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2007 J. Phys.: Condens. Matter 19 026207

(http://iopscience.iop.org/0953-8984/19/2/026207)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **19** (2007) 026207 (9pp) doi:10.1088/0953-8984/19/2/026207

Diffuse phase transition and relaxor behaviour of textured $Sr_{0.63}Ba_{0.37}Nb_2O_6$ ceramics

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Received 6 September 2006
Published 15 December 2006
Online at stacks.iop.org/JPhysCM/19/026207

Abstract

Textured $Sr_{0.63}Ba_{0.37}Nb_2O_6$ ferroelectric ceramics, with relaxor characteristics, were fabricated by the hot forging process. The analysis of the complex dielectric constant as a function of the temperature revealed the presence of three dielectric anomaly regions. In addition, the relaxor behaviour of this ceramic was also observed at microwave frequencies, evidencing the existence of active polar regions in a broad frequency range. Using the Vogel–Fulcher approximation, physical parameters such as the freezing temperature (T_f) were estimated. It was verified that the mechanisms of the dielectric response, in the microwave frequency range, are also affected by the presence of compositional fluctuations and local electric fields. A phenomenological equation was applied in order to investigate the nature of the polarization mechanisms at low frequencies. Also, a qualitative model was proposed to explain the anisotropic behaviour observed in the phase transition diffuseness between the different ceramic directions.

1. Introduction

Strontium barium niobate $Sr_xBa_{1-x}Nb_2O_6$ (SBN$x/1-x$) constitutes a solid solution for $0.25 < x < 0.75$ with tetragonal tungsten bronze structure [1]. These materials have a high potential to be used in important technological applications, such as electro-optic, pyroelectric, piezoelectric and photo-refractive devices [2–4]. In addition, the macroscopic properties of SBN single crystals are known to be anisotropic, with strongest dielectric and pyroelectric responses obtained along the [001] direction (the direction of the macroscopic polarization) [5]. SBN materials have also shown strong frequency dependence of the complex dielectric constant ($\varepsilon^* = \varepsilon' - j\varepsilon''$; real, ε' and imaginary, ε'' components), which is a typical feature of relaxor ferroelectrics. Fan *et al* [6] identified three dielectric relaxation processes in the SBN system at different temperature ranges. On the other hand, Huang *et al* [5] observed a vitreous behaviour in SBN single crystals, which was attributed to the chemical disorder inherent to the SBN structure, causing polarization fluctuations. Dec *et al* [7], using the concept of dynamically correlated domains [8], concluded that the SBN system has relaxor characteristics, which were associated to the spatial fluctuations of random electric fields.

For relaxor ferroelectrics and glassy systems the dielectric relaxation can be described according to the Vogel–Fulcher (VF) expression [9, 10];

$$\nu = \nu_0 \exp\left[-\frac{E_a}{k_B(T - T_f)}\right] \tag{1}$$

where ν_0 represents the inverse of the relaxation time (Debye's frequency); E_a is the average of the activation energies for polarization fluctuations of an isolated polar cluster (nanometre-scale polar region); T_f the static freezing temperature and k_B Boltzmann's constant. The VF expression may be interpreted as a typical Debye relaxation process with a temperature-dependent activation energy [10].

The parameterization of the ε' versus T (real dielectric constant versus the temperature) curves, for temperatures above the temperature of the maximum real dielectric constant (T_m), is one of the most used tools to investigate the characteristics of the diffuse phase transition. In this way, some propositions have been reported in the literature, such as that developed by Kirilov and Isupov [11], which is based on the compositional fluctuation model [12]. Recently, Santos and Eiras [13, 14] proposed a phenomenological equation, which allows one to fit the ε' versus T curves around and above T_m. The Santos–Eiras expression (equation (2)) uses two parameters (Δ and ξ), which are related to the transition diffuseness and to the character of the phase transition, respectively.

$$\varepsilon' = \frac{\varepsilon'_m}{1 + (\frac{T - T_m}{\Delta})^{\xi}}. \tag{2}$$

Because of the anisotropic behaviour observed in the physical properties of the SBN system, the fabrication process of textured SBN ceramics (ceramic bodies with oriented grains) has become an interesting issue [15–17]. Taking into account that the grains in the polycrystalline SBN materials preferentially grow along the [001] direction [18], one of the methods used to obtain textured SBN ceramics is the hot forging technique. The pressure applied during the firing process limits the grain growth along the pressing direction in favour of grain growth in the perpendicular directions with respect to the pressing axis [17]. Therefore, textured SBN ceramics made by the hot forging technique show an anisotropic response of the dielectric properties between the parallel and the perpendicular directions with respect to the pressing axis [16, 17].

