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Dielectric and Raman spectroscopy studies of $(Na_{0.5}Bi_{0.5})TiO_3$ lead-free ceramic

(Estudos de espectroscopia dielétrica e Raman de cerâmica $(Na_{0,5}Bi_{0,5})TiO_3$ isenta de chumbo)

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Abstract

In this study, samples of sodium bismuth titanate $(Na_{0.5}Bi_{0.5})TiO_3$ (NBT) have been prepared using the solid-state technique. Sintering was done at 1200 °C for 4 h in air atmosphere. X-ray diffraction analysis carried out at room temperature showed the formation of a single-phase compound with a rhombohedral crystal system. Dielectric and Raman spectroscopic characterizations have been performed as a function of temperature. The dielectric study showed the existence of a diffuse phase transition around 330 °C. The Raman spectra was fitted to the individual Raman peaks. The obtained peaks were analyzed by observing the changes in their respective peak positions and intensities with increasing of temperature. At high temperatures, the results showed discontinuous changes in the phonon frequencies across the rhombohedral-tetragonal transition.

Keywords: NBT ceramic, perovskite, dielectric properties, Raman spectroscopy.

Resumo

Neste estudo, amostras de titanato de bismuto e sódio $(Na_{0,5}Bi_{0,5})TiO_3$ *(NBT) foram preparadas usando a técnica de estado sólido. A sinterização foi feita a 1200 °C por 4 h ao ar. A análise de difração de raios X realizada à temperatura ambiente mostrou a formação de um composto de fase única com um sistema cristalino romboédrico. Caracterizações dielétricas e espectroscópica Raman foram realizadas em função da temperatura. Estudo dielétrico mostrou uma existência de transição de fase difusa em torno de 330 °C. Os espectros Raman foram ajustados aos picos Raman individuais. Os picos obtidos foram analisados observando-se as mudanças em suas respectivas posições e intensidades de pico com o aumento da temperatura. Em altas temperaturas, os resultados mostraram mudanças descontínuas nas frequências de fônons ao longo da transição tetragonal-romboédrica.*

***Palavras-chave**: cerâmica NBT, perovskita, propriedades dielétricas, espectroscopia Raman.*

INTRODUCTION

Due to the toxicity and high vapor pressure of lead (Pb) oxide during processing in lead-based piezoelectric ceramics, researchers have shown their keen interest in developing lead-free piezoelectric ceramics which are biocompatible and environment-friendly [1]. Among various lead-free materials, sodium bismuth titanate, $(Na_{0.5}Bi_{0.5})TiO_3$ (NBT) is considered to be one of the important ferroelectric materials due to its: i) strong ferroelectric properties at room temperature; ii) high remnant polarization (Pr=38 $\mu C.cm^{-2}$); and iii) high Curie temperature [2, 3]. Sodium bismuth titanate (NBT) was first studied by Smolensk et al. in 1961 [4]. It was studied continuously by several authors in recent years [5, 6]. In the lead-based ferroelectric system, Pb^{2+} (with [Xe]= $4f^{14}\,5d^{10}\,6s^2$ electronic configuration) is responsible for high polarization due to its lone pair effect of $6s^2$ valence shell electron. It may be pointed out that Bi^{3+} has an electronic configuration similar to that of lead in $(Na_{0.5}Bi_{0.5})TiO_3$. This motivated the scientific community to study the NBT system as a replacement of

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lead-based materials.

The NBT shows a sequence of phase transitions as a function of temperature [7]. The crystal structure of NBT on decreasing temperature is transformed from: i) cubic (Pm3m) to tetragonal (P4bm) around 540-520 °C; and ii) tetragonal to rhombohedral (R3c) around 320 °C with a diffuse phase transition (DPT). The diffuse phase transition occurs due to the coexistence of phases in the temperature range 225-400 °C [8]. NBT is ferroelectric at room temperature. On increasing temperature ferroelectric to antiferroelectric phase transition occurs at 200 °C [9]. The second transition occurs around 320 °C which corresponds to a transition from the antiferroelectric to paraelectric phase [10]. The high-temperature anomaly (around 530 °C) may correspond to the transformation of tetragonal to cubic structure [10, 11]. This system attracts great attention and continues to be studied as possible lead-free piezoelectric compounds.

