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2008 J. Phys.: Condens. Matter 20 135209

(http://iopscience.iop.org/0953-8984/20/13/135209)

J. Phys.: Condens. Matter **20** (2008) 135209 (4pp) doi:10.1088/0953-8984/20/13/135209

Mesoscopic structure evidenced by AC dielectric nonlinearities in $Sr_{0.75}Ba_{0.25}Nb_2O_6$ relaxor ferroelectric thin films

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Received 21 August 2007, in final form 12 February 2008
Published 7 March 2008
Online at stacks.iop.org/JPhysCM/20/135209

Abstract
The AC electric field and temperature dependences of the dielectric permittivity for strontium barium niobate ($Sr_{0.75}Ba_{0.25}Nb_2O_6$) relaxor ferroelectric thin films have been investigated. The results indicate the existence of a true mesoscopic structure evidenced by the nonlinear dielectric response of these films, which is similar to those observed for bulk relaxor ferroelectrics. A tendency for a temperature dependent crossover from a linear to a quadratic behaviour of the dielectric nonlinearity was observed, indicating an evolution from paraelectric to glass-like behaviour on cooling the samples towards the freezing temperature transition.

1. Introduction

The high electric field level dielectric response of ferroelectric thin film heterostructures has led to rising attention from both theoreticians and experimentalists in the last few years [1, 2]. This is because the dielectric nonlinearities can shed some light on the influence of the film/electrode interface, grain size and strain effects on the film dielectric properties [3, 4]. The knowledge of these dielectric nonlinearities is of very great practical interest, whereas the use of ferroelectric films as modern nonvolatile random access memories has revolutionized microelectronics and microelectromechanical device performances [5, 6]. Recent works have also shown that the usually observed low dielectric permittivity, broad dielectric dispersion region (with diffuse phase transition), including the temperature range above T_m, should be related to inactive thin dielectric layers that are found in interfaces of heterostructures containing ferroelectric thin films [2, 3]. In fact, some authors have conjectured that the relaxor-like dielectric response of heterostructures can be associated with layer interfaces instead of a true dielectric response of films [7]. On the other hand, some reports had hinted that, in epitaxial or polycrystalline ferroelectric thin films, the principal contributions for low dielectric permittivity values and broadened paraelectric–ferroelectric phase transitions are usually the small grain size distribution and the strains, which can be attributed to the difference in thermal expansion coefficient (TEC) between films and substrates [8, 9]. Strontium barium niobate ($Sr_xBa_{1-x}Nb_2O_6$–SBNx/$1-x$, for short), which has attracted much attention as regards practical applications in the last few years, is a solid solution for $0.75 < x < 0.25$, with an unfilled tetragonal tungsten bronze (TTB) structure at room temperature. Due to their very good photorefractive effects, materials in the SBN family are among the most promising for holographic recording applications [10]. In addition, SBN materials also present high dielectric permittivity (with relaxor characteristics), as well as a high pyroelectric coefficient and electro-optic effect, very important for technological applications, mainly when produced in thin film form, where thermal detection, sensing and capacitive memory applications are also feasible. SBN thin films have been synthesized by various methods, such as radio-frequency sputtering [11], sol–gel [12], and laser ablation [13] techniques, where only the structural and/or ferroelectric properties have been taken into account. Recently, a modified chemical route was successfully employed to obtain high

quality SBN thin films [14], which presented structural and ferroelectric characteristics compatible with those obtained by other traditional routes [12–15]. Despite their very attractive physical properties, and to the best of our knowledge, there have been few experimental works concerning the dielectric nonlinearities in SBN thin films. In this paper, the temperature, frequency and AC probing electric field amplitude (E_m) dependences of the dielectric properties of SBN thin films, prepared by the aforementioned alternative chemical route, are presented and discussed. The relaxor-like dielectric response, as well as the crossover from linear to quadratic dependence of the AC dielectric nonlinearity as a function of the temperature, suggests the interpretation of a true mesoscopic structure evidenced by the nonlinear dielectric response of the SBN thin films investigated. Indeed, a crossover from paraelectric to glass-like behaviour was observed on cooling the thin films towards the freezing transition temperature.