Despite the existence of some works concerning the relaxor behaviour and the transition diffuseness in SBN materials, these were limited to the frequency range below 20 MHz [5–7, 13]. To the best knowledge of the authors, there are no reports in the current literature including microwave dielectric properties in SBN materials. Therefore, the objective of the present work is to investigate in detail the relaxor character and the diffuse phase transition of SBN63/37 textured ceramics, through the temperature and the frequency dependence of the real and imaginary components of the dielectric constant in a broad frequency interval, including low and high (microwave) frequencies. In order to better understand the physical mechanism responsible for the relaxor character and the correlation between the low and the high frequency dielectric response, the results obtained were analysed according to the models currently discussed in the literature.

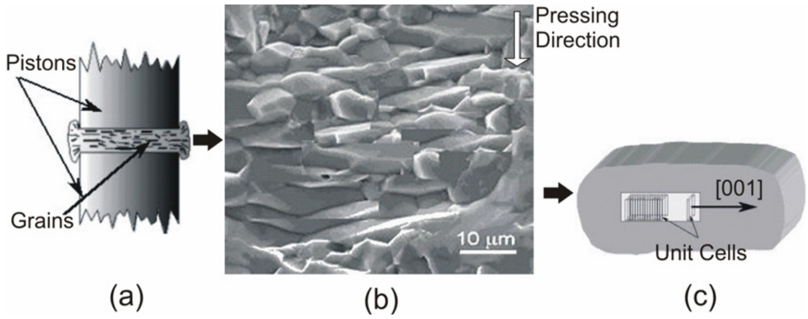

Figure 1. (a) Schematic representation of the grain arrangement during the hot forging process. (b) Fracture surface of the SBN ceramic used in this work. (c) Schematic representation of the grain growth habit along the [001] direction.

2. Experimental procedure

Ceramic powders with nominal formula $Sr_{0.63}Ba_{0.37}Nb_2O_6$ were prepared by the solid state reaction method, as previously reported [19]. Analytical grade precursors, such as $Ba(NO_3)_2$, Nb_2O_5 and $SrCO_3$, were mixed in a ball mill within polyethylene pots, containing isopropyl alcohol and stabilized ZrO_2 rods. The mixture was dried, calcined twice at 1200 °C for 3 h and milled again for 24 h. The powders were compacted into discs (14 and 12 mm in diameter and thickness, respectively) by uniaxial pressing (250 MPa). After that, isostatic pressing (125 MPa) was applied in order to minimize the density gradients. The texture of the SBN63/37 ceramic was obtained through the hot forging technique. The applied pressure, during the sintering of the SBN ceramic (see figure 1(a)), conditioned the preferential grain growth along the perpendicular directions with respect to the pressing direction, as illustrated in figure 1(b) for the fracture surface of the SBN ceramic. In addition, the grain growth habit in SBN ceramics, schematically illustrated in figure 1(c), allowed the crystallographic texture of the material because the (001) planes were preferentially positioned in the perpendicular directions with respect to the pressing axis (∼40% higher than in a conventionally sintered SBN ceramic [17]). Therefore, when the ceramics were measured in the perpendicular or parallel directions relative to the pressing axis, an anisotropic response of the dielectric properties was observed. Detailed descriptions of the method used, and the density, microstructure, structural characteristics and texture level for this ceramic, were reported in a previous work [17].

For the physical characterizations, hot forged ceramic samples were cut from the original pellet and labelled as SBN (∥) and SBN (⊥) in which the direction is related to the pressing axis, as illustrated in figure 2.

Computer assisted dielectric characterization was performed on the gold sputtered ceramics, as a function of the temperature, using an HP 4194A impedance gain phase analyser, covering a frequency range of 100 Hz–10 MHz. The measurements were performed over a temperature range of 20–450 K, on cooling, at a constant rate of 4 K min^{-1}.

