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Dielectric Properties of Bismuth Niobate Ceramics

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Additional information is available at the end of the chapter

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Abstract

The development of new dielectric materials that allow the reduction of size and weight of electronic components has been in the scope of the researchers. The bismuth-based dielectric ceramics are extensively studied for this purpose, namely, the bismuth niobate (BiNbO_4). The first attempt to improve BiNbO_4 occurred in 1992 when Kagata reported the microwave dielectric properties of bismuth niobate doped with the addition of oxides. This chapter will present a brief review of the several attempts that have been carried out to enhance the dielectric properties of BiNbO_4 by modifying their structure through addition, doping, or atom(s) substitution. This manuscript focuses on a case study that involves bismuth substitution by europium ions. To investigate the inclusion of europium in BiNbO_4 ceramics, $(\text{Bi}_{1-x}\text{Eu}_x)\text{NbO}_4$ samples were prepared using the sol-gel method, in particular, the citrate route. The structure of the prepared samples was studied by X-ray diffraction (XRD) and Raman spectroscopy and the morphology by scanning electron microscopy (SEM). The dielectric properties were studied, in the microwave frequency range (MW), using the resonant cavity method, and in the radio frequency range (RF), with the impedance spectroscopy technique.

Keywords: bismuth niobate, europium, sol-gel, dielectric properties

1. Introduction

ABO_4 ternary oxides proved to be attractive materials from the chemical perspective since they have the capacity to combine chemical elements in this basic formula, which lead to an extensive wide array of structures and phases with different properties [1].

They present stibiotantalite structure, where “A” can be bismuth (Bi^{3+}) and “B” niobium (Nb^{5+}) cations, composing the bismuth niobate, BiNbO_4 [2, 3].

The bismuth niobate exists in two polymorph structures, an orthorhombic (α) phase and a triclinic (β) phase. According to previous studies, the transition of β -BiNbO₄ to α -BiNbO₄ occurs at temperatures around 700/750°C, with the opposite, and irreversible transition occurring at 1020/1050°C [3].

The bismuth-containing oxides have large structural diversity and promising physical properties for applications in optics, nanoelectronics and nanophotonics [4].

In the last three decades, the bismuth niobate ceramics have been studied as a dielectric material for applications in radio and microwave frequency range, since the development of the communication systems forced the device miniaturisation, and, for that, new dielectric materials are needed [3, 5].

The general requirements of a ceramic dielectric for radio and microwave applications are high dielectric constant and low losses [5, 6]. However, there are other important parameters that require improvement, such as the density, since dense BiNbO₄ (BNO) ceramics are difficult to obtain [7, 8].

Since 1992, when Kagata [9] reported for the first time the microwave dielectric properties of BiNbO₄ doped with CuO and V₂O₅, numerous attempts have been carried out to improve the dielectric properties of this ceramic material.

Several authors studied the influence of the preparation process of BiNbO₄, the influence of sintering process, the addition of different oxides and also the substitution of bismuth or niobium by other cations.

The relation between the structural characteristics and the dielectric properties should also be considered and that is why the influence of the phase transition on the dielectric properties of the material is normally presented [10].

In the next section, state of the art, specific previous studies will be presented, where the dielectric characterisation of BiNbO₄ in the radio and microwave frequency regions is made in BNO samples where the addition of oxides or the substitution of bismuth ion was performed.

The last section of this chapter is devoted to the description of a case study, where the inclusion of europium in BiNbO₄ ceramics, (Bi_{1-x}Eu_x)NbO₄ samples, prepared using the sol-gel method and then subjected to different heat treatments is analysed. The dielectric properties were studied in the radio and in the microwave frequency range.

2. State of the art

As mentioned, in 1992 Kagata [9] doped BiNbO₄ with small amounts of CuO or V₂O₅ with the aim of densifying the ceramic material. In that work, the samples were prepared using the solid-state reaction method, and the dielectric characterisation was performed in the microwave frequency range ($f \approx 4.3$ GHz), using Hakki-Coleman's method. According to the authors, with the addition of these oxides, the samples became dense, even with heat treatments below 1000°C, presenting dielectric constants of about 43 at room temperature.

In 1999, Yang [11] presented the dielectric properties of BiNbO_4 ceramics doped with different amounts of CuO , V_2O_5 , or $\text{CuO-V}_2\text{O}_5$ mixtures. The samples were prepared using the solid-state reaction method, and the dielectric characterisation, in the microwave frequency regime ($f \approx 6.1$ GHz), was performed using Hakki-Coleman's method improved by Courtney and Kobayashi. According to this study, the samples became dense, even with heat treatments below 920°C , and also presented dielectric constants of about 43 at the same environmental conditions.

Tzou and coworkers [6] also used, in 2000, V_2O_5 as a support to lower the sintering temperature of BiNbO_4 ceramics. The samples were prepared by the solid-state reaction method, and to study the microwave (5.7–6.2 GHz) dielectric properties and relate them to the amount of V_2O_5 , the Hakki-Coleman's method, improved by Courtney and Kobayashi, was used. A bulk density of 98% of the theoretical density was achieved for treatment temperatures of 920, 940 and 960°C . The obtained results suggested that large amount of V_2O_5 is avoidable since the Q values decrease critically.

In 2001 Huang [12] investigated the behaviour and the microwave dielectric properties of $\text{BiNb}_{(1-x)}\text{Ta}_x\text{O}_4$ doped with CuO . The powders were prepared by the solid-state reaction method, and the dielectric measurements, in the frequency range of 6–8 GHz, were performed using the Hakki-Coleman's technique. The dielectric constant of these samples was not significantly influenced by the Ta^{5+} substitution and saturated at a value between 44 and 45, again at room temperature.

Shihua, Xi and Yong [13] sintered, in 2004, BiNbO_4 doped with Bi_2O_3 , by the solid-state reaction process. Those powders were sintered in air and in N_2 atmosphere. The microwave dielectric properties, at approximately 5 GHz, were measured using the Hakki-Coleman dielectric resonator methods. For low frequencies, the temperature dependence of dielectric properties was measured from 20 to 500°C in a frequency range of 1–100 kHz. This study revealed that the dielectric constant and loss at low frequencies increased rapidly and the microwave dielectric properties deteriorated with increasing of B_2O_3 content when sintered in N_2 .

Shihua and coworkers [14] studied, in 2006, the microwave ($f \approx 6$ GHz) dielectric properties of $(\text{Bi}_{1-x}\text{R}_x)\text{NbO}_4$ ($\text{R} = \text{Ce}, \text{Nd}, \text{Dy}, \text{Er}$) using CuO and V_2O_5 as sintered aids. In this work, the samples were prepared using the solid-state reaction method, and the dielectric properties were obtained by the Hakki-Coleman resonator method. The mentioned ions were introduced to substitute for Bi^{3+} ions. The dielectric constant varied from approximately 37.5 to 41.58.

In 2008, Zhou et al. [15] designed $\text{Bi}(\text{V}_x\text{Nb}_{1-x})\text{O}_4$ ceramics by using V^{5+} substituting for Nb^{5+} . The samples were prepared by the solid-state reaction method, and the dielectric behaviour at microwave frequencies (5–6 GHz) was studied by two different processes, Hakki-Coleman's dielectric resonator method improved by Kobayashi and the shielded cavity method. The results obtained by the two methods were similar, with the dielectric constant and the quality factor strongly dependent on the sintering temperature. For values of x between 0.002 and 0.064, the dielectric constant varied between 38 and 46.

