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Temperature dependence of ferroelectric properties of SBT thin films

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Abstract

Strontium bismuth tantalate (SBT) thin films have been deposited on $Pt/TiO_2(100)Si$ substrates by a metal–organic decomposition (MOD) method, using a non-stoichiometric composition. The measured net spontaneous polarization is a consequence of the parallel alignment of 180° domains, as it is confirmed by the random distribution of the pole figures. Measurements of temperature dependence of permitivitty, ε', and remnant polarization, P_r, show diverse anomalies. The large shift of the temperature $T_{C,}$ is explained by the structure distortion associated with Bi:Sr ratio of the film. A strong decrease of P_r with T is observed that could be related with possible phase transitions, although more information on atomic level is needed to know the mechanisms involved.

Keywords: Ferroelectric properties; Films; Functional applications; Tantalates; Temperature

1. Introduction

Up to date, studies of the temperature behavior of strontium bismuth tantalate (SBT) thin films are scarce and issues on the phase transitions and their mechanisms are still open. Values of Curie temperature, T_C of 210°C have been reported by Newnham et al.[1] for $(Sr_{0.9}Ba_{0.1})$-$Bi_2Ta_2O_9$ single crystals. Shimakawa et al.[2] reported values of T_C of about 300 and 400°C for powder samples of stoichiometric ($SrBi_2Ta_2O_9$) and non-stoichiometric ($Sr_{0.8}Bi_{2.2}Ta_2O_9$) compositions, respectively, invoking the structural distortion to justify the observed T_C temperature shift. Shoji et al.[3] have found T_C value close to 322°C for stoichiometric ceramic samples. Onodera et al.[4] have also reported thermal anomalies in the specific heat at 237 and 397°C for a ceramic sample of composition $Sr_{0.85}Bi_{2.1}Ta_2O_9$. They also carried out a XRD thermal study of the mentioned samples, comparing them with a sample of stoichiometric composition showing different sequences of structural phase transitions at high temperatures. However, no anomalies in the dielectric constant and spontaneous polarization were reported.

In these compounds, despite of the high values of spontaneous polarization, P_s, calculated for these materials, only a small part of P_r has been measured in thin films (not higher than 1/3 of the calculated one). Some authors attributed this fact to an unfavorable texture [*c*-axis laying normal to the film plane, meanwhile the *a*-axis is in the polar direction, as reported by Gruverman et al.[5] based on Scanning Force Microscopy (SFM) studies] or to the formation of a low permittivity layer at the interface, despite of the high $<100>$ oriented films claimed by Hu et al.[6] On the other hand the absence of 90° domain wall reported for single crystals by Newnham et al.[1] and Rae et al.[7] could justify the low fatigue and the moderate polarization values obtained in these materials, since 180° domains should be only ones involved in the switching process.

The aim of this work is two-fold, on the one hand we investigate the role that 180° domains play in SBT thin film obtained by a MOD method by means of XRD and net polarisation measurements. On the other hand, we study the variation of the dielectric constant with temperature and the thermal evolution of remnant polarisation in order to gain a deeper insight on the temperature influence on ferroelectric properties of SBT compounds prepared as thin films, to be used for non-volatile ferroelectric random access memories (NVFeRAM) applications.

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2. Experimental

The films have been obtained following the MOD process previously described by the authors[8] that lead to single phase thin films, showing P_r values in the range of 4–6 μC cm^{-2}, good retention of P_r after 10^5 s and a moderate fatigue after 10^{10} cycles. A solution of nominal composition $Sr_{0.7}Bi_{2.2}Ta_2O_9$ is deposited by spin-coating on to a $Pt/TiO_2(100)Si$ substrate. After drying the wet layer at 225°C, films were crystallized at 750°C/1 h after a 30 min firing step at 550°C under a flowing O_2. To monitor the crystalline phases X-ray diffraction measurements were carried out using the Bragg–Brentano ($\theta-2\theta$ coupled) and the grazing incidence (GIXRD), $\alpha = 2°$, configurations. At this fixed angle, the equivalent penetration of X-ray beam ($I/I_0 = 1/e$) is equal to 230 nm which is close to the thickness of the film. Pole figures were also obtained, in order to correlate the texture with the net polarisation of the samples. They were carried out with a Huber four-circle goniommeter to acquire a complete diffraction pattern at each position of the sample. Film thickness were measured by using a Taylor–Hobson mechanical stylus, resulting an average value of 300 nm. Final composition was deduced from Rutherford backscattering spectroscopy (RBS), being the estimated error, after the fitting of data against the model, better than 10% for Bi. Atomic force microscopy (AFM) measurements were also carried out to observe the film surface microstructure.