2. Experimental details

$Sr_{0.75}Ba_{0.25}Nb_2O_6$ (hereafter labelled as SBN75/25) thin films, with 500 ± 20 nm thickness, determined by scanning electron microscopy, were prepared by a chemical route and deposited on Pt/Ti/SiO_2/Si substrates as previously reported [14]. X-ray diffraction patterns (not shown here) and energy dispersive x-ray spectroscopy analysis revealed a single polycrystalline tetragonal SBN phase and the expected nominal composition. For dielectric investigations, gold electrodes (0.5 mm in diameter) were sputtered on thin film surfaces forming a metal–film–metal configuration, as previously reported [14]. Computer assisted dielectric measurements were performed as a function of temperature, frequency (1 kHz–1 MHZ) and measurement AC electric field amplitude (E_m), up to 20 kV cm^{-1}, using an HP4194A impedance gain/phase analyser. For low temperature measurements, samples were placed in a test chamber (APD201; Cryogenics Inc.), which can be operated in a temperature range of 20–450 K.

3. Results and discussion

The temperature, frequency and E_m dependences of the dielectric permittivity for SBN75/25 thin films are shown in figure 1. As can be seen in figure 1(a), for the lowest AC electric field amplitude (0.2 kV cm^{-1}), the composition studied shows the main relaxor ferroelectric characteristics, i.e., frequency dependence of the maximum dielectric permittivity (ε'_m) and its corresponding temperature (T_m). A close inspection of the frequency dependence of T_m was carried out by fitting the experimental data with the Vogel–Fulcher relationship ($\nu = \nu_0 \exp[-T_0/(T_m - T_f)]$), as shown in the inset figure 1(b). The fitting parameters obtained, namely $T_0 = E_a/k_B$ (where E_a is a measure of the mean activation energy and k_B the Boltzmann constant), the attempt frequency (ν_0) and the freezing temperature (T_f), were 1052 K, 26×10^9 Hz and 224 K, respectively, which are in good agreement with others previously reported for bulk SBN [15]. As can be seen, the attempt frequency value ($\sim 10^9$) is way below the soft mode frequencies, which are in the order of 10^{11}–10^{12} Hz.

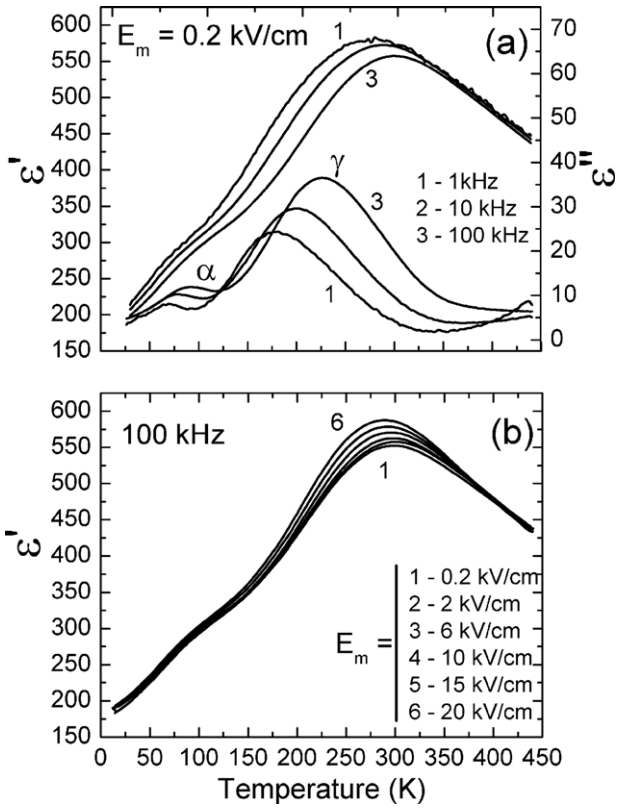

Figure 1. Temperature dependence of the dielectric permittivity for the SBN75/25 thin films, as a function of the frequency (a) and the AC measurement electric field amplitude (E_m) (b). The inset shows the fitting of the results for the lowest E_m level with the Vogel–Fulcher relation.

This can be attributed to the random field-correlated polar clusters beyond the atomic SBN scale. In this way, a broad distribution of relaxation times can supposed for the linear dielectric response of the films studied. Thus, a nonlinear dielectric response, similar to that observed for bulk relaxors and which can be related to the mesoscopic structure, can be supposed for the SBN thin films.

