Microwave Dielectric Properties of $BiNbO_4$ Ceramics

C. S. Ferreira, M. P. F. Graça, T. Santos, and L. C. Costa
I3N and Physics Department, University of Aveiro, Aveiro 3810-193, Portugal

Abstract— $BiNbO_4$ ceramics were prepared by the solid state reaction, and the as-prepared samples were treated at temperatures between 600 and 1200°C. The samples structure was analyzed by X-Ray Diffraction and the morphology was studied using Scanning Electron Microscopy. The low-perturbation resonant cavity method was used to calculate the dielectric properties of the ceramic material. The samples heat treated at temperatures above 800°C present the $BiNbO_4$ crystal phase, being the predominant phase on the samples treated above 950°C. The samples treated below 900°C present the $Bi_5Nb_3O_{15}$ secondary phase, which seems to be responsible for the highest dielectric constant values observed at room temperature. The dielectric losses of all samples are always lower than 10^{-4}. The electromagnetic fields, inside the cavity, without and with the cylindrical sample were simulated using the COMSOL Multiphysics software.

1. INTRODUCTION

The progress in communications technology led to extensive researches for the development of miniaturized electronic devices. The study of the properties of potential materials and the development of new materials with specific properties have been the subject of interest [1]. One of the most promising is the bismuth niobate ($BiNbO_4$), that presents good properties in the microwave range [2, 3], with applications in multilayer capacitors [4].

Several authors have studied the influence of the preparation process of $BiNbO_4$, the influence of sintering temperatures and the addition of different oxides [5–7]. The method of solid state reaction has been the most used in the preparation of bismuth niobate.

The measurement of the materials dielectric properties at microwave frequencies can be done in a resonant cavity, using the small perturbation theory [8, 9]. In this method, the changes in the resonance peak frequency and in the quality factor of the cavity, due to the insertion of a sample, can be used to obtain the complex dielectric permittivity of the material, $\varepsilon^* = \epsilon' - i\epsilon''$. The shift in the resonant frequency of the cavity, Δf, can be related to the real part of the complex permittivity, ε', and the change in the inverse of the quality factor of the cavity, $\Delta(1/Q)$, gives the imaginary part, ε''. The relations are simple when can be considered only the first order perturbation in the electric field caused by the sample [10].

In this work, the dielectric properties were measured at 2.7 GHz, using a resonant cavity.

X-Ray diffraction (XRD) and scanning electron microscopy (SEM) were used to find the influence of the microstructures in the microwave dielectric properties.

2. EXPERIMENTAL

Bismuth niobate ($BiNbO_4$) powders were prepared by the solid state method. The raw materials used were bismuth oxide (Bi_2O_3) and niobium pentoxide (Nb_2O_5). After weighting the raw materials in the stoichiometry amount, they were mixed, in agata vessels with agata balls during 2 hours at 250 rpm using the same volume of powders and balls in a Fritsch planetary ball mill.

The obtained powder was thermally analysed by differential thermal analysis (DTA), using a Linseis apparatus, from room temperature until 1200°C, with heating rates of 10 and 20°C/min. The obtained results allowed us to define the treatment temperatures. Therefore, pellets from the base powder were made in cylinders with 4 mm in diameter and 8 mm in height, and heat-treated at 200, 500, 600, 700, 800, 900, 1100 and 1200°C, using a dwell time of 4 hours. The heating rate used in the treatments was 5°C/min.

The X-Ray diffraction (XRD) patterns were obtained on a X'Pert MPD Philips difractometer (CuKα radiation, $\lambda = 1.54060$ Å) at 45 kV, and 40 mA, with a curved graphite monochromator, an automatic divergence slit (irradiated length 20.00 mm), a progressive receiving slit (height 0.05 mm) and a flat plane sample holder in a Bragg-Brentano parafocusing optic configuration. Intensity data were collected by the step counting method (step 0.02° in 1 s), in the 2θ angle range from 10 to 60°.

The morphology of the obtained samples was analyzed by scanning electron microscopy (SEM). The measurements were performed on a Hitachi S4100-1, on free and fracture surfaces. The samples were covered with carbon before microscopic observation.

The measurement of the complex permittivity, was made by using a cavity, operating in TE_{015} mode, with a resonant frequency of 2.7 GHz. The cavity transmission was measured using an HP 8753D Network Analyzer.

The COMSOL RF module was used to simulate the electromagnetic field inside the cavity, with and without a material sample.

3. RESULTS AND DISCUSSION

Figure 1 shows the most relevant diffraction patterns of the heat treated samples. The one treated at 600°C presents the $Bi_5Nb_3O_{15}$ phase, which is maintained in the highest treatment temperatures. The orthorhombic α-$BiNbO_4$ phase is mostly presented in the sample treated at 900°C, and for higher temperatures it is observed the triclinic β-$BiNbO_4$ phase.