The study developed by Zhong and coworkers [16], in 2010, involved two kinds of $\text{CuO-V}_2\text{O}_5$ dopants with the aim of reducing the sintering temperature of BiNbO_4 : one was the mechanical mixture of CuO and V_2O_5 , and the other was the compound CuV_2O_6 . The samples were

prepared by the solid-state reaction method and sintered in N_2 atmosphere. The dielectric characterisation at microwave frequencies ($f = 4.3$ GHz) was performed using the Hakki-Coleman dielectric resonator method. The addition of CuV_2O_6 led to uniform and dense microstructures, with higher dielectric constant than those of the samples added with $CuO-V_2O_5$. The sample with better microwave dielectric properties was sintered at $860^\circ C$ and was doped with 0.5 wt.% of CuV_2O_6 ; $\epsilon' = 47$ and $Q \times f = 11,950$ GHz.

In the same year, Butee and coworkers [17] investigated ceramic samples of $BiNbO_4$ and $(Bi_{0.95}Ln_{0.05})NbO_4$ ($Ln = Dy^{3+}$, Gd^{3+} , Nd^{3+} or La^{3+}) with V_2O_5 addition. The samples were obtained by the solid-state reaction method. The dielectric measurements were made at low frequencies (1 kHz–1 MHz) with a Solartron impedance gain phase analyser and, at microwave frequencies (≈ 4 –5 GHz), with the dielectric post resonator technique. The obtained values in the microwave frequency region for the dielectric constant were 46.5 (pure $BiNbO_4$), 40.8 ($Ln = Dy^{3+}$), 41.7 ($Ln = Gd^{3+}$), 43.4 ($Ln = Nd^{3+}$) and 47.5 ($Ln = La^{3+}$). The dielectric measurements made on the sintered samples at RF frequencies showed dielectric constants between 44.7 and 53.4.

In 2011, Almeida et al. [18] sintered $BiNbO_4$ ceramics with different amounts of PbO and Bi_2O_3 , by the solid-state reaction method. The dielectric characterisation was performed with the impedance spectroscopy technique, in the frequency range of 10^2 – 10^8 Hz. Since the studied samples presented relaxation processes, the activation energies were calculated and varied between 0.55 eV (pure triclinic BNO) and 0.67 (BNO with 10 wt.% of PbO).

Sales and coworkers [3] investigated, in 2012, the dielectric, electrical modulus and impedance properties of $BiNbO_4$ ceramics, doped with different amounts of CuO and prepared by the solid-state reaction method. The frequency range of this study was between 100 Hz and 10 MHz. The highest values of dielectric permittivity occurred at 10 kHz, for the samples of BNO with 3 wt.%, 5 wt.% and 10 wt.% of CuO , with the values of 87.15, 88.63 and 140.73, respectively. The lowest values of the lost tangent occurred for the same samples but at 10 MHz.

In 2014, Czekaj et al. [19] studied the immittance properties of $BiNbO_4$ ceramics fabricated by the solid-state reaction route, with an excess of Bi_2O_3 , followed by pressureless sintering. The immittance properties, complex impedance, complex modulus, complex admittance, complex dielectric permittivity and dielectric losses were studied by impedance spectroscopy, in a frequency range of 20 Hz to 1 MHz. Since the investigated samples presented relaxation processes, the Arrhenius relation was applied in order to calculate the activation energies. The values of the activation energy varied between 0.81 and 1.04 when obtained with the impedance formalism and between 0.85 and 1.12 with the modulus formalism.

Devesa and coworkers [7] investigated, in 2015, $(Bi_{1-x}Fe_x)NbO_4$ samples prepared using the sol-gel method. The measurements of the complex permittivity were made in a resonant cavity, using the small perturbation method, at frequencies of 2.7 and 5.0 GHz. With the substitution of bismuth by iron, it was possible to reduce the sintering temperature and simultaneously to decrease the dielectric losses. The dielectric constant of the samples with different percentages of iron was practically independent of the sintering temperature.

In 2016, Butee et al. [20] studied $(Bi_{1-x}Pb_x)NbO_4$ samples, prepared by the solid-state reaction method, with the addition of V_2O_5 . The dielectric post (DP) resonator technique was employed for the microwave characterisation of the samples that was performed at room

temperature and at ~4–5 GHz. In this study, dielectric constant values between 42 ($x = 0$) and 71 ($x = 0.2$) were obtained. According to the authors, such increase has never been reported in a BNO system and can be attributed to the formation of the $\text{Pb}_2\text{Nb}_2\text{O}_7$ secondary phase.

Analysing the referenced works, we can see that the solid-state reaction method is the most common preparation process. Furthermore, the dielectric characterisation studies are mainly focused in the microwave frequency regime, which means that the information of the dielectric behaviour of ceramic materials based on bismuth niobate in the RF frequency regime is reduced. Concerning the MW dielectric studies, it is also perceptible that the improved Hakki-Coleman's dielectric resonator method is the most used.

To end this brief state of the art, it is important to note that, for some reason that the authors do not understand, a significant number of microwave dielectric studies of BNO ceramics do not refer the measuring frequency. None of those incomplete works was included in this manuscript.

In **Table 1**, the **key progress of the modified BiNbO_4** is presented.

3. Case study

In this work, $(\text{Bi}_{1-x}\text{Eu}_x)\text{NbO}_4$ ($x = 0.00, 0.10, 0.20, 0.50$) samples were prepared using the sol-gel method and thermally treated at different temperatures, between 650 and 1050°C.

In fact, the solid-state reaction method has been the most applied technique to process ceramic powders; however, more recently the sol-gel method, through citrate route, became considered a promising process and a simple way to obtain stoichiometric fine powders, with high homogeneity, since the formation of citrate complexes allows mixing the component cations in an atomic scale; thus they can immediately react with each other at relatively low temperatures [6].

The structure was studied by X-ray diffraction (XRD) and Raman spectroscopy and the morphology by scanning electron microscopy (SEM).

The measurements of the complex permittivity were performed in a frequency range from 100 Hz to 1 MHz (RF, radio frequency range), using the impedance spectroscopy technique, and at 2.7 GHz (MW, microwave frequency range), using the small perturbation theory.

In the case of the microwave dielectric characterisation, through the small perturbation method, a more detailed study can be consulted in a previous work of Devesa et al. [21], from 2017.

