2O_6) linked with the $\text{A}_2\text{O}'$ tetrahedra in the interstices.

Pyrochlore and pyrochlore-related oxide system Bi_2O_3 -ZnO- Nb_2O_5 (BZN) has received special attention in last years due to its high dielectric constants (ϵ), low dielectric losses, and compositionally tunable temperature coefficients of the capacitance (TCC). These properties, allied to the low sintering temperatures (less than 950 °C), make these compounds attractive candidates for capacitor and high-frequency multilayer structures co-fired with metal electrodes.²

Two basic phases of the BZN system, the cubic-pyrochlore-structure with composition $\text{Bi}_{1.5}\text{Zn}_{0.5}(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$ (α -phase), and the low-symmetry-structure with composition $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$ (β -phase) have been most studied. Their electrical properties are quite different for each phase (TCC is

about $-400 \text{ ppm}/^{\circ}\text{C}$ for the α -phase and $-200 \text{ ppm}/^{\circ}\text{C}$ for the β -phase), what is attractive for manufacturing of controllable temperature coefficient of capacitance devices.³

BZN-based dielectrics ceramics have been systematically prepared by the solid state reaction, which is known to yield large sized particles and local chemical heterogeneity. Commonly this route leads to multiphase powders.⁴⁻⁷

Alternatively chemical methods have been employed to achieve smaller sized particles with chemical homogeneity. Nanocrystalline materials obtained by the solution-based chemical methods are normally chemically homogeneous, with a narrow size distribution of particles and lead to low crystallization and sintering temperatures.

The aim of this work was to achieve chemically homogeneous BZN nanopowders (α and β phases), for that the polymeric precursor method was employed. The polymeric precursor method is a chemical method based on the Pechini process⁸, and has been successfully used for the synthesis of several complex oxides.⁹⁻¹¹

II- EXPERIMENTAL

Firstly, niobium ammonium oxalate ($\text{NH}_4\text{H}_2[\text{NbO}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$, 99.5 %, CBMM - Araxá, Brazil) was dissolved in water and $\text{Nb}(\text{OH})_5$ was precipitated by addition of NH_4OH . After filtration, niobium hydroxide was dissolved in an aqueous solution of citric acid to form niobium citrate. The content of Nb was gravimetrically determined as Nb_2O_5 . To the niobium citrate solution, heated at $60 \text{ }^{\circ}\text{C}$, were added stoichiometric (for α and β phases) amounts of zinc acetate dihydrate ($\text{C}_4\text{H}_6\text{O}_4\text{Zn}\cdot 2\text{H}_2\text{O}$, 99.5%, Carlo Erba) as salt and Bi_2O_3 (99.99 %, Aldrich) dissolved in water with HNO_3 to form a (Zn, Nb, Bi) complex precursor. In this synthesis the citric acid/metal ratio (CA/Me, molar ratio) was 3. The solution was kept under stirring at $60 \text{ }^{\circ}\text{C}$ and the pH was adjusted at 8-9 with ethylenediamine. To this solution was added ethylene glycol to promote polymerization of the mixed citrate, and the citric acid/ethylene glycol ratio (CA/EG, mass ratio) was 60/40. The resin was kept on a hot plate until a viscous gel was obtained and subsequently suffered a thermal treatment at 300°C for 4 h in a furnace. The obtained powders were treated at temperatures from 400 to $900 \text{ }^{\circ}\text{C}$ for 2 h to follow the crystallization process.

The thermal decomposition of BZN precursors was studied using a differential scanning calorimetry (TG/DSC) (NETZSCH, STA404), at a heating rate of $10 \text{ }^{\circ}\text{C}/\text{min}$, under air flux. The crystalline phases were determined by X-ray diffraction (DRX) using an INEL curved position-sensitive detector, operating with the $\text{CuK}\alpha$ radiation. The Fourier transformed infrared (FTIR) spectra in the

range 400-4000 cm^{-1} were recorded on NICOLET-MAGMA 760 spectrometer in the transmission mode (KBr method) with a resolution of 4 cm^{-1} . Raman spectra in the range 100-1000 nm were collected on a BRUKER spectrometer (FRA-106/S), using the 1064-nm excitation line of Nd-YAG Laser. The data were collected keeping the power at 60 mW, 100 scans and 4 cm^{-1} resolution. Scanning electron microscopy (SEM) JEOL 6400 was used to observe the morphology of the powders treated at different temperatures. The chemical composition was determined by ICP and EDX.