Figure 2 shows SEM images of heat treated samples at different temperatures. At the lowest temperature treatment we can see stacked rods of the $Bi_5Nb_3O_{15}$ phase. For 900°C of temperature, a kind of aggregation of particles is observed and for the highest temperature, the coalescence and high densification is then detected.

Figure 3 shows the resonant cavity, which was used to measure the dielectric properties, and the simulated electric field inside it, when a small sample is introduced in its center.

The measurement of the complex permittivity, $\varepsilon^* = \epsilon' - i\epsilon''$, was made by using the small perturbation theory. When we consider only the first order perturbation in the electric field caused

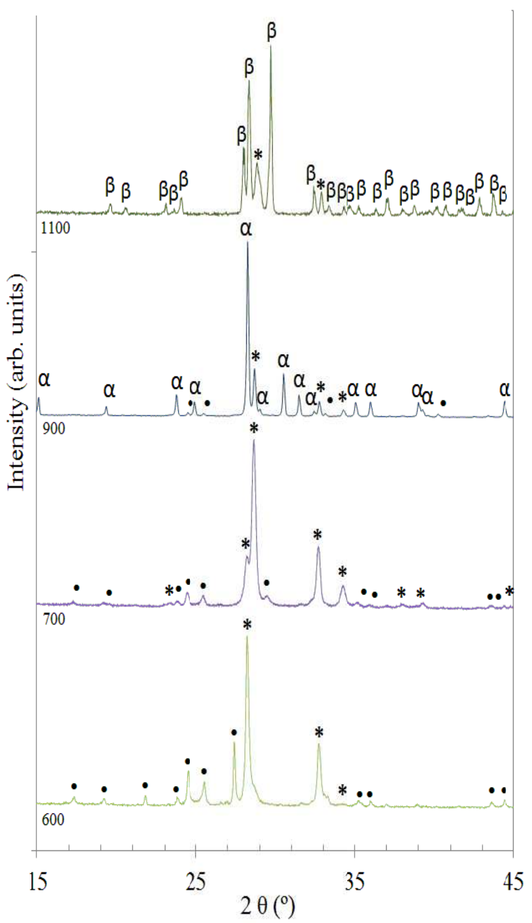

Figure 1: X-Ray diffraction patterns of different samples (•: Nb_2O_5; ∗: $Bi_5Nb_3O_{15}$; α: α-$BiNbO_4$; β: β-$BiNbO_4$).

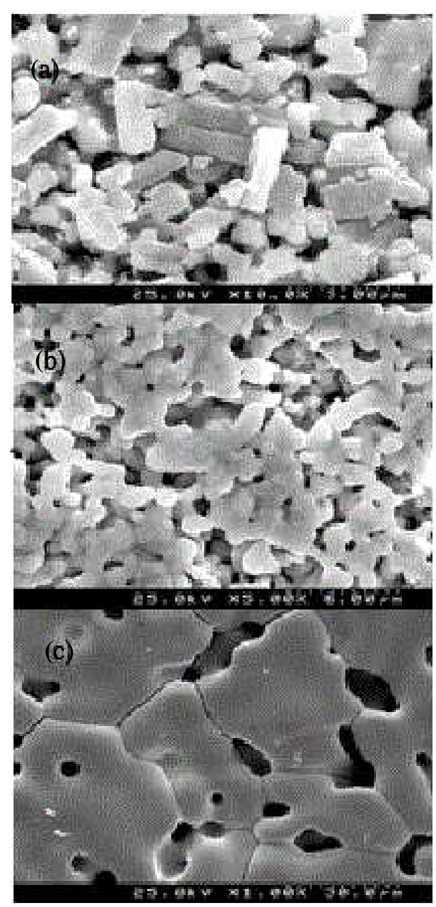

Figure 2: SEM images of heat treated samples: (a) 600°C; (b) 900°C; (c) 1200°C.