In order to perform ferroelectric measurements, top platinum electrodes were deposited by cold sputtering using a shadow mask, which yielded 5 10^{-4} cm^2 area dots. Net polarization of the as-grown samples was obtained from the first traced cycle using a new method of pulsed hysteresis loops recently developed by the authors.[9] Pyroelectric currents were measured after applying a triangular thermal wave of amplitude 2.5°C and 2.10^{-3} Hz, at room temperature. Variation of remnant polarization with temperature was calculated from two sorts of measurements: (a) from the pulsed hysteresis loops (PHL) with pulse width of 100 μs and 50 ms apart, (b) from the switching currents (SC) curves with write pulses of 10 μs and read pulses of 50 and 100 μs apart. The applied electric field for the P_r vs temperature measurements was larger than four times the value of the coercive field, E_c, at room temperature.

3. Results and discussion

Although the nominal composition of the film is $Sr_{0.7}Bi_{2.2}Ta_2O_9$, after crystallisation its composition as deduced from RBS was $Sr_{0.7}Bi_{1.9}Ta_2O_{8.2}$, far from stoichiometry. The AFM image, inset in Fig. 1, revealed the formation of densely packed elongated grains.

The XRD patterns show a well conformed single phase compound corresponding to the layered perovskite structure [GIXRD pattern, Fig. 1(a)], without any significant texture [$\theta-2\theta$ pattern, Fig. 1(b)]. The intensity peaks correspond to those of the calculated pattern using the parameters reported by Shimakawa et al.[2] as revealed by the bars included over Fig. 1(a).

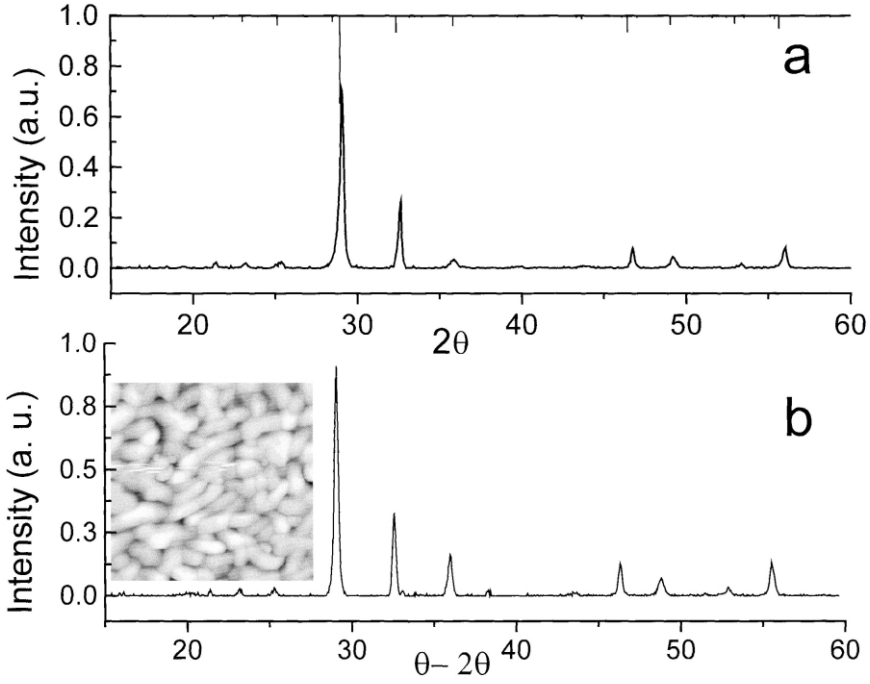

Fig. 1. XRD data. (a) GIXRD 2θ pattern of the SBT film (the bars correspond to the pattern calculated from the structural data[2] (b) $\theta - 2\theta$ pattern of the SBT film. The inset shows the AFM image of the SBT film (image size: 1.5×1.5 μm^2).