The powders treated at 700 °C were pressed into pellets 12 mm in diameter and 2.0 mm in the thickness. Discs were sintered in air at 950 °C for 2 h. and the volumetric density was determined.

III- RESULTS AND DISCUSSIONS

After thermal treatment of the resin at 300 °C for 4 h, a soft black powder was obtained. Portions of this black powder were heat treated for 2 h at temperatures from 400 to 900 °C.

The Zn and Nb content were determined by inductive coupled plasma (ICP) while the Bi content was obtained EDX. The results are summarized in Table I, which represent the mean value of three determinations for powder samples treated at 700 °C for 2 h.

Table I – Chemical composition of BZN compositions for powders treated at 700 °C for 2 h.

Element	α -BZN		β -BZN	
	Calculate (% mass)	Determined (% mass)	Calculate (% mass)	Determined (% mass)
Zn (ICP)	10.4	11.3 ± 0.4	6.2	7.8 ± 0.6
Nb (ICP)	22.1	24.1 ± 0.8	17.8	15.8 ± 0.6
Bi (EDX)	49.8	49.3 ± 0.6	59.9	57.9 ± 0.6

It can be observed that for α -BZN composition, the results show a light excess in Zn and Nb, while a good agreement for Bi was achieved. On the other hand, for the β -BZN composition, the results show high deficiency in Nb and Bi, and excess of Zn.

Fig. 1 shows the TG-DSC curves of the BZN powders previously treated at 400 °C for 2 h. The DSC result reveals exothermic peaks centered at 500 °C and 538 °C for α -BZN and β -BZN, respectively, which correspond to the elimination of the organic material. Due to the high content of organic material still present (weight loss higher than 65%, not shown here), it is not possible to observe

the crystallization of the pyrochlore phases, except for a small peak centered at 585 °C, for the α -BZN composition, which may correspond to the crystallization of the cubic phase.

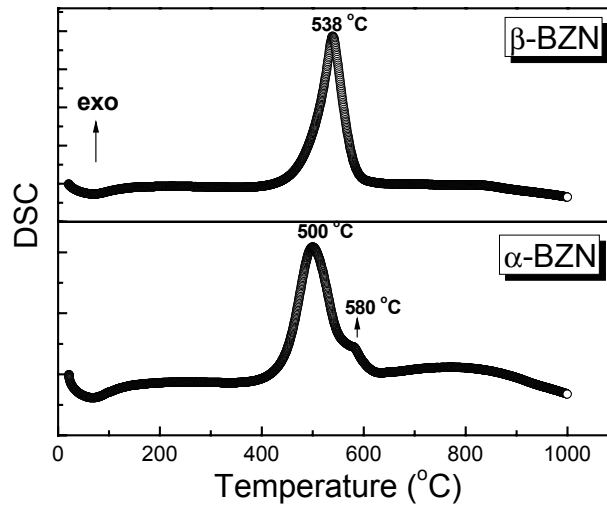


Fig. 1- Thermal analysis of the BZN powders treated at 400 °C for 4 h.

The crystalline phase evolution process for the α -BZN pyrochlore was followed by XRD, as shown in Fig. 2. At 400 °C it was observed the presence of Bi_2O_3 phase (JCPDS 27-0050). At 500 °C the pyrochlore phase is already formed and coexists with Bi_2O_3 reminiscent; at 600 °C the pyrochlore peaks are some broad indicating small and disordered crystallites. As expected, increasing the annealing temperature to 700 °C, leads to an increase in the crystallinity degree of the samples.

Similar studies for BZN prepared by solid state reaction report that the pyrochlore phase crystallizes through the formation of an intermediary BiNbO_4 phase. Bi and Nb cations react to form the BiNbO_4 compound at low temperatures, and the pyrochlore phase formation occurs through the reaction of BiNbO_4 and ZnO .^{4,6}

In this study no detectable intermediary phases as BiNbO_4 or $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ nor pseudo-orthorhombic pyrochlore phase were ever observed in α -BZN composition, indicating that the chemical synthesis conferred a higher chemical homogeneity and reactivity to the powder, modifying the crystallization route of the pyrochlore phase

On the contrary, for the β -BZN composition, it was also observed the Bi_2O_3 phase at 400 °C but different secondary phases appear as the temperature increased. For the powder treated at 700 °C an unknown phase still remains, as showed in Fig. 3. For the pellet treated at 950 °C for 2 h the pyrochlore phase is the major phase, although the traces of the secondary phase can be observed.