3.1. Sample preparation

The $(\text{Bi}_{1-x}\text{Eu}_x)\text{NbO}_4$ powders were prepared using the sol-gel method, through the citrate route. Bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), niobium chloride (NbCl_5) and europium nitrate ($\text{Eu}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$) were used as starting materials and citric acid and ethylene glycol as chelating agent and reaction medium, respectively. All reagents used in the whole procedure were of analytical grade. A suspension containing stoichiometric amounts of starting materials was previously prepared in a minor amount of hydrogen peroxide and dispersed in a mixture of

Reference	Composition of BiNbO ₄	Preparation method	Frequency	Dielectric measurement method	Dielectric constant	Quality factor	Dielectric loss (tgδ)
[9]	Doped with CuO	Solid-state reaction	4.3 GHz	Hakki-Coleman's	44	2240	_____
	Doped with V ₂ O ₅				44	2750	_____
	Doped with CuO and V ₂ O ₅				43	4260	_____
[11]	Doped with CuO, V ₂ O ₅ and CuO-V ₂ O ₅ mixture	Solid-state reaction	6.1 GHz	Hakki-Coleman's improved by Courtney and Kobayashi	43.2	3310	_____
[6]	Doped with V ₂ O ₅	Solid-state reaction	5.7~6.2 GHz	Hakki-Coleman's improved by Courtney and Kobayashi	43.6	3410	_____
[12]	BiNb _(1-x) Ta _x O ₄ doped with CuO	Solid-state reaction	6–8 GHz	Hakki-Coleman's	44–45	Tem q*f!	_____
[13]	Doped with Bi ₂ O ₃	Solid-state reaction	≈ 5 GHz	Hakki-Coleman's	41.5	4400	_____
			1–100 kHz	_____	1874	_____	_____
[14]	(Bi _{1-x} R _x)NbO ₄ (R = Ce, Nd, Dy, Er) doped with CuO and V ₂ O ₅	Solid-state reaction	≈ 6 GHz	Hakki-Coleman's	41.58	5000	_____
[15]	Bi(V _x Nb _{1-x})O ₄	Solid-state reaction	5~6 GHz	Hakki-Coleman's improved by Kobayashi and shielded cavity method	38–46	1000–4000	_____
[16]	Doped with CuO and V ₂ O ₅ or CuV ₂ O ₆	Solid-state reaction	4.3 GHz	Hakki-Coleman's	47	2779	_____
[17]	BiNbO ₄ and (Bi _{0.95} Ln _{0.05})NbO ₄ (Ln = Dy ³⁺ , Gd ³⁺ , Nd ³⁺ or La ³⁺) doped with V ₂ O ₅	Solid-state reaction	≈ 4–5 GHz	Dielectric post resonator	40.8–47.5	_____	_____
			10 ³ –10 ⁶ Hz	Solartron impedance gain phase analyser	44.7–53.4	_____	_____
[18]	Doped with PbO and Bi ₂ O ₃	Solid-state reaction	10 ² –10 ⁸ Hz	Impedance spectroscopy	78.44	_____	6.26 × 10 ⁻²
[3]	Doped with CuO	Solid-state reaction	10 ² –10 ⁷ Hz	Impedance spectroscopy	140.73	_____	1–2

Reference	Composition of BiNbO ₄	Preparation method	Frequency	Dielectric measurement method	Dielectric constant	Quality factor	Dielectric loss (tgδ)
[19]	With excess of Bi ₂ O ₃	Solid-state reaction	20–10 ⁶ Hz	Impedance spectroscopy	_____	_____	_____
[7]	(Bi _{1-x} Fe _x)NbO ₄	Sol-gel method	2.7 and 5 GHz	Small perturbation	4.24	_____	2 × 10 ⁻²
[20]	(Bi _{1-x} Pb _x)NbO ₄ doped with V ₂ O ₅	Solid-state reaction	~4–5 GHz	Dielectric post (DP) resonator	71	_____	_____

Table 1. Summary of the most significant progress of the modified BiNbO₄.

citric acid and ethylene glycol in a molar ratio 1:3. In order to promote the solubility, the mixture was stirred, during 7 days, until a clear colloidal suspension was obtained. The obtained solution was dried at 400°C for 48 h to evaporate the solvent, and the obtained powders were thermally analysed by differential thermal analysis (DTA), performed in a *Linseis Apparatus L92/095*, in the temperature range of 20–1200°C, with a heating rate of 10°C/min, using Al₂O₃ as reference. Subsequently, the dry powders were pressed into pellets and cylinders and finally heat-treated, according to the differential thermal analysis (DTA) results, at 650, 850 and 1050°C, using a dwell time of 4 h, with a heating rate of 5°C/min.

3.2. Experimental methods

The structural characterisation of the obtained ceramics was performed using XRD. The pattern data were obtained on an Empyrean diffractometer (CuK α radiation, $\lambda = 1.54060 \text{ \AA}$) 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 2 θ angle range of 10–60°

The Raman spectroscopy measurements were performed at room temperature, in backscattering geometry, with a 442 nm laser line using an HR-800-UV Jobin-Yvon Horiba spectrometer. A microscope objective focused the exciting light onto the sample.

The morphology of the obtained samples was analysed by SEM. The measurements were performed on a TESCAN-Vega III. The samples were covered with carbon before microscopic observation to improve the surface electron conduction.

For the electrical measurements in the frequency range from 100 Hz to 1 MHz, pellets in disc form and with a thickness of about 1 mm and diameter of 10 mm were prepared, and their opposite side surfaces were painted with silver conducting paste. During the electrical measurements, the samples were maintained in a helium atmosphere in order to improve the heat transfer and eliminate the moisture. These measurements were made using a precision impedance analyser (Agilent 4294A) in the Cp-Rp configuration, in the temperature range of 200–400 K. The real part of the complex permittivity, ϵ' , and the imaginary part, ϵ'' , were calculated using Eq. (1) [22]:

$$\epsilon^* = \epsilon' - i\epsilon'' = \frac{C_p d}{A \epsilon_0} - i \frac{d}{\omega R_p A \epsilon_0} \quad (1)$$

where A and d represent the sample area and thickness, respectively, ϵ_0 the free space permittivity and ω the angular frequency.

The microwave characterisation was performed using the resonant cavity method, with the cavity operating at 2.7 GHz in the TE₁₀₅ mode. The measurements were made at room temperature, using a network analyser (HP 8753D) coupled to the cavity.

The insertion of the cylindrical sample at the position where the electric field is maximal causes a perturbation, changing the transmission of the cavity.

Considering only the first-order perturbation in the electric field caused by the sample [7], 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, $\Delta(1/Q)$, can be related to the imaginary part, ϵ'' [7, 21]:

$$\epsilon' = K \frac{\Delta f}{f_0} \frac{V}{v} + 1 \quad (2)$$

$$\epsilon'' = \frac{K}{2} \Delta\left(\frac{1}{Q}\right) \frac{V}{v} \quad (3)$$

where K is a constant related to the depolarization factor, which depends on the geometric parameters; v and V are the volumes of the sample and the cavity, respectively and f_0 is the resonance frequency of the cavity.

$$\Delta f = f_0 - f_l \quad (4)$$

$$\Delta\left(\frac{1}{Q}\right) = \frac{1}{Q_l} - \frac{1}{Q_0} \quad (5)$$

where the indexes 0 and l refer to the empty and loaded cavity, respectively.

Using a sample of known dielectric constant, in this study polytetrafluoroethylene (PTFE), the constant K can be calculated.

3.3. Results and discussion

3.3.1. Differential thermal analysis

The DTA data of the obtained powders, shown in **Figure 1**, revealed, for the sample with $x = 0.00$, three exothermic phenomena centred at 646, 1043 and 1181°C. When $x = 0.10$, besides the three exothermic phenomena mentioned above, that can clearly be identified although the small displacements, it is visible two new exothermic phenomena centered at 546 and 607°C, and an endothermic peak at 443°C. The powder with $x = 0.20$ shows an endothermic peak at 443°C, and four exothermic phenomena centred at 530, 667, 1033 and 1189°C. For $x = 0.50$, there is an endothermic phenomenon centred at 590°C and an exothermic at 978°C.

The heat treatments were made in agreement with these results.

3.3.2. X-ray diffraction pattern analysis

The crystalline phases were identified by X-ray diffraction patterns and are shown in **Figure 2**.