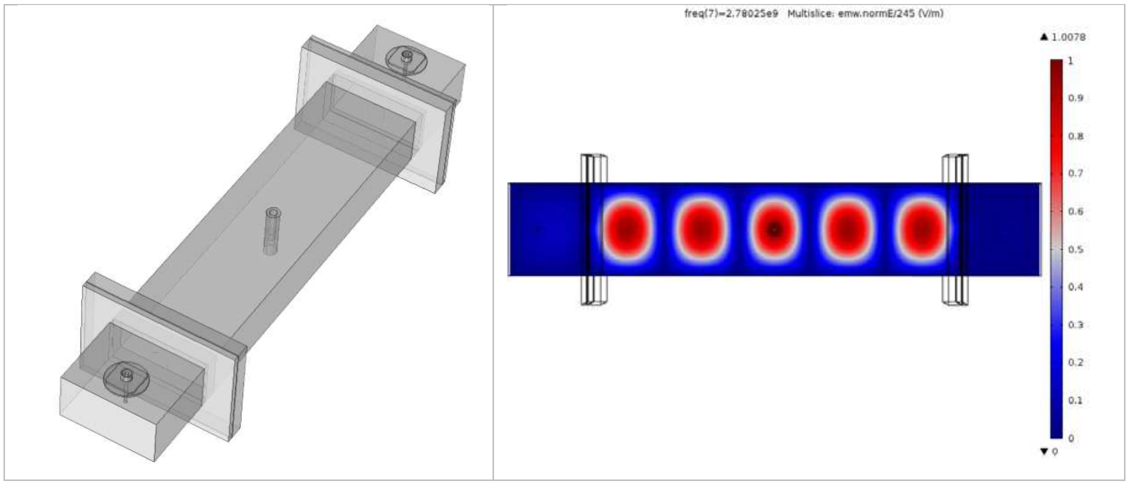

Figure 3: 2.7 GHz resonant cavity and simulated electric field inside it, when a small sample is introduced in its center.

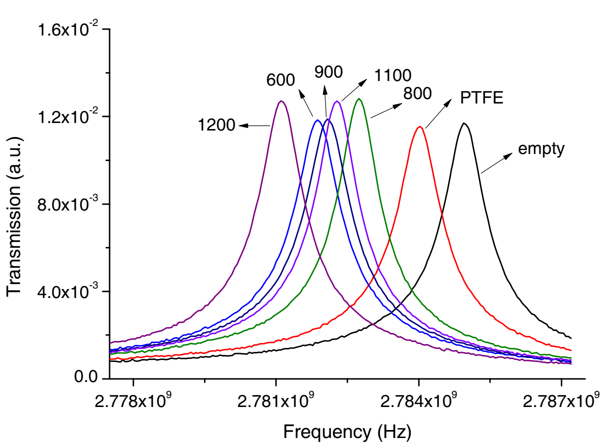

Figure 4: Transmission of the cavity, empty and with different samples.

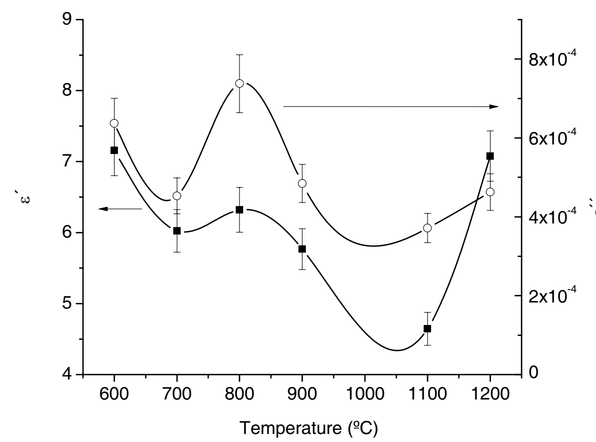

Figure 5: Calculated values of the complex permittivity, for the different samples.

by the sample [11],

$$\varepsilon' = K \frac{\Delta f}{f_0} \frac{V}{v} + 1 \tag{1}$$

$$\varepsilon'' = \frac{K}{2} \Delta \left(\frac{1}{Q}\right) \frac{V}{v} \tag{2}$$

where f_0 is the resonance frequency of the cavity, v the volume of the sample, V the volume of the cavity, and K is a constant related to the depolarization factor, which depends upon the geometric parameters. Using a sample of known complex permittivity we can calculate K. In our case we used a polytetrafluorethylene (PTFE) cylinder, with the same size and shape of the samples.

Figure 4 shows the transmission of the cavity, empty and with different samples. The most perturbing sample is the 1200°C, indicating that the dielectric constant is high.

Figure 5 shows the calculated values of the complex permittivity. The highest value for the dielectric constant is observed for the sample heat treated at 600°C, which can be assigned to $Bi_5Nb_3O_{15}$ phase, the one that is predominant in this sample. It is also observable that the 1200°C treated sample shows high value for ε'. The triclinic β-$BiNbO_4$ phase and the particular morphology can justify this behavior. However, this sample also shows very low ε'', and consequently low loss tangent, $\text{tg}\delta = \varepsilon''/\varepsilon'$. This fact is relevant for technological applications.

4. CONCLUSIONS

$BiNbO_4$ ceramics were prepared by the solid state reaction, and treated at temperatures between 600 and 1200°C. The samples heat treated at higher temperatures present the $BiNbO_4$ crystal phase, being the predominant phase on the samples treated above 950°C. The samples treated at lower temperatures present the $Bi_5Nb_3O_{15}$ phase, which seems to be responsible for the highest dielectric constant values. The 1200°C heat treated samples present the lower dielectric losses, with high dielectric constant, which make them useful for electronic applications.

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