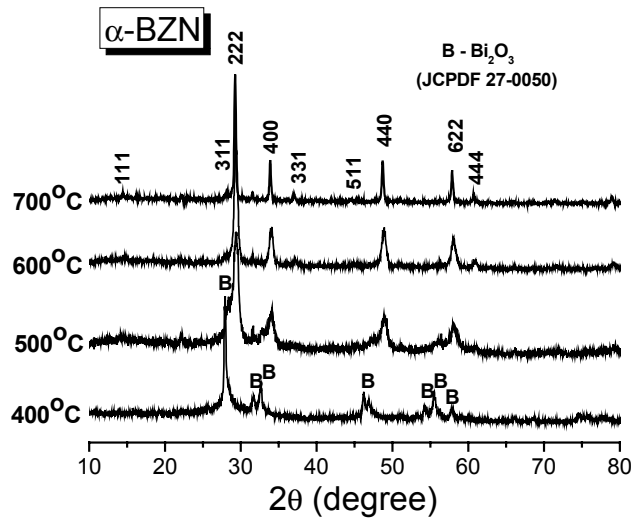


Fig. 2: XRD results for α -BZN powders treated at 700 °C for 2 h.

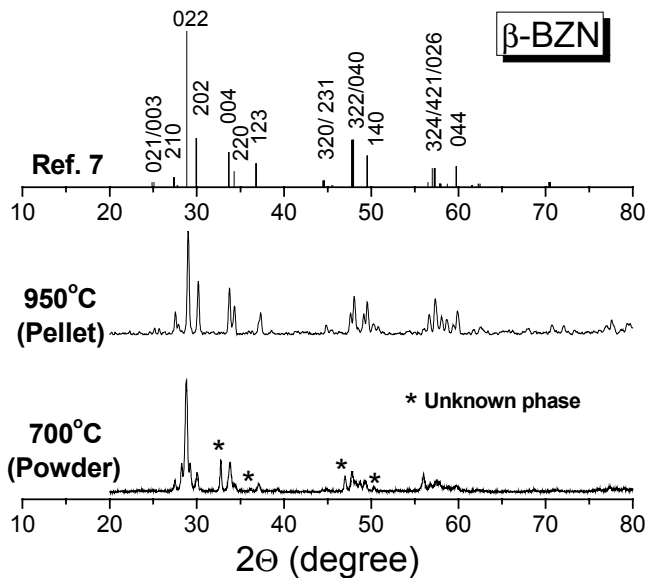


Fig. 3- XRD results for β -BZN powder treated at 700 °C for 2 h and β -BZN pellet treated at 950 °C for 2 h.

Fig. 4a shows the FT-IR spectra for α - and β -BZN powders heated at 500 °C. No significant difference was observed in both spectra, where it is observed the bands related to O-H stretching modes and CH stretching modes, at 3437 cm^{-1} and 2920 cm^{-1} , respectively. In the region from 2000 to 1500 cm^{-1} , the band around 1640 cm^{-1} is related to the OH stretching mode, and between 1500 and 1200 cm^{-1} , it can be observed the bands at 1498, 1380 and 1280 cm^{-1} (carboxyl group stretching modes), 1280 cm^{-1} (CO stretching modes). At lower wavenumbers several bands characteristic of the oxygen-metals/stretching mode, 645 and 523 cm^{-1} for β -BZN, and 595 cm^{-1} for α -BZN. ^{12, 13}

Similarly, the Raman spectra (Fig. 4b) of the powders treated at 700 °C presented no strong difference for both compositions except for the intensity and for the band at 845 cm^{-1} , observed only for the β -BZN composition. The reported bands for the BZN pyrochlore are located at 139, 195, 251, 271, 337, 369, 537, 623, and 764 cm^{-1} . The band at 251 cm^{-1} was assigned to the Zn-O stretching mode while the bands at 195 and 764 cm^{-1} correspond to Bi-O and Nb-O stretching modes, respectively. According to Wang *et al.*⁷, the band at 336 cm^{-1} can be assigned to O-B-O bond bending (which includes Nb-O and Zn-O bonds), while those at 369, 421, 537, 623, and 895 cm^{-1} were not defined; the band at 870 cm^{-1} can be assigned to B-O bonds¹⁴. The authors stated that Zn^{+2} is inclined to occupy A site only after B site was fully occupied, so it can be considered that the bands at 894, 625 and 370 cm^{-1} could be related to Zn-O bonds in B site.