In the host samples, $x = 0.00$, a combination of orthorhombic and triclinic BiNbO_4 was obtained for the heat treatment of 650°C, orthorhombic BiNbO_4 for the heat treatment of 850°C and triclinic BiNbO_4 for the heat treatment of 1050°C.

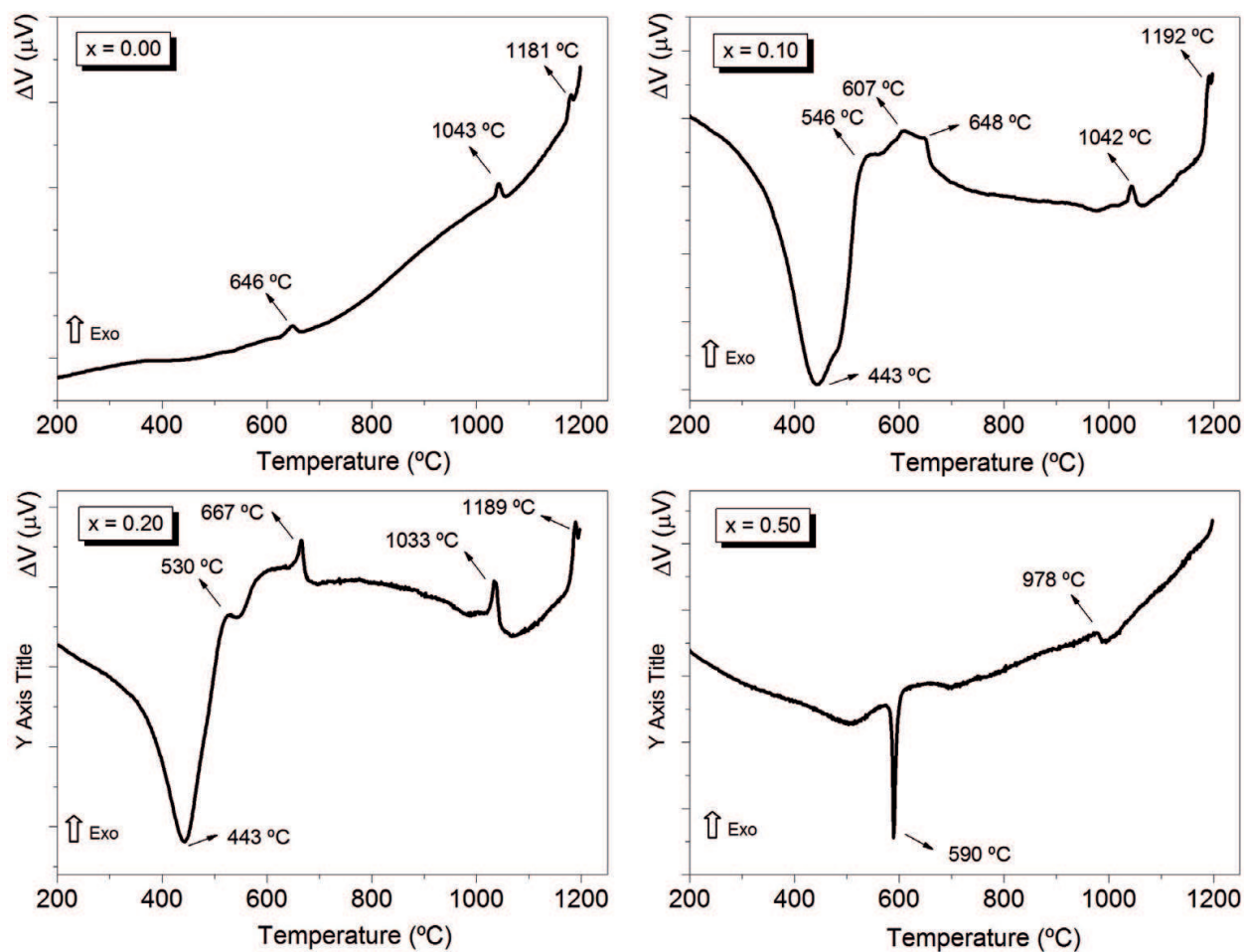


Figure 1. DTA of $(\text{Bi}_{1-x}\text{Eu}_x)\text{NbO}_4$ powders, heated at the rate of $10^\circ\text{C}/\text{min}$.

When $x = 0.10$, besides the $\alpha\text{-BiNbO}_4$ and $\beta\text{-BiNbO}_4$, EuNbO_4 and EuNb_2O_6 , a nonstoichiometric phase of bismuth niobate was formed for the heat treatment of 1050°C . The formation of nonstoichiometric phases of bismuth niobate is associated with the volatile nature of Bi^{3+} ions at high temperature.

With the increase of x to 0.20, besides the $\alpha\text{-BiNbO}_4$, $\beta\text{-BiNbO}_4$ and EuNbO_4 , for the higher treatment temperature, there are two unidentified peaks that should be associated with a different nonstoichiometric phase of bismuth niobate.

For $x = 0.50$, $\alpha\text{-BiNbO}_4$, $\beta\text{-BiNbO}_4$, $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ and EuNbO_4 were identified.

The results show that Eu^{3+} ions substituted in BiNbO_4 tend to form a separate crystal structure rather simply replacing Bi^{3+} ions.

Analysing the X-ray diffraction data and the DTA results, the consistency of the information is visible.

For $x = 0.00$, the first peak shows the formation of $\beta\text{-BiNbO}_4$ and the second can be associated with the conversion of $\alpha\text{-BiNbO}_4$ in $\beta\text{-BiNbO}_4$.