Two dielectric dispersion regions (termed α and γ) can be clearly observed in the imaginary part of the dielectric permittivity, also showed in figure 1(a). This result contrasts with that reported by Santos *et al* [16] for SBN single crystals and ceramics, where three distinct dielectric relaxation regions were observed. The absence of a third dispersion region observed in the interval 200–250 K, and termed β in a previous report [17–20] can be associated with weak tensile strains on the thin films due to the substrate, and the narrow grain size distribution of nanograins [19]. In fact, these tensile strains can suppress the extensively reported planar defects that give rise to an incommensurate superstructure in bulk SBN ([17] and [18]) and, consequently, the formation of the β dispersion region. Detailed discussion concerning the dielectric dispersion regions in SBN thin films can be found in [19].

It can also be observed that with the increase of E_m, the T_m shifts to lower temperatures, while the ε'_m value increases (figure 1(b)). These results, which mimic the

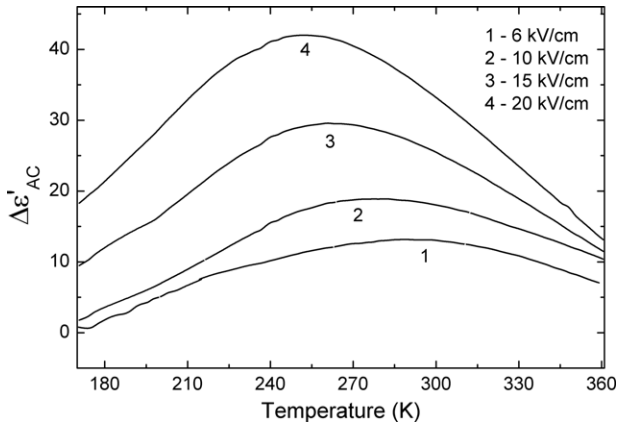

Figure 2. Dielectric nonlinearity ($\Delta\varepsilon'_{AC}$) as a function of temperature and AC measurement electric field amplitude, for the SBN75 thin films at 100 kHz.

relaxor behaviour observed at low AC electric field amplitudes (figure 1(a)), are similar to those usually observed for bulk relaxor ferroelectrics [20]. Bearing this result in mind, and taking into account the almost complete absence of the frequency dielectric dispersion for temperatures above T_m (see figure 1(a)—ε''), it can be inferred that the interfacial effects, usually observed in epitaxial ferroelectric thin film heterostructures, are extremely weakened in the samples studied. In this way, the considerably low values obtained for the dielectric permittivity and its corresponding T_m can be associated with the above mentioned tensile strains and the narrow grain size distribution of nanograins in the thin films [19]. Indeed, these two factors contribute strongly to the enhancing of the diffuseness degree of the phase transition, as observed in the SBN75/25 results when compared with bulk SBN [19]. The temperature and E_m dependences of the AC dielectric nonlinearity, which can be defined as $\Delta\varepsilon'_{AC} = \varepsilon'(E_m) - \varepsilon'(E_0)$, E_0 being the small signal AC electric field ($E_m \sim 0.2$ kV cm^{-1}) [20], are shown in figure 2 at 100 kHz. With the increase of the AC electric field amplitude, a characteristic relaxor ferroelectric behaviour can be observed; for instance, the maximum of $\Delta\varepsilon'_{AC}$ increases, while the corresponding temperature of the maximum decreases, with the increase of E_m. These results are also very similar to those observed for bulk relaxor ferroelectrics [20], and corroborate the previous assumption that the observed dielectric nonlinearities are a true thin film dielectric response, which for bulk SBN can be attributed to a strong polydispersity of clusters and domains [21, 22]. Figure 3(a) shows the E_m dependence of $\Delta\varepsilon'_{AC}$ on a log–log scale for different temperatures (185, 200, 250, 300 and 350 K), at 100 kHz. The curves were fitted with the scaling relation $\Delta\varepsilon'_{AC} \sim E^{\xi}$. By considering the thermal evolution of the ξ exponent (figure 3(b)), an almost linear relationship ($\xi = 0.80 \pm 0.03$) between $\Delta\varepsilon'_{AC}$ and E_m is observed at 350 K. With the decrease of the temperature, the ξ exponent starts to increase at temperatures where the linear dielectric dispersion also starts to appear (∼325 K). At 200 K, ξ reaches values close to 2 ($\xi = 1.80 \pm 0.12$), revealing a typical quadratic behaviour between $\Delta\varepsilon'_{AC}$