On the other hand, high frequency dielectric measurements were performed in the temperature range of 300–450 K using an HP 8719C network analyser in the frequency range of 50 MHz–2 GHz. In order to obtain the dielectric response, a 50 Ω coaxial line was employed by using the reflectometry technique [20]. For determining the frequency dependence of the reflection coefficients (Γ', Γ''), a careful compensation procedure was carried out to avoid spurious reflections that might result by transmission line discontinuities and to eliminate the

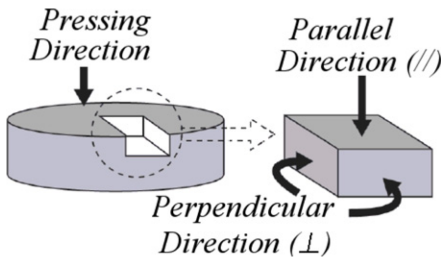

Figure 2. Cut directions for SBN hot forged ceramics.

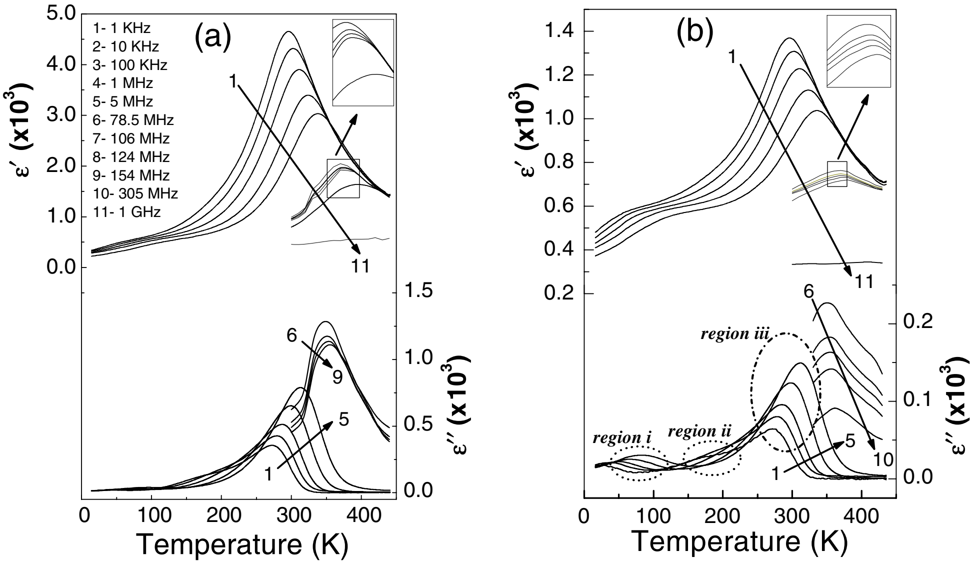

Figure 3. Complex dielectric constant as a function of the temperature and frequency for different cuts of the SBN63/37 textured ceramic. (a) SBN (⊥) and (b) SBN (‖).

effect of the resistances and capacitances of the sample holder [21]. Three different HP standard terminations (open, short and 50 Ω), with reflection coefficients of 1, −1 and 0, respectively, were used to calibrate the system in the frequency range investigated. The complex dielectric constant was determined from the measured complex reflection coefficient [21].

3. Results and discussions

Figure 3 illustrates the behaviour of the real and imaginary components of the dielectric constant as a function of the temperature and the frequency of the textured SBN63/37 ceramic, for the different cut directions. The overall dielectric behaviour agrees with that expected for the SBN system, where three dispersion regions in the whole temperature range studied can be observed: the first, for temperatures below 100 K, labelled as region i, the second, between 130 and 230 K, labelled as region ii, and the third, observed around T_m, labelled as region iii. The relaxation process observed in region i has been observed by several authors [6, 22] and it is regularly associated to a structural phase transition from the tetragonal (4*mm*) to the monoclinic (m) phase, because of the oxygen octahedra rotation in the *a*–*b* plane of the unit cell. Therefore,

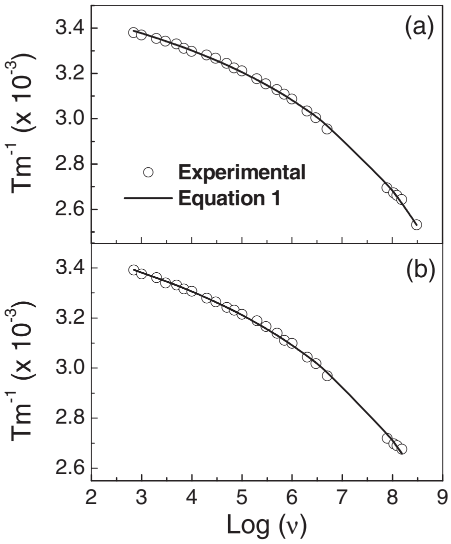

Figure 4. Frequency dependence of T_m (T_m^{-1} versus log ν) for the SBN63/37 ceramics. The fitting curves were generated using equation (1). (a) SBN (⊥); (b) SBN (∥).