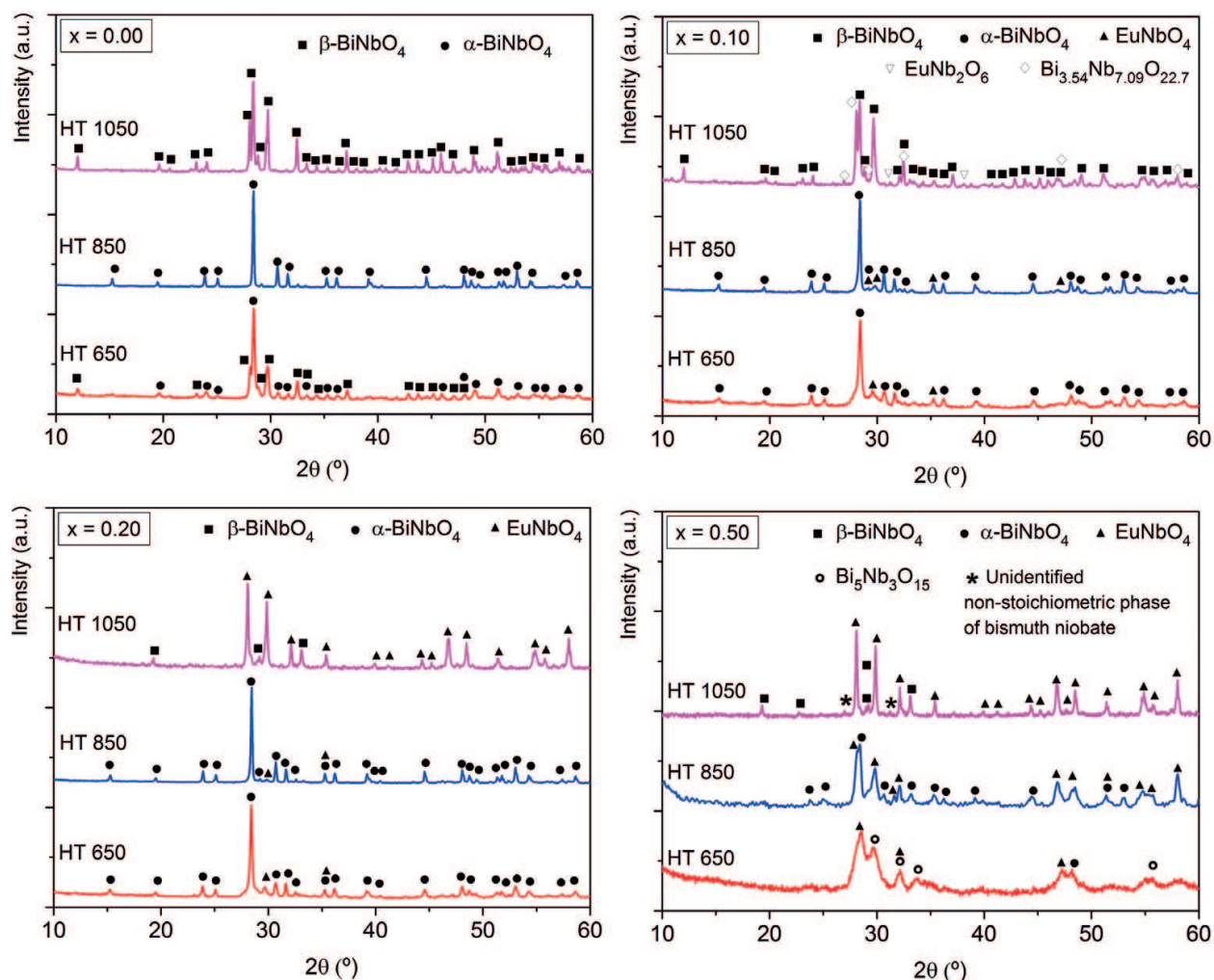


Figure 2. X-ray diffraction patterns of $(\text{Bi}_{1-x}\text{Eu}_x)\text{NbO}_4$ samples heat-treated at 650, 850 and 1050°C.

According to the literature, the formation of $\alpha\text{-BiNbO}_4$ is expected for temperatures above 500°C, evidenced by small exothermic peaks between 500 and 600°C [23], which are visible in the DTA of the powders with $x = 0.10$ and 0.20.

As in the reference powders, all of the powders with europium show one peak close to 1000°C that can be related to the transition of $\beta\text{-BiNbO}_4$ to $\alpha\text{-BiNbO}_4$. The existence of one endothermic peak in this set of powders can be related to the decomposition of intermediate phases.

The increase of the crystallinity is also perceptible for the heat treatment of 850°C, with the increase of the height and the decrease of the half-high width of the peaks.

The thermal treatment performed at 1200°C caused the fusion of the powders, and therefore there is no information about the exothermic phenomenon that occurs near this temperature.

3.3.3. Raman spectroscopy analysis

The Raman spectra are presented in **Figure 3**.

When $x = 0.00$, the samples treated at 650 and 1150°C show peaks at 102, 450 and 687 cm^{-1} that are characteristics of the vibration modes of $\beta\text{-BiNbO}_4$. In the case of the sample treated at 850°C, where the single phase $\alpha\text{-BiNbO}_4$ was identified, none of these peaks is present. Besides, the peaks at 139 and 199 cm^{-1} are distinctive of the orthorhombic BiNbO_4 , a fact that justifies their absence in the spectrum of the sample treated at 1050°C, where all are attributed to triclinic BiNbO_4 [5, 24]. This means that none of the detected vibrations can be assigned to nonstoichiometric phase $\text{Bi}_{3.54}\text{Nb}_{7.09}\text{O}_{22.7}$.

For $x = 0.10$ and 0.20, the peaks identified in the samples treated at 650 and 850°C can be attributed to the vibration modes of BiNbO_4 , with vibrations at 140 and 200 cm^{-1} being characteristic of the orthorhombic BiNbO_4 . For the sample treated at 1050°C, these two vibrations are absent, though at 690 cm^{-1} it is possible to identify a distinctive peak of the triclinic BiNbO_4 [25, 26].

The vibrations present at 120, 133, 175, 290 and 782 cm^{-1} in the sample with $x = 0.20$ can be attributed to the vibration modes of EuNbO_4 [1].

For the samples with $x = 0.50$, this analysis is still valid, and it is possible to notice that the vibration modes of the nonstoichiometric phase $\text{Bi}_5\text{Nb}_3\text{O}_{15}$ are very similar to the ones obtained for the orthorhombic BiNbO_4 .