Complex impedance spectroscopy is helpful for understanding the dielectric properties of ferroelectric materials [12]. Raman spectroscopy has been used as an effective technique to investigate the structural evolution in perovskite-type solid solution ceramics. In literature, there is not an important number of quantitative analysis of the spectra at elevated temperatures concerning the identification of the phase transition [13]. In this paper, we report our work on the dielectric characterization of $(Na_{0.5}Bi_{0.5})TiO_3$ lead-free ceramic synthesized and prepared by solid-state reaction processing technique. Considering the peculiar phase transition of NBT, this work is also an attempt to study the behavior of phonons at different temperatures using Raman spectroscopy.

EXPERIMENTAL PROCEDURE

Sodium bismuth titanate NBT was synthesized following the solid-state reaction route. The starting powders Na_2CO_3 (reagent grade, Sigma-Aldrich, 99.5%), Bi_2O_3 (Aldrich, 99.9%) and TiO_2 (Riedel-Dehaen) were weighed in the proper amounts to form $Bi_{0.5}Na_{0.5}TiO_3$. The powders were mixed with planetary milling in ethanol using agate balls as milling media for 1 h. The milled powders were calcined at 825 °C for 4 h in air atmosphere. After calcining, the powder was ball-milled again and then isostatically pressed. The compacted samples were sintered at 1200 °C for 4 h in air atmosphere. The as-prepared samples were cut in disks shape of 12 mm in diameter and 1 mm in thickness. The crystal structures of sintered ceramics were determined by means of X-ray diffractometer (Rigaku, Miniflex) using CuKα radiation. The microstructure of the sintered ceramics was observed with a scanning electron microscope (SEM, Hitachi, S-3500N). Raman scattering experiments were performed using a micro Raman spectrometer (Labram, HR800), working in a back-scattering configuration, equipped with a He-Ne (λ=633 nm) laser. The spectral resolution of the system was 3 cm^{-1}. Silver electrodes were applied on polished samples to provide good electrical contact. The variation of dielectric constant with temperature at different frequencies was studied from room temperature to 550 °C using a computer-controlled impedance analyzer (Agilent, 4284A).

RESULTS AND DISCUSSION

Structure and microstructure: Fig. 1a shows the X-ray diffraction (XRD) pattern of the NBT sample at room temperature. It indicates the formation of a single phase with perovskite structure. The XRD pattern was indexed on the basis of rhombohedral symmetry with space group R3C (JCPDS file No. 36-340). A good agreement was observed between the X-ray peak positions and the reference pattern. Fig. 1b shows the microstructure of NBT ceramic. The result showed that grains were large, having a diameter in the range of 3 to 4 μm.

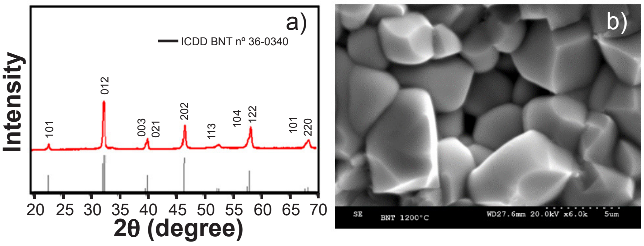

Figure 1: X-ray diffraction pattern (a) and scanning electron micrograph (b) of the NBT ceramic.
[Figura 1: Padrão de difração de raios-X (a) e micrografia eletrônica de varredura (b) da cerâmica NBT.]