the polarization vector leans towards a small angle in the [110] direction, causing the dielectric dispersion in that temperature range. On the other hand, a similar relaxor process to that observed for region ii was reported by Bursill and Lin [23, 24], which was associated to the existence of incommensurable superstructures in the SBN system, for the temperature range 93–423 K. According to these authors, in this temperature region the oxygen ion modulation in the $(0, 0, z/2)$ plane is the base of that incommensurability. The modulation causes the duplication of the tetragonal unit cell in the [001] direction, favouring the inclination of the oxygen octahedron in the *a–b* plane, and consequently a relaxation process may be observed in this temperature range (region ii).

The ferroelectric–paraelectric phase transition occurs in a wide temperature range around T_m, which is a characteristic of systems with a diffuse phase transition (region iii). On the other hand, a decrease of ε', together with the increase of T_m, was verified with the increase of frequency. A difference of about 90 K for T_m, between the measurements performed at 1 kHz and 300 MHz, can be observed. As can be seen, the relaxor behaviour remains up to microwave frequencies (about 300 MHz), which evidences the existence of polar regions that can be still activated in the high frequency region for this material. This observed behaviour is an interesting result, which has not been explored in the literature, possibly due to the difficulties associated with the instrumentation procedures for high frequency measurements [21]. The analysis of the dielectric behaviour of the high frequency activated polar regions could be a starting point for a better understanding of the responsible mechanisms for the dielectric relaxation in relaxor materials, which nowadays constitutes a topic that still remains in discussion.

Figure 4 shows the frequency (ν) dependence of T_m plotted in the T_m^{-1} versus log ν form, for the SBN63/37 textured ceramics. The fitting results obtained by using the VF equation (see equation (1)) have also been added to figure 4 and are represented by solid lines. As can be seen, the VF fitting reproduces the experimental results with good accuracy, for all the frequency range analysed. The activation energy distribution obeys the same VF law for both low and high (microwave) frequencies ranges, evidencing that the mechanisms responsible for the dielectric

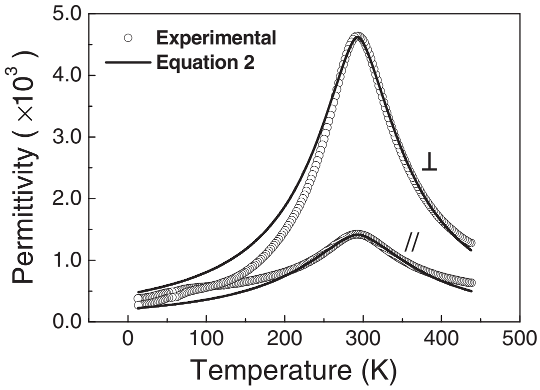

Figure 5. Real component of the dielectric constant (ε') as a function of the temperature (at 1 kHz) and generated curves using equation (2) for the SBN63/37 ceramic cut in different directions.

Table 1. Parameters from the fitting curves (equation (1)).

Sample	ν_0 ($\times 10^9$ Hz)	T_f (K)	E_a (eV)
SBN ⊥	6.3 ± 0.1	247 ± 2	0.035 ± 0.001
SBN ‖	7.0 ± 0.1	243 ± 3	0.037 ± 0.001

Table 2. Parameters (ξ, Δ and Γ) obtained from the fitting of the ε' versus T curves, at 1 kHz, using equation (2) (calculated (Γ_{TH}) and experimental (Γ_{EXP}) half-widths at half-height).

Sample	$\xi \pm 0.01$	Δ (K)	Γ_{TH} (K)	Γ_{EXP} (K)
SBN63/37 ⊥	1.60	73 ± 1	58 ± 1	58 ± 3
SBN63/37 ‖	1.60	98 ± 1	78 ± 1	79 ± 3

behaviour in the microwave region are also affected by the presence of random electric fields and compositional fluctuations. These factors cause the relaxor behaviour at low frequencies, which are now also verified for microwaves frequencies. The fitting parameters are shown in table 1. The average activation energy is the same for both parallel and perpendicular directions, when uncertainties are taken into account, indicating that the energy necessary to change the polarization configuration of the polar region is not dependent on the crystallographic orientation for the SBN textured ceramic (at least for the texture level reached in this work). In addition, the freezing temperature (T_f) is found to be approximately 50 K lower than T_m ($T_m = 296$ K, at 1 kHz), indicating the transition diffuseness.