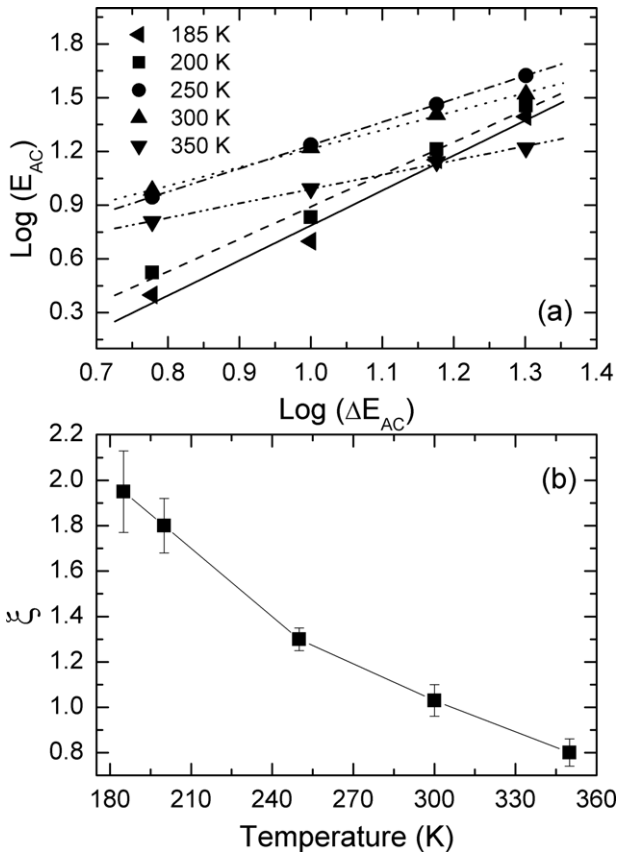

Figure 3. Nonlinear dielectric response analysis results (100 kHz). (a) AC measurement electric field amplitude (E_m) dependence of the dielectric nonlinearity ($\Delta\varepsilon'_{AC}$) on a log–log scale. The lines represent the fits by using the power law $\Delta\varepsilon'_{AC} \sim E_m^{\xi}$. (b) Temperature dependence of the ξ exponent.

and E_m for temperatures near the freezing temperature ($T_f = 224$ K). In fact, the ξ values for temperatures below T_f are similar to those observed for PLZT ceramics and PMN single crystals [23, 24]. It is important to point out that crescent deviations from the expected square law, $\Delta\varepsilon'_{AC} \sim E_m^2$, were observed for the SBN75/25 thin films at temperatures below 200 K ($\xi = 1.95 \pm 0.18$ for $T = 185$ K). In this temperature region the existence of the α dielectric dispersion phenomenon complicates the analyses, since it can be the reason for the dispersion observed in the ξ values. However, the Rayleigh-type non-analytical behaviour for $\Delta\varepsilon'_{AC}$ for ferroelectric thin films can also be ruled out in the presented analysis, enforcing the hypothesis that the observed dielectric nonlinearities for the SBN thin films are related to a true mesoscopic structure characteristic of relaxor materials.

4. Conclusions

The AC dielectric nonlinearities for SBN75/25 relaxor ferroelectric thin films were carefully determined as a function of temperature, frequency and AC measuring field. The set of results indicates the existence of a true relaxor behaviour of SBN75/25 thin films, which is very similar to that observed for bulk relaxor ferroelectrics, and can be associated with the existence of clusters and domains beyond the SBN atomic

scale. A temperature dependent crossover from a linear to a quadratic behaviour of the dielectric nonlinearity has also been observed, indicating an evolution from paraelectric to the glass-like behaviour on cooling of the thin films towards the freezing temperature.

Acknowledgments

The authors would like to thank FAPESP (contracts 04/09612-0 and 00/09722-9) and CNPq (470862/2006-8) Brazilian agencies for financial support.

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