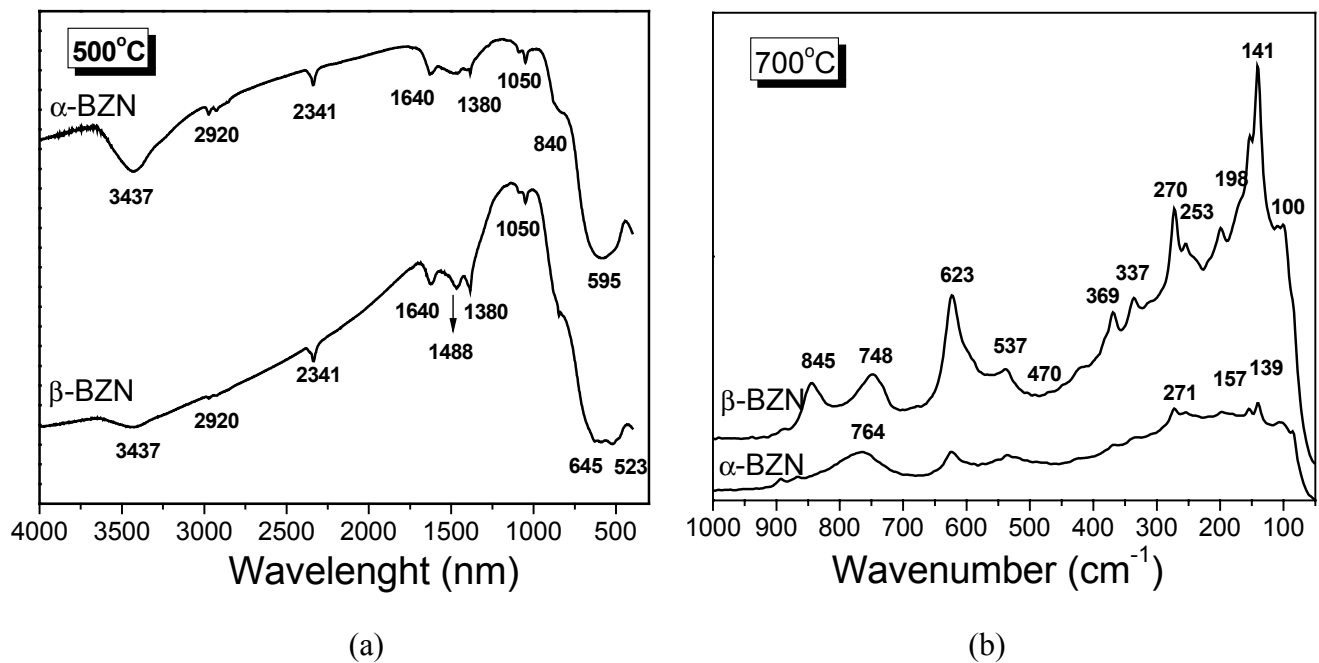
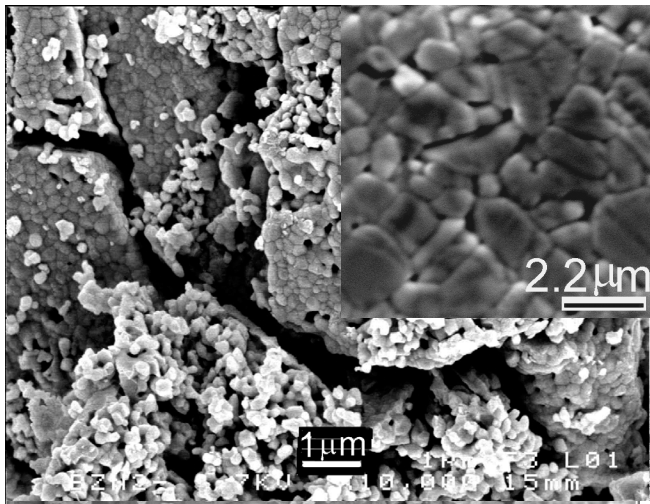


Fig. 4: FT-IR (a) and Raman (b) spectra for α - and β -BZN powders heated at 500 °C and 700 °C, respectively.

The particle morphology observed by SEM is showed in Fig. 5. The samples prepared at 800 °C are formed by large agglomerated clusters with dimension in the order of hundred nanometers. The inset shows the microstructure of the pellets sintered at 950 °C for 2 h, the relative density of pellets was 88.6 % for α -BZN ($\rho_T = 7.11 \text{ g/cm}^3$) and 83.6 % for β -BZN ($\rho_T = 7.194 \text{ g/cm}^3$). It can be observed a heterogeneous microstructure of small grains for β -BZN pellet which may be due to the reminiscent secondary phase observed by XRD. For α -BZN, it is observed a microstructure with grains larger than 3 μm mixed with smaller grains.