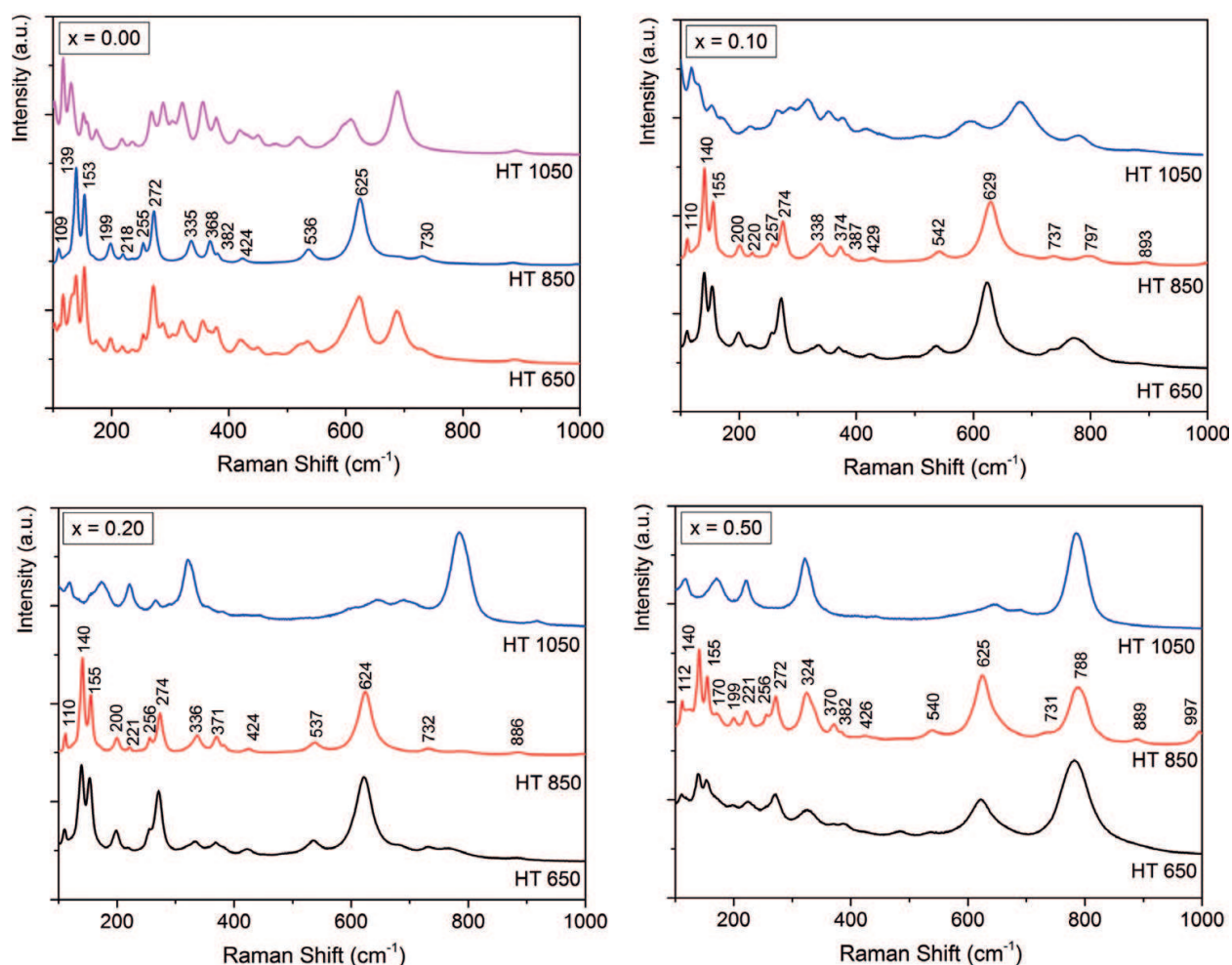


Figure 3. Raman spectra of $(\text{Bi}_{1-x}\text{Eu}_x)\text{NbO}_4$ samples heat-treated at 650, 850 and 1050°C.

3.3.4. Morphological characterisation

SEM micrographs of $(\text{Bi}_{1-x}\text{Eu}_x)\text{NbO}_4$ powders are shown in **Figure 4**. The images for treatment temperature of 650°C revealed that the increase of europium content promotes changes in the morphology of the samples. These changes are more perceptible when x increases from 0.20 to 0.50, with the grain size increasing. For the samples treated at 850°C , one can see that the increase of europium promotes the occurrence of coalescence. The heat treatment of 1050°C promotes the formation of high-temperature triclinic BiNbO_4 , which leads to a dramatic change in the morphology of the samples, with the grain size showing a very expressive increase.

3.3.5. Dielectric characterisation

Figure 5 shows the real part of the dielectric permittivity as a function of the frequency, at constant temperature $T = 300\text{ K}$, in the RF frequency range, for the prepared samples. It can be verified that it is not significantly influenced by the frequency.

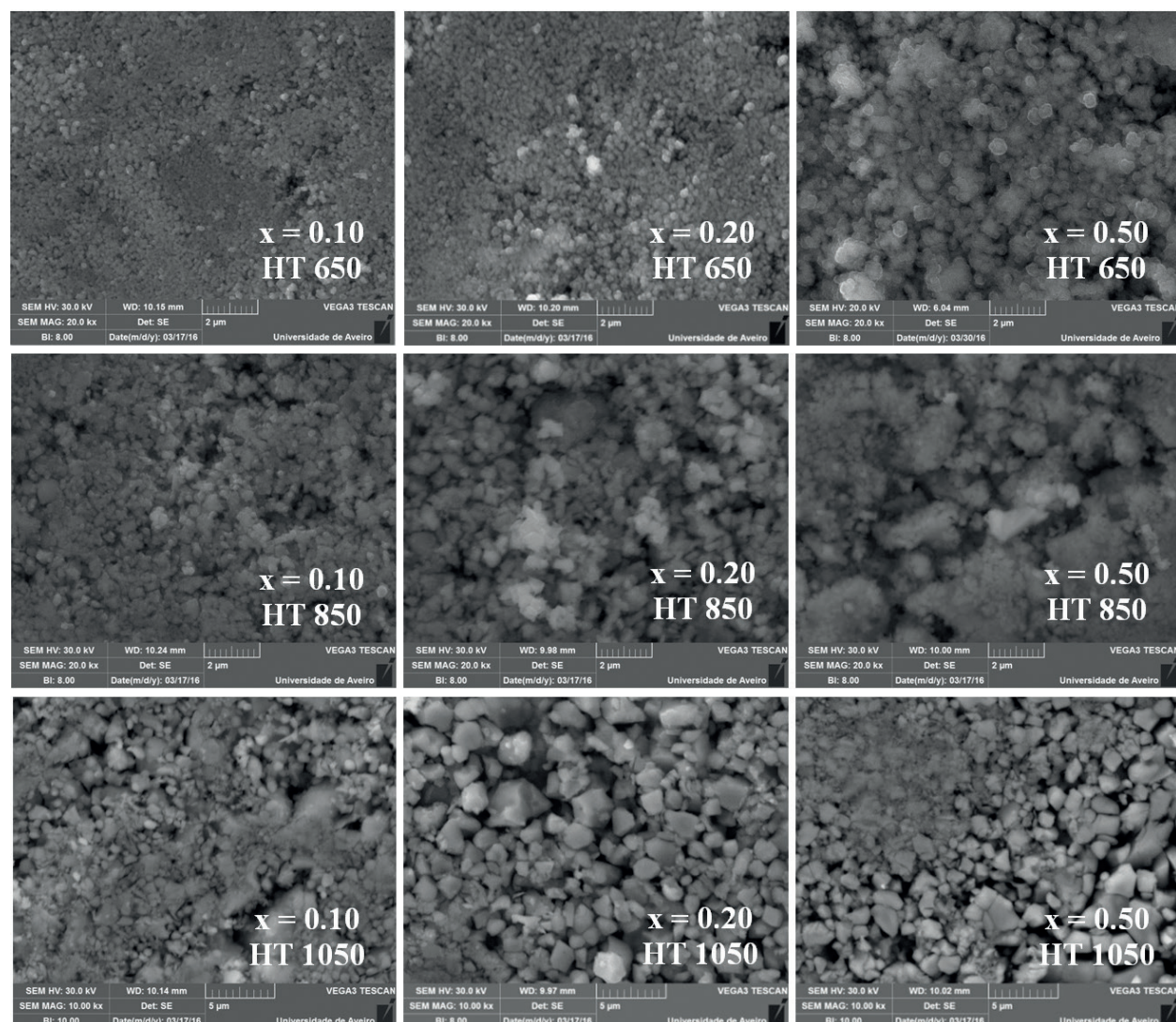


Figure 4. SEM micrographs of $(\text{Bi}_{1-x}\text{Eu}_x)\text{NbO}_4$ samples.