The pole figures presented in Fig. 2 for the sample are in good agreement with a random orientation of grains in the film, because of the low value of the texture index (m.r.d.)^2 for {001} and {100}+{100} recalculated pole figures

The results obtained from the first cycle measurements, before any electrical treatment (Fig. 3), indicate that the film has a spontaneous net polarisation, pointing to the top electrode, which corresponds to a mean value of 60% of the switchable polarisation. In the figure, the 12th cycle is also plotted in order to test that all the switcheable polarization is present in the first cycle, validating the results obtained from the first cycle measurement.

Fig. 4 shows the dielectric permittivity variation with temperature for the film, measured at 1 kHz, showing the maximum at $T_C = 365$°C in heating and at 375°C on cooling.

Values of polarization, P_r, deduced from measurements of SC and PHL with temperature are depicted in Fig. 5. Due to experimental difficulties of the PHL method (large dielectric losses) it was not possible to surpass the 200°C with this technique. The following experimental facts are revealed: the polarisation decreases linearly with increasing temperature up to 175°C in PHL measurements and close to 200°C in SC measurements (see Fig. 4) while P_r exists up to 400°C, beyond the T_C value.

It should be noted that the SC measurement may induce imprint[10] and loss in the ferroelectric polarisation due to space charge redistribution and pinning of the ferroelectric domains produced by the uncompensated charge in the film. These effects should be stronger when the temperature increases as a result of the higher charge mobility and the nature of the measurement that leaves the polarisation fixed to one sense during the temperature stabilization (30 min approx.). In our measurements the variation of the polarisation is practically the same in heating the sample than in cooling, showing

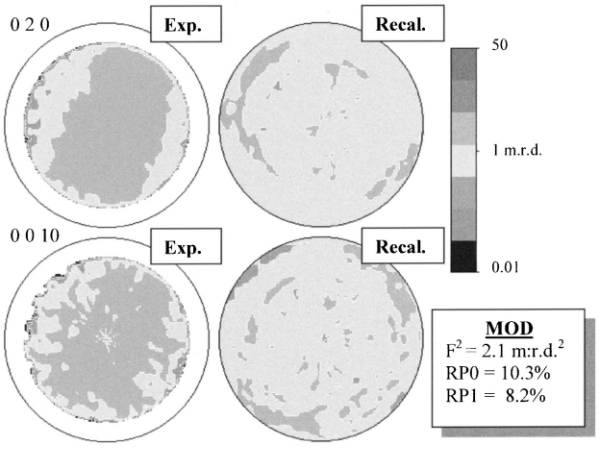

Fig. 2. {001} and {100}+{100} recalculated pole figures of SBT film. Equal area projection and logarithmic density scale.

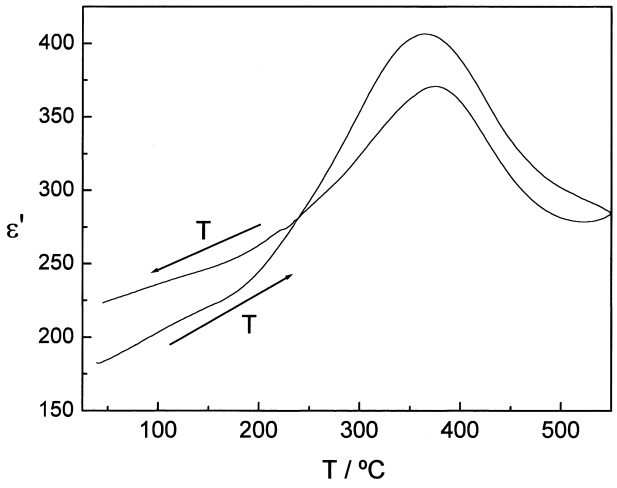

Fig. 4. Temperature dependence of permittivity ε', for SBT film. Arrows indicate the temperature evolution of measurements.