Dielectric properties: Fig. 2 shows the variations of the dielectric permittivity, ε_r, and dielectric loss, tgδ, as a function of temperature for various frequencies (10 kHz to 1 MHz). It can be seen that ε_r increased with increase in temperature, attained its maximum value at temperature T_m (~330 °C) and then decreased (Fig. 2a). This dielectric anomaly is representing the antiferroelectric-paraelectric phase transition of diffuse nature. All the peaks appeared at the same temperature irrespective of the frequency. It was also observed that at around 190 °C (called depolarization temperature, T_d), there was a bifurcation in dielectric constants for different frequencies. This may be due to the ferroelectric to antiferroelectric phase transition of NBT. The dielectric loss, tgδ, increased with the increase of temperature particularly beyond 250 °C (Fig. 2b). The increase in dielectric loss at higher temperature might be due to the increase in electrical conductivity. The important mechanism of ionic conductivity in this system is the movement of ions which are the current carriers. It has been long known that the alkali ion is a good current carrier in ceramics; therefore, this ion plays an important role in the conductivity of NBT ceramics, since the Na^+ ions move easily upon heating, resulting in the increase in conductivity with increasing temperature of the sample. The order of diffusivity or disorderness in the materials is analyzed by modified Curie-Wiess law: $(1/\varepsilon_r-1/\varepsilon_m)=(T-T_m)^\gamma/C$, where γ is the diffusivity and C is the Curie-Weiss constant, ε_r is the dielectric constant at temperature T, and ε_m is its maximum at T_m. The value of γ (diffusivity) is calculated from the slope of $\ln(1/\varepsilon_r-1/\varepsilon_m)$ with $\ln(T-T_m)$. In general, the diffusivity lies between 1 and 2. In the case of $\gamma=1$, a normal Curie-Weiss law is obtained and represents a normal ferroelectric-paraelectric phase transition. For complete diffusive phase transitions the value of $\gamma=2$. The value of γ can be employed to describe the degree of diffusivity of the phase transition. Here the calculated value of γ was found to be 1.58 for 100 kHz, which clearly showed that the phase transition in NBT is a diffuse phase transition (DPT) [14].

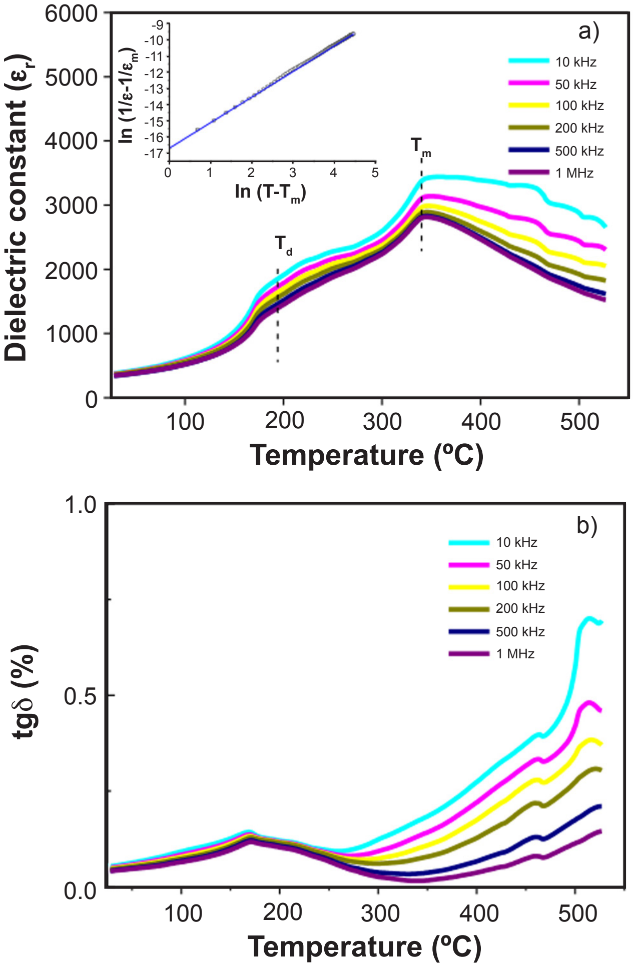

Figure 2: Temperature dependence of: a) dielectric constant, ε_r (inset: diffusivity curve at 100 kHz); and b) dielectric loss, tgδ, of NBT ceramic at different frequency.

[Figura 2: Dependência da temperatura da: a) constante dielétrica, ε_r *(inserto: curva de difusividade em 100 kHz); e b) perda dielétrica, tgδ, da cerâmica NBT em diferentes frequências.]*

Raman investigation: NBT is the classic example of rhombohedral ferroelectric material at room temperature and belongs to the space group R3c. The irreducible representation of optical phonons in this phase is $\Gamma_{opt}=4A_1+5A_2+9E$, where the A_1 and E modes are both Raman and infrared active, whereas the A_2 mode is inactive both in Raman and infrared [13]. Fig. 3 represents the Raman spectrum of NBT ceramics at room temperature performed in the range from 90 to 1000 cm^{-1}. The deconvolution of the spectrum of pure NBT with LabSpec 5 software using pseudo-Voigt function showed six vibration modes observed at 133, 276, 520, 584, 780 and 845 cm^{-1}. These results were in good agreement with those reported by other authors [13, 15-17]. The number of modes observed was less than that predicted. This could be either due to accidental degeneracy of phonon frequencies or insufficient intensities arising from small polarizability of several modes. These modes were assigned to the Na-O, Ti-O and to the oxygen octahedral vibrations/rotations, respectively. We noted that in the recent literature the bands observed at high frequencies (780 and 845 cm^{-1}) are attributed also to some oxygen defects [18]. Due to the high mass of the bismuth atom, a Bi-O band would be located at very low frequencies and was not observed in our experimental conditions.