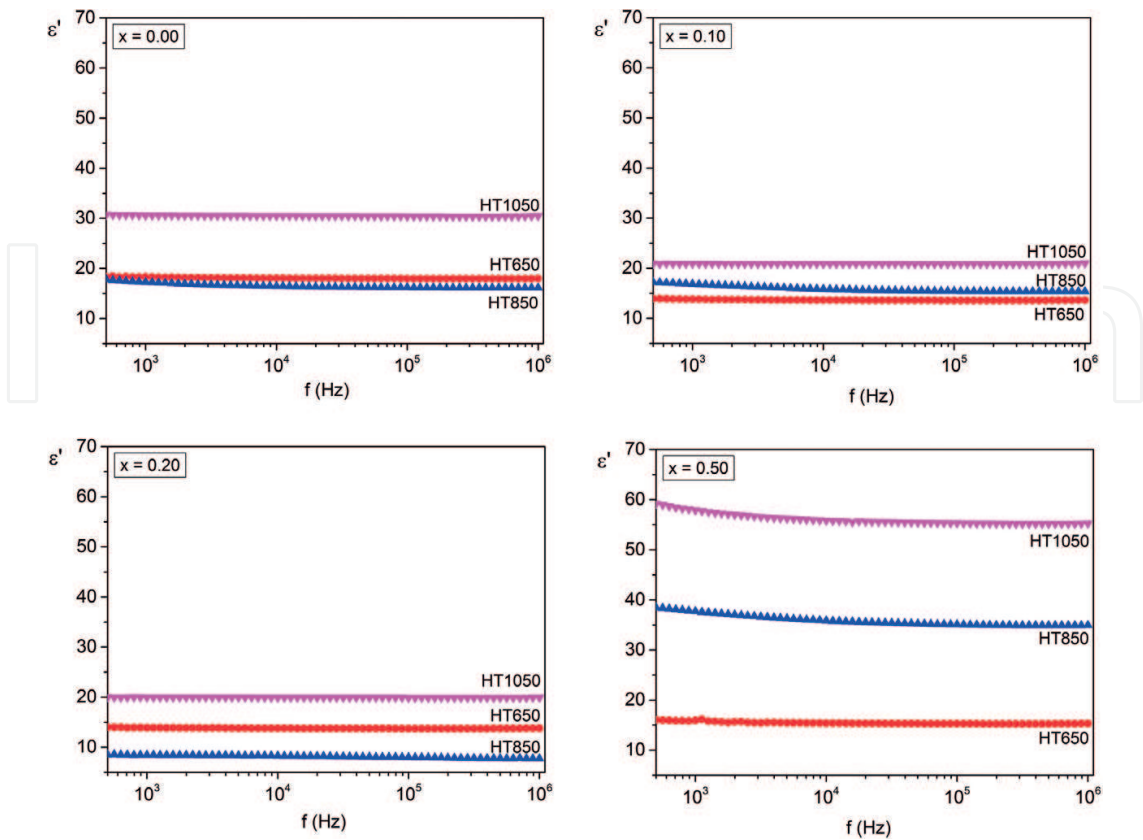


Figure 5. Frequency dependence of the real part of the complex permittivity, ϵ' , at $T = 300$ K.

For the host samples and for the samples with different amounts of europium, it is perceptible that the presence of triclinic BiNbO_4 leads to higher ϵ' values.

The highest dielectric constant occurs for the sample with $x = 0.50$, treated at 1050°C , where besides $\alpha\text{-BiNbO}_4$ and EuNbO_4 , an unidentified nonstoichiometric phase of bismuth niobate was detected.

The variation of the imaginary part of the complex permittivity with frequency, also at constant temperature $T = 300$ K and in the RF frequency range, is shown in **Figure 6**.

Except in the case of the sample with highest ϵ' , all the other samples are showing ϵ'' values lower than 1.

In general, the losses decrease with frequency, except in the sample with $x = 0.20$, treated at 850°C , where the shape of the curve indicates the occurrence of a relaxation process.

Figure 7 presents the real part of the complex permittivity at 2.7 GHz, at constant temperature $T = 300$ K, as function of x , for the prepared samples. The samples treated at 1050°C show the highest ϵ' , with the maximum ϵ' , 8.41 , occurring for the sample with $x = 0.20$. The calculated values indicate that the more influent parameter is the treatment temperature since the permittivity does not vary significantly with the amount of europium.

This increase of ϵ' for the highest treatment temperature can be attributed to the increase of crystallinity, combined with the formation of the high-temperature triclinic BiNbO_4 .

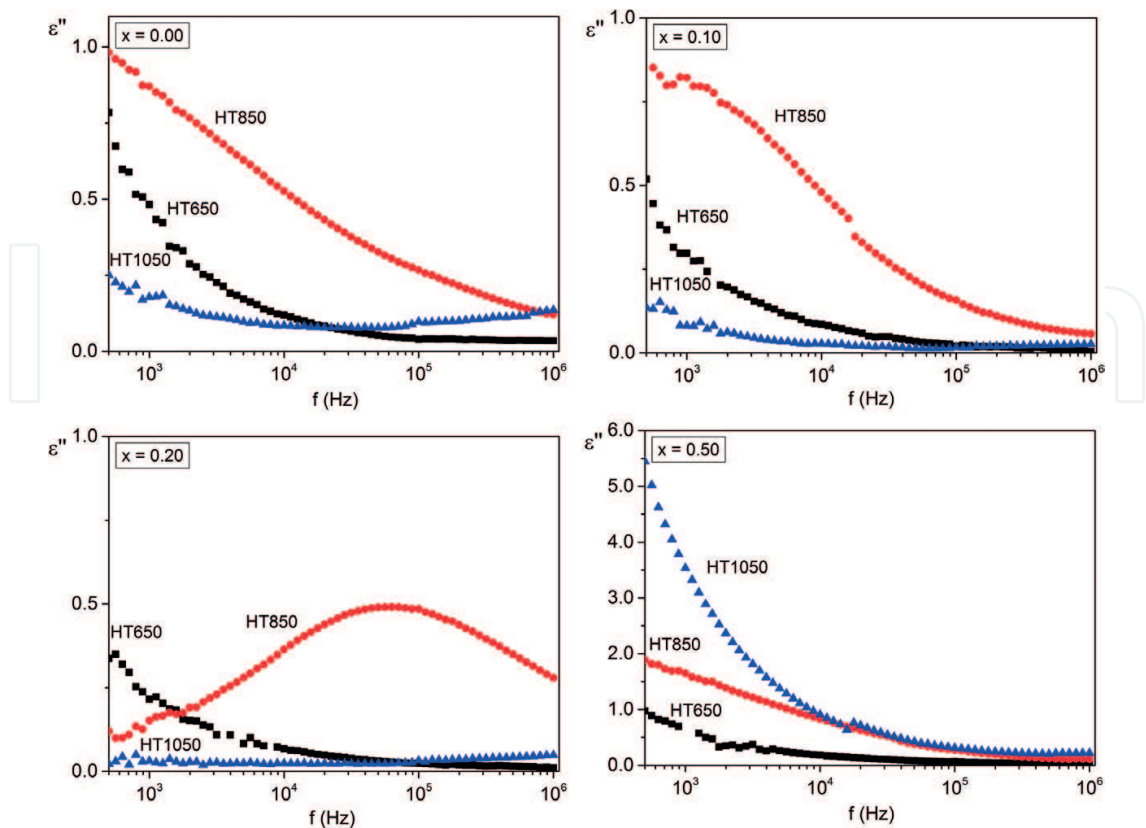


Figure 6. Frequency dependence of the imaginary part of the complex permittivity, ϵ'' , at $T = 300$ K.

In **Figure 8**, the variation of the imaginary part of the complex permittivity with frequency is presented. It can be seen that ϵ'' values are influenced by the amount of europium and also by the increase of the treatment temperature.

Table 2 resumes ϵ' and $\tan \delta = \frac{\epsilon''}{\epsilon'}$, for the different samples.