The temperature dependence of the real component of the dielectric constant for the SBN63/37 ceramic, at 1 kHz, can be observed in figure 5. In addition, the fitting of the experimental curves by using equation (2) is also shown in the same figure 5. In all the cases, the experimental points were successfully reproduced by the generated curves for temperatures around and above T_m, which is the temperature range of interest. The fitting parameters ξ, Δ and Γ (defined as the half-width at half-height), are listed in table 2. The likeness between Γ_{TH} and Γ_{EXP} proves the applicability of the Santos–Eiras equation [13, 14] for the textured SBN ceramics.

The same value for the ξ parameter (1.60) was obtained for both parallel and perpendicular directions of the SBN63/37 ceramic. The ξ parameter ($1 \leqslant \xi \leqslant 2$) represents the character of the phase transition. It can take the limit values of 1 for normal ferroelectrics with a non-

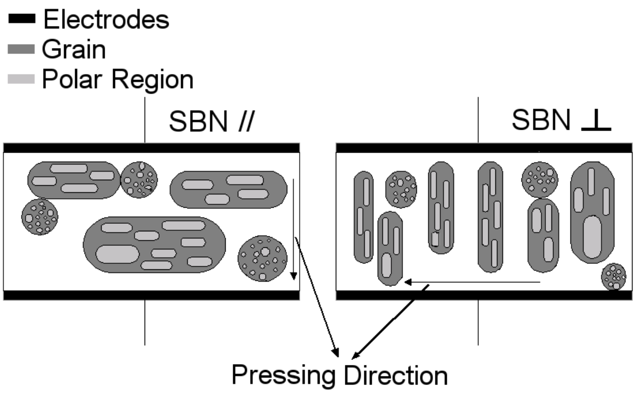

Figure 6. Schematic representation of the polar region configuration for the textured portion of the SBN ceramics in different cut directions.

diffuse phase transition, which obey the Curie–Weiss law, and 2 for relaxor ferroelectrics with a complete diffuse phase transition, where the interactions between the polar regions are neglected or frustrated [13]. Therefore, it can be considered that the low frequency dielectric behaviour, observed for the SBN ceramic studied, at temperatures around and above T_m, originates from an intermediate configuration of the polar regions, between the aforementioned limit cases, showing a so-called 'incomplete' diffuse phase transition. In this situation, when the material is cooled from the paraelectric to the ferroelectric region, the interacting ferroelectric clusters start to be formed at temperatures higher than T_m. Furthermore, due to the interaction between the ferroelectric clusters, other micro-regions are induced to be formed, consequently increasing the number, interaction and creation rate. In SBN ceramics, the compositional disorder caused by the random occupation of the Sr^{2+} and Ba^{2+} ions in the A_2 sites, together with the structural defects inherent to the ceramic processing, give rise to the different size and shape of the polar regions inside the material. On the other hand, local random electric fields appear to involve these polar regions. These aspects cause a distribution of activation energies, that is to say, a distribution of the energy necessary to change the polar region orientation. Consequently, the relaxor behaviour and a diffuse phase transition can be observed for this material.

From the analysis of the Δ parameter, which characterizes the transition diffuseness, an increase of this parameter for the SBN (∥) sample with respect to that obtained for the SBN (⊥) sample can be observed. An analogous behaviour has been reported for SBN single crystals [25], where an increase of the Δ parameter in the *a* (or *b*) direction of the unit cell, with respect to the observed for the *c* direction (polarization direction), was obtained. In SBN materials the polar regions have a needle-like shape [26, 27] arranged along the grain length [18, 26], with the polarization direction along its length (see figure 1(c)). Therefore, the textured portion of the SBN ceramic (∼40%) must have a configuration of the polar regions, for the different cut directions, similar to that illustrated in figure 6, where the grains represented with circles have a long shape with length perpendicular to the sheet plane.