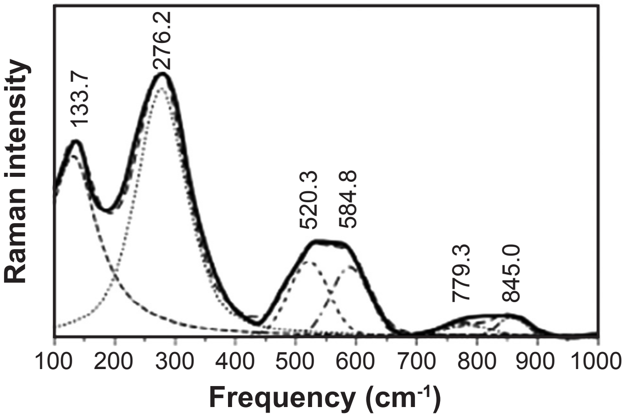

Figure 3: Raman spectrum of NBT at room temperature and the fitting of the spectrum to the pseudo-Voigt function.

[Figura 3: Espectro Raman de NBT à temperatura ambiente e o ajuste do espectro à função pseudo-Voigt.]

The Raman spectra at different temperatures (25 to 450 °C) are depicted in Fig. 4. The dependences of the mode frequencies during the heating cycle are shown in Fig. 5. As mentioned earlier, NBT undergoes a phase transition to the tetragonal structure (P4bm) at around 320 °C. For this structure the expected optical phonons are $\Gamma_{opt}=4A_1+3A_2+1B_1+3B_2+8E$, where A_1, B_1, B_2 and E modes are Raman active [13]; thus, as many as 16 Raman active modes are expected in this phase. The present Raman spectra show only three modes above 350 ºC. The first lattice mode at 133 cm^{-1} (labeled by an arrow) located at the region between 100 and 200 cm^{-1} attributed to the Na-O bonds of the A-site vibration was found to disappear at high temperature (Fig. 5a); this is discussed later. The Ti-O vibration mode (at 276 cm^{-1}) located at the region from 200 to 300 cm^{-1} (Fig. 5a) displayed a gradual broadening and decreased in intensity with increasing temperature up to 350 ºC. This behavior was due to the increase of the structural disorder of the Ti-O bond of the TiO_6 octahedra; such behavior may be associated with the nucleation of nanodomains within the ferroelectric matrix, as suggested in previous works [19-22]. Above 350 °C, no changes were observed.

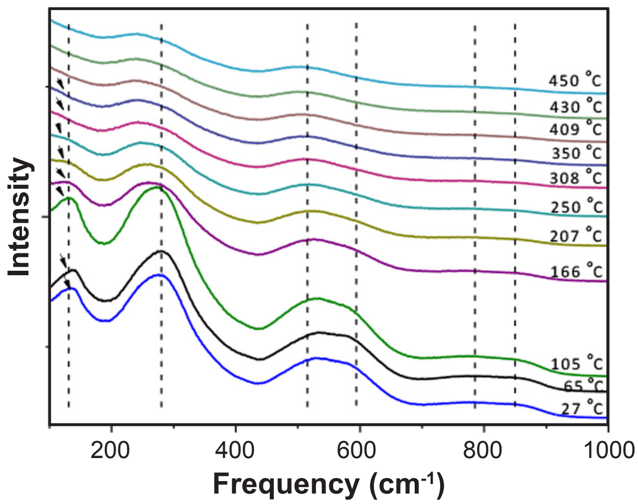

Figure 4: Raman spectra of NBT at different temperatures.
[Figura 4: Espectros Raman de NBT em diferentes temperaturas.]