(a)

(b)

Fig. 5: SEM images of powders treated for 2 h at 800 °C: (a) α -BZN, (b) β -BZN. The inset shows the microstructure of the pellets sintered at 950 °C for 2 h.

IV. CONCLUSIONS

Bismuth zinc niobate pyrochlores $\text{Bi}_{1.5}\text{Zn}_{0.5}(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$ - α -BZN, and $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$ - β -BZN were synthesized by chemical method based on the polymeric precursors. The phase formation study for α -BZN reveals that a single-phased nanopowder is obtained after calcination at 700 °C, and no intermediary phase (reported for solid state reaction) was observed. For β -BZN it was found some secondary phases due to the lack of stoichiometry in the obtained powder.

The work was supported by the Brazilian financing agency FAPESP. The authors would like to thank LCSIM – Université de Rennes I - France, for the XRD and SEM facilities, and LIEC – UFSCar – Brazil, for the Raman measurements.

REFERENCES

1. Levin, I., Amos, T.G., Nino, J.C., Vanderah, T.A., Randall, C.A. & Lanagan, M.T., Structural study of an unusual cubic pyrochlore $\text{Bi}_{1.5}\text{Zn}_{0.92}\text{Nb}_{1.5}\text{O}_{6.92}$. *J. Sol. State Chem.*, 2002, **168**, 69-75.
2. Valant, M. & Davies, P.K., Synthesis and dielectric properties of pyrochlore solid solutions in the Bi_2O_3 -ZnO-Nb₂O₅-TiO₂ system. *J. Mater. Sci.*, 1999, **34**, 5437-5442.

3. Wei, J., Zhang, L. & Yao, X., Melting properties of Bi₂O₃-ZnO-Nb₂O₅-based dielectric ceramics. *J. Am. Ceram. Soc.*, 1999, **82**, 2551-2552.
4. Nino, J.C., Lanagan, M.T. & Randall, C.A., Phase formation and reactions in the Bi₂O₃-ZnO-Nb₂O₅-Ag pyrochlore system. *J. Mater. Res.*, 2001, **16**, 1460-1464.
5. Chen, S.Y., Lee, S.Y. & Lin, Y.J., Phase transformation, reaction kinetics and microwave characteristics of Bi₂O₃-ZnO-Nb₂O₅ ceramics. *J. Eur. Ceram. Soc.*, 2003, **23**, 873-881.
6. Wang, X.L., Wang, H. & Yao, X., Structures, phase transformations, and dielectric properties of pyrochlores containing bismuth. *J. Am. Ceram. Soc.*, 1997, **80**, 2745-2748.
7. Wang, H., Du, H. L. & Yao, X., Structural study of Bi₂O₃-ZnO-Nb₂O₅ based pyrochlores. *Mat. Sci. Eng. B*, 2003, **99**, 20-24.
8. Pechini, M. P., Method of preparing lead and alkaline earth titanates and niobates and coating methods to form the capacitor. US Patent no. 3.330.697, 1967.
9. Zanetti, S. M., Leite, E. R., Longo, E. & J. A. Varela, SrBi₂Nb₂O₉ thin films deposited by dip coating using aqueous solution. *J. Eur. Ceram. Soc.*, 1999, **19**, 1409-1412.
10. Zanetti, S. M., Leite, E. R., Longo, E., Araújo, E. B., Chiquito, A. J., Eiras, J. A. & Varela, J. A., An alternative chemical route for synthesis of SrBi₂Ta₂O₉ thin films. *J. Mater. Res.*, 2000, **15**, 2091-2095.
11. Paris, E.C., Leite, E.R., Longo, E. & Varela, J.A., Synthesis of PbTiO₃ by use of polymeric precursors. *Mater. Lett.*, 1998, **37**, 1-5.
12. Du, H., Yao X. & Zhang, L., Structure IR spectra and dielectric properties of Bi₂O₃-ZnO-SnO₂-Nb₂O₅ quaternary pyrochlore. *Ceram. Int.*, 2002, **28**, 231-348.
14. Nino, J.C., Lanagan, M.T., Randall, C.A. & Kamba; S., Correlation between infrared phonon modes and dielectric relaxation in Bi₂O₃-ZnO-Nb₂O₅ cubic pyrochlore. *Appl. Phys. Lett.*, 2002, **81**, 4404-4406.