Considering the experimental result, apparently the polar region configuration of the SBN (∥) ceramic favours the transition diffuseness. According to the model assumed in this work, the main causes of the relaxor behaviour and the transition diffuseness are the random size of the polar regions and the presence of local electric fields around these regions, as mentioned above. It has been reported in the SBN system that quadrupolar fields, which

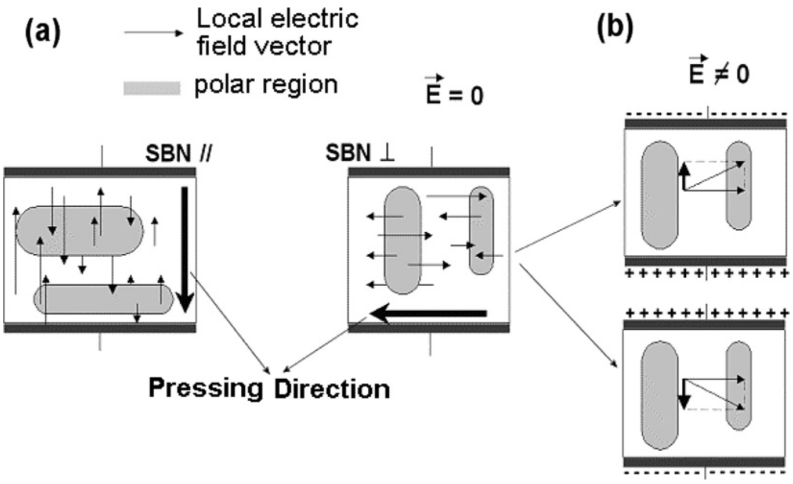

Figure 7. (a) Schematic representation of the local electric field orientation for SBN ceramics cut in different directions. (b) SBN (⊥) configuration under the action of an alternate external electric field.

are random in the *a–b* plane, may break the translational invariance of the polarization in the *a–b* plane [26]. However, long-range translational invariance might remain in the *c* direction, being the main cause for the formation of nano-polar regions with a needle-like morphology. In this way, the situation for the different measured directions (∥ or ⊥) should be similar to that schematically represented in figure 7(a). If the low electric field intensity, used for the dielectric measurement, is sufficient to perturb some local electric fields in the SBN (∥) sample, visible changes should not be observed, because the local electric fields for this ceramic are situated preferentially in the same direction of the external electric field and they could not change their orientation. On the other hand, the local electric fields in the SBN (⊥) ceramic, could be slightly perturbed by the external field action (see figure 7(b)) and consequently, they would have a component in the polarization direction of the polar regions ([001] direction). In this case, the action of these components could favour interaction between neighbouring polar regions and, therefore, a reduction of the transition diffuseness should be observed for the SBN (⊥) sample.

The previous discussion suggests thinking that a similar analysis in single crystals could lead to a higher difference of the Δ parameter between different crystallographic directions. In fact, Santos *et al* [25] verified that the Δ parameter, calculated from the dielectric measurements along the *a* (or *b*) direction, is about six times higher than that calculated from the measurement along the *c* direction, in SBN64/36 single crystals.

4. Conclusions

The behaviour of the complex dielectric constant as a function of temperature for textured SBN ceramics revealed the presence of three dielectric anomaly regions. For temperatures around the transition temperature, the existence of polar regions with random size was assumed; these regions are enclosed by local electric fields that inhibit the correlation between the polar regions, promoting the diffuse character of the transition. The relaxor behaviour of this ceramic was also observed at microwave frequencies, evidencing the existence of polar regions, which can be still activated at high frequencies. Using the Vogel–Fulcher approximation, it was possible to estimate physical parameters such as the freezing temperature for SBN ceramics. Furthermore, it was verified that the mechanisms responsible for the dielectric behaviour, in the microwave frequency range, are also affected by the presence of compositional fluctuations and local electric fields for the SBN63/37 relaxor material. The low frequency dielectric behaviour, around and above T_m, for the SBN63/37 material apparently originates from an intermediate configuration of the polar regions between the normal ferroelectric case (which obeys the Curie–Weiss law for temperatures above T_m) and a relaxor ferroelectric (with the so-called complete diffuse phase transition) case. The sample measured in the direction parallel to the pressing axis has a higher transition diffuseness when compared to that measured in the perpendicular direction. In order to explain this experimental observation, it was suggested that interaction between the local electric fields and the external electric field is the main factor responsible for the behaviour.

Acknowledgments

The authors thank CNPq and FAPESP (Proc. No. 04/09612-0) (Brazilian agencies) for financial support. The authors also thank Francisco J Picon for the technical assistance.

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