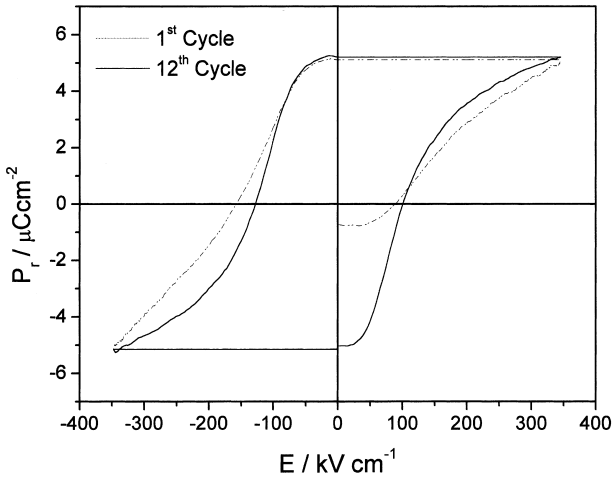

Fig. 3. Pulsed hysteresis loop results of the SBT film. Continuous line is the 12th cycle, dashed line is the very first one, showing the net polarisation of the sample.

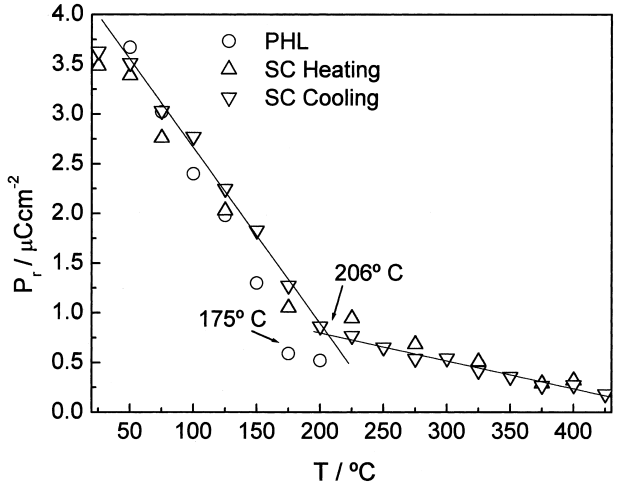

Fig. 5. Remnant polarization vs temperature (P_r–T) diagram. Polarization obtained from pulsed hysteresis loops (PHL) and switching current (SC) during heating and cooling down.

that the possible imprint is not responsible of the strong decrease in P_r.

The existence of a self-polarisation in the samples (net polarization) as deduced from the measured value of pyroelectric coefficient, $\gamma = 2.10^{-9}$ C cm^{-2} °C^{-1} and first cycles measurements can only be explained by the formation of 180° domain walls, mainly aligned with a common sign, since XRD data show a random orientation of the films. This is compatible with the X-ray diffraction data, since here parallel and anti-parallel 180° domain walls are undistinguished according to Friedel law.[11] Furthermore, as it was mentioned above, only a moderated amount of domains are expected to be aligned by an external electric field, because of the absence of 90° domain walls. These findings justify the low P_r values obtained from switching or hysteresis loops, as compared with the calculated saturation values (in the range of 18 and 20 μC cm^{-2}).[2] On the other hand, the Curie temperatures, T_C, behavior agrees with that reported for ceramic samples of similar compositions by Shimakawa et al.[2] and could be ascribed to the degree of structural distortion of the film. The RBS measurements indicate that the approximate Bi:Sr ratios of the film is 2.71, slightly lower than 2.75 reported for ceramic of composition ($Sr_{0.8}Bi_{2.2}Ta_2O_9$). Since the Sr^{2+} radius is larger than that of the Bi^{3+} ion it results in a stronger structural distortion of the film. For ferroelectric perovskite structures,[12] the phase transition temperature increases as the distortion increases, like in the present case (see Fig. 4). The small perturbation measured in specific heat reported by Onodera[4] in non-stoichiometric ceramic SBT can be related to the change in the P_r vs T slope at temperatures close to 200°C, although no changes in the permittivity have been observed to be associated with a phase transition. On the other hand, the existence of P_r above the maximum of permittivity versus temperature suggests its diffusive character.

4. Summary

From the experimental results described above, the temperature dependence of the dielectric constant seems to be more sensitive to phase transitions than the remnant polarization. A change in the slope of P_r vs temperature is found in the SBT film that can be related to a possible low temperature phase transition claimed by Onodera.[4] The rapid decrease of P_r with temperature up to 200^{0}C is of practical interest, considering the application of these films to NVFeRAM memories.

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