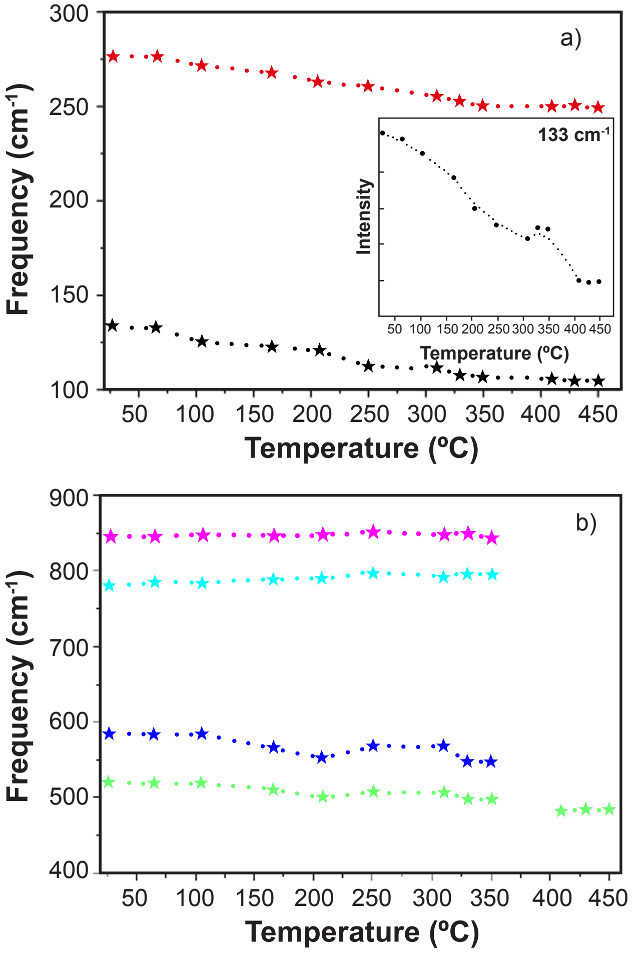

Figure 5: Evolution of the Raman mode frequencies with temperature: a) 100-300 cm^{-1}; and b) 400-900 cm^{-1}.
[Figura 5: Evolução das frequências do modo Raman com a temperatura: a) 100-300 cm^{-1}; e b) 400-900 cm^{-1}.]

The spectral region from 400 to 700 cm^{-1} (Fig. 5b) was particularly interesting because it is well known in perovskite oxides that the high-frequency modes are commonly dominated by vibrations of oxygen atoms when the cations are almost at rest [23]. For this reason, one can expect that they do not depend on the mass of anion. The broad double peak in this region was deconvoluted into two peaks at room temperature. The first peak at approximately 520 cm^{-1} (Fig. 5b) exhibited no noticeable position shift with temperature up to 350 °C, but it gradually became broader. Above this temperature, a small shift to lower frequencies was observed. One can also see that this peak displayed a discontinuous decrease in the frequencies. This suggests that the phase transition occurred at around 350 °C, close to that reported using neutron diffraction result [8]. The second peak at 584 cm^{-1} showed a decrease in intensity and vanished above 350 °C. No remarkable changes with temperature were observed for the two deconvoluted peaks at 780 and 845 cm^{-1} for NBT, apart from their broadening and weakening in the frequency region between 700 and 900 cm^{-1} (Fig. 5b). Above 350 °C these peaks became undetectable. As mentioned earlier, the 133 cm^{-1} peak exhibited dramatic changes in intensity and shape upon heating. The integrated intensity for the 133 cm^{-1} peak as a function of temperature is shown in the inset of Fig. 5a for NBT. The 133 cm^{-1} peak showed a high decrease in intensity on heating up to 350 °C; above this temperature, the intensity was very low. One can also see that the intensity exhibited anomaly around 350 °C consistent with the changes in the frequencies of other modes (Fig. 5) across the transition. The persistence of the 133 cm^{-1} mode intensity above 350 °C could be due to the coexistence of two phases [8].

CONCLUSIONS

The polycrystalline sample of $(Na_{0.5}Bi_{0.5})TiO_3$ (NBT) was studied by dielectric and Raman spectrum measurements as a function of temperature. The dielectric study showed the phase transition of NBT is of diffuse type. The Raman spectra showed several prominent modes assigned to the Na-O, Ti-O and oxygen octahedral vibrations/rotations. The modes in the high-frequency range exhibited discontinuous changes across the rhombohedral-tetragonal transition while a lattice mode at 133 cm^{-1} was found to exhibit anomaly in its intensity.

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