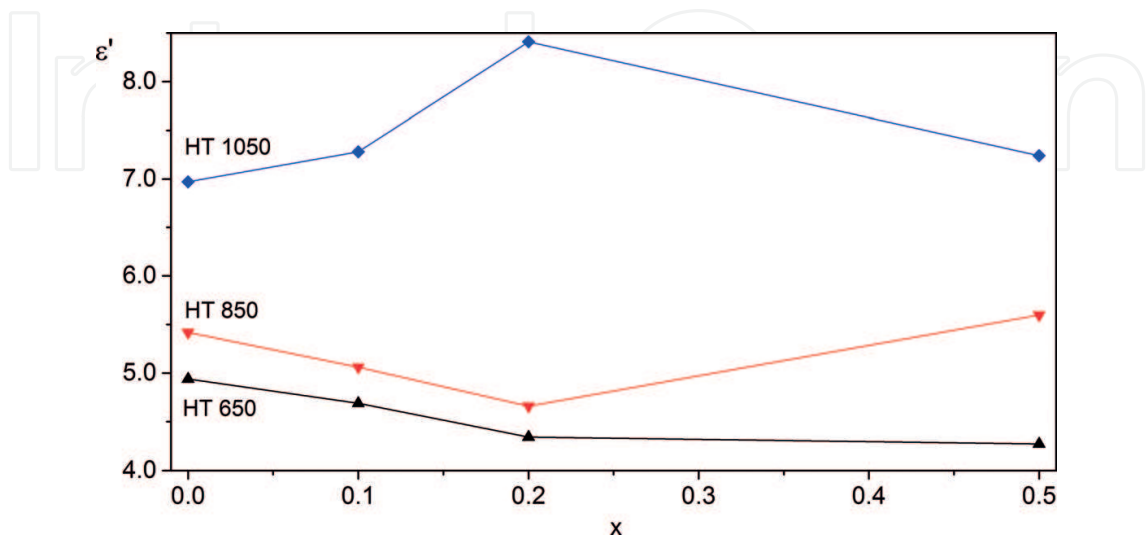


Figure 7. Calculated ϵ' for all treatment temperatures as a function of x value, at 2.7 GHz and 300 K.

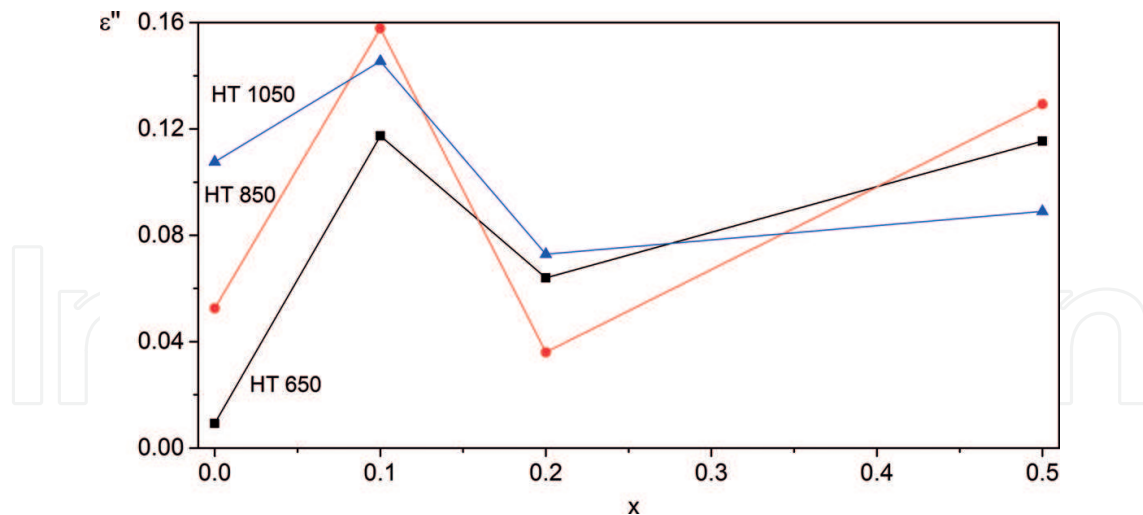


Figure 8. Calculated ϵ'' for all treatment temperatures as a function of x value, at 2.7 GHz and 300 K.

x	HT (°C)	100 kHz		1 MHz		2.7 GHz	
		ϵ'	$\text{tg } \delta$	ϵ'	$\text{tg } \delta$	ϵ'	$\text{tg } \delta$
0.00	650	17.95	2.2×10^{-3}	17.96	1.9×10^{-3}	4.94	1.9×10^{-3}
	850	16.18	1.6×10^{-2}	16.13	7.5×10^{-3}	5.42	9.7×10^{-3}
	1050	30.39	3.2×10^{-3}	30.48	4.5×10^{-3}	6.97	1.5×10^{-2}
0.10	650	13.56	1.5×10^{-3}	13.64	2.8×10^{-4}	4.69	2.5×10^{-2}
	850	15.42	1.0×10^{-2}	15.36	3.7×10^{-3}	5.06	3.1×10^{-2}
	1050	20.85	8.4×10^{-4}	20.97	1.2×10^{-3}	7.28	2.0×10^{-2}
0.20	650	13.71	1.7×10^{-3}	13.79	8.0×10^{-4}	4.34	1.5×10^{-2}
	850	7.98	6.1×10^{-2}	7.74	3.6×10^{-2}	4.66	7.7×10^{-3}
	1050	19.87	1.6×10^{-3}	19.89	2.5×10^{-3}	8.41	8.7×10^{-3}
0.50	650	15.27	4.3×10^{-3}	15.32	1.7×10^{-3}	4.27	2.7×10^{-2}
	850	35.08	7.8×10^{-3}	34.95	3.2×10^{-3}	5.6	2.3×10^{-2}
	1050	55.32	5.7×10^{-3}	55.25	4.0×10^{-3}	7.24	1.2×10^{-2}

Table 2. Calculated ϵ' and $\text{tg } \delta$ for the different samples, at 100 kHz, 1 MHz and 2.7 GHz, at 300 K.

Analysing the presented values, we can see that, for all the presented frequencies, the formation of high-temperature triclinic BiNbO_4 contributes to the increase of the permittivity, without the exacerbation of the dielectric losses.

The substitution of bismuth by europium does not contribute to significant changes in the dielectric losses of the samples, being the treatment temperature the most influent parameter.

Considering the samples treated at 650°C, it is visible that the introduction of europium is not advantageous, since the ϵ' values decrease and, in general, the losses increase. For this same

temperature, the increase of europium promotes the increase of the grains size, a morphologic alteration which is not reflected in the dielectric properties.

In the samples treated at 850°C, the reflection of the morphology changes in dielectric properties is perceptible mostly in the sample with $x = 0.50$. In these set of samples, the coalescence is noticeable; however, it is in the sample with the higher amount of europium that this phenomenon is more evident, which can explain the increase of the dielectric constant.

The samples treated at 1050°C show the higher dielectric constants, which can be related not only with the formation of the high-temperature triclinic BiNbO_4 but also with the growing of the grain size.

For the RF frequency regime, it is also perceptible that, for the samples treated at 1050°C, the increase of the dielectric constant can be related to the amount of europium introduced.

3.4. Conclusion

In this study, we have presented a structural, morphological and dielectric characterisation, in the RF and MW frequency regime, of $(\text{Bi}_{1-x}\text{Eu}_x)\text{NbO}_4$ samples, prepared by the sol-gel method and treated at three different temperatures, between 650 and 1050°C.

For the lowest treatment temperature, one can conclude that the introduction of europium is not an advantage since there is no improvement in the dielectric properties of the samples.

In the case of the intermediate heat treatment, the introduction of europium is advantageous but only for the sample with $x = 0.50$, with the increase of the dielectric constant, without significant increase of the losses.

The samples treated at 1050°C, where the triclinic bismuth niobate was identified, show the highest dielectric constant. In particular, in the case of the RF frequency regime, these sets of samples revealed that the introduction of a higher amount of europium can improve significantly the dielectric constant, without compromising the losses.

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